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Enhanced Automation using SampleSense prep*FAST* and PerkinElmer Avio 500 ICP for US EPA Method 200.7 Compliance

Introduction

The measurement of trace metals in environmental waters is of great importance to ecosystems and human health, not only for the provision of safe drinking water to communities, but also to protect the natural world from the toxic effects of excess pollution from industrial discharge and treated wastewater effluent. Therefore, the levels of many trace metals are often regulated by law for waters discharged into the environment as a result of human activities. One of the most widely used regulated analytical methods for these measurements is the United States Environmental Protection Agency Method 200.7: *Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma-Atomic Emission Spectrometry.*

This work demonstrates the Elemental Scientific prep*FAST* automated sampling system featuring novel SampleSense™ technology coupled with a PerkinElmer Avio 500 ICP performing analysis in compliance with this US EPA method.

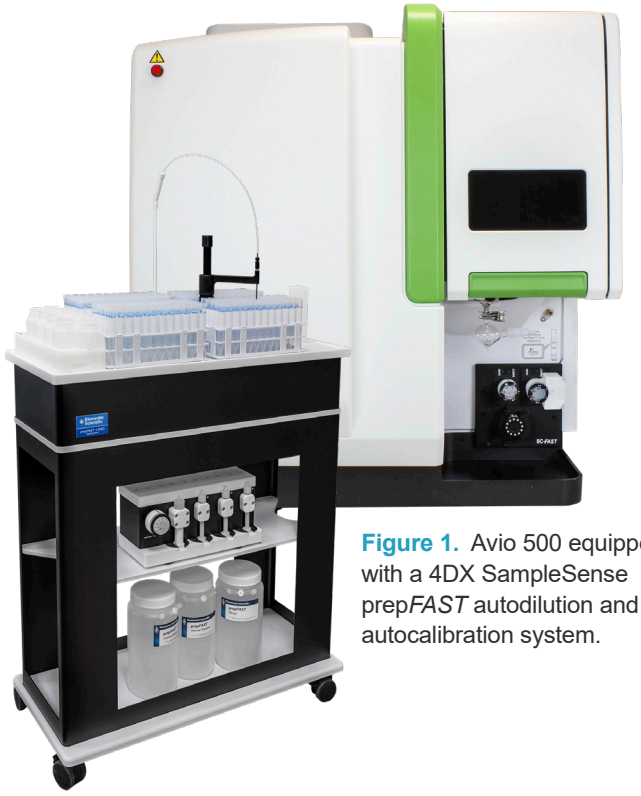

Figure 1. Avio 500 equipped with a 4DX SampleSense prep*FAST* autodilution and autocalibration system.

Experimental

SampleSense prep*FAST*

The prep*FAST* is a sample preparation system consisting of an intelligent autosampler (2, 4, 8, or 14-rack capacities available) coupled with a syringe pump module and DXi integrated valve and peripump assembly mounted on the Avio 500. prep*FAST* fully automates laboratory dilutions while providing high sample throughput. It offers high-precision inline autodilution up to 400x and autocalibration from one or more stock standards.

SampleSense combines an autosampler with an inert injection valve featuring integrated optical sensors that automatically detect both the arrival of a sample in the valve and when the loop is completely filled. This allows rapid sample loading using a high-speed vacuum pump. The sensed sample is automatically injected from the valve loop and the analysis is triggered in a tightly timed analytical sequence free of predetermined delay timings.

This technology is available for Elemental Scientific's *FAST* and prep*FAST* systems to further increase instrument productivity and fully automate the sample uptake process. Key highlights of the system include:

- Eliminates all sample uptake method development – no uptake delays required
- Optimizes loading conditions for each sample matrix
- Allows sample loop sizes to be changed without needing to alter method settings
- Automatically compensates for drift caused by kinked lines or partial blockages
- Provides positive confirmation of sample loading; if a sample fails to load for any reason, the failed sample is logged and the user is alerted.

Samples and Sample Preparation

Numerous reference materials for environmental analysis were obtained and analyzed according to the supplied instructions; these included solutions intended to simulate typical wastewater, sediment and soil samples. Calibration and Quality Control solutions were obtained from two separate suppliers.

