

# Productive Analysis of High Matrix Samples using ICP-MS with Advanced Dilution System

Autodilution of sediments and soils by Agilent ADS 2 before analysis by Agilent 7850 ICP-MS



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## Introduction

The analysis of high matrix samples like soils and sediments by ICP-MS can be challenging and time-consuming, especially for laboratories with a high sample load. The multi-element measurement capability of ICP-MS means that analysts can quantify many elements in a sample. However, determining a large suite of elements typically requires the analyst to prepare multiple suitable calibration standards for those elements. Also, given the complexity and high total solids content of some environmental samples, a lot of analyst time is needed to prepare the samples for analysis. Once prepared, analysts may need to further dilute the samples to ensure that all elements are being measured within the calibration range, which takes more time and resources, and disrupts the analytical workflow.

To reduce the analyst's workload, Agilent ICP-MS (and ICP-OES) instruments can be fitted with the new Agilent Advanced Dilution System (ADS 2), which is a preconfigured, two-syringe modular dilution system that includes an Advanced Valve System for ICP-MS (AVS MS\*)<sup>1</sup>. The ADS 2 enables analysts to easily perform three important time-saving functions, reducing turnaround time on sample results and lowering the cost-per-analysis:

- Automatically prepare a multipoint calibration from single stock standards. Automating the preparation of calibration standards eliminates time-consuming work and minimizes the potential for errors associated with manual operations.
- Automatically dilute samples by a prescribed factor, eliminating the need for manual dilution and reducing the risk of contamination.
- Automatically perform intelligent reactive dilution for targeted analytes when results are out of the calibration range or when the internal standard (ISTD) elements exhibit suppression or enhancement, even during unattended operation.<sup>2,3</sup>

The ADS 2 complements the already high performance characteristics of Agilent ICP-MS instruments and Agilent ICP-MS MassHunter for the analysis of high matrix samples including soils. These sample types can cause issues for ICP-MS such as signal drift, suppression, and polyatomic and doubly-charged ion ( $M^{2+}$ ) interferences. However, as previous studies have shown,<sup>4</sup> the Agilent 7850 ICP-MS can overcome these challenges using various hardware and software functions, including:

- Robust operating conditions (low CeO/Ce ratio) that provide optimum matrix tolerance when analyzing high matrix soil samples, minimizing drift and reducing the frequency of routine maintenance.

- Ultra High Matrix Introduction (UHMI) technology to increase overall matrix tolerance of the ICP-MS. UHMI enables samples with high and variable matrix levels to be measured, without requiring sample-specific dilutions, or matrix matching of the calibration standards.
- AVS MS – previously known as ISIS 3. The seven-port AVS MS reduces the time that the sample matrix is introduced into the instrument, providing superior stability, minimizing quality control (QC) errors, and reducing system maintenance.
- Octopole Reaction System (ORS<sup>4</sup>) helium (He) collision mode to control common spectral interferences by Kinetic Energy Discrimination (KED), ensuring data accuracy.
- Automatic  $M^{2+}$  correction to improve data accuracy for elements such as arsenic and selenium.
- Early Maintenance Feedback (EMF) sensors and counters and post-run performance checks that help maintain instrument performance by alerting the analyst when maintenance is needed. These functions reduce unnecessary maintenance, avoid instrument downtime, and further improve productivity.

As shown in Figure 1, the ADS 2 is positioned between the Agilent SPS 4 autosampler and the AVS MS of the 7850 ICP-MS. The system is fully integrated, operated, and controlled by the ICP-MS MassHunter software. The ADS 2 uses two syringes and four valves to direct the flow of sample, diluent, and carrier to where it is required. This design ensures the benefits of fast sample uptake and high sample throughput are maintained when samples do not require dilution.



**Figure 1.** Agilent 7850 ICP-MS with integrated AVS MS (right), Agilent ADS 2 autodilutor (middle), and Agilent SPS 4 autosampler (left).

\*AVS MS formerly called ISIS 3.

