

Inductively Coupled Plasma –
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Increased Sample Throughput for ICP-OES Applied to U.S. EPA Method 200.7

Abstract

The application of an SC-FAST sample introduction system to the analysis of natural and certified water samples is described. The SC-FAST system consists of an autosampler, sample loop, switching valve, high efficiency nebulizer and a glass cyclonic spray chamber to perform analysis by direct nebulization. The potential benefits of this introduction system are numerous and include: increased throughput, reduced memory effects, increased stability, lower reagent consumption and reduced instrument maintenance. These parameters are evaluated as the system is applied to U.S. EPA Method 200.7 Version 4.4.

Results indicate that sample throughput can be nearly tripled while still meeting the requirements outlined in Method 200.7. Sample-to-sample analysis (according to Method 200.7 protocol) is accomplished in 77 s with significantly improved washout compared to ICP-OES analysis by conventional introduction.

Introduction

The analysis of drinking water and wastewater for trace metal contamination is an important step in ensuring human and environmental health. More productive analyses make better use of public dollars and provide laboratories with a better cost of ownership for instrumentation. One way to improve productivity for metals analysis is by using a more sophisticated and automated sample introduction system to maximize the time spent on measurements and minimize the time spent on wash-in and wash-out of the sample. This work describes the coupling of the Optima™ 7300 DV with the ESI SC-FAST sample introduction system applied to a rigorous U.S. EPA method, drinking water/wastewater 200.7. Initial demonstration of capability and continuing quality control checks are measured as a demonstration of the method performance.

The SC-FAST sample introduction system consists of an autosampler, sample loop, vacuum pump, 6-port switching valve, a sea spray nebulizer and utilizes flow injection to perform analysis by direct nebulization. The FAST 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 sample loop is in close proximity to the nebulizer which reduces the time required for sample uptake. Furthermore, the sample loop prevents samples from contacting the peristaltic pump tubing, which greatly improves sample washout. In addition to higher throughput and reduced memory effects, the FAST system allows for the online addition of internal standards which simplifies sample preparation and helps minimize errors and contamination.

Summary of Method

EPA Method 200.7 contains a lengthy description of procedures that should be followed when collecting, preserving and preparing samples for analysis. The details concerning instrument performance, quality control, and daily analysis routines are loosely defined and are, therefore, open to various interpretations¹. For the sake of clarity, the procedure followed in this work is summarized in Table 1.

Table 1. Summary of U.S. EPA Method 200.7.

Establish Initial Performance Data

1. Linear Range
2. Perform IDLs and MDLs
3. Analyze Quality Control Samples with acceptable performance

Daily Analysis

1. Light plasma, allow 15 minutes for warm-up
2. Record Instrument Sensitivity
 - a. Use 1 ppm Mn for axial view, 10 ppm Mn for radial view
 - b. Record the counts for each and watch for significant changes as compared to signals obtained in previous days/weeks
3. Calibrate using blank and standards
4. Examine data and adjust background and measured wavelengths as needed
5. Screen new samples for relative levels and natural presence of internal std elements
6. Run instrument performance QCS
7. Run analytical QCS
8. Run samples
9. Review results of quality control samples for PASS/FAIL criteria

Experimental

Instrument

An Optima 7300 DV (PerkinElmer®, Shelton, CT) was used for the analysis of all samples described in this work. An SC-FAST (Elemental Scientific Inc., Omaha, NE) was coupled to the ICP-OES for sample introduction. The FAST system is controlled through the Optima WinLab32™ software and is shown schematically in Figure 1. The wavelengths monitored and the viewing modes used for the analytes in Method 200.7 are listed in Table 2. Instrument conditions for the Optima ICP-OES and FAST, as well as experimental parameters used throughout this work, are listed in Table 3.

Standards

All solutions were prepared using ASTM Type I (>18 MΩ-cm) water and double-distilled nitric acid. All acid concentrations reported in this document are described as a relative (v/v) percentage. Reference materials for this work were obtained from High Purity Standards (Charleston, SC) and from NIST, (Gaithersburg, MD).