Instrument Conditions

The prep*FAST* was configured with 2.0 mL loops and automatically triggered the Avio 500 analysis after the sample was loaded and diluted. SampleSense's automated loading and triggering function actively monitors the loading of each sample, automatically compensating for changes in sample viscosity (i.e. between clean water samples and digested solid samples). As a result, method development in the host instrument is greatly simplified—all uptake and stabilization delays were set to "0" in the PerkinElmer Syngistix™ software. The PFA-ICN integrated capillary nebulizer minimizes the number of connections between the valve and the nebulizer, reducing dead volume and uptake time. Total sample consumption from each vial was < 5 mL, leaving sufficient sample volume for reanalysis or QC-triggered autodilution without the need to refill any vials.

Table 1. Instrument analysis settings.

Parameter	Value
Nebulizer	ESI PFA with Integrated Capillary
Spray Chamber	Baffled glass cyclonic
Sample Uptake Rate	1.0 mL/min
RF Power	1500 W
Injector	2.0 mm id Alumina
Nebulizer Gas Flow	0.70 L/min
Auxiliary Gas Flow	0.2 L/min
Plasma Gas Flow	8 L/min
Integration Range	1 – 10 sec
Sample Uptake Tubing	Black/Black PVC (0.76 mm id)
Drain Tubing	Grey/Grey Santoprene (1.14 mm id)
Replicates	4

Table 2. Wavelengths and elements monitored in this work.

Wavelengths measured (nm)			
Y 371.029 Ax (IS)	Ca 315.887	Mg 285.213	Se 196.026
Y 371.029 Rad (IS)	Cd 214.440	Mn 257.610	Si 251.611
Ag 328.068	Co 228.616	Mo 203.845	Sn 189.927
Al 394.401	Cr 267.716	Na 589.592	Sr 421.552
As 188.979	Cu 324.752	Ni 231.604	Ti 334.940
B 249.677	Fe 238.204	P 178.221	Tl 190.801
Ba 493.408	K 766.490	Pb 220.353	V 292.402
Be 313.107	Li 670.784	Sb 206.836	Zn 206.200

