Application Note

Environmental

Agilent

Trusted Answers

Intelligent Analysis of Wastewaters using an Agilent ICP-MS with Integrated Autodilutor

Improved productivity of routine environmental analyses using an Agilent 7900 ICP-MS with Advanced Dilution System

Authors

Aimei Zou, Michiko Yamanaka

Agilent Technologies, Inc.

Introduction

Inductively Coupled Plasma Mass Spectrometry (ICP-MS) is a versatile multi-elemental analysis technique that is widely used across various sectors due to its high sensitivity and selectivity. Many environmental, food, pharmaceutical, and material testing laboratories that rely on high-throughput methods have benefited from the robustness, reliability, and high performance of Agilent ICP-MS instruments. As laboratories look to further reduce inefficiencies in their workflows and lower demands on staff, there is a shift towards automating manual tasks to improve overall productivity.

Because of its high sensitivity, the concentrations of elements in ICP-MS standard solutions are normally low, so many labs prepare fresh standards every day. Preparation of low concentration standards is labor intensive as care is needed to avoid human errors or avoid contaminating the standards. Also, when measuring environmental samples such as wastewater, soils, and sediments, the concentration of target elements sometimes unexpectedly exceeds the calibration range. In these situations, the analyst would have to dilute the sample manually to bring it into range, adding to their workload.

To help labs reduce sample turnaround time and cost-per-analysis, Agilent has developed an Advanced Dilution System, the ADS 2, specifically for Agilent ICP-MS (and ICP-OES) instruments.[1] Laboratories can use the ADS 2 autodilution system for the following important tasks:

- Automatically prepare a multipoint calibration from single stock standards. Automating the preparation of calibration standards eliminates tedious manual work, reduces the potential introduction of human errors, and minimizes the risk of contamination from manual operation.
- Automatically dilute samples by a known (prescribed) factor, eliminating the need for manual dilution.
- Automatically perform intelligent reactive dilution for targeted analytes when results are out of the calibration range even during unattended overnight operation, leading to higher productivity.

These features reduce the analyst's workload, while ensuring that the ICP-MS autodilution method achieves good accuracy and precision for the quantitative measurement of target elements in a sample. The ADS 2 is especially useful for labs that run routine analyses of large numbers of varied samples where the concentrations of the analytes can vary significantly.

Agilent ICP-MS instruments set the performance benchmark for routine environmental sample analysis, due to their high matrix tolerance and advanced collision/reaction cell (CRC) technology. The fourth generation Octopole Reaction System (ORS^4) CRC removes polyatomic interferences that can affect many of the regulated trace elements, such as Cr, As, Se, and Cd, in environmental samples. The ORS^4 provides optimized operating conditions for helium (He) collision mode, which enables the removal of many interferences by kinetic energy discrimination (KED), referred to as He-KED.

In this study, wastewater samples were selected as a representative sample type commonly analyzed by routine environmental testing labs. The Agilent 7900 ICP-MS fitted with the ADS 2 was used to determine 31 elements in wastewater.

Experimental

Samples and standards

Two certified wastewater reference materials (CRMs), including ERM CA713 (IRMM, Belgium) and CWW-TM-C (High Purity Standards, US) were used to check the accuracy of the method. A matrix spike recovery test of actual wastewater samples was also undertaken. The wastewater samples were provided by a local government agency. No pretreatment was required for the wastewater samples before analysis, apart from filtration to remove any undissolved solid matter.

Agilent multi-element and single-element standards were used to prepare a mixed stock solution for autocalibration using the ADS 2. The concentration of each element in the mixed stock solution is shown in Table 1.

Table 1. Agilent standards, part-numbers (p/n), and analyte concentration in the mixed stock solution.