In this study, the 7850 ICP-MS fitted with the ADS 2 was used to measure 26 elements in representative high matrix environmental samples. The method was developed using the Method Wizard function of ICP-MS MassHunter. The accuracy of the autocalibration, automatic prescriptive dilution of samples, and long-term stability of the 7850 ICP-MS with the ADS 2 was evaluated throughout the analysis of solutions comprising a river sediment certified reference material (CRM), a spiked solution, and repeat measurements of digested soil samples.

## Experimental

### Instrumentation

A 7850 ICP-MS equipped with the standard UHMI system and ORS<sup>4</sup> cell was used for the analysis. Automated sample introduction was performed using an SPS 4 autosampler, ADS 2, and AVS MS. The 7850 ICP-MS was fitted with a standard MicroMist nebulizer, Scott-type spray chamber, and one-piece quartz torch with 2.5 mm id injector. The interface consisted of a nickel-plated copper sampling cone and a nickel skimmer cone. The ADS 2 was fitted with a 1.50 mL, 1.00 mm internal diameter (id) loop. The ORS<sup>4</sup> uses a small cell volume and octopole ion guide for optimum performance in He collision mode. He mode reduces the transmission of all polyatomic ions by KED, minimizing errors due to common matrix-based polyatomic interferences. An enhanced, high energy He mode (HEHe mode) is also available to deal with overlaps from high-intensity background species such as Ar<sub>2</sub> on Se at *m/z* 78, N<sub>2</sub> on <sup>28</sup>Si, and NO/NOH on <sup>31</sup>P. The 7850 ICP-MS in HEHe mode reduces the intensity of the interferences without the need to use a reactive cell gas in the ORS<sup>4</sup>, such as O<sub>2</sub>, H<sub>2</sub>, or NH<sub>3</sub>. Avoiding reactive cell gases not only simplifies the operation of the 7850 ICP-MS but ensures that no new molecular interferences are formed in the cell through interaction of analyte ions with the cell gas. Using only He-based modes therefore improves data quality, particularly for multi-element analysis of complex sample matrices. In this work, 25 elements were measured in He mode, and Se was measured in HEHe mode.

To create an analytical method quickly and easily, the Method Wizard within the Agilent ICP-MS MassHunter software was used. The Method Wizard guides users through a series of questions to select analytes and internal standard elements (often using predefined lists and Agilent solution part numbers). For this application “UHMI-4” preset conditions were selected, which provides robust plasma conditions (low CeO<sup>+</sup>/Ce<sup>+</sup> ratio).

The ICP-MS MassHunter software also includes IntelliQuant, which can perform a full mass-spectrum scan of a sample, requiring two seconds measurement time.<sup>5</sup> Acquiring quick scan data of unknown samples using IntelliQuant is a simple way to identify and semiquantify any REEs in the samples. If REEs such as Nd, Sm, Gd, and Dy are present in a sample at a high enough concentration, M<sup>2+</sup> interferences can affect the accuracy of the measurement of elements such as As and Se. The IntelliQuant data presented as a periodic table heat map in Figure 2, shows the presence of Nd, Gd, and Dy in a soil sample so “REE<sup>2+</sup> Correction” was selected in the Method Wizard.

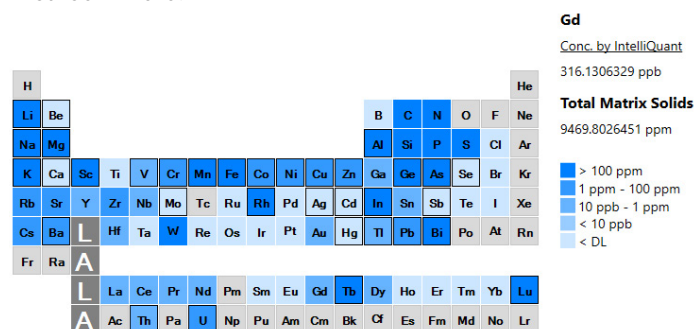


Figure 2. IntelliQuant heat map for a soil sample.

The REE<sup>2+</sup> Correction software routine automatically sets all the parameters needed for the correction of M<sup>2+</sup> interferences, making it fast to set up and easy to use. The parameters include which masses to measure, peak resolution (narrow peak mode), and correction equations. In this method, REE<sup>2+</sup> correction was applied to the measurement of <sup>75</sup>As and <sup>78</sup>Se to correct the contribution from REE<sup>2+</sup> ions, and for <sup>66</sup>Zn to correct for <sup>132</sup>Ba<sup>++</sup>.

