

Automating EPA 6020 Compliant Analysis with the Agilent 7900 ICP-MS and ESI prepFAST Autodilution System

Application Note

Environmental

Authors

Austin Schultz and Jake Unnerstall,
Elemental Scientific,
Omaha NE, USA

Steve Wilbur,
Agilent Technologies Inc.,
Washington, USA



Introduction

Elemental Scientific's (ESI) prepFAST M5 autodilution system can be integrated with Agilent ICP-MS systems to provide a fully automated approach to US Environmental Protection Agency (EPA) 6020 compliant analysis. Using a new software plug-in developed in collaboration between Agilent and ESI, prepFAST can be controlled directly from the Agilent ICP-MS MassHunter software. The software enables analysts to benefit from precision syringe loading of samples, automated preparation of calibration standards, preemptive autodilution of samples, and fully integrated autodilution of over-range QCs and samples. prepFAST-ICP-MS is highly suited to the rapid analysis of environmental samples while maintaining data quality in full compliance with standard and regulatory methods, such as EPA methods [1].

EPA Method 6020A is a performance-based ICP-MS method that can be applied to the determination of over 60 elements in various matrices. Typical sample types include surface water, groundwater, industrial wastes, soils, sludges, sediments, and other solid wastes for which determination of total (acid-leachable) elemental concentrations are required [2].

Laboratories operating according to EPA 6020 typically analyze long sequences of samples with high Total Dissolved Solids (TDS) content, so require robust methodology to handle the workload. The Agilent 7900 ICP-MS uses a unique Ultra High Matrix Introduction (UHMI) system, together with fourth generation helium collision/reaction cell technology (ORS⁴) to deliver accurate results in complex high matrix environmental samples [3].

This study demonstrates the benefits of combining He mode for interference removal, aerosol dilution using UHMI, and auto dilution and autocalibration using prepFAST. The method achieves excellent productivity and high-quality data for samples with high and variable analyte and matrix concentrations.

Experimental

Samples and solutions

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 elements such as Ag, Sb, and Hg in solution.

Six different certified reference materials (CRMs) were prepared for analysis as follows: NIST 1640a Trace Elements in Natural Water (run at dilutions of 1x (undiluted) and 2x); Estuarine Sediment (10x); River Sediment A CRM (10x); River Sediment B CRM (10x); Soil A CRM (10x); Soil B CRM – (10x). CRMs were obtained from High Purity Standards (Charleston SC, USA).

An internal standard (ISTD) mix containing ⁴⁵Sc, ⁷²Ge, ⁸⁹Y, ¹⁰³Rh, and ¹⁷⁵Lu was automatically added to the samples using the prepFAST M5.

Instrumentation

An Agilent 7900 ICP-MS with standard nickel cones was used for the analysis. The instrument was fitted with the UHMI option and the PFA-ST nebulizer that is included with the prepFAST M5 system. UHMI maximizes the plasma robustness of the 7900 ICP-MS through a combination of aerosol dilution and automated plasma temperature optimization. UHMI provides a series of calibrated and reproducible aerosol dilution factors (up to 100x) allowing the measurement of samples containing up to 25% dissolved salt. In this study, a constant aerosol dilution setting of UHMI 10x was used to enable the long-term analysis of the high matrix sample digests.

Table 1. Agilent 7900 ICP-MS operating parameters.

Parameter	No gas	He
RF power (W)	1500	
Carrier gas flow rate (L/min)	0.84	
Dilution gas flow rate (L/min)	0.48	
Lens tune	Autotune	
Cell gas flow rate (mL/min)	0	0.45
Energy discrimination (V)	5	
Number of elements	1, 1 ISTD	26, 5 ISTDs

The 7900 ICP-MS was coupled to the ESI prepFAST M5 system for automatic dilution of samples and standards, as shown schematically in Figure 1. Samples from each autosampler location are loaded into the first sample loop at a fast rate of 0.5 mL/sec using a syringe pump. The prepFAST M5 syringe pump improves sample loading accuracy as well as reducing the sample consumption compared to a vacuum pump. Once loaded into the first loop, the sample is injected by the switching valve into a carrier stream containing the diluent and internal standards. The mixed solution is then transported to the second valve and loaded in the final injection loop. From there the mixed solution is injected into the carrier flow and transported to the ICP-MS nebulizer.

prepFAST M5 ensures rapid, reliable dilutions by using a S500V2 syringe pump. The pump is capable of precise (<± 0.05% RSD) and accurate (<± 0.2% bias) delivery of solution over a wide range of flow rates from 1 µL/min to 40 mL/min.

