

High Throughput Water Analysis using Agilent 7900 ICP-MS coupled with ESI prepFAST

Application Note

Environmental

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Introduction

Agilent ICP-MS users can simplify the routine elemental analysis of environmental, food, pharmaceutical, and other sample types using Elemental Scientific's (ESI) fully automated prepFAST M5 autodilution system. Based on the ESI FAST autosampler, prepFAST M5 is capable of discrete sampling, automated dilution of calibration standards, and autodiluting out-of-range samples using a precise and accurate syringe-based dilution approach [1].

Utilizing Agilent's ICP-MS MassHunter Software Developer's Kit (SDK), ESI has integrated operation and control of prepFAST into Agilent's ICP-MS MassHunter software (from revision 4.3 onwards). The ESI software plug-in for ICP-MS MassHunter allows all prepFAST functions to be operated seamlessly from within the MassHunter Batch software. By fully integrating prepFAST control in this way, autocalibration and autodilution functionality become part of the method.

As a discrete sampling device for ICP-MS, prepFAST is ideally suited to the rapid analysis of high numbers of environmental samples in compliance with standard and regulatory methods. Many labs use the long-established US Environmental Protection Agency (EPA) Method 200.8 for guidance on the analysis of groundwaters, surface waters, drinking waters, and wastewaters by ICP-MS [2].



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Laboratories that use method 200.8 are required to carry out several performance and quality control (QC) tests to verify the quality of the data.

In this study, an Agilent 7900 ICP-MS, equipped with an ESI prepFAST autodilution system, was used for the analysis of drinking and bottled water samples in accordance with EPA Method 200.8 QC criteria. These criteria include:

- A check on over-range sample concentration results, with an upper limit set at 120% of the top calibration point, above which the sample must be diluted and re-run.
- Internal Standard (ISTD) recovery limits of 60 to 125%, with out-of-range recoveries triggering sample dilution.
- Automated analysis of Continuing Calibration Verification (CCV) and Continuing Calibration Blank (CCB) solutions after every 10 samples. CCV recoveries must be within $\pm 10\%$ of the reference value.

Experimental

Samples and solutions

The sample list comprised three drinking water samples: a filtered Omaha tap water, tap water A, and tap water B; seven commercially available bottled water samples; and Standard Reference Material (SRM) NIST 1643f Trace Elements in Water (undiluted and 2x diluted). The prepFAST autosampler rack was loaded with two vials of each of the 11 samples. The complete set of 22 samples was analyzed 10 times, with the sample order being the same for each run. There were 10 replicates of each sample, not including any reanalysis resulting from out-of-range QC failures.

All solutions (diluent, carrier, rinse, internal standard, calibration standards) were prepared using 2% HNO₃ and 1% HCl. HCl was included to ensure the stability of the elements Ag, Sb, and Hg in solution.

The 29 elements listed in Table 2 were calibrated from a single mixed stock standard, which was automatically diluted at factors of 100x, 50x, 20x, 10x, 5x, 2x, and 1x (undiluted) using the prepFAST system.

The ISTD mix, containing ⁷²Ge, ⁸⁹Y, ¹⁰³Rh, and ¹⁷⁵Lu, was automatically added to the samples at 20 ppb using prepFAST. To simulate an ISTD out-of-range sample, one of the bottled water samples was spiked with an extra 21 ppb of Y.

Instrumentation

An Agilent 7900 ICP-MS with standard nickel cones was used for the analysis. The instrument was fitted with the PFA-ST nebulizer that is included with the prepFAST system. Agilent ICP-MS systems include four argon gas lines as standard. In

addition to the plasma and auxiliary gas flows, both a nebulizer gas and a make-up gas line are supplied. This arrangement allows the nebulizer gas flow to be optimized independently from the total gas flow that carries the aerosol from the spray chamber into the plasma. In the case of the PFA-ST nebulizer, the optimum nebulizer gas flow is 0.7 L/min, so an additional 0.5 L/min make-up flow was used to give the optimum total carrier flow. The 7900 features a fourth-generation Octopole Reaction System (ORS⁴) collision/reaction cell, which includes a helium (He) mode cell gas line for the removal of common polyatomic interferences on most analyte elements.

The General Purpose plasma mode was used, as defined in the Preset Method for drinking water analysis that is included in the ICP-MS MassHunter software. Cell modes (no gas and He) were autotuned independently, although parameters related to sample introduction and plasma conditions were consistent for both modes. The cell gas flow and energy discrimination values are also pre-defined in the Preset Method. Instrument operating conditions are shown in Table 1.