The autotune function of ICP-MS MassHunter was used to automatically optimize ion lenses. The autotune software optimizes counts for <sup>7</sup>Li, <sup>89</sup>Y, and <sup>205</sup>Tl in the tuning solution.

The parameters in the shaded rows in Table 1 were predefined in the preset method and lens voltages were autotuned. Operating conditions for the ADS 2 are shown in Table 2.

**Table 1.** Agilent ICP-MS 7850 operating parameters.

	He Mode	HEHe Mode
Plasma Mode	UHMI-4	
RF Power (W)	1600	
Carrier Gas Flow (L/min)	0.8	
Dilution Gas Flow (L/min)	0.15	
Spraychamber temp (°C)	2	
Sampling Depth (mm)	10	
Lens Tune	Autotune	
Cell Gas Flow (mL/min)	4.3	10
Energy Discrimination (V)	5	7
Number of Elements	25	Se

The shaded parameters are defined automatically using UHMI.

**Table 2.** Agilent AVS and ADS 2 sample introduction parameters.

Phase	Time (s)	AVS MS Uptake Pump Speed (%)	Autosampler Needle Position	Valve Position
Sample Load	10	80	Sample	Load
Stabilize	10	10	Rinse port	Inject
Probe Rinse	30	10	Rinse port	Inject
Probe Rinse 1	30	10	Rinse port	Inject
Probe Rinse 2	0	0	Rinse port	Inject
Rinse 3	0	0	Rinse port	Inject
Optional Loop Probe Wash	0	0	Rinse port	Inject
Optional Loop Wash	0	0	Rinse port	Inject

The 7850 was fitted with standard Agilent peristaltic pump tubing, white-white for sample and orange-blue for the internal standard. The internal standard comprised a 2 mg/L solution made from Agilent internal standard mix containing <sup>6</sup>Li, Sc, Ge, Rh, In, Tb, Lu, and Bi (100 mg/L, part number 5188-6525) the solution was diluted ~15x online into the sample.

## Reagents

All solutions (carrier, diluent, rinse, internal standard, and calibration standards) were prepared using 1% nitric acid (HNO<sub>3</sub>).

## Automatic preparation of calibration standards by ADS 2

Three calibration standard stock solutions were prepared from Agilent standards including Environmental Calibration Solution (p/n 5183-4688) and single-element standards for Al (1000 mg/L, p/n ICP-013) and Hg (10 mg/L, p/n 5190-8575). A 100 µg/L Hg solution was prepared from the Hg stock solution in 1% HNO<sub>3</sub> and 18 MΩ de-ionized (DI) water (Millipore). The calibration curves were automatically made from the three stock standards using the ADS 2, by diluting them at 200x, 100x, 50x, and 10x. The dilution parameters and calibration range of each element are listed in Table 3.

## Reference material

The calibration and the accuracy of the method were evaluated by analyzing River Sediment B (High Purity Standards, USA)—a CRM that was developed to simulate a river sediment sample. The CRM contained most elements required for this application, apart from Ag, Be, Hg, and Mo. So, known amounts of certified single element solutions of each of these elements were spiked into the CRM.