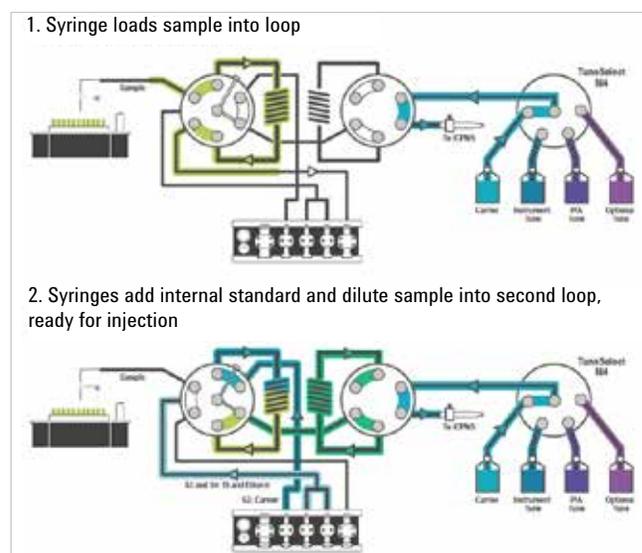


Figure 1. The ESI prepFAST M5 system schematic, illustrating sample loading during spray chamber rinse, followed by sample dilution, internal standardization, and injection.

Autocalibration

The 27 elements listed in Table 2 were automatically calibrated from a single mixed stock standard diluted by factors of 100x, 50x, 20x, 10x, 5x, 2x, and undiluted. The robustness and matrix tolerance of the prepFAST/7900 ICP-MS system meant that no matrix matching of the calibration standards was required. Example calibration curves for several major and trace elements across the mass range are shown in Figure 2.

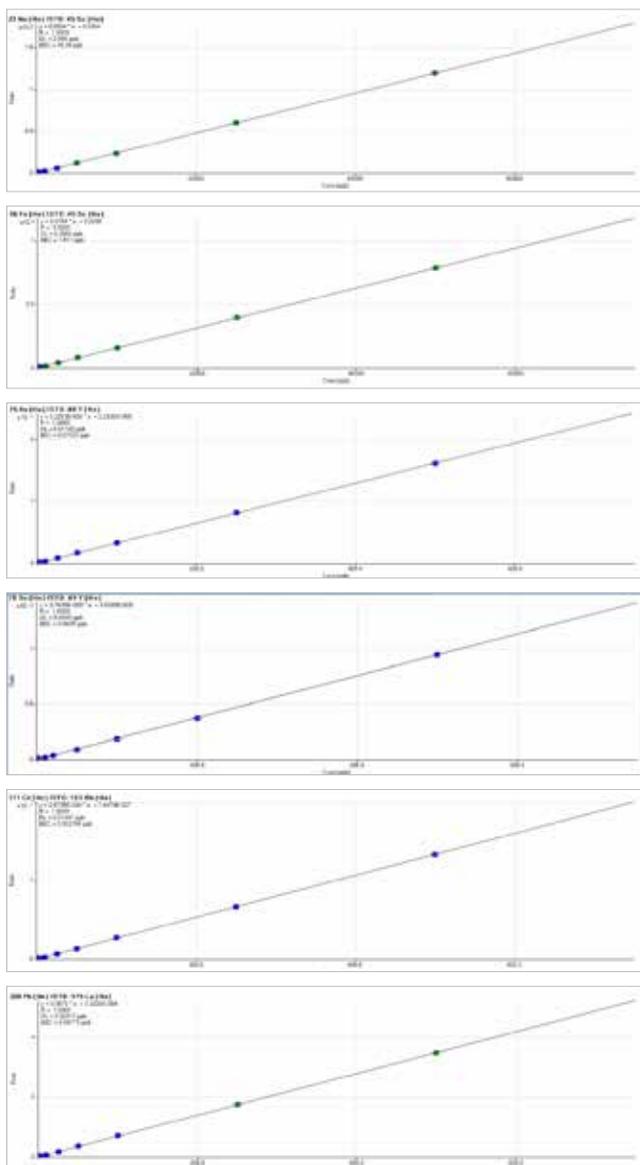
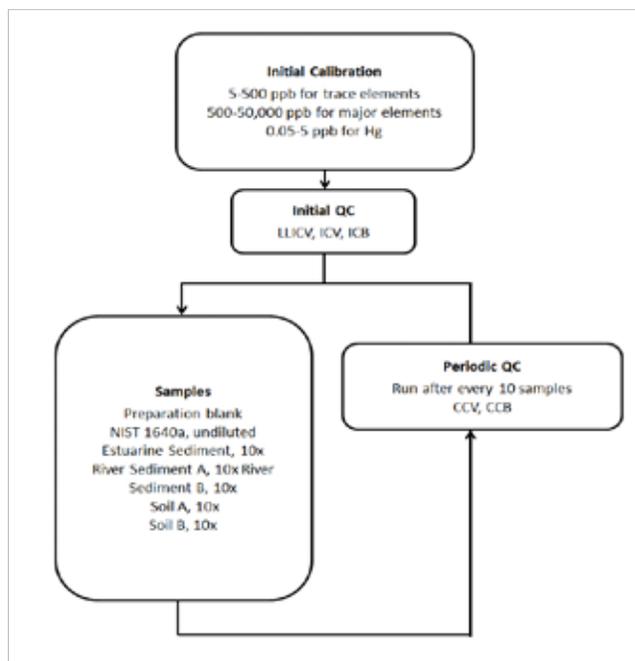