Table 1. Agilent 7900 ICP-MS operating conditions.

Parameter	No gas	He
Plasma mode	General purpose	
RF power (W)	1500	
Sample depth (mm)	11	
Carrier gas flow rate (L/min)	0.7	
Make up gas flow rate (L/min)	0.5	
Lens tune	Autotune	
Cell gas flow rate (mL/min)	0	4.5
Energy discrimination (V)	5	

Shaded parameters are predefined in the Preset Method for drinking water



Figure 1. The prepFAST system attached to the 7900 ICP-MS

The 7900 ICP-MS was connected to the ESI prepFAST M5 autodilution system (Figure 1). The integrated system offers the following advantages for trace elemental analysis of environmental samples:

- Discrete sampling to reduce the analysis time to approximately 2 minutes per sample.
- Automated, real-time preparation of calibration standards from a single stock solution located in the autosampler rack.
- prepFAST M5 can dilute a calibration stock standard by up to a factor of 400, to give a multi-level calibration. If a wider calibration range is needed, two separate stock standards at different concentrations can each be diluted up to 400x to give a combined calibration range covering more than 4 orders of magnitude.
- Prescriptive autodilution: the analyst specifies the dilution factor for each sample ahead of time in the method Batch file, and prepFAST dilutes the sample accordingly, directly from the autosampler.
- Intelligent autodilution: the operator specifies QC limits for out-of-range analytes and internal standards. ICP-MS MassHunter intelligently calculates the necessary dilution factors for any out-of-range samples based on these criteria. The user can select which elements or ISTDs to check for outlier conditions. ICP-MS MassHunter automatically checks the results and control limits for the selected elements, and calculates the minimum dilution factor required to bring the furthest outlier into range. prepFAST dilutes the sample using the calculated dilution factor, and adds it to the sample list for reanalysis.
- The integrated TuneSelect valve provides selection of up to four different carrier or tune solutions for automated tuning or other tasks such as "Startup" tasks and EPA Tune Check. The TuneSelect valve supports unattended tuning and optimization of the ICP-MS without requiring any manual movement of the carrier line or changes to the plumbing.

Results and Discussion

Calibration

Representative calibration curves for several trace elements are shown in Figure 2 (V and As) and Figure 3 (Cd and Hg). All curves show excellent linearity across the calibration range. Both V and As are subject to polyatomic overlap in chloride matrices (from ClO⁺ on V⁺ at *m/z* 51, and ArCl⁺ on As⁺ at *m/z* 75).

Instrument detection limits (IDLs) of 0.036 µg/L (ppb) for V and 0.022 µg/L for As were obtained. The IDLs were based on three replicates, due to the limited measurement time available with discrete sampling. The low IDLs and sub-ppb background equivalent concentrations (BECs) of 0.35 ppb for V and 0.06 ppb for As demonstrate the efficient removal of the Cl-based interferences in He mode on the 7900 ICP-MS.

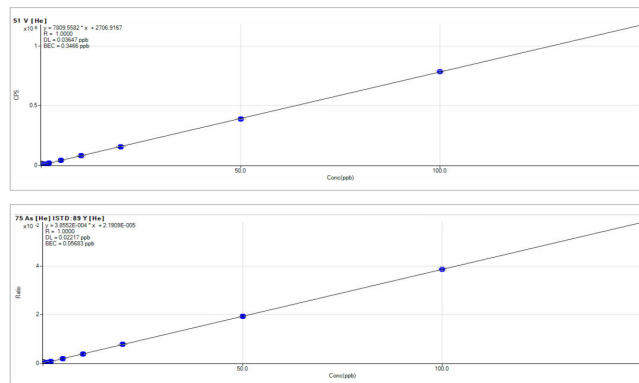


Figure 2. Calibration curves for V and As in He mode, showing effective reduction of Cl interferences. All standards contain 2% HNO₃ and 1% HCl.

Cd and Hg are environmentally critical elements, and are controlled at the lowest maximum allowable concentrations in most drinking water regulations [3]. These elements are often measured in no gas mode to maximize sensitivity, but both can suffer from polyatomic overlaps in some natural matrices (from MoO⁺ on Cd⁺ at *m/z* 111 and WO⁺ on Hg⁺ at *m/z* 202). It is therefore beneficial to measure both elements in He mode if sensitivity can be maintained. The sub-ng/L (ppt) IDLs (0.5 ppt for Cd and 0.8 ppt for Hg) and low ppt BECs (5.2 ppt for Cd and 7.5 ppt for Hg) demonstrate the excellent sensitivity and low background achieved for these trace analytes in He mode.