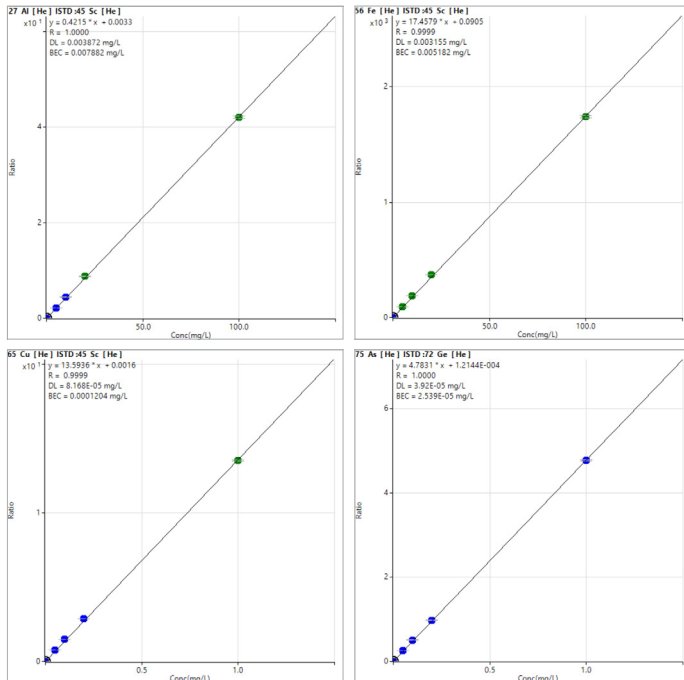
**Table 3.** Agilent ADS 2 autodilution factors applied to the three stock solutions to prepare the calibration curves. All units mg/L.

Stock Solution	Original Concentration	200x	100x	50x	10x (*Al 20x)
Ag, As, Ba, Be, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sb, Se, Th, Ti, U, V, Zn	10	0.05	0.1	0.2	1
Ca, Fe, K, Mg, Na	1000	5	10	20	100
Hg	0.1	0.0005	0.001	0.002	0.01
Al	1000	5	10	20	*50

## Results and discussion

### Calibration

ADS 2 autocalibration was used to prepare four-point curves for all elements listed in Table 4. All curves showed excellent linearity, with calibration coefficients greater than 0.9995. Representative calibration curves for Al, Fe, Cu, and As are shown in Figure 3.



**Figure 3.** Calibration curves for Al, Fe, Cu, and As using standards that were auto-prepared from stock solutions using the Agilent ADS 2 at 200x to 10x dilution.

### Detection limits

Typical 7850 ICP-MS instrument detection limits (IDLs) calculated from the ICP-MS MassHunter calibrations are shown in Table 4. The IDLs were calculated as three sigma of 10 measurements of a blank solution.

**Table 4.** Agilent 7850 ICP-MS detection limits.

Element	Mode	ISTD	IDL (µg/L)
9 Be	He	<sup>45</sup> Sc	0.17
23 Na	He	<sup>45</sup> Sc	7.7
24 Mg	He	<sup>45</sup> Sc	1.4
27 Al	He	<sup>45</sup> Sc	1.3
39 K	He	<sup>45</sup> Sc	8.9
44 Ca	He	<sup>45</sup> Sc	7.1
51 V	He	<sup>72</sup> Ge	0.012
52 Cr	He	<sup>72</sup> Ge	0.14
55 Mn	He	<sup>72</sup> Ge	0.044
56 Fe	He	<sup>72</sup> Ge	0.14
59 Co	He	<sup>72</sup> Ge	0.086
60 Ni	He	<sup>72</sup> Ge	0.031
63 Cu	He	<sup>72</sup> Ge	0.016
66 Zn	He	<sup>72</sup> Ge	0.052
75 As	He	<sup>72</sup> Ge	0.024
78 Se	HEHe	<sup>72</sup> Ge	0.14
95 Mo	He	<sup>115</sup> In	0.0031
107 Ag	He	<sup>115</sup> In	0.070
111 Cd	He	<sup>115</sup> In	0.0074
121 Sb	He	<sup>115</sup> In	0.0076
137 Ba	He	<sup>115</sup> In	0.0097
202 Hg	He	<sup>209</sup> Bi	0.052
205 Tl	He	<sup>209</sup> Bi	0.15
Pb*	He	<sup>209</sup> Bi	0.052
232 Th	He	<sup>209</sup> Bi	0.0028
238 U	He	<sup>209</sup> Bi	0.0022

\*Pb data is based on the sum of the 206, 207 and 208 isotopes.

## Spike recoveries

To represent the typical elemental content of soil, a sample was prepared by spiking known amounts of the analytes into a 1% HNO<sub>3</sub> solution. This spiked solution, which was made at a concentration applicable to soil analysis, was diluted 10x using the prescriptive dilution function of the ADS 2 during analysis. Table 5 shows the expected and measured concentrations of the spikes, and recoveries for all analytes. Recoveries for most elements fell within ±10%, while recoveries for all elements were within ±15% of the expected values. This evaluation of the 7850 ICP-MS method using a relatively high, but simple synthetic standard confirmed the calibration.