Figure 2. Typical calibration curves for Na, Fe, As, Se, Cd, and Pb.

Analytical workflow

Accuracy, productivity, and long-term stability were tested by analyzing a sequence of typical environmental samples for an extended period. The sequence of samples, calibrants, and QC solutions detailed in Figure 3 was used to represent a typical routine workload performed in contract environmental laboratories.



Key: Quality Control (QC), Initial Calibration Verification (ICV), Low Level Initial Calibration Verification (LLICV), Initial Calibration Blank (ICB), Continuing Calibration Verification (CCV), Continuing Calibration Blank (CCB).

Figure 3. Sequence of calibrants, samples, and QC solutions analyzed in a continuous 8-hour sequence. The “samples” block was run repeatedly with automatic insertion of “Periodic QC” block after every 10 sample runs. Total number of analyses over the course of the sequence was 230.

Results and Discussion

Method detection limits

Method Detection Limits (MDLs) were calculated from 3.14 x the standard deviation of the concentrations measured in seven replicates of the blank. All regulated elements can be measured in helium mode, but, for highest sensitivity and lowest DLs, beryllium was acquired in no gas mode. The other elements were all acquired in He mode, with the cell mode being switched during the analysis of each sample. The ability to switch cell modes during the short duration signal derived from loop injection is enabled by the very short cell gas stabilization time of the small volume ORS⁴ cell. Integration times were kept as short as possible to minimize the total acquisition time.

Table 2. Analysis parameters and 3 sigma MDLs.

Element	Mass	Analysis mode	Integration time (s)	MDL (ppb)
Be	9	No gas	0.3	0.01
Na	23	He	0.1	1.4
Mg	24	He	0.1	0.5
Al	27	He	0.3	0.5
K	39	He	0.1	7.8
Ca	44	He	0.3	3.4
V	51	He	0.3	0.05
Cr	52	He	0.3	0.03
Mn	55	He	0.3	0.02
Fe	56	He	0.3	0.14
Co	59	He	0.3	0.006
Ni	60	He	0.3	0.01
Cu	63	He	0.3	0.02
Zn	66	He	0.3	0.07
As	75	He	1	0.04
Se	78	He	4	0.50
Sr	88	He	0.3	0.02
Mo	95	He	0.3	0.007
Ag	107	He	0.3	0.002
Cd	111	He	0.5	0.004
Sn	118	He	0.3	0.03
Ba	137	He	0.3	0.02
Hg	202	He	2	0.002
Tl	205	He	0.1	0.004
Pb	206+207+208	He	0.3 (3*0.1)	0.009
Th	232	He	0.1	0.02
U	238	He	0.1	0.002

Meeting EPA 6020 quality control (QC) requirements

Method 6020A specifies that ISTD recoveries for all samples must exceed 30% of the ISTD response in the calibration blank. If an ISTD falls below the 30% limit the sample must be diluted and reanalyzed.

In addition, CCV QC samples must be analyzed after every 10 real samples. The CCVs must be prepared near the midpoint concentration of the calibration and must be recovered within ±10% of the true value. If the CCV recovery criteria are not met, the instrument must be recalibrated and the block of samples run after the last successful QC must be reanalyzed. Recoveries for all 15 CCVs run over the course of the 8-hour sequence (total of 230 soil and sediment digest samples) are shown in Figure 4. All elements were within +10% throughout the run.

