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High throughput sample introduction system for the analysis of drinking waters and wastewaters by ICP-MS

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High throughput sample introduction system for the analysis of drinking waters and wastewaters by ICP-MS†

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The application of a high-throughput introduction system to the analysis of natural and certified water samples is described. The introduction system consists of an autosampler, a switching valve, a high efficiency PFA-ST nebulizer and Peltier-cooled cyclonic spray chamber to perform analysis by direct nebulization. The potential benefits of this introduction system include increased throughput, reduced memory effects, increased stability, lower reagent consumption and less instrument maintenance. These parameters were evaluated as the system was applied to U.S. EPA Method 200.8. Particular attention was paid to the retention of Hg and long term stability during the analysis of samples containing high total dissolved salts. Analyses (according to Method 200.8 protocol) were accomplished in 90 s with significantly improved washout compared with that of conventional introduction, thereby doubling the throughput.

1. Introduction

Inductively-coupled plasma mass spectrometry (ICP-MS) is a sensitive technique that is widely used for the analysis of liquid samples;[1] however, its "Achilles heel" lies with sample introduction.[2] As with all analytical atomic spectroscopic techniques, sample introduction is a critical step that strongly influences, and often dictates, analytical figures of merit such as sensitivity, precision and stability.[1] Improving the efficiency of sample introduction is an on-going research topic; however, it has proven to be a non-trivial task as the processes involved within both the nebulizer and spray chamber are numerous and complicated.[3]

Both the nebulizer and spray chamber play a crucial role in sample introduction. The main role of the nebulizer is to generate an aerosol, with a narrow drop size distribution, of small droplets from a continuous solution stream.[4] A spray chamber then efficiently filters out the large aerosol droplets.[5] Since the droplets must be desolvated, and the resulting salt vaporized, atomized and ionized during the short residence time in the plasma, the spray chamber passes only small droplets (typical diameter <10 μm).[6,7]

In an effort to overcome the limits associated with sample introduction, much effort has been put into the design of nebulizers and spray chambers. The relative simplicity and low cost of pneumatic nebulization[8] make it the preferred choice for ICP sample introduction; however, its drawbacks include low analyte transport efficiency (1–2%), high sample consumption (1–2 ml min^{-1}) and relatively high retention of some elements.[9]

Microconcentric nebulizers (MCN)[10,11] were designed to improve the gas–liquid interaction and reduce the size distribution of droplets formed in the aerosol.[12,13] These nebulizers, which operate at lower sample flow rates compared to those typically used with pneumatic nebulizers, include: high efficiency nebulizers (HEN),[14,15] oscillating capillary nebulizers (OCN)[16,17] and sonic spray nebulizers (SSN).[18] These nebulizers have a relatively low dead volumes and operate at normal or elevated nebulizer gas pressures to improve analyte transport efficiency regardless of whether organic or aqueous solvents are used.[19,20]

Ultrasonic nebulizers (USN)[21,22] efficiently produce a large volume of small droplets[23] for which a desolvation system is needed to decrease the water vapor load, in the case of aqueous sample analyses,[24,25] and to decrease solvent load and carbon deposition for samples containing organic solvents or high concentrations of dissolved salts.[26,27]

Direct injection nebulizers (DIN)[28,29] and direct injection high efficiency nebulizers (DIHEN)[30,31] improve the sample transport efficiency to 100%, even at relatively low flow rates, and do not require a spray chamber, thereby decreasing the dead volume, increasing the response time, and reducing memory effects.[32,33] A significant drawback of DINs is their vulnerability toward samples containing high concentrations of dissolved salts or volatile solvents which cause plasma instability and tip clogging.[34] The large bore direct injection high efficiency nebulizer (LB-DIHEN)[35] was designed to reduce its susceptibility to blockage; however, the larger inside diameter of the nebulizer capillary produces a relatively large droplet size distribution which degrades both the precision and detection limits.[36]

