# APPLICATION NOTE



# ICP-Optical Emission Spectroscopy

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The Analysis of Water and Wastes by U.S. EPA Method 200.7 Using the Optima 8300 ICP-OES and prep*FAST* Auto-Dilution/ Calibration System

# Introduction

The prevention and control of water pollution is of critical importance to protecting human and environmental health. Monitoring of water and wastes is an efficacious way to prevent the introduction of pollutants and costly remediation of drinking and environmentally

important waters. The United States Environmental Protection Agency (U.S. EPA), along with local regulatory bodies, is responsible for regulating water and wastes under the Clean Water Act and the Safe Drinking Water Act. Depending on the number and type of analytes, the number of samples and the productivity requirements, several different analytical techniques can be applied to measure trace elements in water and wastes.

U.S. EPA Method 200.7 Version 4.4 covers the use of inductively coupled plasma optical emission spectroscopy (ICP-OES) in radial and/or axial viewing for the determination of metals and some non-metals in water and wastes for regulatory compliance.<sup>1</sup> Method 200.7 contains a lengthy description of procedures for the collection, preservation and preparation of samples for analysis. The objective of this work was to complete the method using the PerkinElmer<sup>®</sup> Optima<sup>®</sup> 8300 ICP-OES coupled with the prep*FAST*<sup>TM</sup> Automated In-Line Auto-Dilution/Calibration System (Elemental Scientific Inc., Omaha, NE).



The prep*FAST*<sup>™</sup> system provides a number of advantages over conventional ICP-OES introduction systems, the most significant of which is higher sample throughput and reduced memory effects. The prep*FAST*<sup>™</sup> system allows accurate, syringe-driven auto dilution of samples and standards, eliminating manual dilution errors and increasing calibration range. Reducing costly high-purity reagent and sample consumption, the prep*FAST*<sup>™</sup> Auto-Dilution/ Calibration System is one of the best ways to improve laboratory productivity.

### Summary of Method 200.7

The direct analysis of samples was performed according to Method 200.7. For samples that require *total recoverable analysis*, refer to section 11.2 of EPA Method 200.7 rev 4.4. Below is a summary of the steps required for compliance with EPA 200.7 revision 4.4.

- 1) For *direct analysis* (samples with < 1 NTU), dilute, if necessary, to an appropriate volume and preserve samples to a pH < 2 with ultrapure  $HNO_3$ .
- 2) Optimize the instrument using the *plasma solution* (section 10.2.3) after allowing 15-30 minutes for the plasma to stabilize to the environment.
- 3) Calibrate the instrument using at least one blank and one calibration standard.
- 4) Run the instrument performance check (IPC sample) immediately following daily calibration and verify its recovery within 5%. The IPC should also be run after every 10<sup>th</sup> sample and at the end of a sample run and recovered within 10%.
- Prepare an inter-element correction (IEC) table, if necessary, and analyze the spectral interference check (SIC) solution to verify lack of spectral interferents in the method. This should be repeated on a periodic basis.
- 6) Perform the initial demonstration of performance (IDP)
  - a. Instrument detection limit (IDL) Calculated as 3x the standard deviation of 10 replicate measurements of the calibration blank.
  - b. Method detection limit (MDL) Calculated as 3.14x the standard deviation of seven replicate aliquots of fortified (2-3x estimated IDL) reagent water.
  - c. Quality control sample (QCS) Prepared from a second source. Verify that the mean concentration of three analyses is recovered within 5%. Also run QCS quarterly or after new calibration standards are made.
  - d. Linear dynamic range (LDR) Analyze successively higher standard concentrations until they return 90% of the stated concentration based on a typical standard curve. Verify annually.

- 7) Laboratory reagent blank (LRB) Analyze one every 20 samples. Should be below MDL.
- 8) Laboratory fortified blank (LFB) Analyze one with each batch of samples. Verify within 85-115% recovery.
- 9) Laboratory fortified matrix (LFM) Spike 10% of the samples prior to sample prep. Verify within 70-130% recovery. Concentration should be ≥ 30% of background concentration.
- 10) Reference materials Should be run when available.

### **Experimental Conditions**

### Instrumentation

All samples were analyzed with a PerkinElmer Optima 8300<sup>®</sup> ICP-OES (Figure 1) equipped with an ESI prep*FAST*<sup>™</sup> Auto-Dilution System with an ESI SC-2 DX Autosampler (Figure 2). Instrumental parameters are listed in Table 1.

Elements determined and wavelengths used in this study, the peak area, points per peak, and number of background points used for each wavelength are listed in Table 2. All elements were viewed axially. For some elements, alternate wavelengths were investigated in this study. The use of an alternate wavelength may be desirable for a variety of reasons – better sensitivity and greater freedom from spectral interferences are the two primary reasons. The wavelengths cited in Method 200.7 are 'recommended' with the following footnote: "The wavelengths listed are recommended because of their sensitivity and overall acceptability. Other wavelengths may be substituted if they can provide the needed sensitivity and are treated with the same corrective techniques for spectral interference (see Section 4.1)." It is worth investigating these alternate wavelengths for their applicability to the method. The wavelengths recommended by Method 200.7 are denoted in the table, as well as the reason for choosing an alternate wavelength in this study.



Figure 1. The PerkinElmer Optima 8300 ICP-OES with Flat Plate<sup>™</sup> plasma technology.



*Figure 2*. The prep*FAST*<sup>™</sup> Auto-Dilution System with an ESI SC-2 DX Autosampler illustrating a two-step process of loading the sample into a loop and in-line dilution.