Element	Standard	Concentration in Mixed Stock Solution (ppm)
Na, Mg, K, Ca, Fe	Multi-element standard (p/n: 5183-4688)	20
Be, Al, V, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Sr, Mo, Ag, Cd, Sb, Ba, Tl, Pb, Th, U	Multi-element standard (p/n: 5183-4688)	0.2
B	p/n: 5190-8254	0.2
Sr	p/n: 5190-8581	0.2
Ti	p/n: 5190-8545	0.2
Sn	p/n: 5190-8543	0.2
Te	p/n: 5190-8533	0.2
Hg	p/n: 5190-8575	0.01

Agilent internal standard (ISTD) mix (p/n: 5183-4681) containing 10 ppm each of ^{6}Li, Sc, Ge, Y, In, Tb, and Bi was used. A 100 ppb working solution was prepared by 100x manual dilution and added online to the 7900 ICP-MS via the integrated Advanced Valve System for ICP-MS (AVS MS)* and peristaltic pump. An approximate 15x dilution of the ISTD working solution was obtained using narrow-bore tubing, helping to minimize sample dilution.

*AVS MS formerly called ISIS 3

A solution of 2% HNO_3 (v/v) with 0.5% HCl (v/v) was used for the preparation of the mixed stock solution, diluent, carrier, and ISTD stock. HCl was added to ensure the stability of Ag, Sb, Sn, Te, and Hg in solution. 3% HNO_3 with 0.5% HCl was used as the rinsing solution to thoroughly flush the system between the analysis of different solutions.

The 31 elements listed in Table 1 were autocalibrated by the ADS 2 from the stock standard, using dilution factors of 200x, 100x, 40x, 20x, 10x, 4x, and 2x.

Instrumentation

All analyses were carried out using a 7900 ICP-MS equipped with the standard sample introduction system consisting of a glass concentric nebulizer, quartz spray chamber, and torch (2.5 mm injector diameter). The instrument was fitted with a nickel-plated copper sampling cone and a nickel skimmer cone. Figure 1 shows the instrumentation used in this study.

By selecting General Purpose plasma conditions in the Agilent ICP-MS MassHunter software, the shaded parameters shown in Table 2 were set automatically. The ion lens voltages were also automatically optimized to maximize sensitivity. The 7900 ICP-MS operating conditions and ADS 2 sample introduction parameters are shown in Tables 2 and 3, respectively.

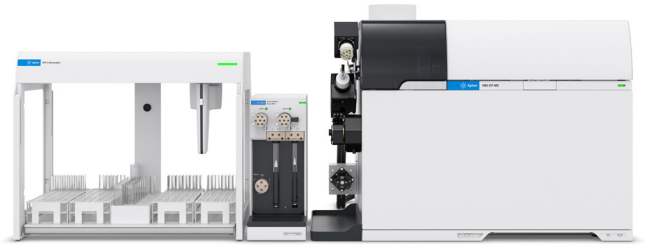

Figure 1. Showing the Agilent 7900 ICP-MS with integrated AVS MS switching valve connected to the Agilent ADS 2 and Agilent SPS 4 autosampler.

Table 2. Agilent 7900 ICP-MS operating conditions.

Parameter	No Gas	He
Plasma Mode	General Purpose	
RF Power (W)	1550	
Sampling Depth (mm)	10	
Nebulizer Gas Flow Rate (L/min)	1.20	
Lens Tune	Autotune	
Cell Gas Flow Rate (mL/min)	0	5
Energy Discrimination (V)	5	

Table 3. Agilent ADS 2 sample introduction parameters.

	Time (s)	AVS MS Uptake Pump Speed (%)	Autosampler Needle Position	Valve Position
Sample Load	20	25	Sample	Load
Stabilize	10	5	Rinse port	Inject
Probe Rinse	15	5	Rinse port	Inject
Probe Rinse 1	5	35	Rinse port	Inject
Probe Rinse 2	20	0	Rinse port	Inject
Rinse 3	1	0	Home	Inject
Optional Loop Probe Wash	10	50	Rinse port	Load
Optional Loop Wash	1	5	Rinse port	Inject

The 7900 ICP-MS with ADS 2 provides valuable benefits for routine laboratories, including:

- Automatic preparation of multilevel calibrations from single or multiple stock standards by up to a factor of 400x dilution. Preparation and analysis of calibration standards can be completed automatically, within 20 minutes, improving lab efficiency.
- Intelligent reactive autodilution of samples if any targeted analytes are measured at concentrations above the calibration range. The diluted sample will be automatically added to the real-time sample list and online analysis data of the diluted sample will be generated accordingly.
- Result-based reactive autodilution of samples with analytes that need different dilution factors due to matrices that contain elements with a range of concentrations.