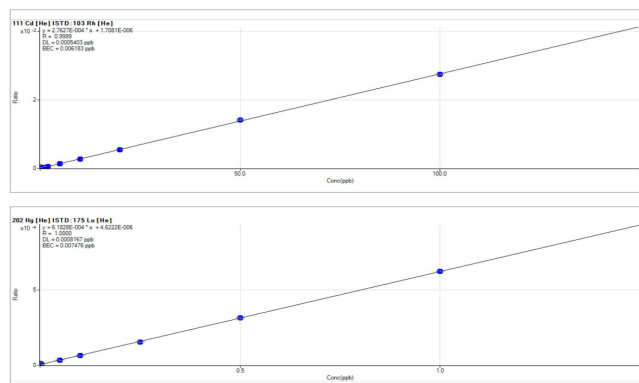


Figure 3. Calibration curves for low-level elements Cd and Hg, illustrating sub-ppt instrumental DLs in He mode and excellent precision and linearity at low concentrations.

Method detection limits

Method detection limits (MDLs) were determined for 29 elements including all analytes specified in EPA Method 200.8. The 3 σ MDLs were calculated from the analysis of seven replicate aliquots of the spiked calibration blank (2% HNO₃ and 1% HCl). According to method 200.8 requirements, MDL replicates were spiked at ~2-5x the estimated MDL concentration.

Table 2. List of analytes and 7900 ICP-MS MDLs.

Analyte	Preferred isotope	Mode	7900 ICP-MS MDL (ppb)
Lithium (Li)	7	No gas	0.002
Beryllium (Be)	9	No gas	0.001
Boron (B)	11	No gas	0.06
Sodium (Na)	23	He	0.2
Magnesium (Mg)	24	He	0.04
Aluminum (Al)	27	He	0.1
Potassium (K)	39	He	3.3
Calcium (Ca)	44	He	4.0
Vanadium (V)	51	He	0.03
Chromium (Cr)	52	He	0.01
Manganese (Mn)	55	He	0.004
Iron (Fe)	56	He	0.05
Cobalt (Co)	59	He	0.001
Nickel (Ni)	60	He	0.02
Copper (Cu)	63	He	0.007
Zinc (Zn)	66	He	0.03
Arsenic (As)	75	He	0.01
Selenium (Se)	78	He	0.3
Strontium (Sr)	88	He	0.03
Molybdenum (Mo)	95	He	0.003
Silver (Ag)	107	He	0.003
Cadmium (Cd)	111	He	0.002
Antimony (Sb)	121	He	0.008
Barium (Ba)	137	He	0.008
Mercury (Hg)	202	He	0.01
Thallium (Tl)	205	He	0.0005
Lead (Pb)	208*	He	0.0004
Thorium (Th)	232	He	0.002
Uranium (U)	238	He	0.0004

*Shaded cells indicate additional analytes to those specified in Method 200.8

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

Intelligent autodilution of out-of-range analytes and ISTDs

Operation and control of the prepFAST is seamlessly integrated into the Agilent ICP-MS MassHunter software. The analyst specifies the required QC limits in the ICP-MS MassHunter prepFAST Batch window. If the out-of-range limits are exceeded, MassHunter calculates the appropriate dilution factor needed to bring the out-of-range analytes within the calibration range, and sends this to prepFAST. In a real-time update to the sample list, prepFAST then re-runs the sample with the calculated dilution factor as a QC Action on Failure (AOF). This function is similar to standard QC AOF in ICP-MS MassHunter, and requires no intervention from the analyst. Similarly, if an ISTD signal exceeds the user-set recovery range, the sample is autodiluted 5x (and then 10x if needed) to bring the ISTD recovery within the defined range.

In this study, the ISTD recovery range was set to much tighter limits of 80-120% instead of the 60-125% range specified in 200.8. The tighter limits reflect the QC requirements specified in some labs' operating procedures. One of the bottled water samples was spiked with Y at 21 ppb. The spike was in addition to the 20 ppb Y ISTD automatically added to each sample. The theoretical concentrations and ratios given in Table 3 show that a 10x dilution of the spiked sample would be required to bring the total Y concentration within 20% of the ISTD reference level (of 20 ppb). This theory was confirmed from the analytical results for the bottled water sample spiked with an extra 21 ppb Y, as shown in Table 4. At 5x dilution, the added Y still causes the Y ISTD recovery to exceed the 120% limit, so a 10x dilution was required to ensure that the sample passed the QC check. The recoveries of the other internal standards remained within the QC limits for all dilutions of the sample.