#### Sample and Standard Preparation

The solutions that were prepared and used for this study are listed in Table 3. All solutions were diluted in 2% HNO<sub>3</sub>. For Sn analysis, solutions were acidified to 1%HCl/2%HNO<sub>3</sub>. For calibration, a 1 mg/L (standard 5) and a 5 mg/L (standard 10) standard, depending on the element, were prepared and the prepFAST<sup>™</sup> system was used to automatically dilute these solutions to prepare standards 1-4 (from standard 5) and standards 6-9 (from standard 10). The concentration of each calibration standard, the prepFAST<sup>™</sup> dilution factor, and the elements applied to each standard are shown in Table 4. The prepFAST™ system was also set up to automatically dilute samples which were over the range of the calibration curve. For this reason, several standard solutions, analyzed as samples, were deliberately prepared so that the results would be high and the prepFAST™ system would perform a dilution. Yttrium was used as the internal standard during sample analysis.

#### Table 1. Instrumental Parameters

| Parameter               | Value                        |
|-------------------------|------------------------------|
| Nebulizer Type          | ESI PFA                      |
| Spray Chamber           | Non-baffled cyclonic         |
| Injector                | Sapphire                     |
| Plasma Gas Flow (L/min) | 8                            |
| Aux Gas Flow (L/min)    | 0.2                          |
| Neb Gas Flow (L/min)    | 0.55                         |
| RF Power (watts)        | 1500                         |
| Resolution              | Normal                       |
| Read Delay (sec)        | 50                           |
| Peak Processing         | Peak area                    |
| Calibration Type        | Linear, calculated intercept |
| Torch Cassette Position | -3                           |
| ESI Flow Rate (µL/min)  | 500                          |
| ESI Loop Size (µL)      | 3000                         |

*Table 2.* Analytical parameters used for EPA Method 200.7 with the Optima 8300 ICP-OES

| Analyte | Wavelength<br>(nm) | Points/<br>Pe <u>ak</u> | Background<br>Correction<br>Points | Comments  |
|---------|--------------------|-------------------------|------------------------------------|---|
| Al      | 396.153*           | 1                       | 1                                  | Greater intensity   |
| Al      | 308.215            | 3                       | 2                                  | ,   |
| Sb      | 206.836            | 1                       | 2                                  |   |
| As      | 188.979*           | 1                       | 1                                  | Greater freedom from spectral interferences                             |
| As      | 193.696            | 1                       | 2                                  |   |
| Ва      | 493.408            | 1                       | 2                                  |   |
| Ве      | 313.042            | 1                       | 1                                  |   |
| В       | 249.677            | 1                       | 2                                  |   |
| Cd      | 226.502            | 1                       | 2                                  |   |
| Са      | 315.887            | 1                       | 1                                  |   |
| Ce      | 413.764            | 1                       | 1                                  |   |
| Cr      | 267.716*           | 1                       | 2                                  | Greater intensity and<br>greater freedom from<br>spectral interferences |
| Cr      | 205.560            | 1                       | 1                                  |   |
| Со      | 228.616            | 1                       | 2                                  |   |
| Cu      | 324.755            | 3                       | 2                                  |   |
| Fe      | 259.939            | 1                       | 2                                  |   |
| Pb      | 220.353            | 1                       | 2                                  |   |
| Li      | 670.794            | 1                       | 2                                  |   |
| Mg      | 285.213*           | 1                       | 2                                  | Greater intensity   |
| Mg      | 279.077            | 1                       | 2                                  |   |
| Mn      | 257.610            | 1                       | 1                                  |   |
| Мо      | 203.845            | 1                       | 2                                  |   |
| Ni      | 231.604            | 1                       | 2                                  |   |
| Р       | 213.617*           | 1                       | 2                                  | Software-suggested<br>wavelength  |
| Р       | 214.914            | 1                       | 1                                  |   |
| Р       | 178.223*           | 1                       | 2                                  | Greater freedom from spectral interferences                             |
| Р       | 177.435*           | 1                       | 2                                  | Greater freedom from spectral interferences                             |
| К       | 766.490            | 3                       | 2                                  |   |
| Se      | 196.026            | 1                       | 1                                  |   |
| Si      | 251.611            | 1                       | 2                                  |   |
| Ag      | 328.068            | 1                       | 1                                  |   |
| Na      | 589.592*           | 1                       | 2                                  | Argon interference<br>(shoulder)  |
| Na      | 588.995            | 1                       | 1                                  |   |
| Sr      | 421.552            | 1                       | 2                                  |   |
| TI      | 190.805            | 5                       | 2                                  |   |
| Sn      | 189.927            | 1                       | 2                                  |   |
| Ti      | 334.942            | 1                       | 1                                  |   |
| V       | 292.402            | 1                       | 2                                  |   |
| Zn      | 206.200*           | 1                       | 2                                  | Greater freedom from spectral interferences                             |
| Zn      | 213,857            | 1                       | 2                                  |   |

\* Alternate wavelengths

Table 3. Solutions used for the calibration and QC procedures in the analysis of water by EPA Method 200.7

