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Application Note

Automating the Preparation of Water Samples for EPA 200.8

Mary Jo Menke-Wright
Jacob Herrington
Teledyne CETAC Technologies
Omaha, NE USA
Jacob.Herrington@Teledyne.com

Introduction

Sample dilution and curve preparation are a necessary part of data analysis for many different methodologies. In environmental laboratories, samples requiring EPA 200.8 are typically diluted to decrease interferences and prevent degradation of instrument performance by the sample matrix. However, dilutions are not always ideal as they are labor intensive as well as prone to error and accidental contamination.

The SimPrep Automated Liquid Handling Station is a stand-alone autodilutor capable of automating not only sample dilutions but also calibration curve preparation and reagent addition. In this application note, calibration curves, standard reference materials (SRMs), and typical 200.8 samples will be prepared by the SimPrep to demonstrate its accuracy and precision.

Figure 1: SimPrep Automated Liquid Handling Station

Sample Preparation

Two samples were collected for analysis. Sample A is a drinking water from a local park which failed EPA short-term health advisory limits for Manganese with a detect of 0.52 mg/L. Sample B is an urban, surface river water (Fox River) sampled in the City of Waukesha, Wisconsin. Sample A was not turbid and thus was analyzed without digestion. Sample B was digested according to EPA 200.8 along with NRC NASS-7 Seawater Certified Reference Material. In addition, two NIST standard reference materials (SRMs) were tested: 1640a, Trace Elements in Natural Water NIST and 1643f, Trace Elements in Water, were tested.

Instrument Conditions

Samples were analyzed following EPA method 200.8 protocol using a Thermo RQ ICP-MS paired with an ASX-560 Autosampler. The ICP-MS was equipped with standard accessories such as nickel cones, a micromist nebulizer (0.4 mL/min flow), and a 2 mm injector. The instrument was tuned daily following manufacturer guidelines. Interference correction formulas, where applicable, were supplied by the manufacturer. If interferences could not be resolved with a formula, kinetic energy discrimination (KED) mode was used with Helium as the cell gas.

The SimPrep added 0.5 mL of an internal standard (IS) solution to each sample/standard. The IS solution contained Scandium (Sc), Yttrium (Y), Indium (In), Terbium (Tb), and Bismuth (Bi). Final concentration of each IS element was 50 ppb. Internal standard recoveries must be 60-125% for data to be considered valid. Isotopes analyzed for this application note are listed in Table 1. Internal standard selection for each isotope was determined by interpolation.

The instrument was calibrated using a blank and 6 standards prepared in 1% nitric acid (HNO_3). The calibration curve was prepared by hand and by the SimPrep to compare performance. The SimPrep method used to prepare the calibration is shown in Figure 2. The lowest volume that could be dispensed using the standard 1 mL and 10 mL syringes is 50 µL. Thus, the 0.5 ppb and 1 ppb were prepared using a serial dilution.

Calibration curves had a correlation coefficient of 0.999 or greater for all isotopes except Zinc in the hand prepared calibration. At least one of the calibration points was contaminated for Zinc by the analyst during the calibration preparation. By using the SimPrep, this user error was avoided. (See Figure 3.)

Figure 2: SimPrep Calibration Sequence

Sample		Dilution 1				
Position	Name	Position	Volume [µl]	Vol Sample	Vol Std	Name Std
	Blank	R1-01	10000			
	Blank	R1-02	10000			
	5ppb	R1-23	10000		50	Cal Parent
R1-23	0.5ppb	R1-03	10000	1000		
	10ppb	R1-24	10000		100	Cal Parent
R1-24	1ppb	R1-04	10000	1000		
	5ppb	R1-05	10000		50	Cal Parent
	10ppb	R1-06	10000		100	Cal Parent
	50ppb	R1-07	10000		500	Cal Parent
	100ppb	R1-08	10000		1000	Cal Parent
	ICV	R1-10	10000		500	Second Source Parent
	Blank	R1-11	10000			