Much effort has been put into spray chamber design, as spray chambers are responsible for the loss of > 90% of the aerosol produced by the nebulizer.[7] Improvements have focused on controlling the flow of aerosol from the nebulizer to maximize the efficiency with which larger droplets are filtered out.[37]

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Reverse flow, or Scott-type double-pass,[38,39] spray chambers are simple, low-cost and popular. The design is particularly useful for samples containing high concentrations of dissolved salts, as the transport efficiency is relatively low compared to that of other spray chamber designs.[40]

Cyclonic designs have improved transport efficiency, precision and detection limits.[41,42] Popular cyclonic spray chamber designs include a flow spoiler or dimple.[43] Computer modeling of the fluid dynamics within cyclonic spray chambers suggests that the presence of three spoilers creates a "virtual cyclone",[44] which reduces interaction between the aerosol and the walls of the spray chamber, thereby improving transport efficiency and reducing memory effects.

Single-pass or cylindrical-type spray chambers, designed for low-flow introduction,[45,46] provide high efficiency and reduced memory effects;[46] however, these designs are unsuitable for conventional ICP analysis and are typically used when electrophoretic or chromatographic separations are employed in conjunction with ICP detection.[47,48]

Spray chambers have also been blamed for the retention of elements such as B and Hg.[49,50] As discussed above, one approach to solving this problem has been in the removal of the spray chamber. Other approaches have involved the use of a controlled temperature spray chamber. Cooled spray chambers reduce aerosol desolvation and deposition on the walls of the spray chamber, thereby reducing memory effects and reducing oxide formation in the plasma.[51–53] Heated spray chambers improve the efficiency of aerosol generation in aqueous samples by desolvation.[54,55]

In addition to nebulizer and spray chamber design, internal standardization and stream switching have been employed to improve plasma spectrochemical measurements. When chosen appropriately, internal standardization has been shown to improve measurement precision[56–58] and to reduce the effects of instrument fluctuation and drift.[59] Online addition of internal standards combines the advantages associated with internal standardization without adding complexity or error to the sample preparation procedure.[60,61]

Stream switching provides a continuous flow of solution to the nebulizer, which allows sample uptake and stabilization in the plasma to take place more rapidly, thereby increasing sample throughput. Other discrete sample introduction techniques, including air-segmented introduction, have been used to increase sample throughput with the added benefit of decreased signal tailing.[62,63] A drawback to these techniques is the introduced sample is of finite volume, and the measured signal becomes transient. This is an undesirable situation when measuring a large suite of elements with a sequential instrument as many of the elements will be measured off the peak maximum, which degrades the signal-to-noise ratio and the sensitivity.[64,65] To retain both steady-state signal analysis and rapid wash-in and washout, a relatively large-volume sample loop is needed.

The driving forces behind the design of sample introduction systems include: improved sensitivity and detection limits, improved precision across the working mass range, and fewer interferences from matrix effects. Much of the design efforts have centered around improvements in nebulizers and spray chambers; however, significant progress has diminished in the recent years.[66]

We have evaluated a new introduction system that incorporates a number of the introduction features discussed above for analysis with increased throughput and decreased sample carryover. The system consists of an automatic sample changer, a low-flow, microconcentric PFA-ST nebulizer, a Peltier-cooled, baffled, glass cyclonic spray chamber and on-line internal standard addition. Washout is improved by the use of a stream switching valve and sample loop, which inserts a small, well-defined volume of solution into a continuously flowing carrier that merges with an internal standard stream. The sample loop prevents samples from contacting the peristaltic pump tubing and reduces the amount of salt introduced into the instrument.

This method has been demonstrated in the context of U.S. EPA Method 200.8, which is a procedure for trace element determination in drinking water and wastewater. Laboratories that perform environmental analysis in compliance with Method 200.8 must establish instrument and method performance, followed by validation using certified reference materials. Method 200.8 also requires that quality control analysis be performed periodically.