| Designation   | Analytes  | Part Number   | Preparation   |
|---|---|---|---|
| Cal Standard 1-5,<br>IPC Solution<br>LFM                                    | 100 mg/L: Al, Sb, Ba, Be, Cd, Ca, Cr, Co, Cu, Fe,<br>Pb, Mg, Mn, Mo, Ni, K, Se, Ag, Na, Sr, Tl, Sn, Ti, V, Zn<br>1000 mg/L: Ce<br>1000 mg/L: Li | Instrument Cal. Std. 2:<br>N9301721<br>N9300110<br>N9300129 | Diluted to 1 mg/L for S5  |
| Cal Standard 6-10<br>IPC Solution<br>LFM                                    | 1000 mg/L: B<br>1000 mg/L: P<br>1000 mg/L: Si   | N9303760<br>N9300139<br>N9300150                            | Diluted to 5 mg/L for S10   |
| QCS 1   | 100 mg/L: As, Be, Ca, Cd, Co, Cr, Cu, Fe, Li, Mg, Mn,<br>Mo, Ni, Pb, Sb, Se, Sr, Ti, Tl, V, Zn  | QC Standard 21:<br>N9300281                                 | Diluted to 0.4 mg/L   |
| QCS 2   | 1000 mg/L: K<br>500 mg/L: Si<br>100 mg/L: Al, B, Ba, Na<br>50 mg/L: Ag  | QC Standard 7A:<br>N9300280                                 | Diluted 1000x   |
| QCS 3   | 1000 mg/L P   | N9303788  | Diluted to 0.4mg/L  |
| QCS 4   | 1000 mg/L Sn  | N9303801  | Diluted to 0.4 mg/L   |
| SIC A & SIC B   | 5000 mg/L: Al, Ca, Mg<br>2000 mg/L: Fe<br>1000 mg/L: Fe Stock   | Interferents A<br>N9300226<br>N9300126                      | Prepared to 200 mg/L: Al, Ca, Mg;<br>300 mg/L: Fe<br>The SIC B was spiked with the solutions<br>used to prepare the calibration standards |
| Sample  | 100 mg/L: Cd, Ni, Zn<br>60 mg/L: Sb<br>5 mg/L: Pb<br>50 mg/L: Ba, Be, Co, Cr, Cu, Mn, V<br>20 mg/L: Ag<br>10 mg/L: As                           | Analytes B Solution:<br>N9300227                            | Diluted 10x   |
| Sample  | See Tables for Elements and Concentrations  | Initial Calibration Verification (ICV):<br>N9300224         | Diluted 10x   |
| Sample  | See Tables for Elements and Concentrations  | HPS DWSS Secondary Drinking<br>Water Standard               | Diluted 10x   |
| Sample  | See Tables for Elements and Concentrations  | HPS DWPS Primary Drinking<br>Water Sol. A                   | Diluted 100x  |
| Sample  | See Tables for Elements and Concentrations  | HPS CRM TMDW Trace Metals in<br>Drinking Water              | No dilution   |
| Lab Sample: Sample (LM),<br>Sample Duplicate (LMdup),<br>Sample Spike (LFM) | First Morning Tap Water   |   | No dilution, acidification to 2% with ${\rm HNO}_{\rm 3}$   |

## Results

As an initial qualification of the system, the IDLs and MDLs were determined for each of the wavelengths. The IDLs were determined over two separate days. All results are shown in Table 5. Concentrations of the analytes in the fortified solution used for the MDLs are also listed in Table 5.

To validate the calibration curve, the QCS solution was analyzed after calibration was complete. The QCS solution was prepared from an alternate stock source, as is required by U.S. EPA Method 200.7. Results are shown in Table 6. The solution used for the alternate source QCS did not contain Ce. Rather than risk having contamination occur by spiking in stock, it was decided to leave the solution without this element.

The QCS should be within 5% of the known value. All of the values were within this variance except for Na and K. When calibration was carried to 0.5 mg/L (rather than 1 mg/L), both of these elements were also within 5%.

The ruggedness of the prep*FAST*<sup>TM</sup> system to dilute solutions was tested in two different ways. First, standard calibration curves created by using the prep*FAST*<sup>TM</sup> system were run over several days. In all cases, for all the wavelengths used, the correlation coefficient was > 0.999, and in most cases > 0.9999. Next, an instrument performance check (IPC) was

Table 4. Standards and dilutions

| Analyte   | <u>Standard</u><br>Std. Number | Conc. (µg/L)                      | prep <i>FAST</i> ™<br>Dilution Factor |
|---|--------------------------------|-----------------------------------|---------------------------------------|
| Al, Sb, As, Ba, Be,<br>Cd, Ce, Ca, Cr, Co,<br>Cu, Fe, Pb, Li, Mg,<br>Mn, Mo, Ni, K, Se,<br>Ag, Na, Sr, Tl, Sn,<br>Ti, V, Zn | 1<br>2<br>3<br>4<br>5          | 20<br>50<br>100<br>500<br>1000    | 50x<br>20x<br>10x<br>2x<br>1x         |
| B, P, Si  | 6<br>7<br>8<br>9<br>10         | 50<br>100<br>500<br>1000<br>50000 | 100x<br>50x<br>10x<br>5x<br>1x        |

| Table 5. Detection limits using the Optima 8300 ICP-OES with the prepFAST <sup>™</sup> |  |
|--|--|
| Auto-Dilution/Calibration System and EPA Method 200.7 parameters                       |  |

| Table 6. | Ouality | Control | Sample   | (OCS) |
|----------|---------|---------|----------|-------|
| 100000   | Quanty  | 001101  | oumpre , |       |