Final volume

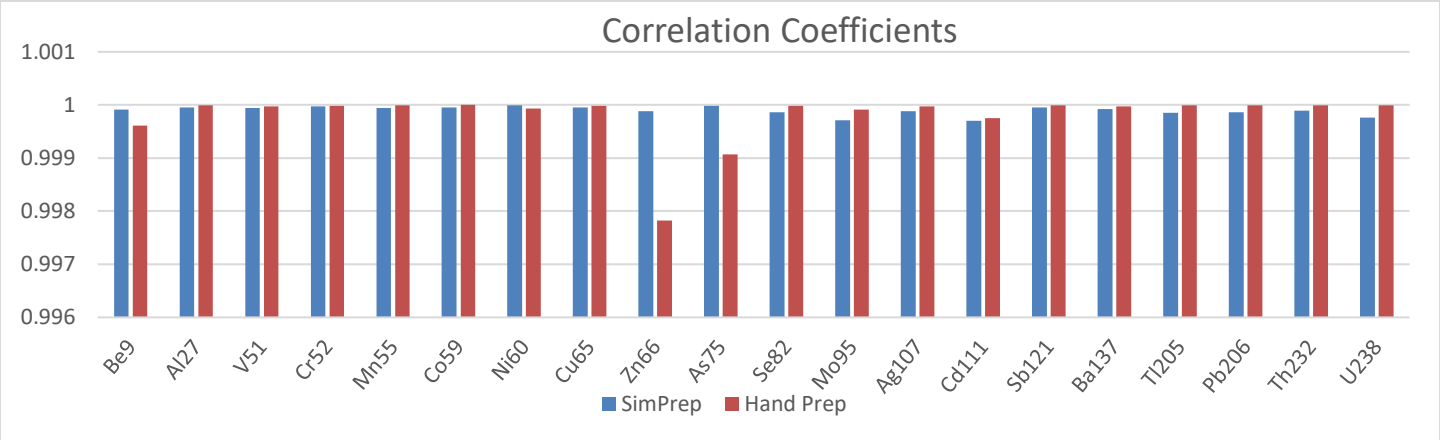
Serial dilution parent

1000 µL is taken from R1-24 to make a 10× dilution of the 10 ppb

Table 1: Analytes and Isotopes

Element	Mass
Aluminum	27
Antimony	121
Arsenic	75
Barium	137
Beryllium	9
Bismuth	209
Cadmium	111
Chromium	52
Cobalt	59
Copper	65
Indium	115
Lead	206
Manganese	55
Molybdenum	95
Nickel	60
Scandium	45
Selenium	82
Silver	107
Terbium	159
Thallium	205
Thorium	232
Uranium	238
Vanadium	51
Yttrium	89
Zinc	66

Figure 3: Calibration Curve Correlation Coefficients for SimPrep vs Hand Prep



Results

Time Savings

A sequence consisting of the calibration curve, QC, and 10–10× dilutions of Sample A was prepared by hand and the SimPrep. The processes were timed with the results in Figure 4. The initial programming of the sequence into the SimPrep required 4.75 minutes. However, for subsequent preparations, the same sequence was used reducing total time to 3.5 minutes. Once the SimPrep was setup, it saved over 15 minutes of time for this short sequence.

Precision

The 10× dilutions prepared by hand and by the SimPrep were analyzed against the same calibration curve to determine the % RSD. A 50 mL 10× dilution of Sample A was prepared and analyzed 10× to act as a control. In addition, Sample A was diluted at 10×, 20×, 50×, and 100× both ways. The SimPrep reproducibility is comparable to that of the hand prep while saving a significant amount of laboratory personnel time (Figure 5).

Accuracy

The calibration curve was verified by running an instrument calibration verification (ICV) standard prepared at 50 µg/L. A continuing calibration verification (CCV), also at 50 µg/L, was prepared from the same source as the calibration standards and analyzed every 10 samples. Acceptance criteria was 90–110%. Most analytes are between 95–105% as shown in Figure 6.