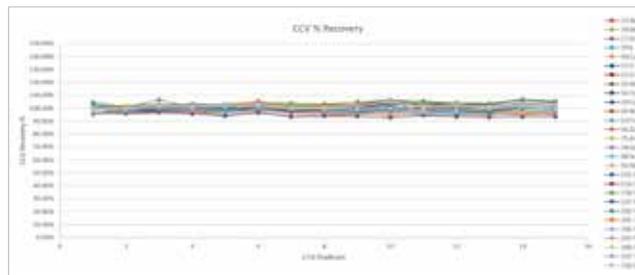


Figure 4. Continuing calibration verification (CCV) recoveries over the course of the sequence.

ISTD recoveries are shown in Figure 5. The near horizontal slope of the ISTD plot indicates that there was no significant loss in sensitivity, indicating minimal matrix accumulation on the interface or lenses during the entire sequence. In addition, there were no internal standard failures in any of the samples, which demonstrates the exceptional matrix tolerance delivered by the 7900 ICP-MS system with UHMI.

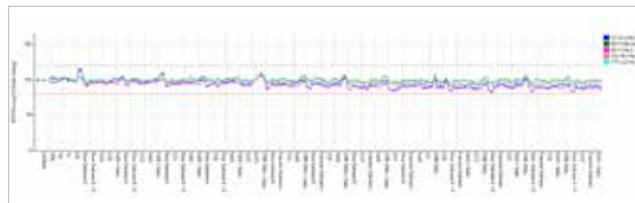


Figure 5. Internal standard recoveries normalized to the calibration blank for all samples. No internal standard failures occurred throughout the sequence.

Recovery of certified reference values

Four certified reference material (CRM) samples were analyzed repeatedly to test the accuracy of the method. NIST 1640a was analyzed undiluted, while the other reference materials were analyzed after 10x autodilution. The mean concentration and % recovery compared to the expected values are shown for each analyte in Table 3. Not all reference materials are certified for all analytes – blank cells indicate the absence of a certified value. Most recoveries are within 10% of the certified values, including analytes that suffer polyatomic interferences such as V, Cr, Cu, As, Se, Mo, Cd, and others.

The high recoveries for Cd in the Estuarine Sediment and Soil A CRMs were due to contamination of the respective reference materials. The contamination was indicated by the fact that results were consistent for all the main Cd isotopes (preferred isotope and secondary or confirmatory isotopes), and this contamination was also confirmed by the manufacturer.

Matrix spike recoveries

Each of the four CRMs was spiked near the midpoint of the calibration curve in the undiluted sample: 250 ppb for trace elements, 25,000 ppb for mineral elements (Na, Mg, Al, K, Ca and Fe), and 2.5 ppb for Hg. The matrix spiked samples were analyzed periodically, interspersed with the other samples throughout the sequence.

Most elements met the EPA limits of 75 to 125% recovery for matrix spikes, as shown in Table 3. The only analytes for which recoveries were outside this range had spike levels that were very low (less than 1/10) relative to the existing, unspiked concentration, as indicated in Tables 3a and 3b.

Table 3a. Mean measured values, mean recoveries, and matrix spike recoveries for all certified elements in four CRMs. Blank cells indicate no certified value.

Element	NIST 1640a, undiluted, n=12 unspiked and spiked					Estuarine Sediment, 10x autodiluted, n=12 unspiked and spiked				
	Measured conc. (ppb)	Expected value (ppb)	% Recovery	Spike level (ppb)	Spike recovery (%)	Measured conc. (ppb)	Expected value (ppb)	% Recovery	Spike level (ppb)	Spike recovery (%)
9 Be	2.7	3.026	88	250	95	18.2			250	88
23 Na	3,047.4	3081	99	25000	94	202958	200000	101	25000	83
24 Mg	1,035.1	1039.6	100	25000	94	100320	100000	100	25000	89
27 Al	57.5	52	111	25000	93	693495	700000	99	25000*	54*
39 K	566.0	569	99	25000	94	149752	150000	100	25000	85
44 Ca	5,762.1	5514	104	25000	93	77567	80000	97	25000	90
51 V	14.5	14.9	97	250	97	984.7	1000	98	250	91
52 Cr	39.5	40.13	99	250	98	801.9	800	100	250	92
55 Mn	39.3	39.99	98	250	98	4001.2	4000	100	250*	73*
56 Fe	40.9	36.4	112	25000	95	353213	350000	101	25000*	75*
59 Co	20.5	20.04	102	250	95	105.4			250	96
60 Ni	23.5	24.77	95	250	97	304.6	300	102	250	96
63 Cu	80.9	84.9	95	250	98	204.8	200	102	250	96
66 Zn	55.0	55.08	100	250	100	1525.1	1500	102	250	87
75 As	8.2	7.995	102	250	97	99.6	100	100	250	95
78 Se	20.1	19.93	100	250	100	49.4	50	99	250	94
88 Sr	121.3	124.78	97	250	96	0.9			250	97
95 Mo	42.0	45.14	93	250	97	1.5			250	97
107 Ag	8.5	8	107	250	94	4.0			250	75
111 Cd	3.9	3.952	98	250	99	1.1	0.4	278**	250	100
118 Sn	0.0			250	96	0.4			250	98
137 Ba	138.9	150.29	92	250	101	3.3			250	98
202 Hg	0.0			2.5	89	0.2			2.5	102
205 Tl	1.6	1.603	101	250	98	0.3			250	98
208 Pb	12.4	11.98	104	250	98	303.4	300	101	250	95
232 Th	0.1			250	93	108.2	100	108	250	99
238 U	26.1	25.1	104	250	97	0.2			250	98