2. Experimental

2.1 Instrumentation

Samples were analyzed with a PerkinElmer SCIEX (Shelton, CT) ELAN 9000 plasma source mass spectrometer fitted with an Elemental Scientific, Inc. (Omaha, NE) sampler changer (SC)-FAST sample introduction system. The FAST system, shown in Fig. 1, consists of an autosampler, a switching valve, a high-efficiency PFA-ST nebulizer and a Peltier-cooled cyclonic spray chamber. The system is designed to be inserted between the instrument's peristaltic pump and the spectrometer and is controlled through the ELAN software. Instrument conditions for the ELAN, FAST, and other experimental parameters, are presented in Table 1.

The contents of the sample loop, which is large enough to provide a steady state signal, are injected into an acid carrier stream that merges with the internal standard solution. The lengths of tubing are short so that the time between injection and measurement is minimized. The instrument response as a function of time is illustrated schematically in Fig. 2.

The FAST system allows for a programmable, multi-step rinse procedure that can be controlled through both the ELAN and

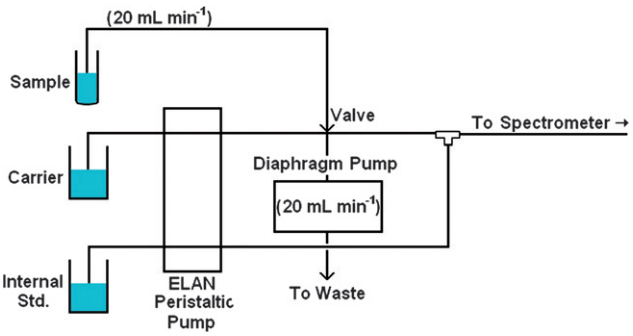

Fig. 1 Schematic diagram of a FAST introduction system.

Table 1 FAST-ELAN 9000 instrumental conditions and experimental parameters

ELAN 9000 parameters	
RF power	1500 W
Plasma gas flow	15 l min^{-1}
Auxiliary gas flow	1 l min^{-1}
Nebulizer gas flow	0.83–0.88 l min^{-1}
Sample flow rate	0.5 ml min^{-1}
Nebulizer/spray chamber	PFA-ST/Peltier-cooled cyclonic
Spray chamber temp.	2 °C
Detector mode	Dual mode
Lens	AutoLens Enabled
Sampler/skimmer cones	Nickel
Scanning mode	Peak hopping
Number of points/peak	1
Dwell time	10–50 ms per point
Number of sweeps/reading	10
Number of readings/replicate	1
Number of replicates	3
FAST parameters	
Sample loop volume	1 ml
Sample loop fill rate	20 ml min^{-1}
Carrier pump tubing	Black/black (0.76 mm id)
Carrier flow rate	0.4 ml min^{-1}
Internal std pump tubing	Orange/green (0.38 mm id)
Internal std flow rate	0.1 ml min^{-1}
Read delay	20 s
Rinse	5 s
Analysis time (total)	90 s (sample-to-sample)
Experimental parameters	
Carrier solution	3% HNO_3
Internal std. solution[a]	1% HNO_3 + 100 μg l^{-1} Au
Rinse solution	3% HNO_3
Acidity of stds/samples	3% HNO_3

[a] Sc was used as an internal standard for the determination of Be and Al because Li, often present in real samples, resulted in poor recoveries.

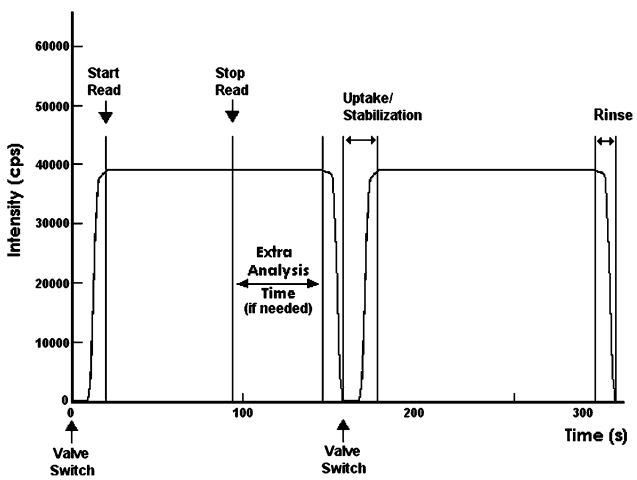

Fig. 2 Profile for back-to-back sample injections of 1 μg l^{-1} U.