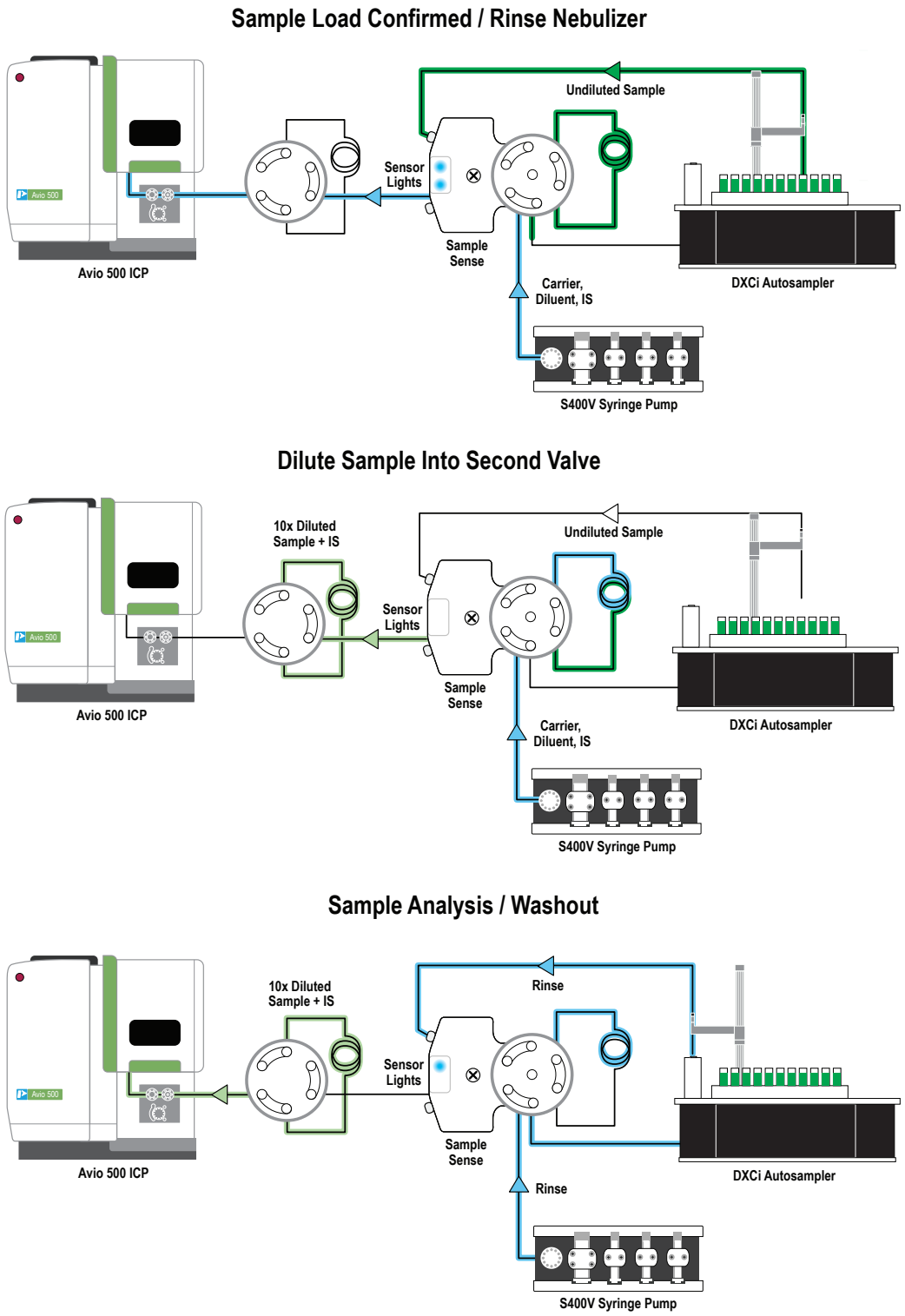

Figure 2. Schematic overview of the SampleSense prep*FAST* shows the following steps: (i) sample loading, with the valve automatically injecting upon detection of a full loop; (ii) dilution and addition of internal standard; (iii) analysis of the sample and simultaneous washing of the probe and SampleSense valve.

Analytical Sequence

Table 3. Analytical sequence of repeated QC samples and reference materials.

Sample Name	Sample Type
IPC	Instrument Performance Check
CCB	Continuing Check Blank
LFB	Laboratory Fortified Blank
TMDW	Trace Metals in Drinking Water
TM-C	Trace Metals in Wastewater
TM-D	Trace Metals in Wastewater
SOIL-B	Simulated Soil Digest
ESTUARINE SED	Simulated Estuarine Sediment Digest
RIVER SED B	Simulated River Sediment Digest

The analytical sequence performed in this study utilized the QC and sample list shown in the table above. After measuring the required calibration checks (IPC and CCB), the prep*FAST* analyzed the remaining QC and samples in the order shown. This solution list was then repeated 7 times within a 5-hour period to demonstrate system performance in a typical analysis procedure.

Results and Discussion

The Avio 500 was set up according to the manufacturer's recommendations for environmental analysis. The analytical sequence was configured to follow the protocols defined in the US EPA Method 200.7. The selected reference materials were analyzed in a repeating sequence over several hours to evaluate long-term method stability. The sample-to-sample cycle time during this experiment—including four replicate measurements in both axial and radial views—was 2 minutes and 15 seconds.

Washout

The prep*FAST* system demonstrates excellent washout characteristics. The washout from a 20 ppm multielement calibration standard (100 ppm for K) to the subsequent check blank was > 1000x for most elements in the analysis and exceeded 10,000x for some analytes. For laboratories requiring additional washout to reach specific blank concentration levels, additional rinse time may be added to the procedure. The immediate rinsing of the spray chamber after ICP analysis and elimination of sample contact with peristaltic pump tubing—notorious as a source of carryover from chemical interactions between the sample and the tubing—achieve this impressive washout and permit short wash times, improving overall sample throughput and reducing operating costs.

prepFAST calibration linearity

The prep*FAST* system can automatically prepare a complete calibration curve from a single mixed-element stock standard. For all elements measured in this experiment, the linear correlation coefficient, R, was > 0.9995. A summary of the linearity obtained is shown at right, and a calibration curve for As is displayed below.

