

Routine Analysis of Soils using ICP-MS and Discrete Sampling

Agilent 7850 ICP-MS provides the stability and robustness needed for the long-term accurate analysis of high matrix samples



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Introduction

ICP-MS is a fast, multi-element technique that is often used to measure 30 or more analytes in a wide range of complex, high matrix environmental samples such as soil and sludge digests (1–3). Commercial laboratories performing contract analysis of environmental samples strive for a simple and consistent analytical workflow. To support such routine operation, Agilent ICP-MS systems use Ultra High Matrix Introduction (UHMI) technology to increase overall matrix tolerance. UHMI enables samples with high and variable matrix levels to be measured, without requiring sample-specific dilutions, or matrix matching of the calibration standards. Routine analysis of high matrix samples can also lead to concerns about signal stability and increased instrument maintenance with long analytical runs. Robust operating conditions (low CeO/Ce ratio) provide optimum matrix tolerance when analyzing high matrix soil digests, minimizing drift and reducing the frequency of routine maintenance (4).

Agilent ICP-MS systems also include the ORS⁴ collision/reaction cell (CRC), which is optimized for removal of all common polyatomic overlaps using helium (He) collision mode. He mode allows the same cell settings to be used for most elements in many common sample types, again simplifying routine analysis. Furthermore, because He mode is effective for all polyatomic ions, it gives access to secondary, or qualifier, isotopes for many analytes. Analysts can therefore verify the accuracy of their data by comparing the results from the primary and qualifier isotopes. Agilent ICP-MS MassHunter software also supports simple, easy to use methods, with features such as preset methods, autotuning, and a software interface that guides analysts through typical analytical workflows.

This unique combination of hardware performance and software functionality is one of the reasons that hundreds of laboratories worldwide use Agilent ICP-MS instruments for routine analysis of environmental samples. However, many of these labs, especially those in the commercial sector, are looking for ways to further streamline their analytical workflow, while maintaining productivity and data quality. The Agilent 7850 ICP-MS and ICP-MS MassHunter software (version 5.1 or later) include a series of novel features to help laboratories run their ICP-MS analysis more efficiently. These features assist operators to optimize sample preparation and method development, avoid unnecessary instrument maintenance, and generate high-quality data for challenging samples.

ICP-MS MassHunter IntelliQuant is a useful, time-saving function that calculates semiquantitative concentrations for up to 70 elements in each sample from a two second Quick Scan acquisition in He mode. The IntelliQuant results are calculated for all elements, not just those analytes present in the calibration standards. The results can be viewed as a periodic table heat map, which gives a clear visual indication of the concentration ranges of all elements in each sample (5). The IntelliQuant data can be summed to give a Total Matrix Solids (TMS) level, and used to confirm the presence of unexpected elements, reducing the need for sample remeasurement.

Agilent ICP-MS systems are routinely operated with excellent plasma robustness (low CeO/Ce ratio), so are easily able to tolerate the level of dissolved solids present in most typical ICP-MS samples. However, very high matrix levels can cause signal changes by altering sample uptake and nebulization processes due to differences in sample viscosity. Knowing the TMS level of new or unusual sample types simplifies method development. For example, an analyst can use the TMS level to help choose the appropriate measurement

conditions for a batch of unknown samples. TMS data can also help identify and understand the cause of any in-run or post-run data queries, such as a sudden drop in internal standard signals. Reviewing the TMS data from previous batches can help an analyst make informed decisions on routine maintenance.

ICP-MS MassHunter features also help analysts schedule routine cleaning and maintenance, using early maintenance feedback (EMF) indicators and a post-run tune-check to monitor the condition of the instrument after each sequence (6). Analysts can use the information provided by these functions to optimize instrument performance, saving time and resources by avoiding unnecessary maintenance.

Experimental

Instrumentation

An Agilent 7850 ICP-MS fitted with the ISIS-3 discrete sampling system was used for the analysis of varied soil and sediment digests. The 7850 instrument includes a nickel-tipped copper sampling cone, nickel skimmer cone, UHMI aerosol dilution system, ORS⁴ helium collision cell, and an automated function to correct for doubly charged interferences. Sample delivery was performed using the Agilent SPS 4 autosampler.