Results and discussion

Automatic preparation of calibration standards by ADS 2

Calibration performance of the ADS 2 autodilution system was evaluated in terms of linearity, accuracy, and instrument detection limits (IDLs). Representative calibration curves that were automatically created by the 7900 ICP-MS with ADS 2 are shown in Figure 2. The curves cover low to high-mass elements, Be, As, Cd, and Pb. Excellent linearity was obtained for all analytes across the calibration range, as shown by calibration coefficients of $R \geq 0.9995$.

The dilution accuracy achieved by the ADS 2 was evaluated by dividing the calculated concentration of standards prepared using dilution factors from 2 to 200 for all analytes by the expected concentration. The dilution accuracy of each calibration level was within 90 to 110%, demonstrating the high accuracy of the ADS 2 for the automatic preparation of calibration standards.

IDLs were calculated by the ICP-MS MassHunter software based on three replicate measurements of each standard. Low IDLs were obtained for all the analytes across the mass range, for example, 0.001 ppb for ^{52}Cr and ^{75}As, 0.0003 ppb for ^{111}Cd, and 0.0009 ppb for ^{202}Hg. The low-concentration IDLs show the high precision of sample delivery by the ADS 2 coupled with the SPS 4 autosampler. The IDLs also confirm that the sensitivity of the 7900 ICP-MS is not compromised by the ADS 2 autodilution system.

The efficiency of the ADS 2 was assessed based on the time taken for the autocalibration with the total preparation and analysis time of eight calibration levels at less than 20 minutes. Importantly, calibration was fully automated and did not require operator input other than preparing the initial single stock solution.