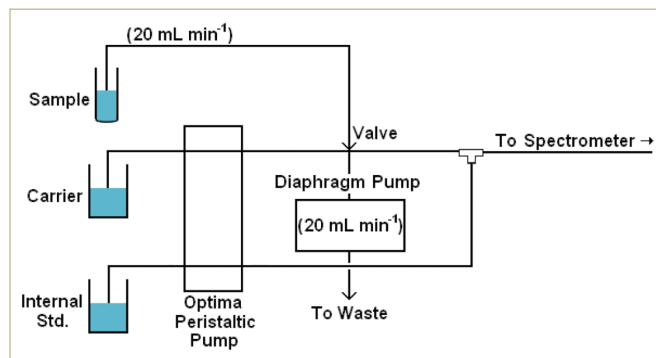


Figure 1. Schematic of a FAST introduction system.

Table 2. Wavelengths Monitored and Viewing Modes Used for Method 200.7.

Analyte	Symbol	Wavelength Monitored (nm)	View
Aluminum	Al	308.215	Radial
Antimony	Sb	206.836	Axial
Arsenic	As	188.979	Axial
Barium	Ba	233.527	Axial
Beryllium	Be	313.042	Radial
Boron	B	249.677	Radial
Cadmium	Cd	226.502	Axial
Calcium	Ca	315.887	Radial
Cerium	Ce	413.765	Radial
Chromium	Cr	267.716	Axial
Cobalt	Co	228.616	Axial
Copper	Cu	327.393	Axial
Iron	Fe	238.204	Radial
Lead	Pb	220.353	Axial
Lithium	Li	670.784	Radial
Magnesium	Mg	285.213	Radial
Manganese	Mn	257.610	Axial
Mercury	Hg	194.168	Axial
Molybdenum	Mo	202.035	Axial
Nickel	Ni	231.604	Axial
Phosphorus	P	213.617	Axial
Potassium	K	766.490	Radial
Selenium	Se	196.026	Axial
Silicon	Si	251.611	Axial
Silver	Ag	328.068	Axial
Sodium	Na	589.592	Radial
Strontium	Sr	407.771	Radial
Thallium	Tl	190.801	Axial
Tin	Sn	189.927	Axial
Titanium	Ti	334.940	Axial
Vanadium	V	292.402	Axial
Zinc	Zn	206.200	Axial
Internal Standards			
Yttrium	Y	371.029	Radial/Axial
Tellurium	Te	214.281	Radial/Axial
Interference Check			
Cerium	Ce	413.764	Radial

Table 3. FAST-Optima 7300 DV Instrumental Conditions and Experimental Parameters.

Optima 7300 DV Parameters	
RF Power	1450 watts
Plasma Gas Flow	15 L min ⁻¹
Auxiliary Gas Flow	0.2 L min ⁻¹
Nebulizer Gas Flow	0.6 L min ⁻¹
Peristaltic Pump Speed	0.85 mL min ⁻¹
Nebulizer/Spray Chamber	Sea Spray
Torch Cassette Position	-3
Purge	Normal
Resolution	Normal
Integration Time	2 s min/5 s max
Read Delay	14 s
Wash Time	1 s
Number of Replicates	3
FAST Parameters	
Sample Loop Volume	2 mL
Sample Loop Fill Rate	27 mL min ⁻¹
Carrier Pump Tubing	Black/Black (0.76 mm i.d.)
Sample Load Time	7 s
Rinse	5 s
Analysis Time (total)	77 s (sample-to-sample)
Experimental Parameters	
Carrier Solution	1% HNO ₃
Rinse Solution	1% HNO ₃
Acidity of Stds/Samples	1% HNO ₃

Sensitivity Check

Solutions containing 1 ppm Mn and 10 ppm Mn were analyzed periodically to monitor the sensitivity of the instrument. The Mn solutions were analyzed weekly and after the initial installation of the introduction system. The 1 ppm and 10 ppm Mn solutions were prepared by diluting 50 µL and 500 µL into 50 mL of 1% HNO₃, respectively.