| Analyte | Wavelength<br>(nm) | IDL<br>(µg/L) | MDL<br>(µg/L) | Spike Concentration<br>for MDL Solution<br>(µg/L) |
|---------|--------------------|---------------|---------------|---|
| Al      | 396.153            | 0.28          | 0.70          | 0.4   |
| Sb      | 206.836            | 1.2           | 1.3           | 3   |
| As      | 188.979            | 0.96          | 1.8           | 3   |
| Ва      | 493.408            | 0.01          | 0.018         | 0.05  |
| Be      | 313.042            | 0.06          | 0.083         | 0.4   |
| В       | 249.677            | 0.66          | 0.55          | 3   |
| Cd      | 226.502            | 0.05          | 0.050         | 0.4   |
| Ca      | 315.887            | 0.39          | 0.58          | 1   |
| Ce      | 413.764            | 0.49          | 0.49          | 1   |
| Cr      | 267.716            | 0.12          | 0.15          | 0.4   |
| Со      | 228.616            | 0.21          | 0.22          | 0.4   |
| Cu      | 324.755            | 0.48          | 0.69          | 1   |
| Fe      | 259.939            | 0.16          | 0.12          | 0.4   |
| Pb      | 220.353            | 1.2           | 1.1           | 3   |
| Li      | 670.794            | 0.02          | 0.023         | 0.05  |
| Mg      | 285.213            | 0.11          | 0.30          | 0.4   |
| Mn      | 257.610            | 0.02          | 0.027         | 0.05  |
| Мо      | 203.845            | 0.37          | 0.78          | 1   |
| Ni      | 231.604            | 0.21          | 0.35          | 1   |
| Р       | 178.223            | 2.5           | 3.8           | 5   |
| K       | 766.490            | 0.37          | 2.4           | 1   |
| Se      | 196.026            | 1.5           | 1.9           | 3   |
| Si      | 251.611            | 1.7           | 3.8           | 5   |
| Ag      | 328.068            | 0.17          | 0.27          | 0.4   |
| Na      | 589.592            | 0.36          | 1.7           | 1   |
| Sr      | 421.552            | 0.004         | 0.011         | 0.05  |
| TI      | 190.805            | 0.04          | 0.91          | 1   |
| Sn      | 189.927            | 0.44          | 0.48          | 1   |
| Ti      | 334.942            | 0.05          | 0.07          | 0.4   |
| V       | 292.402            | 0.15          | 0.26          | 0.4   |
| Zn      | 206.200            | 0.10          | 0.88          | 0.4   |

|         |            |        | Alternate Source | <u>e</u> |
|---------|------------|--------|------------------|----------|
| Analuta | Wavelength | QCS    | Determined       | Recovery |
| Analyte | (1111)     | (µg/L) | (µg/L)           | (70)     |
| Al      | 396.153    | 100    | 97.9             | 97.9     |
| Sb      | 206.836    | 400    | 408              | 102      |
| As      | 188.979    | 400    | 401              | 101      |
| Ва      | 493.408    | 100    | 101              | 101      |
| Be      | 313.042    | 400    | 407              | 102      |
| В       | 249.677    | 100    | 98.6             | 98.6     |
| Cd      | 226.502    | 400    | 415              | 104      |
| Ca      | 315.887    | 400    | 413              | 103      |
| Ce      | 413.764    |        |                  |          |
| Cr      | 267.716    | 400    | 417              | 104      |
| Со      | 228.616    | 400    | 408              | 102      |
| Cu      | 324.752    | 400    | 416              | 104      |
| Fe      | 259.939    | 400    | 415              | 104      |
| Pb      | 220.353    | 400    | 414              | 104      |
| Li      | 670.784    | 400    | 396              | 99.1     |
| Mg      | 285.213    | 400    | 419              | 105      |
| Mn      | 257.610    | 400    | 416              | 104      |
| Мо      | 203.845    | 400    | 401              | 100      |
| Ni      | 231.604    | 400    | 409              | 102      |
| Р       | 178.221    | 400    | 400              | 100      |
| К       | 766.490    | 1000   | 1045             | 105      |
| Se      | 196.026    | 400    | 406              | 102      |
| Si      | 251.611    | 500    | 526              | 105      |
| Ag      | 328.068    | 50.0   | 52.1             | 104      |
| Na      | 589.592    | 100    | 102              | 102      |
| Sr      | 421.552    | 400    | 419              | 105      |
| TI      | 190.801    | 400    | 405              | 101      |
| Sn      | 189.927    | 1000   | 973              | 97.3     |
| Ti      | 334.940    | 400    | 410              | 103      |
| V       | 292.402    | 400    | 419              | 105      |
| 7       |            |        | 400              | (        |

analyzed after calibration, throughout the analysis, and at the end of the run. These solutions were prepared from standards 5 and 10 (depending on the analyte), using the prep*FAST*<sup>™</sup> system. The results for each wavelength are shown in Table 7. For all analytes except B, P, and Si, the dilution factor was 4x. For B, P, and Si, the dilution factor was 5x. The IPC solution should not vary more than 10% during an analysis. All readings fell into this range with the average recovery reported below. WinLab<sup>™</sup> for ICP software can automatically re-analyze any quality control sample that falls out of range, if necessary.

The effect of potential interferences was investigated. An interferent solution (SIC A) was prepared from a commercial solution, and fortified to an Fe concentration of 300 mg/L, as recommended in the Method (see Table 3). A portion of this solution was also spiked with a known concentration of

most of the analytes and used as SIC B. Only a few of the wavelengths showed visible spectral peak interference: As, Cd and V. Several of the other wavelengths suffered from an effect that produced slight baseline effects. When the analysis of the SIC A solution produced results of more than  $\pm 5.5 \ \mu$ g/L, a baseline effect was decided to have occurred. At that time, an IEC factor was applied to the data. All results are shown in Table 8. In all cases, except for Li, the determined value for the spiked solution, SIC B, was within 10% of the expected value. Contamination occurred during the SIC B solution preparation; therefore, the Li results are not reported.