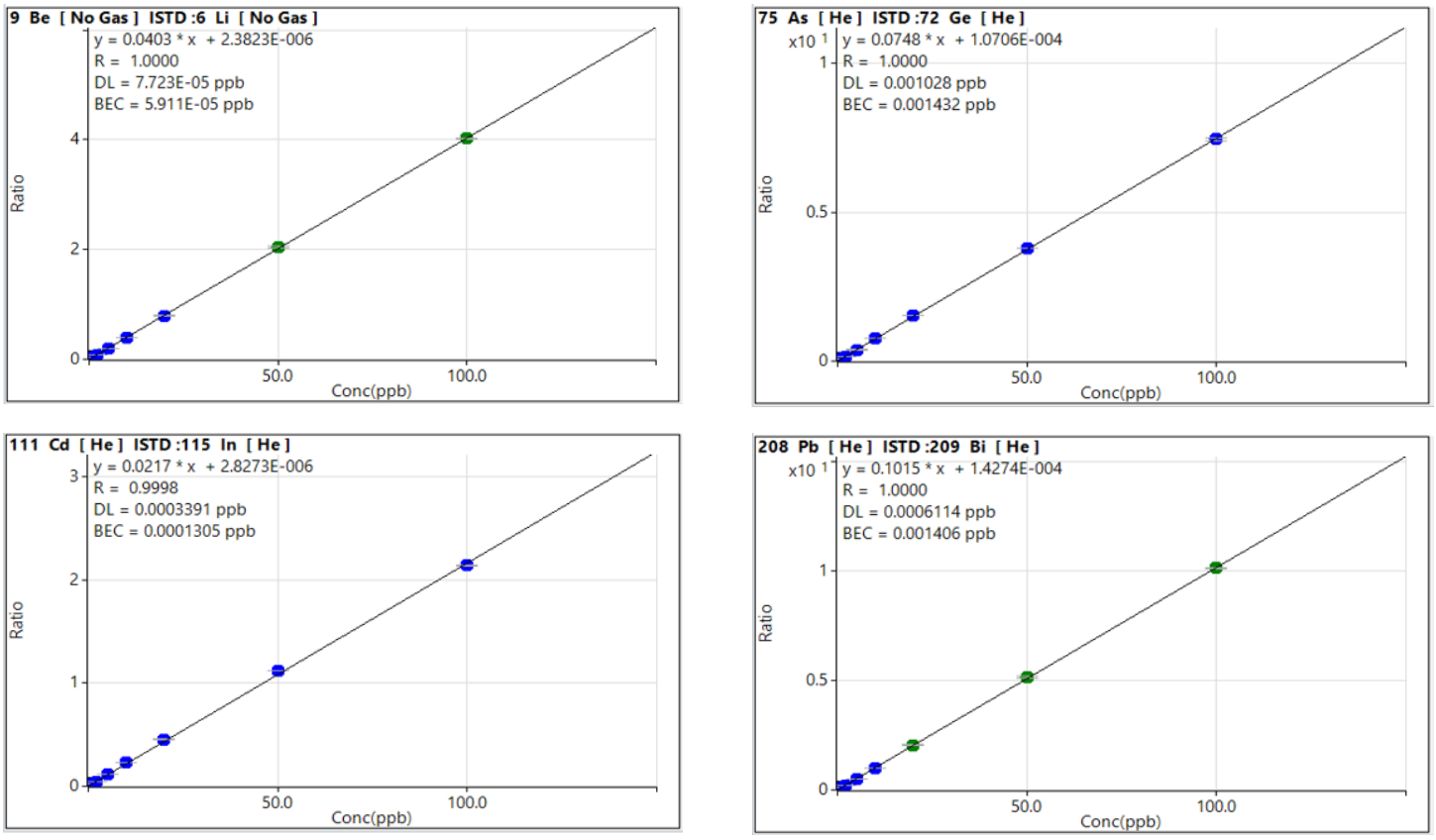

Figure 2. Representative ICP-MS calibration curves for Be, As, Cd, and Pb that were automatically created from a single stock solution by the Agilent ADS 2 fitted to the Agilent 7900 ICP-MS.

Method Detection Limits (MDLs)

MDLs for all 31 elements were determined per guidance provided in EPA Method 200.8.[2] The three sigma MDLs were calculated from the analysis of seven replicate aliquots of a preparation blank (2% HNO_3 with 0.5% HCl) which had been spiked at concentrations of 2 to 5 times the estimated MDL. Beryllium and boron were acquired in no gas mode and the other elements were acquired in He mode. A summary of the MDLs for all analytes is shown in Table 4. Low-level MDLs were achieved for all the trace elements, illustrating the excellent sensitivity of the 7900 ICP-MS with ADS 2 and SPS 4 autosampler.

Table 4. Three sigma method detection limits achieved by the Agilent 7900 ICP-MS fitted with the ADS 2 autodilution system.

Analyte	Mass	Cell Mode	MDL (ppb)
Be	9	No gas	0.0006
B	11	No gas	0.014
Na	23	He	0.30
Mg	24	He	0.25
Al	27	He	0.095
K	39	He	0.82
Ca	44	He	1.4
Ti	47	He	0.032
V	51	He	0.004
Cr	52	He	0.004
Mn	55	He	0.003
Fe	56	He	0.063
Co	59	He	0.001
Ni	60	He	0.018
Cu	63	He	0.006
Zn	66	He	0.022
As	75	He	0.007
Se	78	He	0.11
Sr	88	He	0.005
Mo	95	He	0.002
Ag	107	He	0.002
Cd	111	He	0.002
Sn	118	He	0.006
Sb	121	He	0.003
Te	125	He	0.056
Ba	137	He	0.006
Hg	202	He	0.005
Tl	205	He	0.0006
Pb*	*	He	0.0004
Th	232	He	0.001
U	238	He	0.0003

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

Dilution performance evaluation using CRMs

The two wastewater CRMs (ERM CA713 and CWW-TM-C) were used in this study to evaluate the dilution performance of the ADS 2 in terms of accuracy and recovery. Duplicate aliquots of each CRM were analyzed during the sequence, and the mean concentration and recoveries were calculated for the analytes, as summarized in Table 5.