* Indicates that the spike was less than 1/10 unspiked concentration.

**Isotopic agreement and communication with the manufacturer confirmed that the Cd result was the result of contaminated reference materials.

Table 3b. Mean measured values, mean recoveries, and matrix spike recoveries for all certified elements in four CRMs. Blank cells indicate no certified value.

Element	River Sediment B, 10x autodiluted, n=12 unspiked and spiked					Soil A, 10x autodiluted, n=12 unspiked and spiked				
	Measured conc. (ppb)	Expected value (ppb)	% Recovery	Spike level (ppb)	Spike recovery (%)	Measured conc. (ppb)	Expected value (ppb)	% Recovery	Spike level (ppb)	Spike recovery (%)
9 Be	0.2			250	89	0.1			250	89
23 Na	48,670	50000	97	25000	91	68,256	70000	98	25000	89
24 Mg	116,822	120000	97	25000	89	67,995	70000	97	25000	90
27 Al	578,904	600000	96	25000*	82*	485,979	500000	97	25000*	73*
39 K	196,406.8	200000	98	25000	90	200,580	200000	100	25000	87
44 Ca	283,442	300000	94	25000*	91*	333,531	350000	95	25000*	78*
51 V	959.9	1000	96	250	92	95.0	100	95	250	94
52 Cr	14,608	15000	97	250*	31*	7.5			250	97
55 Mn	5,762	6000	96	250*	74*	103.4	100	103	250	95
56 Fe	397,309	400000	99	25000*	82*	199,348	200000	100	25000	85
59 Co	155.3			250	97	5.8			250	99
60 Ni	465.1	500	93	250	89	285.0	300	95	250	91
63 Cu	940.9	1000	94	250	88	286.8	300	96	250	92
66 Zn	4,712.7	5000	94	250*	67*	954.7	1000	95	250	87
75 As	200.2	200	100	250	95	199.0	200	100	250	96
78 Se	8.9	10	89	250	91	9.3	10	93	250	95
88 Sr	23.5			250	96	2.3			250	96
95 Mo	2.5			250	92	0.8			250	93
107 Ag	0.4			250	101	1.9			150	85
111 Cd	29.4	30	98	250	95	4.5	3	150**	250	96
118 Sn	0.6			250	102	0.6			250	102
137 Ba	3,709.0	4000	93	250*	83*	4,664.3	5000	93	250*	75*
202 Hg	0.2			2.5	100	0.2			2.5	101
205 Tl	10.4	10	104	250	99	0.6			250	100
208 Pb	2,025.5	2000	101	250	95	404.8	400	101	250	97
232 Th	99.1	100	99	250	98	108.1	100	108	250	100
238 U	29.2	30	97	250	96	10.0	10	100	250	97

* Indicates that the spike was less than 1/10 unspiked concentration.

**Isotopic agreement and communication with the manufacturer confirmed that the Cd result was the result of contaminated reference materials.

Autodilution of over-range samples

Initially, Soil B CRM was analyzed following a prescriptive dilution of 10x. However, the measured concentrations for Al, Mn, Zn, Ba, and Pb were over-range compared to the top calibration standard concentrations of 50,000, 500, 500, 500 and 500 ppb, respectively.

Using prepFAST M5, the Soil B sample was automatically reanalyzed at an auto-calculated dilution factor of 200x to bring all elements to a level below 120% of the top calibration standard. The results given in Table 4 show excellent recoveries compared to the certified values for all elements at both dilution factors.