The 7850 ICP-MS includes UHMI technology as standard. The UHMI was used to minimize the need for sample-specific dilution before analysis, avoiding a time-consuming manual process that can introduce error. UHMI uses argon to dilute the sample aerosol, reducing the sample matrix reaching the plasma and avoiding the need for liquid dilution. A preset method with a suitable UHMI aerosol dilution level was selected as appropriate for the sample type and expected matrix level. Plasma parameters were applied automatically based on the preset plasma setting, and all lenses were autotuned.

The 7850 also includes the ORS⁴ CRC for control of polyatomic interferences. Samples with high and variable major element content can be difficult to analyze by ICP-MS due to the formation of variable and unpredictable matrix-based polyatomic interferences. The ORS⁴ cell is the optimum configuration for He mode, effectively reducing all common, matrix-based polyatomic interferences under one set of standard cell conditions. This proven approach enables new as well as experienced analysts to quickly and confidently acquire reliable and accurate data for all elements. He mode is selected as the default mode for Quick Scan data acquisition, ensuring that IntelliQuant data is free from the errors that can be caused by common polyatomic ion overlaps.

ICP-MS MassHunter software includes a function to automatically correct for potential doubly charged ion interferences caused by the rare earth elements (REEs) that can be present in soil samples (7). If present at a high enough concentration in soil samples, the doubly charged REE ions $^{150}\text{Nd}^{2+}$ and $^{150}\text{Sm}^{2+}$ will interfere with $^{75}\text{As}^+$, while $^{156}\text{Gd}^{2+}$ and $^{156}\text{Dy}^{2+}$ will interfere with $^{78}\text{Se}^+$. REE $^{2+}$ interferences are not removed effectively in He mode, so, if uncorrected, these overlaps can lead to false-positive results. Instrument operating conditions are shown in Table 1.

Table 1. 7850 ICP-MS operating conditions.

ICP-MS Parameter	Helium Mode	
Plasma Mode	UHMI-8	
RF Power (W)	1600	
Spray Chamber Temp (°C)	2	
Sampling Depth (mm)	10	
Nebulizer Gas Flow (L/min)	0.69	
Dilution Gas Flow (L/min)	0.28	
Lens Voltages	Autotune	
He Flow (mL/min)	1.0	5.0 (*10)
Energy Discrimination (V)	5.0 (*7.0)	
Elements	Beryllium, 1 ISTD	27 analytes, 3 ISTDs

*The shaded parameters were set automatically. *Enhanced He mode settings used for Se and P. As and Se were measured at the increased resolution settings used for M $^{2+}$ correction.*

The ISIS 3 discrete sampling system speeds up the overall analysis by starting the rinse program while acquiring data for the previous sample. ISIS 3 discrete sampling shortened the analysis time by two minutes compared with conventional sample introduction, while minimizing carry over from previous samples. More details of ISIS 3 configuration and functionality are given elsewhere (2, 3).

Table 2. ISIS 3 operating parameters.

ISIS 3 Parameter	Setting	
Loop Volume (mL)	1.4	
	Time (s)	Pump speed (%)
Sample Load	9	35
Stabilize	23	5
Probe Rinse	25	8
Probe Rinse 2	10	60
Probe Rinse 3	10	5
Optional Loop Probe Wash	13	60
Optional Loop Wash	3	5

Standard and sample preparation

The calibration standards and samples were prepared in an acid matrix of 1% HNO_3 and 0.5% HCl. HCl is routinely added to samples for ICP-MS analysis to ensure the stability of elements such as Ag, Sb, and Hg. The standard He cell mode of the 7850 ICP-MS removes any Cl-based interferences that would be formed from the added chloride matrix. Calibration standards, spikes, and most of the quality control (QC) standards were prepared from Agilent Environmental calibration standard part number (p/n) 5183-4688. Single element standards were used for Al, Mn, Hg, Zn (Kanto Chemicals, Japan), and P (SPEX CertiPrep, Metuchen, NJ, USA). Six point calibrations including calibration blank were prepared at the concentration ranges given in Figure 1. The term “mineral elements” refers to Na, Mg, K, Ca, and Fe.

For in-run quality control (QC), the initial calibration verification (ICV) and continuing calibration verification (CCV) standards were prepared from multi-element Environmental Calibration Standard A (VHG) and single element standards for Al, Mn, P, Hg and Zn. The acid matrix of 1% HNO_3 and 0.5% HCl was used as the initial calibration blank (ICB) and continuing calibration blank (CCB). For the low-level ICV (LLICV) sample, a solution containing 1 ppb for trace elements, 100 ppb for mineral elements, 200 ppb for Ca, 5 ppb for P, and 0.02 ppb for Hg was measured.