**Table 5.** Spike recovery results for a spiked solution that was automatically diluted using the Agilent ADS 2. The data has been corrected for dilution following a prescriptive 10x autodilution by the ADS 2.

Element	Expected Concentration (mg/L)	Average Measured Conc (mg/L) (n=10)	Recovery (%)
9 Be	0.01	0.00981	98
23 Na	100	105	105
24 Mg	100	105	105
27 Al	500	517	103
39 K	150	159	106
44 Ca	250	253	101
51 V	0.5	0.502	100
52 Cr	7.5	7.71	103
55 Mn	7.5	7.57	101
56 Fe	400	399	100
59 Co	0.2	0.201	101
60 Ni	1	1.04	104
63 Cu	2.5	2.67	107
66 Zn	5	5.25	105
75 As	0.5	0.521	104
78 Se	0.1	0.103	103
95 Mo	1	1.04	104
107 Ag	0.05	0.0543	109
111 Cd	0.05	0.0555	111
121 Sb	0.2	0.205	103
137 Ba	2	2.08	104
202 Hg	0.004	0.00391	98
205 Tl	0.1	0.0967	97
Pb*	5	5.02	100
232 Th	0.05	0.0526	105
238 U	0.05	0.0515	103

\*Pb data is based on the sum of the 206, 207 and 208 isotopes.

## Prescriptive dilution of samples using the ADS 2

To evaluate the prescriptive dilution function of the ADS 2 and the accuracy of the method, the autodilution system was used to perform a 25x dilution of the River Sediment B CRM before analysis. Results for the certified elements and additional spiked elements (Be, Mo, Ag, and Hg) are shown in Table 6. All elements were measured within ±15% of the expected concentration, demonstrating the effectiveness of the ADS 2 for the automatic dilution of a high matrix river sediment sample.

**Table 6.** Measured concentrations and recoveries of certified elements in the River Sediment CRM acquired by the Agilent 7850 ICP-MS (n = 3). The data has been corrected for dilution following a prescriptive 25x autodilution by the Agilent ADS 2.

Element	River Sediment B		
	Expected Concentration (mg/L)	Average Measured Conc (mg/L) (n=10)	Recovery (%)
9 Be	**0.1	0.094	94
23 Na	50	53.6	107
24 Mg	120	131	109
27 Al	600	625	104
39 K	200	205	104
44 Ca	300	308	103
51 V	1	1.01	101
52 Cr	15	15.9	106
55 Mn	6	6.25	104
56 Fe	400	429	107
59 Co	0.15	0.152	101
60 Ni	0.5	0.534	107
63 Cu	1	1.1	110
66 Zn	5	5.36	107
75 As	0.2	0.211	105
78 Se	0.01	0.0104	104
95 Mo	**1	1.03	103
107 Ag	**0.05	0.054	108
111 Cd	0.03	0.0326	109
121 Sb	0.04	0.042	105
137 Ba	4	4.12	103
202 Hg	**0.06	0.0596	99
205 Tl	0.01	0.00952	95
Pb*	2	2.04	102
232 Th	0.1	0.092	92
238 U	0.03	0.0266	89

\*Pb data is based on the sum of the 206, 207 and 208 isotopes.

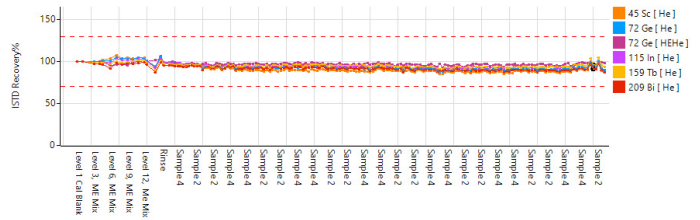
\*\*Since no certified values are provided for Be, Mo, Ag, and Hg, the elements were manually spiked into the CRM at a relevant concentration.