Internal Standards

All solutions were spiked with 1.5 ppm Y and 2.5 ppm of Te. The spiking solution was made from single element stock solutions.

Calibration

Since Method 200.7 outlines the analysis of water (both drinking water and wastewater) and soils, each element was calibrated to levels typically encountered in those samples. The concentrations used in the calibration standards are listed in Table 4. Each standard contained all elements listed in Table 4.

Table 4. Calibration Standard Concentrations.

Analytes	Standard Concentration $\mu\text{g L}^{-1}$
Al, As, Ag, B, Ba, Be, Ca, Cd, Ce, Co, Cr, Cu, Fe, Hg, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Sb, Si, Se, Sn, Sr, Ti, Tl, V, Zn	1000

Monitored Wavelengths

As mentioned earlier, the wavelengths monitored, along with the viewing mode used for each analyte in Method 200.7, are listed in Table 2. All analyses were performed using the instrument's auto-integration feature with a minimum of 2 seconds and a maximum of 5 seconds.

Initial Performance Demonstration

IDLs

Instrument detection limits (IDLs) were estimated using multiple replicate measurements of the calibration blank (1% nitric acid). The IDL was calculated to be the concentration equal to three times the standard deviation of those replicate measurements; results are shown in Table 5. The IDL calculation was followed according to the procedure outlined in Method 200.7¹.

MDLs

Method detection limits (MDLs) were based upon seven replicate measurements of a series of spiked calibration blanks. Each blank solution was spiked with analytes at concentrations between 2 and 10 times the calculated IDLs. The MDL was calculated by multiplying the standard deviation of the seven replicate measurements by the appropriate Student's t test value according to:

$$\text{MDL} = (S) \times (t)$$

Note that the Student's t-value is based on a 99% confidence level. Both the Student's t-value and the standard deviation are based on n-1 degrees of freedom (t = 3.14 for six degrees of freedom).

Linear Range

A linear calibration range was established for each element listed in Method 200.7. No special detector optimization was done prior to conducting this procedure. The linear dynamic range for each analyte was calculated to be the highest concentration for which the recovery was within $\pm 10\%$ of the true (i.e., known) value of the standard. The results from this study are based upon multi-element standards in a 1% nitric acid matrix and are given in Table 5.

The linear range results should be viewed with the understanding that a combination of elements in the presence of a complicated matrix can cause interference effects and reduce the linear range for a number of elements. For results that more accurately reflect an individual experiment, the linear range should be established using standards in a matrix that replicates the sample matrix as closely as possible.

Table 5. Optima 7300 DV IDLs, MDLs and Linear Ranges for Method 200.7.

Analyte	Wavelength	IDL (ppb)	MDL (ppb)	MDL Spike Level	Linear Range
Ag	328.068	0.5	1.1	5	100
Al	308.215	1.5	6.6	20	2000
As	188.979	1.8	1.2	20	100
B	249.677	2.0 (0.4)	1.9 (0.2)	5	2000
Ba	233.527	0.2	0.2	2	25
Be	313.107	0.2	0.5	2	50
Ca	317.933	1.3 (0.3)	1.0 (0.1)	5	900
Cd	226.502	0.4	0.4	2	100
Ce	413.764	7.6 (0.9)	12.8 (1.4)	20	100
Co	228.616	0.3	0.5	2	250
Cr	267.716	0.4	0.6	2	50
Cu	327.393	0.4	0.3	2	300
Fe	259.939	1.0 (0.5)	0.7 (0.2)	5	400
K	766.490	41.1 (2.1)	28.1 (3.6)	100	2000
Mg	279.077	2.5 (0.4)	4.6 (1.0)	20	700
Mn	257.610	0.1	0.5	2	40
Mo	202.031	0.4	0.5	5	125
Na	589.592	7.6 (0.2)	4.7 (0.5)	20	900
Ni	231.604	0.7	0.5	2	125
Pb	220.353	0.6	1.1	20	100
P	213.617	2.9	5.6	20	3000
Li	670.784	0.5 (0.01)	0.5 (0.1)	5	200
Hg	253.652	1.6	9.6	20	100
Sb	206.836	2.6	2.1	20	100
Se	196.026	1.1	1.8	20	100
Si	251.611	2.6 (1.3)	13.3 (4.7)	5	2500
Sr	421.552	1.6 (0.1)	1.6 (0.5)	2	50
Sn	189.927	5.6 (0.5)	6.7 (1.9)	20	2000
Ti	334.940	0.1	0.5	2	50
Tl	190.801	1.1	1.8	20	100
V	292.402	0.2	0.6	2	50
Zn	206.200	0.2	0.4	2	100