Initially, the measured concentration of Cu in the undiluted ERM CA713 wastewater CRM was above the calibration range, so the ADS 2 automatically performed a 10x reactive dilution of the sample. The measured concentrations of most of the certified analytes in the CA713 wastewater CRM were excellent—with recoveries of the certified elements ranging from 97 to 103% and within the acceptable (uncertainty) range. Only the measured result for Hg fell slightly outside the acceptable concentration range, but still within ±10%, which is considered acceptable for an external calibration method.[3]

For the CWW-TM-C wastewater CRM, a 10x reactive autodilution by ADS 2 was triggered for all target analytes, as the initial measured concentrations were out of the calibration range. As shown in Table 5, recoveries between 100 and 106% were achieved for all target analytes, confirming the accuracy of the 7900 ICP-MS with ADS 2 autodilution method.

Table 5. Quantitative results for two wastewater CRMs by the Agilent 7900 ICP-MS with ADS 2.

Analyte	ERM-CA713				CWW-TM-C		
	Certified Value (ppb)	Uncertainty (ppb)	Measured Conc. (ppb)	Recovery (%)	Certified Value (ppb)	Measured Conc. (ppb)#	Recovery (%)
9 Be	NA				150	151	101
11 B	NA				500	504	101
27 Al	NA				500	518	104
51 V	NA				500	501	100
52 Cr	20.9	1.3	21.0	100	500	531	106
55 Mn	95	4	93	98	500	527	105
56 Fe	445	27	433	97	500	507	101
59 Co	NA				500	507	101
60 Ni	50.3	1.4	51.6	103	500	512	102
63 Cu	101	7	101#	100	500	526	105
66 Zn	78	NA	77	99	500	529	106
75 As	10.8	0.3	10.5	97	150	158	105
78 Se	4.9	1.1	4.8	98	150	155	103
88 Sr	NA				500	502	100
95 Mo	NA				500	523	105
107 Ag	NA				150	153	102
111 Cd	5.09	0.2	5.24	103	150	152	101
121 Sb	NA				150	153	102
137 Ba	NA				500	512	102
202 Hg	1.84	0.11	1.99	108	10	9.98	100
205 Tl	NA				150	152	102
Pb*	49.7	1.7	51.2	103	500	519	104

*NA=not applicable. *Pb was measured as the sum of the three most abundant isotopes, 206, 207, and 208. # Measured concentrations following 10x reactive autodilution by the ADS 2.*

Dilution performance evaluation using spiked wastewater

A real wastewater sample was also used for the performance evaluation of the ADS 2. Based on the guidelines outlined in EPA Method 6020B,[3] a matrix spike recovery test was performed by taking three replicate readings of three technical preparations of the spiked wastewater. The spike concentrations of each analyte in the wastewater sample are given in Table 6.

As the measured concentration of Na, K, and Ca in the original wastewater was relatively high, a high concentration spike was used. For those elements that were measured above the calibration range, a 10x reactive dilution was carried out automatically by the ADS 2. The quantitative results are summarized in Table 6.

The accuracy of the reactive dilution step was calculated by dividing the measured concentration following 10x reactive dilution of the wastewater by the measured concentration in undiluted wastewater.

As shown in Table 6, recoveries of 97 to 110% were achieved for the analytes with relatively high concentrations in the wastewater sample, including B, Na, Mg, Al, K, Ca, Mn, Fe, Zn, Sr, and Ba. Also, a preparation blank was measured between wastewater samples, and no carryover was detected. This observation indicates that the post-wash (rinse) of the ADS 2 effectively cleaned the system.

For the matrix spike recovery test, most elements recovered within 100 ± 10%, while the recoveries for higher concentration elements, Na, Mg, Ca, Mn, and Zn, ranged from 85 to 88%. The spike recoveries for all analytes met the EPA 6020B requirements of 100 ± 25%, confirming the suitability of the autodilution method. Precision (%RSDs) of the recoveries was ≤4%, demonstrating the excellent reproducibility, stability, and reliability of the 7900 ICP-MS with ADS 2.