The certified reference materials (CRMs) used in the analysis were River Sediment A, River Sediment B, Estuarine Sediment, Soil A, and Soil B. The CRMs were all supplied as predigested solutions from High Purity Standards (HPS), Charleston SC, USA. The CRMs were diluted 2x using the 1% HNO_3 and 0.5% HCl acid matrix.

The Internal Standard (ISTD) solution (Agilent p/n 5183-4681) containing 1 ppm Li, Y, In, and Bi was automatically added online via the dedicated seventh port of the ISIS valve. The flow rate of the ISTD solution was about 1/15 of the sample flow rate, due to the use of smaller internal diameter pump tubing.

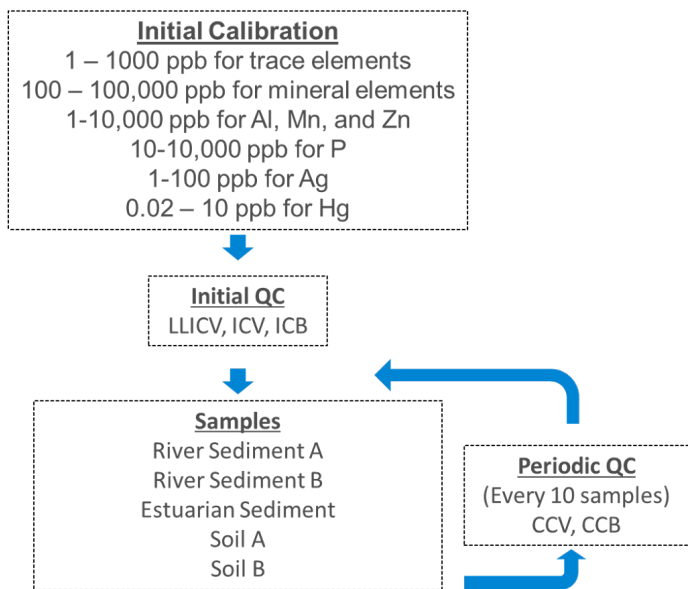


Figure 1. Analytical sequence of calibrants, QC solutions, and samples. The sample block was analyzed repeatedly with automatic insertion of the periodic QC block after every 10 samples.

Results and discussion

All analytes were measured in He mode using the acquisition parameters listed in Table 1. Limits of Detection (LODs) were calculated from three times the standard deviation of 10 measurements of the calibration blank in the acid diluent matrix (Table 3). LODs for the trace analytes were mostly in the low ng/L (ppt) level, confirming the sensitivity of the 7850 ICP-MS for the application.

Long-term stability

To demonstrate the robustness of the 7850 ICP-MS, 100 samples and 30 QC samples were analyzed throughout the day. Analyzing varied, high matrix samples can lead to signal changes due to physical effects—the matrix level affects the viscosity of the sample, altering the flow rate and nebulization. To correct for these effects, ICP-MS analysts typically add ISTDs online. Figure 2 shows that the ISTD recoveries for this sample analysis remained within the QC limits of 70–130% throughout the run, with no mass-dependent drift. The recovery data confirms that the robust, matrix tolerant plasma of the 7850 ensured that minimal matrix deposition occurred. The ISTD plot also shows that the 7850 provides excellent control of signal suppression, with ISTD signals being consistent for elements covering a range of masses and ionization potentials. The results demonstrate the long-term robustness and high matrix tolerance of the 7850 ICP-MS with UHMI.

Table 3. Three sigma method LODs calculated from 10 replicates of the calibration blank, prepared in the same acid matrix as used for sample dilution.

Element and Mass Number	ISTD	LOD (µg/L)
9 Be	⁶ Li	0.004
23 Na	⁸⁹ Y	7.75
24 Mg	⁸⁹ Y	1.02
27 Al	⁸⁹ Y	4.97
31 P	⁸⁹ Y	2.75
39 K	⁸⁹ Y	30.3
44 Ca	⁸⁹ Y	17.1
51 V	⁸⁹ Y	0.016
52 Cr	⁸⁹ Y	0.371
55 Mn	⁸⁹ Y	0.222
56 Fe	⁸⁹ Y	3.27
59 Co	⁸⁹ Y	0.010
60 Ni	⁸⁹ Y	0.044
63 Cu	⁸⁹ Y	0.042
66 Zn	⁸⁹ Y	0.210
75 As	⁸⁹ Y	0.049
78 Se	⁸⁹ Y	0.049
95 Mo	⁸⁹ Y	0.009
107 Ag	¹¹⁵ In	0.016
111 Cd	¹¹⁵ In	0.008
121 Sb	¹¹⁵ In	0.011
137 Ba	¹¹⁵ In	0.059
201 Hg	²⁰⁹ Pb	0.004
205 Tl	²⁰⁹ Pb	0.005
Pb*	²⁰⁹ Pb	0.163
232 Th	²⁰⁹ Pb	0.008
238 U	²⁰⁹ Pb	0.006