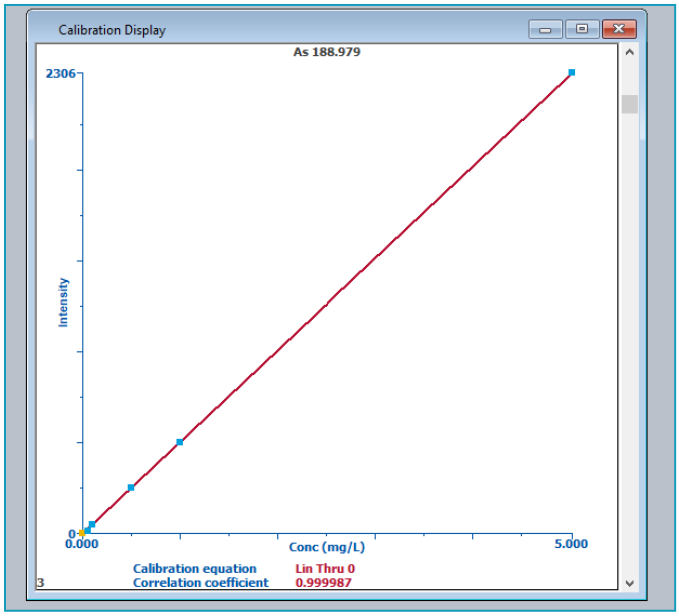

Figure 3. Screenshot of As calibration curve from instrument software.

Addressing overrange samples

The US EPA method requires that samples falling outside of the calibration range be diluted and subsequently reanalyzed. The prep*FAST* does this by automatically diluting (up to 400x) any sample with at least one overrange analyte. Of the sample types used in this work, surface water and wastewater did not have overrange analytes, but several high-level/high-matrix samples (e.g. digested sediments and soils) did, resulting in automatic QC autodilution and reanalysis. Excellent results from selected reference materials representing different concentration ranges are shown in Table 5.

A critical advantage of the prep*FAST* over traditional analysis is the ability to perform overrange dilutions inline and automatically; the reanalyzed samples are inserted and reanalyzed within the original sequence without any user intervention, eliminating the need to perform manual offline dilution for these samples and reanalyze them in a subsequent sequence. Significant time and labor savings are realized while obtaining more accurate results and reducing turnaround time for reporting.

Table 4. Summary of autocalibration linearity.

Element	Correlation (R)	Element	Correlation (R)
Ag	0.999604	Mn	0.999966
Al	0.999974	Mo	0.999953
As	0.999987	Na	0.999969
B	0.999979	Ni	0.999936
Ba	0.999985	P	0.999939
Be	0.999969	Pb	0.999996
Ca	0.999986	Sb	0.999999
Cd	0.999993	Se	0.999850
Co	0.999951	Si	0.999996
Cr	0.999997	Sn	0.999977
Cu	0.999927	Sr	0.999984
Fe	0.999985	Ti	0.999989
K	0.999961	Tl	0.999951
Li	0.999968	V	0.999975
Mg	0.999985	Zn	0.999916

Table 5. Example data showing certified values and average measured recoveries for wastewater and river sediment reference samples. Values in **green** were initially overrange and are reported from the automatically autodiluted and reanalyzed sample.

	Wastewater TM-C		River Sediment B	
	Certfied (mg/L)	Measured %R	Certfied (mg/L)	Measured %R
Ag	0.3	104.0		
Al	1	99.3%	**600**	95.5%
As	0.3	109.6%		
B	1	97.0%		
Ba	1	97.6%	4	100.7%
Be	0.3	110.3%		
Ca			**300**	94.9%
Cd	0.3	106.3%		
Co	1	106.0%	0.15	107.6%
Cr	1	107.4%	15	105.5%
Cu	1	101.5%	1	109.6%
Fe	1	100.1%	**400**	98.9%
K			**200**	91.8%
Mg			**120**	98.0%
Mn	1	103.6%	6	107.3%
Mo	1	109.5%		
Na			**50**	98.1%
Ni	1	107.1%	0.5	109.3%
P			10	107.6%
Pb	1	108.9%	2	102.3%
Sb	0.3	108.2%		
Se	0.3	94.0%		
Sr	1	97.7%		
Tl	0.3	104.6%		
V	1	102.3%	1	98.7%
Zn	1	110.7%	5	105.1%

Quality Control

In accordance with the quality control protocols of Method 200.7, Figures 4 and 5 show selected QC data to demonstrate stability and accuracy over an extended analysis. Figure 4 contains the Instrument Performance Check (IPC) results demonstrating the calibration stability. Figure 5 displays the performance of a Laboratory Fortified Blank (LFB) analyzed throughout the procedure.