() = axial

Data Handling

All data from the Optima 7300 DV was collected using a desktop computer attached to the instrument. The analytical results presented here were computed using the WinLab32 software and exported as report files. The text and supporting data tables were generated using Microsoft® Word and Excel®.

Sample Analysis/Quality Control

The accuracy and precision of the above-described method were verified using certified reference materials and a local

drinking water sample. Certified reference materials were analyzed without modification to determine the accuracy as compared to the certified values. Recoveries of spiked reference materials and the local drinking water sample were calculated. Results from High Purity Standards “Trace Metals in Drinking Water”, NIST SRM 1643e “Trace Metals in Water” and a local drinking water sample are listed in Tables 6, 7 and 8, respectively. The results for the analysis of High Purity Standards interference check standards “INFCS I + INFCS IV” are listed in Table 9. Note that INFCS I was diluted 10,000 fold and INFCS IV was diluted 1,000 fold before the standards were combined into one sample vial.

Table 6. Precision and Recovery Data for High Purity “Trace Metals in Drinking Water” (CRM).

Analyte	Avg Meas. Conc. $\mu\text{g L}^{-1}$	Std. Dev. $\mu\text{g L}^{-1}$	% RSD $\mu\text{g L}^{-1}$	Certified Value $\mu\text{g L}^{-1}$	Recovery of Certified Value (%)	Spike Level $\mu\text{g L}^{-1}$	Avg. Spike Recovery (%)	Std. Dev. of Spike Rec	% RSD
Ag	---	---	---	2	---	100	99.4	0.8	0.6
As	69.9	0.7	1.0	80	87.4	100	102	3.0	2.9
B	---	---	---	NA	---	100	99.7	1.1	1.1
Be	19.8	0.1	0.5	20	99.0	100	102	0.3	0.3
Ca	33400	18	0.1	35000	95.4	100	---	---	---
Cd	9.66	0.2	1.7	10	96.6	100	101	1.0	1.0
Co	23.3	0.2	0.8	25	93.2	100	100	0.2	0.2
Cu	19.8	0.7	3.4	20	99.0	100	102	1.0	1.0
Cr	19.4	0.3	1.5	20	97.0	100	102	0.7	0.7
Fe	93.2	1.9	2.0	100	93.2	100	102	5.0	4.9
K	2380	31	1.3	2500	95.2	100	---	---	---
Li	19.3	0.8	4.3	20	96.5	100	102	1.4	1.4
Mg	8530	125	1.5	9000	94.8	100	---	---	---
Mn	38.6	0.5	1.3	40	96.5	100	103	1.2	1.1
Mo	101	0.7	0.6	100	101	100	101	1.6	1.6
Na	5580	6.9	0.1	6000	93.0	100	---	---	---
Ni	57.8	0.5	0.9	60	96.3	100	98.6	2.5	2.6
Pb	39.7	3.1	7.7	40	99.2	100	103	2.9	2.8
Sb	---	---	---	10	---	100	107	2.8	2.7
Se	---	---	---	10	---	100	110	6.5	5.9
Sn	---	---	---	NA	---	100	100	2.2	2.2
Sr	246	0.4	0.2	250	98.4	100	94.3	3.0	3.2
Ti	---	---	---	NA	---	100	105	0.4	0.4
Tl	---	---	---	10	---	100	99.5	4.7	4.7
V	29.8	0.4	1.4	30	99.3	100	103	0.5	0.5
Zn	69.5	0.6	0.9	70	99.3	100	98.8	1.6	1.7

NA = Not Applicable

Table 7. Precision and Recovery Data for NIST SRM 1643e “Trace Elements in Water”.