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

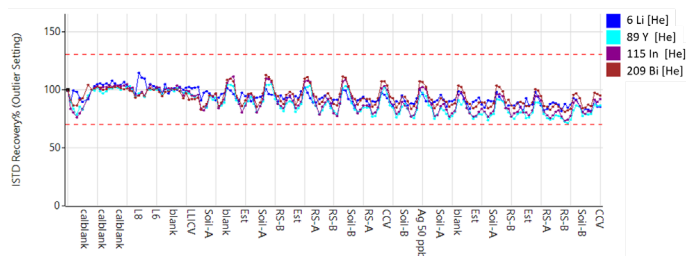


Figure 2. ISTD stability of more than 130 samples measured using the 7850 ICP-MS. ISTD recoveries normalized to the calibration blank for all samples. Due to limited space, not all sample names are shown. Pattern of alternating high and low ISTD signals indicates changes in sample transport and nebulization for groups of low and high matrix samples, respectively.

Table 4. Recovery of certified values for CRMs after correction for the 2x dilution factor. Concentration units mg/L except for elements in shaded rows which are in µg/L.

(n=20)	River Sediment A			River Sediment B			Estuarian Sediment			Soil A			Soil B		
	Mean Conc	Certified Value	Recovery (%)	Mean Conc	Certified Value	Recovery (%)	Mean Conc	Certified Value	Recovery (%)	Mean Conc	Certified Value	Recovery (%)	Mean Conc	Certified Value	Recovery (%)
9 Be	0.151	-	-	0.103	-	-	18.7	20.0±0.6	93	0.063	-	-	0.398	-	-
23 Na	51.8	50.0±0.3	103	54.2	50.0±0.5	108	206	200±2	103	72.2	70.0±0.7	103	99.8	100±1	100
24 Mg	69.6	70.0±0.4	99	127	120±1	106	102	100.0±0.6	102	70.2	70.0±0.4	100	79.0	80.0±0.48	99
27 Al	244	250±1	98	594	600±4	99	710	700±4	102	492	500±3	98	716	700±4	102
31 P	0.017	-	-	9.72	10.0±0.1	97	4.86	5.00±0.05	97	9.84	10.0±0.1	98	9.66	10.0±0.1	97
39 K	149	150±1	99	199	200±3	100	146	150±2	97	197	200±3	98	206	210±3	98
44 Ca	292	300±2	98	294	300±2	98	79	80.0±0.5	99	344	350±2	98	122	125±1	98
51 V	0.252	0.250±0.003	101	1.03	1.00±0.02	103	1.00	1.00±0.02	100	0.100	0.100±0.005	100	0.788	0.800±0.016	99
52 Cr	298	300±2	99	15.8	15.0±0.1	105	0.832	0.800±0.008	104	0.016	-	-	0.404	0.400±0.005	101
55 Mn	7.74	8.00±0.04	97	5.92	6.0±0.1	99	3.86	4.00±0.04	96	0.104	0.100±0.001	104	97.4	100±1	97
56 Fe	1190	1200±6	99	410	400±2	102	348	350±2	99	199	200.0±1.2	99	346	350±2	99
59 Co	100	100±1	100	162	150±3	108	108	100±2	108	2.46	-	-	98.6	100±2	99
60 Ni	0.510	0.50±0.01	102	0.550	0.50±0.01	110	0.320	0.30±0.02	107	0.298	0.30±0.02	99	0.202	0.20±0.01	101
63 Cu	1.01	1.00±0.01	101	1.06	1.00±0.01	106	0.214	0.200±0.003	107	0.300	0.300±0.005	100	2.96	3.00±0.03	98
66 Zn	13.7	15.0±0.2	91	4.70	5.00±0.05	94	1.37	1.50±0.03	92	0.916	1.00±0.002	92	64.0	70.0±0.7	91
75 As	0.594	0.60±0.03	99	0.200	0.20±0.01	100	0.097	0.100±0.005	97	0.190	0.20±0.01	95	5.74	6.00±0.12	96
78 Se	19.7	20±2	98	9.44	10±1	94	45.8	50±5	92	9.42	10±1	94	0.254	-	-
95 Mo	0.592	-	-	2.30	-	-	1.06	-	-	0.234	-	-	1.55	-	-
107 Ag	1.63	-	-	0.318	-	-	0.182	-	-	0.236	-	-	0.500	-	-
111 Cd	102	100±2	102	30.6	30±1	102	0.446†	0.4	-	2.98†	6	-	195	200±4	97
121 Sb	518	500±20	104	41.0	40±2	102	4.42†	4	-	32.6	30±1	109	398	400±12	100
137 Ba	0.514	0.50±0.01	103	4.02	4.00±0.04	100	0.004	-	-	5.06	5.00±0.05	101	6.98	7.00±0.07	100
201 Hg	0.028	-	-	0.021	-	-	0.021	-	-	0.019	-	-	0.020	-	-
205 Tl	9.72	10±1	97	9.76	10±1	98	0.066	-	-	0.066	-	-	0.130	-	-
Pb*	7.12	7.00±0.07	102	2.04	2.0±0.1	102	0.304	0.30±0.02	102	0.400	0.40±0.02	100	58.6	60.0±0.6	98
232 Th	19.9	20±2	99	97.8	100±5	98	97.6	100±5	98	97.6	100±5	98	97.4	100±5	97
238 U	9.82	10±1	98	29.0	30±2	97	0.055	-	-	9.54	10±1	95	242	250±10	97