Figure 4: Time Savings SimPrep vs Hand Prep

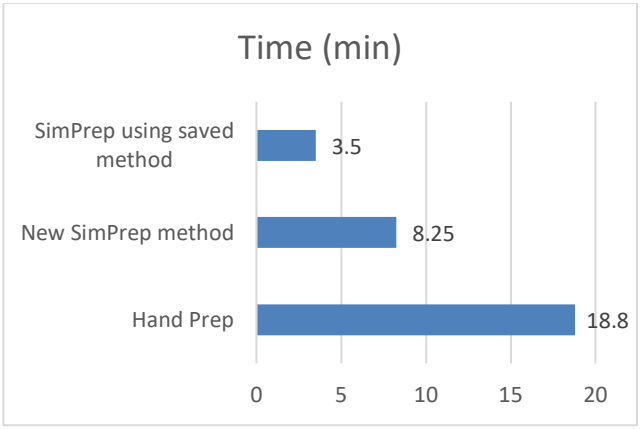


Figure 5: RSD of Different Preparations for Manganese

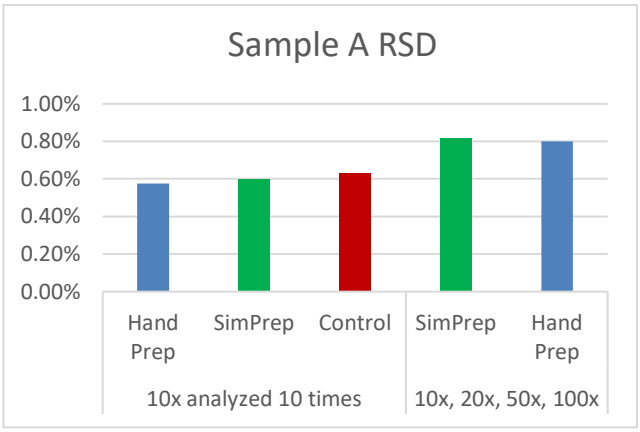
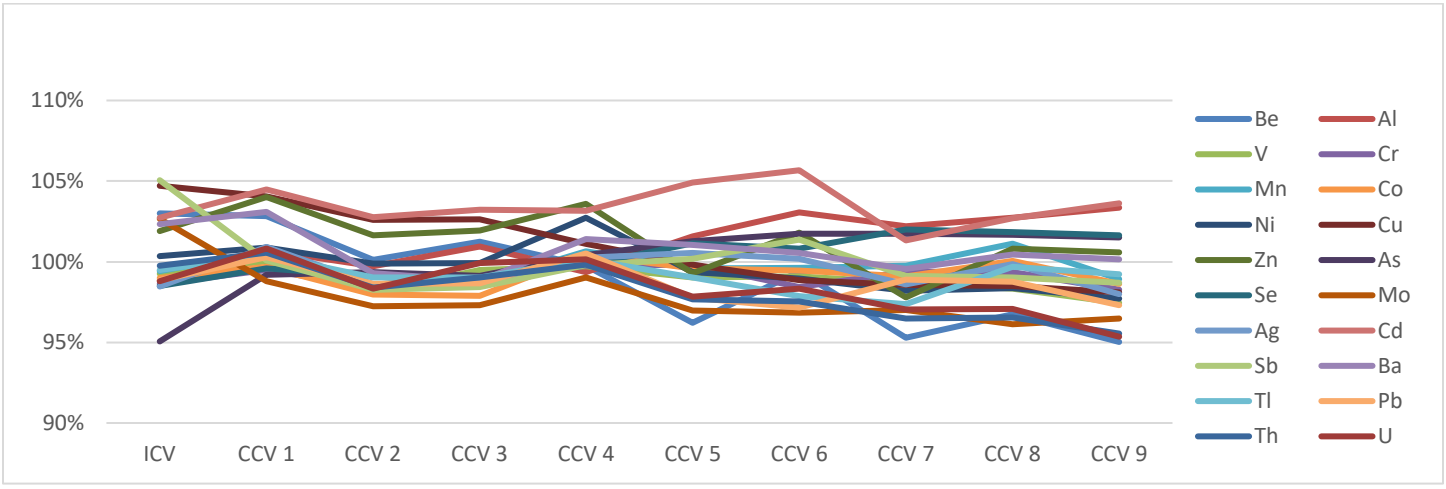


Figure 6: SimPrep Calibration Verification Recoveries



To further demonstrate the dilution accuracy of the SimPrep, two NIST SRMs were diluted at 5× and analyzed. Results are in Table 2. All elements had a recovery between 92-103%. Particularly of note, Thallium in 1640a and Silver in 1643f had excellent recoveries despite having diluted concentrations below the lowest curve standard.

Another SRM, NASS-7 certified seawater, was diluted at 50× by the SimPrep and analyzed (Table 3). Despite the difficult matrix, the recovery is still excellent.

The NASS-7 confirmed the accuracy of the SimPrep for Arsenic and Molybdenum, but the other analytes were too low for our instrumentation. To check the ability of the SimPrep to dilute a complicated matrix for the other analytes, NASS-7 as well as Sample B were spiked in duplicate by an analyst and digested along with a laboratory control sample (LCS). The LCS was diluted at 10×, Sample B at 20×, and NASS-7 at 50× by the SimPrep. The probe depth at each sample location can be programmed into the SimPrep software. The digests were directly loaded onto the SimPrep and dilution aliquots were removed without disturbing settled particulates.