Table 6. Quantitative results for a real wastewater sample measured by the Agilent 7900 ICP-MS with ADS 2.

Analyte	Real Wastewater Sample					
	Measured Conc without Dilution (ppb)	Measured Conc with 10x Reactive Dilution (ppb)	Reactive Dilution Accuracy (%)	Spike Concentration (ppb)	Spike Recovery (%)	%RSD (n=3)
9 Be	< MDL	NA		10	109	2.4
11 B	55.4	56.7	102	40	108	3.8
23 Na	42900	47000	109	50000	86	1.3
24 Mg	1360	1490	110	1000	87	1.3
27 Al	12.6	13.1	104	10	92	1.4
39 K	14200	15300	108	25000	93	1.0
44 Ca	14600	15200	104	25000	85	0.4
47 Ti	0.37	NA		10	96	1.0
51 V	0.28	NA		10	93	1.0
52 Cr	0.23	NA		10	92	1.0
55 Mn	19.7	21.5	109	10	85	2.0
56 Fe	60.1	58.2	97	1000	93	0.5
59 Co	0.07	NA		10	98	0.3
60 Ni	1.21	NA		10	93	0.3
63 Cu	5.57	NA		10	94	1.0
66 Zn	23.1	22.6	98	10	88	1.5
75 As	2.27	NA		10	104	0.2
78 Se	0.31	NA		10	109	1.7
88 Sr	32.7	34.3	105	20	100	1.5
95 Mo	0.38	NA		10	98	0.4
107 Ag	0.03	NA		10	106	2.3
111 Cd	0.01	NA		10	104	0.5
118 Sn	0.26	NA		10	96	0.5
121 Sb	0.40	NA		10	103	0.3
125 Te	< MDL	NA		10	112	1.7
137 Ba	15.2	15.41	102	10	95	2.5
202 Hg	0.03	NA		0.5	97	0.6
205 Tl	0.01	NA		10	100	0.1
Pb*	0.02	NA		10	100	0.1
232 Th	0.01	NA		10	96	0.7
238 U	0.001	NA		10	98	0.5

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

Long-term stability

The long-term stability of the 7900 ICP-MS with ADS 2 autodilution system was investigated based on recoveries of the continuing calibration verification (CCV) and ISTDs. The CCV standard was prepared by the ADS 2, which diluted a mixed stock solution by a factor of 20. The mixed stock solution was the same as the one used to prepare the calibration standards. The CCV standard comprised 1 ppm Ca, Na, Mg, K, and Fe, 0.5 ppb Hg, and 10 ppb for all other elements, which was equivalent to the level 5 calibration standard. The CCV standard was measured after every 10 wastewater samples over more than eight hours. Recoveries of all analytes for all 14 measurements of the CCV were calculated and presented as a stability plot, as shown in Figure 3. All recoveries were within 100 ± 10%, meeting the EPA 6020 criteria and demonstrating the stability of the 7900 ICP-MS with ADS 2 over a continuous run of more than eight hours.

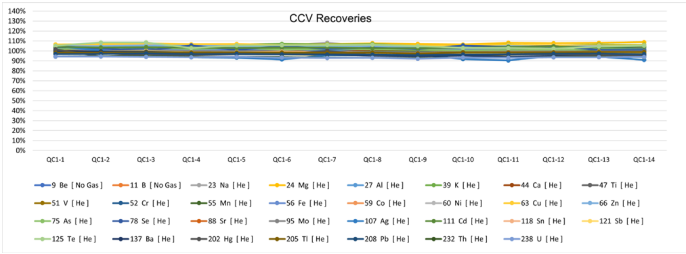

Figure 3. CCV recoveries over more than eight hours of continuous measurement of wastewater samples.