*Pb was measured as the sum of the three most abundant isotopes, 206, 207 and 208. † indicates an uncertified reference value. Blank cells indicate the absence of a reference or certified value.

Accurate analysis of CRMs

The five CRMs were each analyzed 20 times during the sequence, and the mean concentration and recovery was calculated for each analyte (Table 4). All the certified elements, which included major elements at 100s of mg/L (ppm) and trace elements at levels as low as 10 µg/L (ppb), gave recoveries within ±10%. Not all the analytes have certified values in every reference material, so blank cells in Table 4 indicate the absence of a certified value.

Table 5. Matrix Spike (MS)/Matrix Spike Duplicate (MSD) spike concentration recoveries and relative percent difference (RPD) for 2x diluted Soil A CRM.

	Soil A Conc (µg/L)	Soil A MS (µg/L)	Soil A MSD (µg/L)	Soil A MS Recovery (%)	Soil A MSD Recovery (%)	RPD MS/MSD (%)
9 Be	0.18	92.1	90.8	92	91	1.1
51 V	47.4	156	158	108	111	2.7
52 Cr	1.38	104	107	102	105	2.9
55 Mn	52.0	156	163	104	111	6.5
59 Co	1.09	96.8	94.2	96	93	3.2
60 Ni	157	264	268	107	112	4.6
63 Cu	157	266	266	109	109	0.0
66 Zn	524	691	688	111	109	1.8
75 As	93.1	184	184	91	91	0.0
78 Se	4.41	99.7	98.6	95	94	1.1
95 Mo	0.10	100	97.8	100	98	2.0
107 Ag	0.25	97.2	91.3	97	91	6.4
111 Cd	1.43	103	102	101	101	0.0
121 Sb	16.5	119	120	103	104	1.0
201 Hg	0.01	2.06	2.08	102	103	1.0
205 Tl	0.03	103	103	103	103	0.0
Pb*	203	304	302	101	99	2.0
232 Th	48.9	152	153	104	104	0.0
238 U	4.82	107	108	102	103	1.0

All analytes were spiked at 100 µg/L, apart from Zn at 150 µg/L and Hg at 2 µg/L.

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

Matrix spike recoveries

Matrix Spike (MS), Matrix Spike Duplicate (MSD), and relative percent difference (RPD) results for 2x diluted Soil A are given in Table 5. Soil A contains Na, Mg, Al, P, K, Ca, Fe, and Ba at a higher concentration than the 100 µg/L spike amount, so no spike recoveries are given for these elements. However, the CRM recovery results for Soil A in Table 4 show that all these major elements can be analyzed with good accuracy. Recoveries for the other elements were mostly within ±10% of the spike level and the RPD between MS and MSD was less than 10%, demonstrating the accuracy of the method.