the FAST software. The FAST software allows the user to program a "rinse" step that is executed while the ELAN performs data collection. During this step, the sample probe is moved to two reservoirs located at the end of the autosampler. The probe is immersed into each reservoir for 2 s while solution is pumped through the probe tubing. The user is able to control the length of time the probe spends in each reservoir, and a different rinsing solution can be used for each reservoir if desired. This rinse step serves to wash the outer surface of the sample probe along with the walls of the tubing that connect the probe to the switching valve. As the rinsing solution is pumped to waste without passing through the sample loop, it can be relatively aggressive, as it would not pass through the nebulizer and affect subsequent measurements.

The ELAN software also performs a "rinse" step, however, it is significantly different to that performed with the FAST software. The ELAN executes a "rinse" step after data collection and before the next sample is loaded into the sample loop. During this step, the sample probe is held over the next sample vial while air is drawn through the sample loop for 5 s. Evacuating the loop reduces hydrodynamic resistance so that subsequent samples can be rapidly loaded. The length of this step can be adjusted for larger or smaller sample loops, or eliminated entirely. As the FAST system is currently configured, the sample loop cannot be washed with anything other than the next sample.

Since the FAST system allows for direct nebulization using a fixed sample volume, a sample injection profile was first taken to determine an appropriate read delay and analysis window. The read delay and analysis window chosen for a 1 ml sample volume injected by a carrier moving at 0.5 ml min^{-1} were 20 s and 60 s, respectively. The timing parameters of the quantitative analysis were set to be within this read window. Therefore, the read parameters listed in Table 1 were chosen such that three replicate measurements of the twenty-six analytes could be made in 60 s.

2.1.1 FAST procedure. The FAST procedure consisted of three steps. The first step was to load the sample loop. The injection valve remained in the "load" position while a 3 to 4 times the loop volume of sample solution was drawn through the loop at 20 ml min^{-1} *via* a diaphragm pump and delivered to waste. While the loop was loaded, carrier and internal standard solutions were pumped continuously into the nebulizer (see Table 1 for identity, concentration, and flow rate of carrier and internal standard solutions).

The second step involved switching the valve to the "inject" position, which allowed the carrier stream to push the contents of the sample loop into the nebulizer. All data collection occurred during this step. While data was being collected, the sample probe was moved to the rinsing station where a 1% HNO_3 solution was pumped through the tubing that connected the autosampler probe to the switching valve.

The third step was to reload the sample loop. The valve was switched back to the "load" position, and first air, and then the next sample solution were drawn through the loop. In this step, the next sample washed out the remains of previous sample.

2.1.2 Isotopes monitored. The primary and secondary elements outlined in Method 200.8 were monitored in this work. Multiple isotopes for several elements were monitored to correct for isobaric and molecular interferences. Correction equations for these interferences are given elsewhere.[67] Method 200.8 does not include Ca, Fe, K, Mg and Na; however, these elements were monitored for informational purposes at $m/z = 44$, 54, 39, 24 and 23, respectively. All analyses were performed in peak hopping

mode, with a dwell time of between 10 and 50 ms per reading per isotope.

2.2 Reagents

All solutions were prepared using >18 MΩ cm water and double-distilled nitric acid. Reference materials for this work were obtained from High Purity Standards (Charleston, SC) and from NIST, (Gaithersburg, MD). Double distilled nitric and hydrochloric acids were purchased from GFS Chemicals, Inc. (Sidney, BC, Canada). All acidified solutions were made by dilution on a v/v basis.