Several solutions of known concentration were analyzed as samples to determine system reliability. Results are shown in Tables 9-13. The Analytes B solution (Table 9) showed all but one diluted result for Sb within 10% of the expected value.

| Table 7. Initial perform | ance check (IPC) run peri | dically and at end of ru | n; prepared from calibration | standards 5 and 10 by | the prepFAST** | system |
|--------------------------|---------------------------|--------------------------|------------------------------|-----------------------|----------------|--------|
|--------------------------|---------------------------|--------------------------|------------------------------|-----------------------|----------------|--------|

| Analyte | Wavelength<br>(nm) | Check<br>Concentration<br>(µg/L) | After<br>Calibration<br>(µg/L) | Check #1<br>(%) | Check #2<br>(µg/L) | End of Run<br>Recovery<br>(µg/L) | Average<br>(%) |
|---------|--------------------|----------------------------------|--------------------------------|-----------------|--------------------|----------------------------------|----------------|
| Al      | 396.153            | 250                              | 245                            | 243             | 244                | 235                              | 96.7           |
| Sb      | 206.836            | 250                              | 255                            | 253             | 258                | 247                              | 101            |
| As      | 188.979            | 250                              | 253                            | 252             | 255                | 249                              | 101            |
| Ва      | 493.408            | 250                              | 252                            | 250             | 249                | 242                              | 99.3           |
| Ве      | 313.042            | 250                              | 245                            | 244             | 244                | 247                              | 98.0           |
| В       | 249.677            | 1000                             | 1010                           | 1040            | 1050               | 1050                             | 104            |
| Cd      | 226.502            | 250                              | 248                            | 246             | 247                | 246                              | 98.7           |
| Ca      | 315.887            | 250                              | 251                            | 251             | 251                | 249                              | 100            |
| Ce      | 413.764            | 250                              | 252                            | 250             | 248                | 240                              | 99.0           |
| Cr      | 267.716            | 250                              | 249                            | 249             | 249                | 240                              | 98.7           |
| Со      | 228.616            | 250                              | 261                            | 259             | 262                | 255                              | 104            |
| Cu      | 324.752            | 250                              | 251                            | 250             | 252                | 239                              | 99.2           |
| Fe      | 259.939            | 250                              | 249                            | 251             | 249                | 245                              | 99.4           |
| Pb      | 220.353            | 250                              | 257                            | 257             | 260                | 242                              | 102            |
| Li      | 670.784            | 250                              | 239                            | 235             | 237                | 234                              | 94.6           |
| Mg      | 285.213            | 250                              | 248                            | 255             | 251                | 237                              | 99.1           |
| Mn      | 257.610            | 250                              | 248                            | 246             | 246                | 237                              | 97.7           |
| Мо      | 203.845            | 250                              | 254                            | 254             | 256                | 237                              | 100            |
| Ni      | 231.604            | 250                              | 243                            | 243             | 244                | 251                              | 98.1           |
| Р       | 178.221            | 1000                             | 1047                           | 1058            | 1074               | 1094                             | 107            |
| K       | 766.490            | 250                              | 239                            | 238             | 239                | 229                              | 94.4           |
| Se      | 196.026            | 250                              | 253                            | 251             | 255                | 247                              | 101            |
| Si      | 251.611            | 1000                             | 1050                           | 1040            | 1050               | 1070                             | 105            |
| Ag      | 328.068            | 250                              | 253                            | 253             | 255                | 239                              | 100            |
| Na      | 589.592            | 250                              | 244                            | 240             | 244                | 240                              | 96.8           |
| Sr      | 421.552            | 250                              | 257                            | 248             | 254                | 243                              | 100            |
| TI      | 190.801            | 250                              | 253                            | 252             | 256                | 249                              | 101            |
| Sn      | 189.927            | 250                              | 254                            | 252             | 255                | 246                              | 101            |
| Ti      | 334.940            | 250                              | 257                            | 256             | 256                | 243                              | 101            |
| V       | 292.402            | 250                              | 249                            | 249             | 250                | 239                              | 98.7           |
| Zn      | 206.200            | 250                              | 247                            | 246             | 246                | 264                              | 100            |

The same is true for the IPC solution (Table 10) – this solution was diluted 10x by the user and then run using the prep*FAST*<sup>™</sup> system either directly and/or with a 10x or 100x dilution. All recoveries for a drinking water secondary standard (HPS DWSS) were well within acceptable ranges compared to the known values (Table 11). A trace metals drinking water (HPS TMDW) standard was analyzed without dilution of any kind (Table 12). Determined results are within 15% of the certified values, except for Cu and Ag, where contamination was suspected. A drinking water primary standard (HPS DWPS) was also run (Table 13).

A first-morning tap water was collected to use as a sample (laboratory matrix, LM). This solution was run in duplicate and a portion was fortified with the analytes of interest as a laboratory fortified matrix (LFM). Results are shown in Table 14. Duplicates were all within acceptable limits and, with the exception of Ag, all spike results were within 15%. Based on the determined Zn and Cu concentrations in the sample, the spiked concentration should have been higher. The low Ag recovery was caused by a potential precipitation due to a significant chloride concentration in the sample.

Table 8. Recovery of the SIC solution with and without the use of inter-element correction (IEC) factors