Analyte	Avg. Meas.			Certified Value $\mu\text{g L}^{-1}$	Rec. of Certified Value (%)	Spike Level $\mu\text{g L}^{-1}$	Avg. Spike Recovery (%)	Std. Dev. of Spike Rec	% RSD
	Conc. $\mu\text{g L}^{-1}$	Std. Dev. $\mu\text{g L}^{-1}$	% RSD $\mu\text{g L}^{-1}$						
Ag	---	---	---	1.062	---	100	90.3	1.7	1.9
Al	133	0.3	0.3	141.8	94.1	100	94.0	1.1	1.2
As	60.2	1.9	3.7	60.45	99.6	100	109	4.3	4.0
B	150	0.3	0.2	157.9	95.0	100	98.5	2.4	2.4
Ba	504	11	2.1	544.2	92.6	100	---	---	---
Be	13.6	0.1	0.5	13.98	97.3	100	104	0.5	0.4
Ca	29600	95	0.3	32300	91.6	100	---	---	---
Cd	6.00	0.2	4.1	6.568	91.4	100	102	1.6	1.6
Co	25.2	0.2	0.6	27.06	93.1	100	103	0.9	0.9
Cr	20.4	0.2	0.8	20.40	100	100	105	1.0	0.9
Cu	23.6	0.3	1.2	22.76	101	100	108	0.2	0.1
Fe	97.6	7.0	7.2	98.1	99.5	100	99.7	4.8	4.9
K	1920	46	2.4	2034	94.4	100	---	---	---
Li	18.3	0.9	5.0	17.4	105	100	104	0.8	0.8
Mg	7600	70	0.9	8037	94.5	100	---	---	---
Mn	38.7	1.6	4.0	38.97	99.4	100	102	1.1	1.1
Mo	125	0.3	0.2	121.4	103	100	105	1.4	1.3
Na	19100	100	0.5	20740	92.1	100	---	---	---
Ni	59.5	0.9	1.4	62.41	95.3	100	102	1.1	1.1
Pb	19.4	0.5	2.6	19.63	98.8	100	107	2.1	2.0
Sb	59.9	3.7	6.1	58.30	103	100	102	0.8	0.7
Se	---	---	---	11.97	---	100	105	5.3	5.0
Sr	319	0.9	0.3	323.1	98.7	100	101	9.5	9.4
Sn	---	---	---	n/a	---	100	104	0.03	0.03
Ti	---	---	---	n/a	---	100	108	0.3	0.3
Tl	---	---	---	7.445	---	100	106	6.4	6.1
V	37.0	0.2	0.5	37.86	97.7	100	107	0.6	0.6
Zn	76.6	0.7	0.9	78.5	97.6	100	101	0.7	0.6

NA = Not Applicable

Table 8. Results and Spike Recoveries for Local Drinking Water.