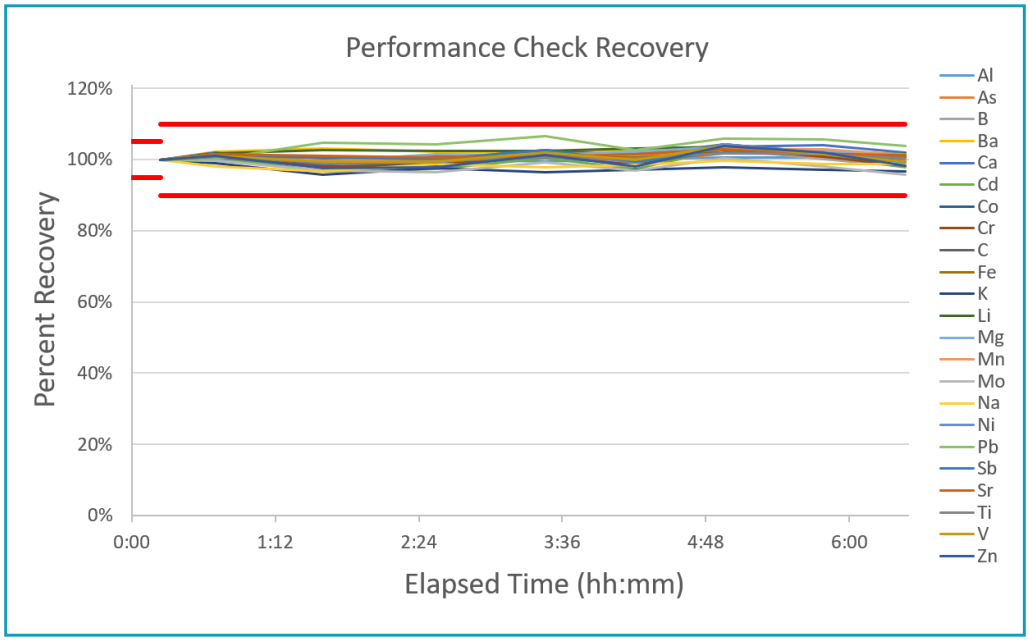

Figure 4. A quality control standard was analyzed at repeated intervals through the experiment to confirm the accuracy of the calibration. All values fall within the initial control window (± 5% immediately after the calibration) and the continuing control window (± 10%) as required by Method 200.7.

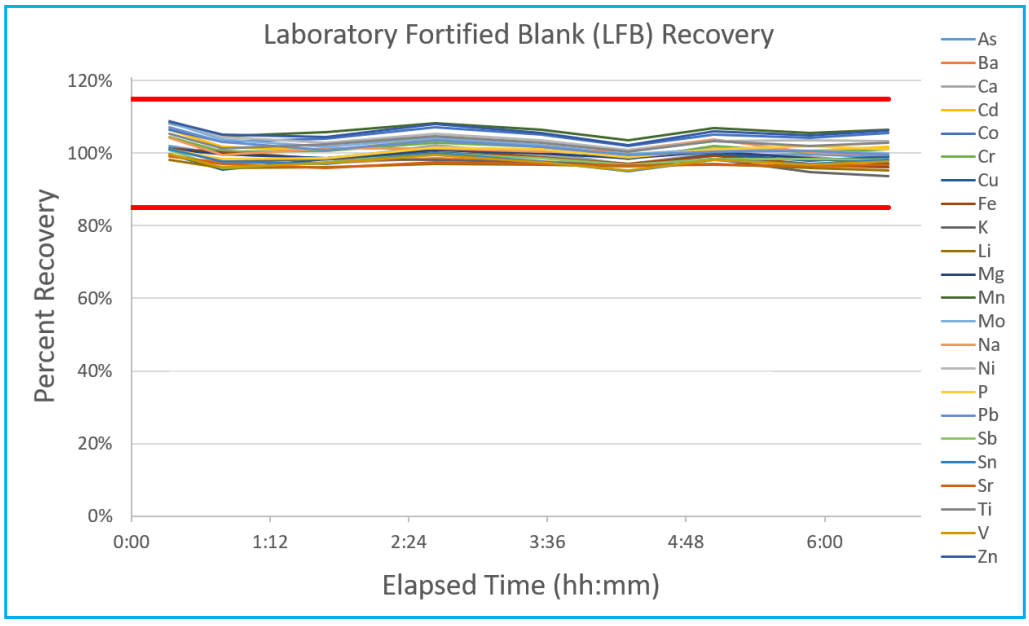

Figure 5. A Laboratory Fortified Blank (LFB) prepared from a secondary source was run at repeated intervals throughout the experiment. All values fall well within the ± 15% acceptance range.

Accuracy and Stability

In order to show the performance of the system throughout the entire analysis, results for wastewater sample TM-D are displayed below in Figure 6. The excellent accuracy and stability demonstrate both the performance of the instrument and SampleSense prep*FAST* for these types of environmental samples.