ISTD stability was also monitored over the same batch of samples for more than eight hours. As shown in Figure 4, ISTD recoveries were within 100 ± 20%, showing the excellent robustness and matrix tolerance of the 7900 ICP-MS. The stability tests confirm that the ICP-MS autodilution method can perform long analytical runs that are typical of routine laboratories.

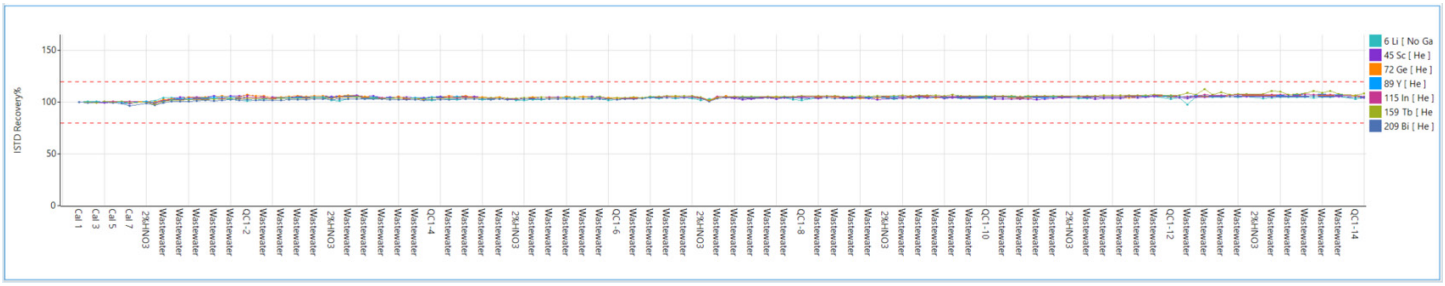

Figure 4. ISTD stability over more than eight hours of measurement of wastewaters. The red dotted lines show the ±20% control limits.

Conclusion

The analytical performance of the Agilent 7900 ICP-MS fitted with the Agilent ADS 2 autodilutor was evaluated for calibration accuracy, recovery of certified elements in two wastewater CRMs, and a matrix spike test of real wastewater.

The ADS 2 autocalibration demonstrated excellent linearity for the entire elemental suite. Quantitative results for the two wastewater CRMs and spiked wastewater sample met the EPA method acceptable criteria for recoveries, following reactive dilution by the ADS 2. The recovery tests confirmed the accuracy of the 7900 ICP-MS method and the intelligent dilution capabilities of the ADS 2 system.

The robustness and reproducibility of the autodilution method over more than eight-hours of continuous measurements was demonstrated by the recoveries of CCVs and ISTDs within the limits specified in EPA method 6020.

The fully integrated Agilent ICP-MS autodilution system offers laboratories a fast, intelligent, and durable automated protocol for the day-to-day analysis of a wide variety of sample types. Through the automation of some labor-intensive tasks, such as preparation of calibration standards, sample dilution, and dilution of overrange samples, laboratories can shorten sample turnaround times, resulting in long-term productivity gains.

References

1. Agilent Advanced Dilution System (ADS 2) – Technical overview, Agilent publication, 5994-7211EN
2. EPA Method 200.8 Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma-Mass Spectrometry, Revision 5.4, EMMC Version, accessed January 2024, EPA Method 200.8: Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma-Mass Spectrometry | US EPA
3. EPA Method 6020B Inductively Coupled Plasma-Mass Spectrometry (ICP-MS), Revision 2, July 2014, accessed January 2024, EPA Method 6020B (SW-846): Inductively Coupled Plasma - Mass Spectrometry | US EPA

Related information

Yamashita, R., Automated Analysis of Low-to-High Matrix Environmental Samples Using a Single ICP-MS Method, Agilent publication, 5994-7114EN

Riles, P., Productive Analysis of High Matrix Samples using ICP-MS with Advanced Dilution System, Agilent publication, 5994-7232EN

Consumables list

Product Type	Agilent Part Number	Description
Sample Loop for AVS MS/ADS 2	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 set-up, 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 set-up, 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/7900icp-ms

DE26776971

Printed in the USA, March 19, 2024
5994-7113EN