Select elements are shown in Figure 7. LCS recoveries are well within the 85–115% limit. All spike recoveries are also within their limits of 70–130% except for Zinc. The Aluminum and Zinc result for the Sample B SD appear to have been contaminated, likely by the sample preparation.

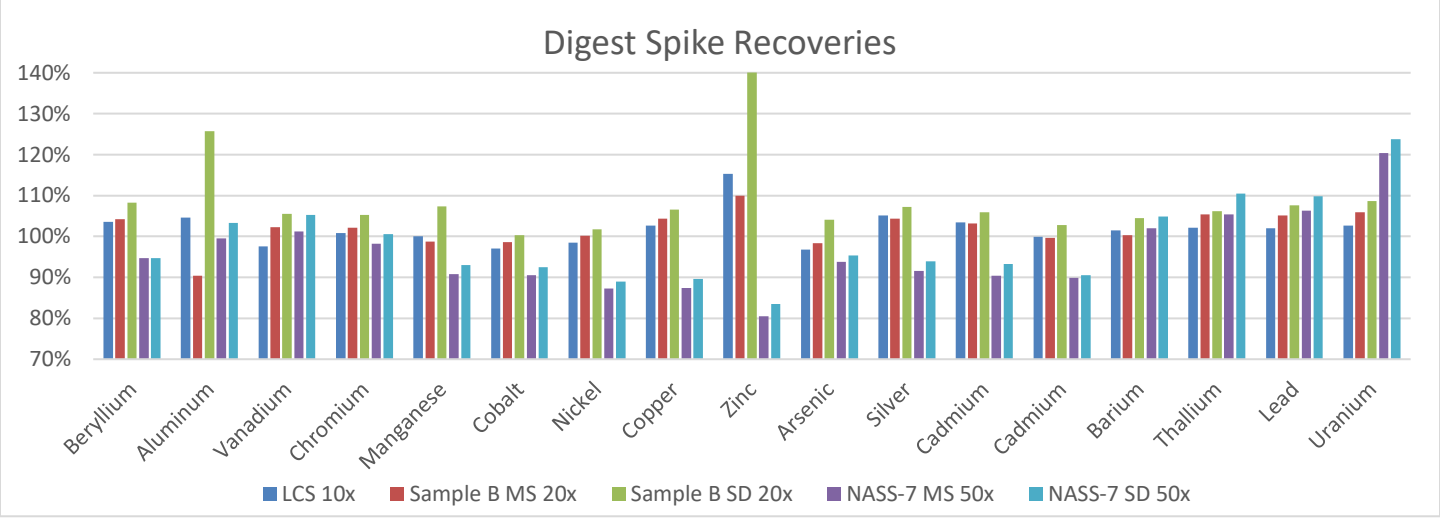
Table 2: Recoveries of NIST SRMs Prepared At 5× Dilution By SimPrep

Element	NIST 1640a			NIST 1643f		
	Certified Value (µg/L)	Measured Value (µg/L)	Recovery %	Certified Value (µg/L)	Measured Value (µg/L)	Recovery %
Aluminum	53.0	52.15	98	133.8	135.6	101
Antimony	5.11	4.93	97	55.45	56.05	101
Arsenic	8.08	7.72	96	57.42	58.95	103
Barium	151.8	151.23	100	518.2	521.47	101
Beryllium	3.03	3.09	102	13.67	13.15	96
Cadmium	3.99	3.97	100	5.89	5.98	102
Chromium	40.54	39.84	98	18.5	18.45	100
Cobalt	20.24	19.53	96	25.3	24.55	97
Copper	85.75	87.69	102	21.66	21.76	100
Lead	12.10	12.31	102	18.49	18.54	100
Manganese	40.39	39.63	98	37.14	36.47	98
Molybdenum	45.6	43.4	95	115.3	112.46	98
Nickel	25.32	24.66	97	59.8	58.48	98
Selenium	20.13	18.42	92	11.7	11.02	94
Silver	8.08	7.95	98	0.97	1.00	103
Thallium	1.62	1.63	101	6.89	6.95	101
Uranium	25.35	24.57	97	-	-	-
Vanadium	15.05	14.07	98	36.07	36.52	101
Zinc	55.64	53.37	96	74.4	71.37	96

Table 3: NRC NASS-7 Seawater Diluted at 50× By SimPrep

Element	Certified Value (µg/L)	Measured Value (µg/L)	Recovery %
Arsenic	1.26	1.28	102
Molybdenum	9.29	10.02	108

Figure 7: Simprep Diluted Digestion Spikes



Results for the digested batch were acceptable for all elements except Zinc. For labs without a clean room, common lab contaminants can be difficult to manage. In contrast to the digested batch, Sample A was spiked in duplicate by the SimPrep. The sequence is shown in Figure 8. The SimPrep diluted the sample and added the spike while maintaining the same 10 mL final volume as the blank and LCS.