### Long-term stability

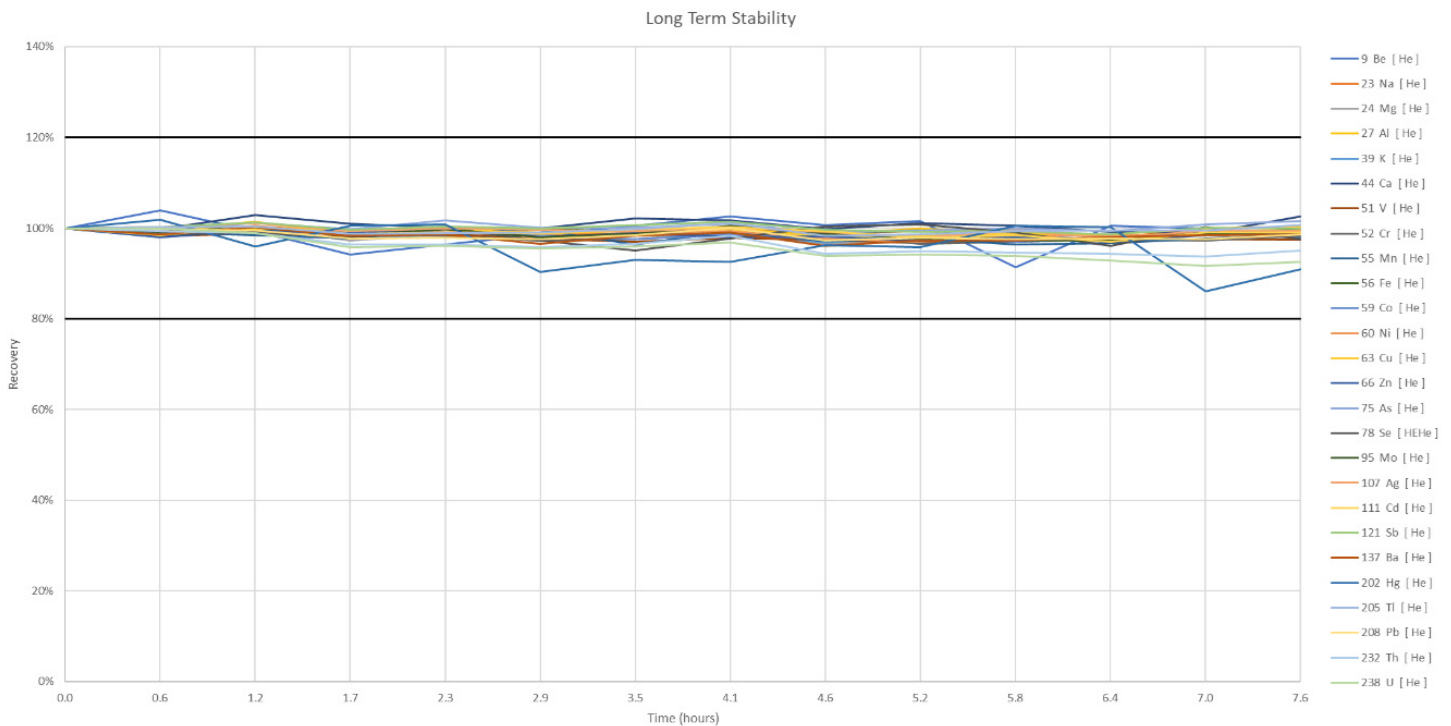
The 7850 ICP-MS analyzed 144 digested soil samples over a period of 7.6 hours, with a QC solution inserted after every 10 samples. The QC solution was prepared in 1% HNO<sub>3</sub> from different batches of the three solutions used to make the calibration standards. The concentration of the elements was as follows: Al, Ca, Fe, K, Mg, Na at 50 mg/L, other elements at 0.5 mg/L, apart from Hg at 0.003 mg/L.

The digested soil samples and QC solution were autodiluted 15 and 5 times respectively by the ADS 2 to bring them into a suitable range for the ICP-MS calibration. Figure 4 shows the internal standard stability graph and Figure 5 shows the QC solution stability plot over the extended batch.

The stability data demonstrates the robustness and stability of the ICP-MS method and confirms the ability of the ADS 2 to perform accurate and repeatable dilutions. All elements reported an RSD of less than 3.5% over 7.6 h, except for Hg, which reported an RSD of 5.4%. This deviation can be attributed to the low concentration (0.6 µg/L) of Hg in solution.