Table 3. Expected concentrations and recoveries for Y ISTD in various dilutions of a water sample spiked with an extra 21 ppb Y.

prepFAST dilution factor	Y from spike (ppb)	Total conc. of Y (ppb)	Expected conc. of Y (ppb)	Ratio of Total Y/ ISTD Y
1	21.0	41.0	20.0	205%
5	4.2	24.2	20.0	121%
10	2.1	22.1	20.0	111%

Table 4. Measured ISTD recoveries (He mode) at various dilutions for a bottled water sample spiked with an extra 21 ppb Y.

Dilution	ISTD Recovery (%)		
	⁸⁹ Y	¹⁰³ Rh	¹⁷⁵ Lu
1	203.5	103.7	103.3
5	124.2	107.0	104.8
10	110.3	103.7	105.4

Dilution accuracy

In this study, NIST SRM 1643f Trace Elements in Water was analyzed undiluted and at 2x dilution. All recoveries were well within the Method 200.8 criteria of $\pm 30\%$, and the recoveries for most of the certified elements were within $\pm 10\%$ in the undiluted and 2x diluted samples, as shown in Table 5.

Since the level of Ba in the undiluted and 2x diluted SRM was more than 20% above the 100 ppb top calibration level, an automatic 10x dilution of the sample was triggered after each analysis of the SRM at 1x or 2x dilution. Again, excellent recoveries for the certified elements were achieved at the 10x dilution level, as shown in Table 5.

Table 5. Recovery tests using different dilutions of NIST 1643f, (n=20).

Element	Mode	Expected value (ppb)	Undiluted 1643f		2x Diluted 1643f		10x Autodiluted 1643f	
			Average found (ppb)	% Recovery	Average found (ppb)	% Recovery	Average found (ppb)	% Recovery
7 Li	No gas	17.4	21.6	124	18.6	107	17.5	101
9 Be	No gas	14.0	15.9	113	14.6	104	14.0	100
11 B	No gas	157.9	171.2	108	147.6	93	170.0	108
23 Na	He	20740.0	20188.3	97	20237.4	98	19652.7	95
24 Mg	He	8037.0	8071.8	100	7863.1	98	7553.2	94
27 Al	He	141.8	148.1	104	146.5	103	140.5	99
39 K	He	2034.0	2135.3	105	2037.8	100	1929.0	95
44 Ca	He	32300.0	30178.4	93	30028.9	93	29053.3	90
51 V	He	37.9	37.9	100	36.6	97	35.0	92
52 Cr	He	20.4	18.8	92	19.2	94	18.4	90
55 Mn	He	39.0	37.6	97	38.1	98	37.1	95
56 Fe	He	98.1	97.5	99	99.0	101	96.1	98
59 Co	He	27.1	25.9	96	26.7	99	26.1	96
60 Ni	He	62.4	60.0	96	61.8	99	60.9	98
63 Cu	He	22.8	22.0	97	21.9	96	21.9	96
66 Zn	He	78.5	76.5	97	78.1	99	77.0	98
75 As	He	60.5	58.3	96	58.9	97	57.1	94
78 Se	He	12.0	12.2	102	12.4	104	11.7	98
88 Sr	He	323.1	329.4	102	325.6	101	307.5	95
95 Mo	He	121.4	116.0	96	114.2	94	108.9	90
107 Ag	He	1.1	0.9	88	1.0	89	0.9	83
111 Cd	He	6.6	6.1	93	6.0	92	5.7	87
121 Sb	He	58.3	59.6	102	58.3	100	55.4	95
137 Ba	He	544.2	516.8	95	515.4	95	490.1	90
202 Hg	He	N/A	<DL	N/A	<DL	N/A	<DL	N/A
205 Tl	He	7.4	7.0	94	7.0	94	6.8	91
208 Pb	He	19.6	18.3	93	18.5	94	17.9	91
238 U	He	N/A	<DL	N/A	<DL	N/A	<DL	N/A

Intelligent autodilution of over-range samples

The ICP-MS MassHunter method was set up to autodilute a sample if the measured concentration of any analyte was more than 20% above the top calibration standard. The AOF specified that the sample should be reanalyzed using a custom dilution factor calculated to bring all elements below the top calibration point.