|         |                    |                 |                 | SIC B           | SIC          | SIC B No IEC       |                 | with IEC        |
|---------|--------------------|-----------------|-----------------|-----------------|--------------|--------------------|-----------------|-----------------|
| Analyte | Wavelength<br>(nm) | SIC A<br>(µg/L) | Comment         | Added<br>(µg/L) | Found<br>(%) | Recovery<br>(µg/L) | Found<br>(µg/L) | Recovery<br>(%) |
| Sb      | 206.836            | 6.4             |                 | 200             | 203          | 102                | 197             | 98.5            |
| As      | 188.979            | *               |                 | 200             | 202          | 101                | N/A             | NA              |
| Ва      | 493.408            | *               |                 | 200             | 201          | 101                | N/A             | N/A             |
| Ве      | 313.042            | *               |                 | 200             | 194          | 97.0               | N/A             | N/A             |
| В       | 249.677            | -12             |                 | 2000            | 2111         | 106                | 2122            | 106             |
| Cd      | 226.502            | 39              | Fe interference | 200             | 221          | 111                | 184             | 92.0            |
| Ce      | 413.764            | -7.3            |                 | 200             | 186          | 93.0               | 193             | 96.5            |
| Cr      | 267.716            | *               |                 | 200             | 189          | 94.5               | N/A             | N/A             |
| Со      | 228.616            | *               |                 | 200             | 187          | 93.5               | N/A             | N/A             |
| Cu      | 324.752            | 10              |                 | 200             | 214          | 107                | 204             | 102             |
| Pb      | 220.353            | *               |                 | 200             | 186          | 93.0               | N/A             | N/A             |
| Mn      | 257.610            | *               |                 | 200             | 186          | 93.0               | N/A             | N/A             |
| Мо      | 203.845            | *               |                 | 200             | 191          | 95.5               | N/A             | N/A             |
| Ni      | 231.604            | -9.3            |                 | 200             | 183          | 91.5               | 191             | 95.5            |
| Р       | 178.221            | 32              |                 | 2000            | 2098         | 105                | 2067            | 103             |
| Se      | 196.026            | -82.87          | Fe interference | 200             | 120.2        | 60.1               | 198             | 99.2            |
| Si      | 251.611            | 16              |                 | 2000            | 2128         | 106                | 2122            | 106             |
| Ag      | 328.068            | *               |                 | 200             | 209          | 104                | N/A             | N/A             |
| Sr      | 421.552            | *               |                 | 200             | 200          | 100                | N/A             | N/A             |
| TI      | 190.801            | 8.7             |                 | 200             | 188          | 94.0               | 180             | 90.0            |
| Sn      | 189.927            | *               |                 | 200             | 182          | 91.0               | N/A             | N/A             |
| Ti      | 334.940            | *               |                 | 200             | 197          | 98.5               | N/A             | N/A             |
| V       | 292.402            | 15              | Fe interference | 200             | 208          | 104                | 194             | 97.0            |
| Zn      | 206.200            | *               |                 | 200             | 197          | 98.5               | N/A             | N/A             |

\* No baseline effect

*Table 9.* Sample analysis: recovery of the Analytes B solution<sup>+</sup> (referenced to a 10x user prepared dilution) run in duplicate, for most elements, with a further 10x prep*FAST*<sup>---</sup> dilution

|         |                    |                          |                      |                 | Replicate 1                                 |                 | Replicate 2                                 |                 |
|---------|--------------------|--------------------------|----------------------|-----------------|---|-----------------|---|-----------------|
| Analyte | Wavelength<br>(nm) | Known<br>Value<br>(µg/L) | Determined<br>(µg/L) | Recovery<br>(%) | prep <i>FAST</i> ™<br>Diluted 10x<br>(µg/L) | Recovery<br>(%) | prep <i>FAST</i> ™<br>Diluted 10x<br>(µg/L) | Recovery<br>(%) |
| Sb      | 206.836            | 6000                     | 5088*                | 84.5            | 5296  | 88              |   |                 |
| As      | 188.979            | 1000                     | 905.3                | 90.5            | 903.9                                       | 90.4            |   |                 |
| Ва      | 493.408            | 5000                     | 4947*                | 98.9            | 5064  | 101             | 4894  | 97.9            |
| Ве      | 313.042            | 5000                     | 4855*                | 97.1            | 4965  | 99.3            | 4830  | 96.6            |
| Cd      | 226.502            | 10000                    | 9830*                | 98.3            | 10320                                       | 103             | 10130                                       | 101             |
| Cr      | 267.716            | 5000                     | 4880*                | 97.6            | 5099  | 102             | 4990  | 99.8            |
| Со      | 228.616            | 5000                     | 4941*                | 98.8            | 4931  | 98.6            | 4854  | 97.1            |
| Cu      | 324.752            | 5000                     | 4788*                | 95.8            | 4860  | 97.2            |   |                 |
| Pb      | 220.353            | 500                      | 499.7                | 100             | 530.5                                       | 106             | 525.2                                       | 105             |
| Mn      | 257.610            | 5000                     | 4834*                | 96.7            | 4743  | 94.8            | 4630  | 92.6            |
| Ni      | 231.604            | 10000                    | 9695*                | 96.9            | 10090                                       | 101             | 9876  | 98.8            |
| Ag      | 328.068            | 2000                     | 1952*                | 97.6            | 2042  | 102             | 1999  | 99.9            |
| V       | 292.402            | 5000                     | 4922*                | 98.4            | 5128  | 103             | 5019  | 100             |
| Zn      | 206.200            | 10000                    | 9763*                | 97.6            | 10160                                       | 102             | 10000                                       | 100             |

 $^{\rm +}$  Solution was run as a sample, not for any method requirement purposes.

\* Indicates over calibration range for sample run directly.