Automatic maintenance alerts

Analyzing complex samples such as soil and sediment digests can be tough on the sample introduction system of an ICP-MS. To maximize analytical performance and minimize unplanned instrument downtime, it can be beneficial to schedule routine maintenance tasks by the number of solutions measured rather than time. With ICP-MS MassHunter, an analyst can accept the default, sample-type specific counters to monitor instrument usage and trigger early maintenance feedback (EMF) alerts. Alternatively, EMF counters based on sample number or elapsed time, can be customized for the lab's specific workload. The ISIS 3 discrete sampling system reduces the sample matrix reaching the cones, allowing those counters to be set to higher values.

An example of the EMF display is shown in Figure 3. Performing maintenance at the right time, not too often or too infrequently, can save the analyst time by preventing unnecessary work and maintaining instrument performance. The clear EMF traffic light color-coded alerts help analysts to optimize their maintenance schedule.

As well as the normal prerun performance check, a post-run check can be scheduled to run after the sample sequence has completed. This performance check gives analysts a clear indication if they need to perform routine maintenance tasks such as cleaning the cones before the next run, making scheduling maintenance easier.

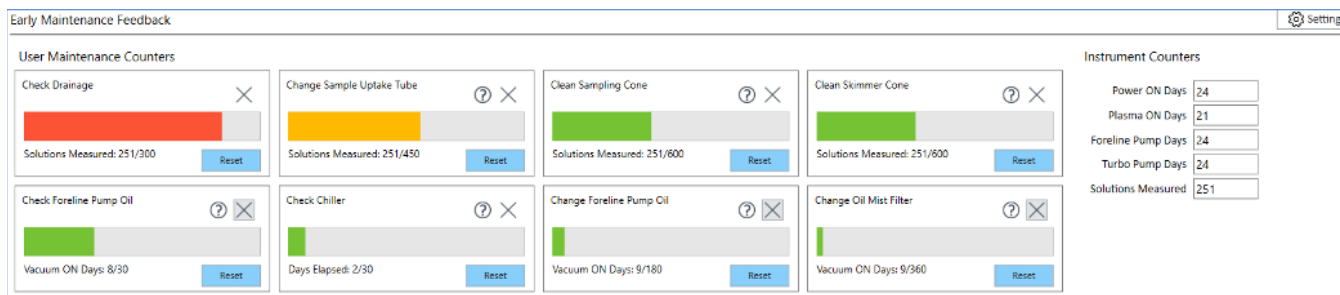


Figure 3. To maintain peak ICP-MS performance, EMF prompts analysts to perform maintenance such as cleaning the interface cones, adjusting or replacing the pump tubing, etc., after a specified time or after a set number of samples have been analyzed.

Conclusion

The Agilent 7850 ICP-MS with ISIS 3 discrete sampling system was used successfully for the high throughput analysis of multiple elements in soil and sediment samples.

Analyzing samples with high matrix levels by ICP-MS can lead to signal drift, suppression, and polyatomic and doubly-charged ion interferences. This study shows the matrix tolerant plasma of the 7850 ICP-MS, He collision mode, and ICP-MS MassHunter software functions address these issues and provide an optimized analytical workflow.

- Many of the method and instrument settings were loaded using a preset method and autotune, saving the analyst time and preventing errors during method development.
- The 7850 uses a robust plasma (low CeO/Ce) that provides optimum matrix tolerance when analyzing high matrix soil digests over many hours, as shown by the ISTD stability results. Instrument stability is important for the productivity of routine, high throughput applications, as it reduces drift, QC failures, sample reanalysis, and maintenance.
- IntelliQuant data can be used to verify the TMS of the samples, information that is useful for optimizing sample preparation and selecting plasma conditions for new and unknown sample types.
- As soil samples can contain a significant concentration of REEs, automatic half mass mode and M^{2+} correction was used for the measurement of As and Se. The automated routine simplifies the method for the analyst, saving time compared to manually correcting for doubly-charged ion interferences.
- All certified elements measured in the five sediment and soil CRMs were within $\pm 10\%$ and matrix spikes were mostly within $\pm 10\%$. These results demonstrate the effective control of polyatomic interferences of the ORS⁴ in helium mode. Getting the right answer first time avoids the need to remeasure samples, which can be a significant burden for routine laboratories that use analytical techniques with less reliable control of spectral overlaps.

- The EMF sensors and counters and post-run performance check help maintain instrument performance by alerting the analyst when maintenance is needed. These functions reduce unnecessary maintenance, avoid instrument downtime, and further improve productivity.

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