Table 4. Sample analysis results for Soil B CRM at the original, prescriptive dilution of 10x, and an automatic, calculated dilution of 200x.

	10x dilution of Soil B CRM, n=5			200x dilution of Soil B CRM, n=5	
	Expected conc. (ppb)	Measured conc. (ppb)	% Recovery	Measured conc. (ppb)	% Recovery
9 Be	--	0	--	0	--
23 Na	100,000	97,439	97	94,129	94
24 Mg	80,000	77,640	97	75,138	94
27 Al	700,000	665,376	95	645,812	92
39 K	210,000	206,783	98	198,732	95
44 Ca	125,000	118,096	94	112,462	90
51 V	800	782.2	98	759.7	95
52 Cr	400	404.5	101	399.7	100
55 Mn	100,000	98,973	99	98,353	98
56 Fe	350,000	355,662	102	352,113	101
59 Co	--	106.7	--	105.6	--
60 Ni	200	207.5	104	204.0	102
63 Cu	3,000	2,935	98	2,933	98
66 Zn	70,000	69,153	99	71,284	102
75 As	6,000	5,747	96	5,740	96
78 Se	--	0	--	0	--
88 Sr	--	10.5	--	7.5	--
95 Mo	--	1.9	--	3.0	--
107 Ag	--	0.7	--	0.6	--
111 Cd	200	213.7	107	210.4	105
118 Sn	--	0	--	0	--
137 Ba	7,000	7,255	104	7,038	101
202 Hg	--	0.1	--	1.0	--
205 Tl	--	0.1	--	0.3	--
208 Pb	60,000	61,733	103	61,297	102
232 Th	100	107.1	107	102.6	103
238 U	250	258.2	103	252.2	101

Conclusions

The multi-elemental determination of analytes in environmental samples can be carried out successfully using a simple, rapid, and highly automated ICP-MS method. The average run-to-run time was 150 seconds, which includes the time taken to analyze some of the samples more than once, due to autodilution.

The Agilent 7900 ICP-MS coupled to ESI's prepFAST M5 system was used to analyze a long sequence of high TDS samples including digested soils and sediments.

Agilent UHMI aerosol dilution technology provided the robust plasma conditions necessary to minimize matrix effects and drift during the analysis of these high matrix samples. Helium collision cell mode proved effective for removing all common matrix-derived polyatomic interferences, providing accurate results across the range of complex sample matrices. The prepFAST M5 7900 ICP-MS method met the performance criteria described in EPA method 6020, providing:

- Automated, real-time preparation of calibration standards from a single stock solution located in the autosampler rack. Autocalibration provided excellent linearity with correlation coefficients of 1.000 for all calibration plots.
- ISTD and CCV recoveries were consistently within the required ranges of >30% and $\pm 10\%$, respectively, over the course of the run.
- Good accuracy was demonstrated by the CRM recovery data.
- Excellent spike recoveries were obtained for spikes at >10% of the unspiked CRM concentrations.
- Automated over-range dilution of high concentration samples demonstrated the ability of the instrumentation to handle samples with high analyte concentrations.

Operation and control of the prepFAST M5 is seamlessly integrated into the Agilent ICP-MS MassHunter software. The ESI software plug-in for ICP-MS MassHunter allows all prepFAST M5 functions to be operated from within the ICP-MS MassHunter Batch software. By fully integrating prepFAST M5 control in this way, autocalibration and autodilution functionality become part of the method.

References

1. Austin Schultz and Paul Field, prepFAST ICP-MS: Environmental, ESI publication, <http://www.icpms.com/products/prepfast.php> (accessed June 2017)
2. U.S. EPA Method 6020A (SW 846) Inductively Coupled Plasma Mass Spectrometry, Revision 1, 1998: <https://www.epa.gov/sites/production/files/2015-07/documents/epa-6020a.pdf> (accessed June 2017)
3. Kazuo Yamanaka and Steve Wilbur, Maximizing productivity for high matrix sample analysis using the Agilent 7900 ICP-MS with ISIS 3 discrete sampling system, Agilent publication, 2014, 5991-5208EN

www.agilent.com/chem

Agilent shall not be liable for errors contained herein or for incidental or consequential damages in connection with the furnishing, performance or use of this material.

Information, descriptions, and specifications in this publication are subject to change without notice.

© Agilent Technologies, Inc. 2017

Published July 3, 2017

Publication number: 5991-8222EN