2.3 Sample preparation

A multi-element internal standard solution containing 20 μg l^{-1} Ga, Ho, In, Ir, Li, Rh, Sc, Tb, Te and Y was used for all analyses. The internal standard solution was prepared from a 10 mg l^{-1} multi-element stock solution by diluting 1 ml of the stock into 500 ml of 1% nitric acid. Gold was added to the internal standard solution in accordance with EPA Method 200.8 protocol. This was accomplished by adding 500 μl from a 100 mg l^{-1} stock solution of Au to yield a final concentration of 100 μg l^{-1}. No internal standards were added to individual blanks, standards and samples, as the internal standard solution was added online.

The calibration blank and standards were prepared in 3% nitric acid for all experiments except for those used to determine detection limits. As illustrated in the results section, a higher acid concentration resulted in improved sample washout and analyte recovery, although detection limits deteriorated slightly. The concentrations used in the calibration standards are listed in Table 2. Each standard contained all the elements listed in Table 2, with the exception of Hg for which standards were run separately to monitor retention, if any, in the sample introduction system. A stock solution of 1 μg l^{-1} Hg was prepared once a week by diluting 500 μl from a 20 μg l^{-1} solution to 10 ml of 1% HNO_3. Standards containing Hg were prepared fresh daily from the 1 μg l^{-1} solution to prevent precipitation.

A 1 μg l^{-1} solution containing Ba, Be, Ce, Co, Cu, Fe, In, K, Mg, Na, Pb, Rh and U in 1% HNO_3 was used for all instrument optimizations. This tuning solution was used to measure all performance aspects of the instrument including: mass calibration, resolution, nebulizer gas flow, AutoLens calibration, and daily performance checks. The tuning solution was prepared by diluting 50 μl of a 10 mg l^{-1} multi-element stock solution to 500 ml of 1% HNO_3. The multi-element stock solution was prepared from 1000 mg l^{-1} single element stock solutions of the elements listed above by diluting 500 μl of each element to 50 ml of 1% HNO_3.

2.4 Method development

2.4.1 Optimization. Optimization of ELAN spectrometer was performed according to manufacturer recommendations. Parameters for the FAST system were varied using a single-cycle alternating variable search method[68] with the assumption that the FAST parameters were independent of each other and of those optimized on the ELAN. The figures of merit used for this investigation were washout time, sample throughput and performance that was compliant with Method 200.8. Parameters evaluated in this investigation were: read delay, pump flow rate, acid identity and concentration in the standards and samples, along with the carrier and rinse solutions, and the addition of Au for effective reduction of Hg retention.

It is not possible to obtain the best detection limits for all elements in a large suite of elements as the operating conditions chosen are a compromise.[65] Optimizing the detection limits for this method may not be necessary, however, as the ELAN 9000 instrument has detection limits that are well below typical sample concentrations.

2.4.2 Analytical performance. Method 200.8 specifies that the analytical performance of the instrument be established before sample analysis is performed.[69] These performance characteristics include detection limits for both the instrument and method, linear working range and rate of wash-in/washout for samples containing relatively high concentrations of relevant analytes. Once instrument performance is established, the accuracy and precision of the method are evaluated with the analysis of appropriate certified reference materials. Additionally, instrument sensitivity drift must be monitored *via* periodic measurements of a quality control standard.

Under optimized conditions, calibration curves for multi-element standards containing 0, 25, 50 and 100 μg l^{-1} were obtained. Sample throughput was calculated relative to that for conventional ICP-MS introduction systems. Both instrument and method detection limits were calculated according to the recommended protocol outlined in EPA Method 200.8. The instrument detection limit (IDL) for each analyte was calculated to be the concentration equal to three times the standard deviation of ten replicate measurements of a calibration blank (1% nitric acid). Method detection limits (MDLs) were based upon seven replicate measurements of a calibration blank spiked with analytes at concentrations between 2 and 5 times the calculated IDLs. The MDL was calculated by multiplying the standard deviation of the seven replicate measurements, S, by the appropriate Student's t test value according to:

$$\mathrm{MDL} = S \times t \quad (1)$$

Table 2 Calibration standard concentrations

Analytes	Standard 1 Concentration/μg l^{-1}	Standard 2 Concentration/μg l^{-1}	Standard 3 Concentration/μg l^{-1}	Standard 4 Concentration/μg l^{-1}
Ag, Al, As, Ba, Be, Cd, Co, Cr, Cu, Mn, Mo, Ni, Sb, Se, Th, Tl, U, V, Zn	1	10	50	100
Hg	0.05	0.1	0.5	1
Ca, Fe, K, Mg, Na	10	100	1000	10 000

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).