One of the tap water samples analyzed in this study had levels of Ca, Na, Mg, and Cu more than 20% higher than the top calibration standard concentration of 10,000 ppb (100 ppb for Cu), and so beyond the acceptable limit above the top calibration point (Table 6). Immediately after the undiluted sample was analyzed, the over-range results triggered an automatic re-run of the sample at a dilution factor of 20x, bringing all analytes within the calibration range.

Table 6. Over-range sample analysis triggered by Ca, Na, Mg, Sr, and Cu.

Element	Mode	Calibration range QC limit (ppb)	Undiluted tap water (ppb)	20x diluted tap water reported (ppb)
7 Li	No gas	120	71.8	67.2
9 Be	No gas	120	0	0
11 B	No gas	12000	153.1	145.3
23 Na	He	12000	75494*	73708
24 Mg	He	12000	44844*	42091
27 Al	He	12000	19.4	18.0
39 K	He	12000	6752	6776
44 Ca	He	12000	129064*	131390
51 V	He	120	0.08	0
52 Cr	He	120	0.1	0.04
55 Mn	He	120	0.7	0.6
56 Fe	He	12000	5.3	4.1
59 Co	He	120	0.05	0.04
60 Ni	He	120	0.4	0.4
63 Cu	He	120	769.8*	852.0
66 Zn	He	120	21.9	22.6
75 As	He	120	0.4	0.2
78 Se	He	120	0.5	0.3
88 Sr	He	120	1254*	1152
95 Mo	He	120	2.8	2.5
107 Ag	He	120	0.01	0.03
111 Cd	He	120	0.005	0.01
121 Sb	He	120	0.09	0
137 Ba	He	120	57.0	52.3
202 Hg	He	120	0.002	0
205 Tl	He	120	0.001	0
208 Pb	He	120	1.30	1.26
238 U	He	120	1.65	1.63

*Indicates those analytes that were >20% above calibration range in the undiluted sample

QC recovery tests

Continuing Calibration Verification (CCV) recoveries for all analytes were automatically measured after every 10 samples during the analytical sequence, as shown in Figure 4. All CCV recoveries were within the $\pm 10\%$ limits defined in EPA method 200.8.

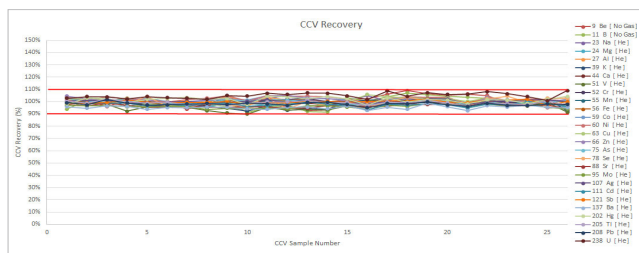


Figure 4. CCV recoveries (2 ppm for B, Na, Ca, Al, K, Mg, and Fe; 1 ppb for Hg; 20 ppb for all other elements) for the 11 hour sequence. The red lines show the $\pm 10\%$ control limits.

The ISTD recovery plot shown in Figure 5 includes three samples that had been deliberately spiked with Y, in addition to the ISTD. Three different levels of Y were added: 7, 14 and 21 ppb, to show that the spiked sample would be diluted appropriately as a result of the out-of-range ISTD.

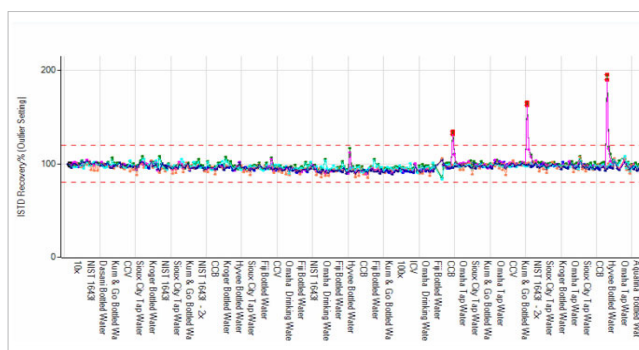


Figure 5. Internal standard recovery plot showing three samples that had been spiked with increasing concentrations of Y at 7, 14 and 21 ppb to trigger an automatic dilution for out-of-range ISTD recovery. The red lines show the custom $\pm 20\%$ control limits used in this work.

For the ISTD recovery plot shown in Figure 6, the three samples that were deliberately spiked with Y have been removed. In this plot, all ISTD recoveries are within the $\pm 20\%$ limits indicated by the red lines.

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