**Figure 4.** ISTD stability during the analysis of 144 soil digests, which were autodiluted 15x using the Agilent ADS 2. ISTD recoveries were normalized to the calibration blank for all samples. The red dotted lines show the ±25% control limits.



**Figure 5.** Recoveries of the 5x diluted QC solution measured during the analysis of 144 soil digests over 7.6 hours. The solid lines show the ±20% control limits.

## Conclusion

The study has shown that the Agilent Advanced Dilution System (ADS 2) can automatically calibrate the Agilent 7850 ICP-MS using a series of online dilutions of calibration stock solutions. The ADS 2 also performed time-consuming prescriptive dilutions of high matrix samples to ensure that all element concentrations were within the range of the calibration.

The accuracy of the autodilution capabilities of the ADS 2 were assessed over a wide range, including with the auto preparation of calibration points between 200x and 10x, and sample measurements between 25x and 5x. This range shows the flexibility of the ADS 2 to speed up critical tasks and reduce the need for labor-intensive manual dilutions. If samples do extend past the linear range of the calibration after dilution, the ADS 2 will automatically dilute the samples using reactive dilution mode.

The 7850 ICP-MS with UHMI technology operates with a robust plasma (low CeO<sup>+</sup>/Ce<sup>+</sup> ratio) providing confidence that the instrument can analyze high matrix samples and reduce remeasurements due to drift. The excellent ISTD and QC stability results show the suitability of the method for routine analysis of soils over an extended run of 7.6 h, without any loss of sensitivity.

IntelliQuant data was used to assess elements that are not included in the quantitative method, such as REEs. Agilent ICP-MS MassHunter applied automated corrections for doubly charged REE ion interferences that impede the measurement of As and Se. This automated routine saves time compared to manually correcting for doubly-charged ion interferences.

## References

1. Agilent Advanced Dilution System (ADS 2) – Technical overview, Agilent publication, [5994-7211EN](#)
2. Yamashita, R., Automated Analysis of Low-to-High Matrix Environmental Samples Using a Single ICP-MS Method, Agilent publication, [5994-7114EN](#)
3. Zou, A.; Yamanaka, M., Intelligent Analysis of Wastewaters using an Agilent ICP-MS with Integrated Autodilutor, Agilent publication, [5994-7113EN](#)
4. Kubota, T., Routine Analysis of Soils using ICP-MS and Discrete Sampling, Agilent publication, [5994-2933EN](#)
5. Agilent IntelliQuant for ICP-MS, Agilent publication, [5994-2796EN](#)

## Consumables list

Product Type	Agilent Part Number	Description
Sample Loop for ADS 2 /AVS MS	5005-0425	1.50 mL 1.00 mm ID 1/pk
Bottle Kits	5005-0435	Diluent/Carrier 6 L bottle kit, includes a 6 L can, GL45 StaySafe cap, fittings, and venting valve
	5005-0436	Diluent 2 L PFA bottle kit for ICP-MS, includes 2 L PFA bottle, GL45 StaySafe cap, fittings, and venting valve
	5005-0437	Waste container kit, includes a 10 L waste can, S60 StaySafe cap, fittings, and acid vapor filter
AVS MS Tubing Kit	G8411-68202	AVS MS preconfigured kit
ADS 2 Tubing Kits	5005-0106	ADS 2 tubing kit, Valve C setup, 2/pk
	5005-0107	ADS 2 tubing kit, Valve C – AVS MS Pump, 1/pk
	5005-0182	ADS 2 tubing kit, Valve C – AVS MS Valve, 1/pk
	5005-0102	ADS 2 tubing kit, Valve B setup, 4/pk
	5005-0103	ADS 2 tubing kit, Valve A – Valve C, 1/pk
	5005-0105	ADS 2 tubing kit, Carrier/Diluent, 2/pk
	G8457-68004	ADS 2 tubing kit, Valve A – AVS MS Valve, 1/pk

[www.agilent.com/chem/7850icp-ms](http://www.agilent.com/chem/7850icp-ms)

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