The stability of the introduction system was evaluated by periodically measuring a quality control (QC) standard during sample analysis. The QC standard, which consisted of a 50 μg l^{-1} multi-element spike (1 μg l^{-1} Hg) in 3% HNO_3, was measured after the analysis of 10 drinking water samples had been completed. Bottled water containing 1600 mg l^{-1} total dissolved salts (TDS) and local tap water were each measured over a period of ten hours, to model a "typical" day of sample analysis.

Memory effects were studied to estimate the rinse time. These studies were performed by measuring a high concentration standard, followed by a series of calibration blanks that were measured until each analyte produced a signal at or below 10 times the MDL calculated previously. Each blank measurement, termed a "cycle", includes 20 s for loading the sample, 65 s for analysis, and 5 s for rinsing, yielding a total analysis time of 90 s. The high concentration standard contained analytes at 10 times the upper bound of the linear range, as suggested in Method 200.8.

A linear calibration range was established for each analyte listed in Method 200.8. The dual (analog and pulse) detector modes of the ELAN were to extend the linear range. The upper linear range was further extended by aspirating a solution containing 200 μg l^{-1} Na and using an analog target gain of 7000 during the analog stage optimization. A dual detector calibration was performed following the detector optimization. A solution containing 200 μg l^{-1} of Method 200.8 elements, 1 mg l^{-1} of Ca, Fe, K, Mg and Na, and 200 μg l^{-1} of the internal standard elements, all in a 1% nitric acid matrix, was used.

Upon completion of the dual detector calibration, the instrument was calibrated with a 3% nitric acid blank and the standards listed in Table 2. A series of standards of increasing concentration was measured as samples, and the calculated concentration of each analyte was compared to the true (i.e. known) concentration of the standard. The top of the linear range for each analyte was the highest concentration for which the measured concentration was within 90% of its known concentration.

2.4.3 Validation. The accuracy of the method was verified using certified reference materials and spiked recoveries of a local drinking water sample. Certified reference materials were analyzed without modification to determine the accuracy. Recoveries of multielement spikes were calculated for the following reference materials: High Purity Standards "Trace Metals in Drinking Water", NIST SRM 1643e "Trace Elements in Water" and a local drinking water sample. An interference check standard (High Purity Standards "INFCS I + INFCS IV") was also analyzed, and the results were compared to the certified values; however, no spike recoveries were performed.

The precision of the method was evaluated using %RSD values from the analysis of certified reference materials as well as from spike recovery measurements.

2.5 Application to water samples

Local drinking water samples were analyzed with 2 sets of spikes, and recoveries were calculated. One set of spikes contained 1 μg l^{-1} Hg and 10 μg l^{-1} of all other analytes of interest. The other set contained 4 μg l^{-1} Hg and 50 μg l^{-1} of all other relevant analytes. Water samples were acidified to 3% with HNO_3 and analyzed with no further pretreatment. Dilution from the addition of acid was assumed to be negligible as microliter quantities of concentrated HNO_3 were added to 500 ml sample solutions.

2.6 Approach to Hg retention

The possible effect of gold on the retention of Hg was investigated with the online addition of gold *via* the internal standard and carrier solutions and with the batchwise addition to standards and samples.

3. Results and discussion

3.2 Method development

3.2.1 Optimization. Optimum conditions for the ELAN and the FAST system are listed in Table 1. A read delay of 20 s provided enough time to load the sample loop, inject its contents into the nebulizer and allow the plasma to reach steady state before analysis commenced. A longer read delay can be used if desired; however, a minimum delay of 20 s must be used to avoid a degradation in precision.