*Table 10.* Sample analysis: recovery of the ICV initial calibration verification solution<sup>+</sup> (referenced to 10x user-prepared dilution) with further prep*FAST*<sup> $\propto$ </sup> dilutions at 10x or 100x, when necessary

|         |                    |                          |                      | Replicate 1     |  |                      | Replicate 2     | Replicate 2                              |  |
|---------|--------------------|--------------------------|----------------------|-----------------|--|----------------------|-----------------|--|--|
| Analyte | Wavelength<br>(nm) | Known<br>Value<br>(µg/L) | Determined<br>(µg/L) | Recovery<br>(%) | prep <i>FAST</i> ™<br>Dilution<br>Factor | Determined<br>(µg/L) | Recovery<br>(%) | prep <i>FAST</i> ™<br>Dilution<br>Factor |  |
| Al      | 396.153            | 20000                    | 19900                | 99.7            | 100x                                     |                      |                 |  |  |
| Sb      | 206.836            | 6000                     | 6260                 | 104             | 10x                                      |                      |                 |  |  |
| As      | 188.979            | 1000                     | 1010                 | 101             | 0x                                       | 999                  | 99.9            | 10x                                      |  |
| Ва      | 493.408            | 20000                    | 20200                | 101             | 100x                                     |                      |                 |  |  |
| Ве      | 313.042            | 500                      | 494                  | 98.6            | 0x                                       | 517                  | 103             | 10x                                      |  |
| Cd      | 226.502            | 500                      | 480                  | 96.0            | 0x                                       | 491                  | 98.1            | 10x                                      |  |
| Ca      | 315.887            | 50000                    | 53000                | 106             | 100x                                     |                      |                 |  |  |
| Cr      | 267.716            | 1000                     | 982                  | 98.2            | 0x                                       | 994                  | 99.4            | 10x                                      |  |
| Со      | 228.616            | 5000                     | 4800                 | 98.8            | 10x                                      |                      |                 |  |  |
| Cu      | 324.752            | 2500                     | 2750                 | 111             | 10x                                      |                      |                 |  |  |
| Fe      | 259.939            | 10000                    | 9660                 | 96.6            | 10x                                      | 10400                | 104             | 100x                                     |  |
| Pb      | 220.353            | 300                      | 291                  | 97.0            | 0x                                       |                      |                 |  |  |
| Mg      | 285.213            | 50000                    | 49300                | 98.6            | 100x                                     |                      |                 |  |  |
| Mn      | 257.610            | 1500                     | 1500                 | 99.8            | 10x                                      |                      |                 |  |  |
| Ni      | 231.604            | 4000                     | 3880                 | 97.0            | 10x                                      |                      |                 |  |  |
| K       | 766.490            | 50000                    | 49200                | 98.5            | 100x                                     |                      |                 |  |  |
| Se      | 196.026            | 500                      | 491                  | 98.1            | Ox                                       | 495                  | 99.0            | 10x                                      |  |
| Ag      | 328.068            | 1000                     | 1018                 | 102             | 0x                                       | 995                  | 99.5            | 10x                                      |  |
| Na      | 589.592            | 50000                    | 47400                | 94.5            | 100x                                     |                      |                 |  |  |
| TI      | 190.801            | 1000                     | 952                  | 95.2            | 0x                                       | 992                  | 99.2            | 10x                                      |  |
| V       | 292.402            | 5000                     | 5200                 | 104             | 10x                                      |                      |                 |  |  |
| Zn      | 206.200            | 2000                     | 1960                 | 97.9            | 10x                                      |                      |                 |  |  |

+ Solution was run as a sample, not for any method requirement purposes.

### Table 11. Recovery of a drinking water secondary standard HPS DWSS (referenced to analyst prepared 10x)

|         |                    |                                  |                      |                 | Replicate 1                                 |                 | Replicate 2                                 |                 |
|---------|--------------------|----------------------------------|----------------------|-----------------|---|-----------------|---|-----------------|
| Analyte | Wavelength<br>(nm) | Known<br>Diluted Value<br>(µg/L) | Determined<br>(µg/L) | Recovery<br>(%) | prep <i>FAST</i> ™<br>Diluted 10x<br>(µg/L) | Recovery<br>(%) | prep <i>FAST</i> ™<br>Diluted 10x<br>(µg/L) | Recovery<br>(%) |
| Cu      | 324.752            | 5,000                            | 4815                 | 96.3            | 5040  | 101             |   |                 |
| Fe      | 259.939            | 10,000                           | 10070                | 101             | 10000                                       | 103             | 9910  | 99.1            |
| Mn      | 257.610            | 5,000                            | 4902                 | 98.0            | 4850  | 97.0            | 4790  | 95.8            |
| Zn      | 206.200            | 5,000                            | 5073                 | 101             | 5170  | 103             | 5190  | 104             |

| Table 12. Recovery of a trace | metals drinking water | standard HPS TMDW |
|-------------------------------|-----------------------|-------------------|
| (no dilutions were made)      |                       |                   |

| Analyte | Wavelength<br>(nm) | Known<br>Value<br>(µg/L) | Determined<br>(µg/L) | Recovery<br>(%) |
|---------|--------------------|--------------------------|----------------------|-----------------|
| Al      | 396.153            | 120                      | 130                  | 110             |
| Sb      | 206.836            | 10                       | 11                   | 110             |
| As      | 188.979            | 80                       | 79                   | 98.4            |
| Ва      | 493.408            | 50                       | 48                   | 96.0            |
| Ве      | 313.042            | 20                       | 23                   | 115             |
| Cd      | 226.502            | 10                       | 11                   | 110             |
| Ca      | 315.887            | 35000                    | 36000                | 102             |
| Cr      | 267.716            | 20                       | 20                   | 100             |
| Со      | 228.616            | 25                       | 23                   | 92.0            |
| Cu      | 324.752            | 20                       | 25                   | 125             |
| Fe      | 259.939            | 100                      | 98                   | 98.0            |
| Pb      | 220.353            | 40                       | 41                   | 102             |
| Mg      | 285.213            | 9000                     | 9000                 | 99.9            |
| Mn      | 257.610            | 40                       | 41                   | 102             |
| Мо      | 203.845            | 100                      | 99                   | 99.0            |
| Ni      | 231.604            | 60                       | 57                   | 95.0            |
| K       | 766.490            | 2500                     | 2658                 | 94.1            |
| Se      | 196.026            | 10                       | 10.06                | 100.1           |
| Ag      | 328.068            | 2                        | 1.5                  | 76.9            |
| Na      | 589.592            | 6000                     | 6800                 | 113             |
| Sr      | 421.552            | 250                      | 250                  | 99.6            |
| TI      | 190.801            | 10                       | 9.2                  | 92.0            |
| V       | 292.402            | 30                       | 30                   | 100             |
| Zn      | 206.200            | 70                       | 74                   | 106             |