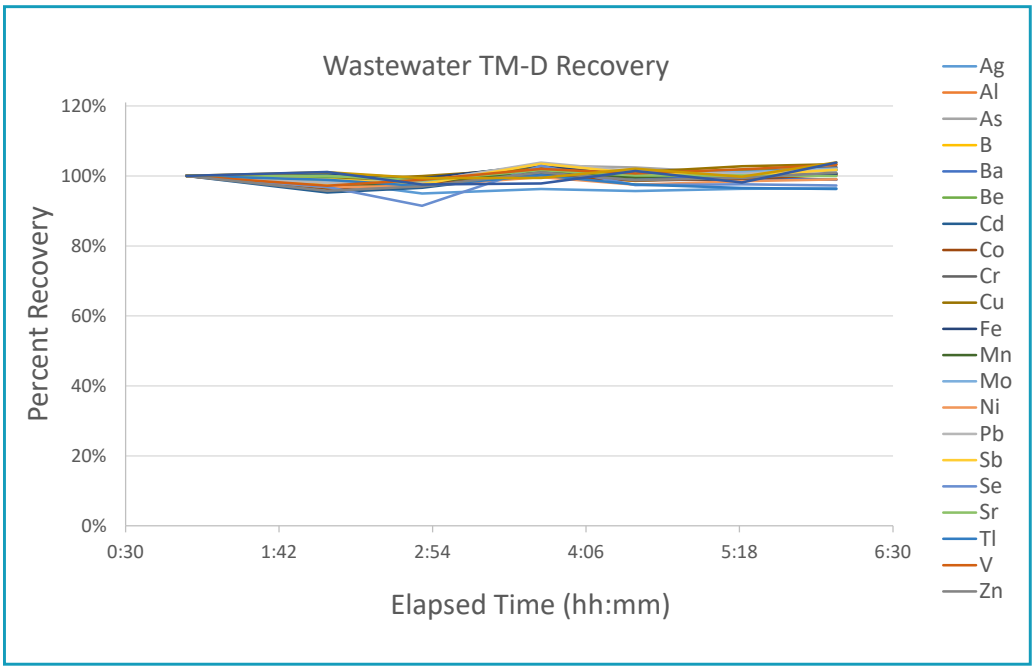

Figure 6. Repeated analysis of reference material TM-D shows excellent stability and recovery over 5 hours of analysis.

Conclusions

The integration of SampleSense prep*FAST* with the PerkinElmer Avio 500 ICP provides the ultimate performance for elemental analysis of environmental waters and waste samples. The SampleSense technology coupled with the powerful autocalibration and autodilution capabilities of the prep*FAST* offers unmatched automation for high-throughput analysis of challenging environmental samples.

Following the US EPA Method 200.7 protocols with four replicates in both axial and radial views, the sample-to-sample cycle time with SampleSense prep*FAST* is 2 minutes and 15 seconds. Total analysis time is typically reduced by 30% while lowering both argon gas consumption and laboratory support costs. Manual sample reanalysis is all but eliminated, and positive confirmation of sample loading ensures the highest confidence in data quality.

Summary

SampleSense prep*FAST* fully automates sample analysis:

- Eliminates all method uptake timing parameters and automatically triggers each ICP analysis
- Optimizes loading conditions for each sample matrix, independent of changing viscosities
- Reduces sample consumption, allowing for reanalysis or autodilution of samples
- Actively detects and reports any sample loading issues
- Automatically compensates for drift in vacuum uptake time caused by kinked lines or partial blockages
- Autocalibrates the ICP with real-time preparation of calibration standards from one or more stock standards
- Autodilutes both prescribed samples and overrange samples automatically during the analysis run

References

1. Analysis of Wastewaters Following U.S. EPA 200.7 using the Avio 500 ICP-OES. PerkinElmer Application Note #013569_01; Ken Neubauer, Angela LaCroix-Fralish, Lenny Pitts. PerkinElmer Inc. Shelton, CT 2017
2. METHOD 200.7 DETERMINATION OF METALS AND TRACE ELEMENTS IN WATER AND WASTES BY INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROMETRY Revision 4.4: T.D. Martin, C.A. Brockhoff, J.T. Creed, and EMMC Methods Work Group - U. S. ENVIRONMENTAL PROTECTION AGENCY CINCINNATI, OHIO 45268, 1994