Analyte	Wavelength (nm)	LDW Conc. $\mu\text{g L}^{-1}$	Low Spike Level $\mu\text{g L}^{-1}$	Low Spike Results $\mu\text{g L}^{-1}$	Low Spike % Recovery	High Spike Level $\mu\text{g L}^{-1}$	High Spike Results $\mu\text{g L}^{-1}$	High Spike % Recovery
Al	308.215	7.50	100	100.3	100.3	500	475	95.0
As	188.979	< MDL	100	102.9	102.9	500	487	97.4
B	249.677	11.2	100	100.1	100.1	500	472	94.4
Ba	233.527	69.0	200	192.9	96.5	1000	946	94.6
Be	313.042	0.120	100	103.8	103.8	500	490	98.0
Ca	315.887	7120	100	---	---	500	---	---
Cd	226.502	< MDL	100	98.8	98.8	500	484	96.8
Co	228.616	< MDL	100	102.1	102.1	500	486	97.2
Cr	267.716	< MDL	100	101.6	101.6	500	484	96.8
Cu	327.393	97.6	100	106	106	500	478	95.6
Fe	238.204	83.5	100	94.5	94.5	500	491	98.2
K	766.490	877.7	100	---	---	500	---	---
Li	670.784	< MDL	100	102	102	500	492	98.4
Mg	285.213	1710	100	---	---	500	---	---
Mn	257.610	16.4	100	102	102	500	503	101
Mo	202.035	< MDL	100	101	101	500	480	96.0
Na	589.592	12800	100	---	---	500	---	---
Ni	231.604	0.730	100	99.4	99.4	500	482	96.4
P	213.617	< MDL	100	99.0	99.0	500	476	95.2
Pb	220.353	< MDL	100	99.7	99.7	500	487	97.4
Sb	206.836	< MDL	100	102	102	500	492	98.4
Se	196.026	< MDL	100	105	105	500	525	105
Sn	189.927	2.94	100	97.4	97.4	500	475	95.0
Sr	407.771	52.4	100	101	101	500	488	97.6
Ti	334.940	< MDL	100	103	103	500	503	101
Tl	190.801	< MDL	100	104	104	500	475	95.0
V	292.402	0.220	100	103	103	500	487	97.4
Zn	206.200	47.2	100	100	100	500	478	95.6

Table 9. Results for High Purity INFCS I + INFCS IV.

Analyte	Wavelength (nm)	INFCS Run #1 µg L ⁻¹	INFCS Run #2 µg L ⁻¹	INFCS Avg. Result µg L ⁻¹	Duplicate RPD	INFCS True Value µg L ⁻¹	% Recovery
As	188.979	110	111	111	0.8	100	111
Ba	233.527	30.0	28.5	29.3	5.2	30	97.7
Be	313.042	10.9	10.9	10.9	0.1	10	109
Ca	315.887	4950	4910	4930	0.8	5000	98.6
Cd	226.502	32.2	33.2	32.7	2.9	30	109
Co	228.616	31.0	31.5	31.3	1.6	30	104
Cr	267.716	31.5	31.4	31.5	0.4	30	105
Cu	327.393	31.3	31.1	31.2	0.5	30	104
Fe	238.204	5230	4910	5070	6.2	5000	101
Hg	194.168	4.97	5.54	5.30	10.8	5	105
K	766.490	2130	2150	2140	0.7	2000	107
Mg	285.213	5070	5050	5060	0.3	5000	101
Mn	257.610	20.8	19.5	20.1	6.4	20	100
Ni	231.604	30.9	31.5	31.2	2.1	30	104
Pb	220.353	105	108	106	2.9	100	106
Se	196.026	53.9	48.8	51.4	10.1	50	103
Tl	190.801	102	103	103	1.1	100	103
V	292.402	31.1	31.1	31.1	0.2	30	104
Zn	206.200	34.8	32.6	33.7	6.7	30	112

Conclusions

The FAST system coupled with the Optima 7300 DV has been shown to produce results that meet the requirements outlined in U.S. EPA Method 200.7 while increasing sample productivity over 200% when compared to analyses with conventional introduction systems. Since the FAST system eliminates virtually all of the rinse and read delay times, most of the time is now spent running samples, therefore increasing productivity. Also, since the FAST reaches a steady state signal much more quickly than conventional sample introduction, instrument and method detection limits are improved almost 2-fold for many analytes. When used in conjunction with the SC autosampler and Optima 7300 DV, the FAST system provides a rugged, automated sample introduction system that can significantly reduce labor costs and improve laboratory productivity.

Acknowledgement

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References

1. EPA Method 200.7, "Determination of Metals and Trace Metals in Water and Wastes by Inductively Coupled Plasma-Atomic Emission Spectrometry," Revision 4.4, 1994, Environmental Monitoring Systems Laboratory, Office of Research and Development, United States Environmental Protection Agency, Cincinnati, OH 45268.