Table 13. Recovery of a drinking water primary standard HPS DWPS (referenced to analyst prepared 100x)

| Analyte | Wavelength<br>(nm) | Known<br>Value<br>(μg/L) | Determined<br>(µg/L) | Recovery<br>(%) |
|---------|--------------------|--------------------------|----------------------|-----------------|
| As      | 188.979            | 1000                     | 1018                 | 102             |
| Ва      | 493.408            | 500                      | 483                  | 96.6            |
| Cd      | 226.502            | 500                      | 508                  | 101             |
| Cr      | 205.560            | 1000                     | 907                  | 90.7            |
| Se      | 196.026            | 500                      | 496                  | 99.4            |
| Ag      | 328.068            | 100                      | 1011                 | 101             |

| Table 14. Lab sample analysis | with sample duplicate and spike |
|-------------------------------|---------------------------------|
|-------------------------------|---------------------------------|

| Analyte | Wavelength<br>(nm) | LM<br>(µg/L) | LM Duplicate<br>(µg/L) | Fortification<br>(µg/L) | LFM Found<br>(µg/L) | Recovery<br>(%) |
|---------|--------------------|--------------|------------------------|-------------------------|---------------------|-----------------|
| Al      | 396.153            | 11.8         | 11.8                   | 200                     | 216                 | 102             |
| Sb      | 206.836            | 13.8         | 14.4                   | 200                     | 184                 | 85.7            |
| As      | 188.979            | 5.6          | 5.3                    | 200                     | 180                 | 87.9            |
| Ва      | 493.408            | 9.52         | 9.70                   | 200                     | 210                 | 100             |
| Ве      | 313.042            | 3.44         | 3.48                   | 200                     | 201                 | 99.0            |
| В       | 249.677            | 17.9         | 18.3                   | 500                     | 539                 | 104             |
| Cd      | 226.502            | 1.18         | 1.16                   | 200                     | 195                 | 97.0            |
| Ce      | 413.764            | 0.790        | 0.904                  | 200                     | 191                 | 95.0            |
| Cr      | 267.716            | 1.57         | 1.56                   | 200                     | 194                 | 96.0            |
| Co      | 228.616            | < MDL        | < MDL                  | 200                     | 195                 | 97.5            |
| Cu      | 324.752            | 1463         | 1466                   | 200                     | 1654                | 101             |
| Fe      | 259.939            | 10.8         | 10.9                   | 200                     | 202                 | 95.5            |
| Pb      | 220.353            | 4.1          | 3.6                    | 200                     | 191                 | 93.8            |
| Mn      | 257.610            | 5.96         | 5.99                   | 200                     | 189                 | 91.5            |
| Мо      | 203.845            | 2.19         | 2.22                   | 200                     | 195                 | 96.5            |
| Na      | 589.592            | 18981        | 18790                  | 200                     | *                   | *               |
| Ni      | 231.604            | 9.15         | 9.43                   | 200                     | 213                 | 102             |
| Р       | 178.221            | 73.3         | 72.7                   | 1000                    | 1152                | 107             |
| К       | 766.490            | 2159         | 2134                   | 200                     | 2390                | 95.2            |
| Se      | 196.026            | 7.09         | 7.79                   | 200                     | 192                 | 92.6            |
| Si      | 251.611            | 1790         | 1820                   | 500                     | 2260                | 94.0            |
| Ag      | 328.068            | 0.112        | 0.018                  | 200                     | 133.5               | 65.5**          |
| Sr      | 421.552            | 56.8         | 57.4                   | 200                     | 252                 | 97.5            |
| TI      | 190.801            | 8.30         | 7.63                   | 200                     | 188                 | 90.4            |
| Sn      | 189.927            | 1.17         | 1.12                   | 200                     | 193                 | 96.0            |
| Ti      | 334.940            | < MDL        | < MDL                  | 200                     | 195                 | 97.5            |
| V       | 292.402            | 2.12         | 2.14                   | 200                     | 197                 | 97.5            |
| Zn      | 206.200            | 413          | 418                    | 200                     | 605                 | 98.4            |

\* Spike to sample ratio was < 1

\*\* See note in text

## Conclusions

This study has demonstrated the capabilities of the PerkinElmer Optima 8300 ICP-OES to produce results that meet the rigorous requirements outlined in U.S. EPA Method 200.7. The accuracy and precision of the instrument allows less time to be spent on meeting the performance requirements. The ESI prep*FAST*<sup>TM</sup> system simplifies sample preparation, allowing higher sample throughput, while reducing memory effects and minimizing errors and contamination. The evaluation has clearly demonstrated that the Optima 8300 ICP-OES coupled with the prep*FAST*<sup>TM</sup> system is well-equipped to handle the real-world

PerkinElmer, Inc. 940 Winter Street Waltham, MA 02451 USA P: (800) 762-4000 or (+1) 203-925-4602 www.perkinelmer.com demands of U.S. EPA Method 200.7 for the analysis of water samples. It has also shown that the analytical accuracy of reference materials is excellent, together with the spike recoveries in real-world drinking water samples.

## References

 EPA Method 200.7 Revision 4.4, "Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma-Atomic Emission Spectrometry." http:// water.epa.gov/scitech/methods/cwa/bioindicators/ upload/2007\_07\_10\_methods\_method\_200\_7.pdf



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