The SimPrep spike recoveries were all within the acceptance limits despite the lack of a cleanroom. In addition, the average relative percent difference (RPD) between the duplicate measurement for all elements was 0.7%.

Conclusion

The SimPrep is an effective tool for automating dilutions, calibration curve preparation, and standard additions. It has been shown to be as reliable as hand preparation while eliminating user generated contamination. With the addition of SimPrep to a laboratory, the monotonous task of sample diluting can be accomplished with minimal user input allowing laboratory staff to focus on other tasks.

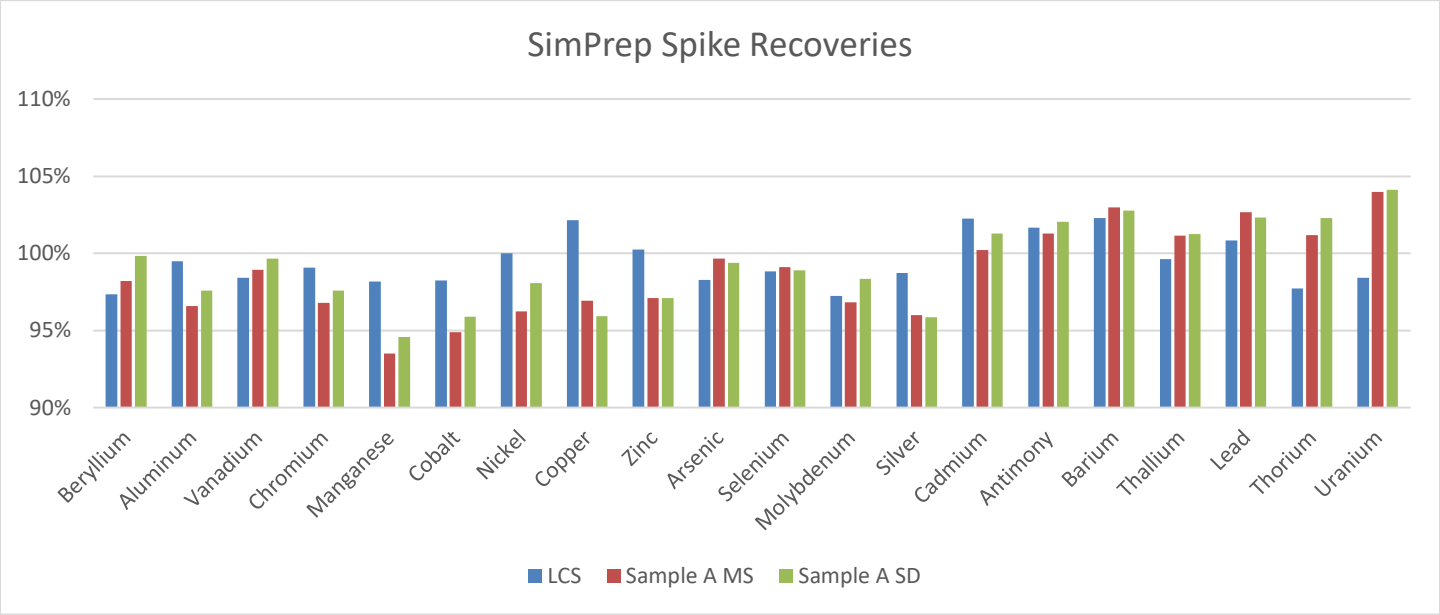
Figure 8: SimPrep Batch Spike Sequence

Sample		Dilution 1				
Position	Name	Position	Volume [µl]	Vol Sample	Vol Std	Name Std
	Blank	R1-01	10000			
	LCS	R1-02	10000		200	Cal Parent
R2-01	Sample A	R1-03	10000	1000		
R2-01	MS	R1-04	10000	1000	200	Cal Parent
R2-01	SD	R1-05	100000	1000	200	Cal Parent

10× dilution

0.2 mL spike addition

Figure 9: LCS and MS/SD Recoveries for Sample a Diluted and Spiked by the SimPrep



Teledyne CETAC Technologies
14306 Industrial Road
Omaha, NE 68144 USA
+1.402.733.2829
teledynecetac.com

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