Various pump speeds up to 8 rpm were investigated to determine whether pump roller noise was reflected in the measurement precision. Pump speeds above 8 rpm were not examined to avoid significant backpressure from the narrow bore tubing and low-dead-volume mixing tee. Results indicated that pump roller noise was not significant at any of the pump speeds examined. A pump speed of 6 rpm (equivalent to a flow rate of 0.5 ml min^{-1}) was chosen.

The acid identity and concentration within the standards, samples, and carrier and rinse solutions was examined to determine the effect, if any, on wash-in/washout and detection limits. Both HNO_3 and HCl were used and the concentrations of each were varied from 1% to 3%. Results from the estimated rinse studies indicated that a higher acid concentration resulted in a slightly faster wash-in/washout; however, detection limits, both IDLs and MDLs, were degraded across the entire mass range. The poorer detection limits were most likely due to higher contamination levels present in the more concentrated acid. For this reason, detection limit studies were performed with standards in 1% nitric acid. The ELAN 9000 is an instrument that provides detection limits well below typical sample concentrations, regardless of the acidity used to calculate the detection limits. If a priority is to reduce memory effects throughout sample analysis, higher acid concentrations improve sample washout at the expense of slightly poorer detection limits.

3.2.2 Analytical performance. Results for IDLs, MDLs and the linear working range are listed in Table 3, along with the spike concentrations used for the MDL study. The spike concentrations cover several orders of magnitude to comply with the Method 200.8 requirement that each analyte be spiked at a level that is 2 to 5 times the IDL. Detection limit studies were performed with standards in a 3% nitric acid matrix.

The results from the linear range study are listed in Table 3. One should view these results with the understanding that

Table 3 ELAN 9000 IDLs, MDLs, and linear ranges for Method 200.8

Analyte	Mass	IDL[a]/μg l^{-1}	MDL[a]/ μg l^{-1}	MDL spike concentration/ μg l^{-1}	Linear range[b]/ mg l^{-1}
Be	9	0.006	0.02	0.05	5
Al	27	0.02	0.03	0.5	10
V	51	0.03	0.05	0.5	5
Cr	52	0.02	0.04	0.5	5
Mn	55	0.003	0.003	0.5	10
Co	59	0.004	0.005	0.005	10
Ni	60	0.01	0.02	0.05	5
Cu	63	0.01	0.02	0.05	5
Zn	66	0.06	0.11	0.5	1
As	75	0.03	0.03	0.5	5
Se	82	0.10	0.19	0.5	5
Mo	98	0.003	0.01	0.05	20
Ag	107	0.007	0.01	0.05	20
Cd	111	0.02	0.02	0.05	5
Sb	123	0.02	0.02	0.005	20
Ba	135	0.02	0.05	0.05	20
Hg	202	0.02	0.003	0.05	1
Tl	205	0.002	0.002	0.005	20
Pb	208	0.002	0.006	0.05	20
Th	232	0.006	0.002	0.005	20
U	238	0.0005	0.003	0.005	20
Ca[c]	44	7	8	50	100
Fe[c]	54	2	1	10	100
K[c]	39	1	2	10	100
Mg[c]	24	0.03	0.1	0.05	100
Na[c]	23	0.2	0.2	10	100

[a] Obtained with standards in a 1% HNO_3 matrix. [b] Indicates the top of the linear range which is defined by the concentrations between the IDL and the linear range. Obtained with standards in a 3% HNO_3 matrix. [c] For information only.

Table 4 Estimated rinse times[a]

Analyte	Tested concentration/ μg l^{-1}	Measured concentration/μg l^{-1} Cycle #1	Cycle #2	Cycle #3	MDL	10 × MDL
Be	5000	1.077	0.043	0.012	0.04	0.4
Al	5000	0.075	0.011	0.019	0.04	0.4
V	5000	0.995	0.02	0.002	0.06	0.6
Cr	5000	0.946	0.024	0.003	0.04	0.4
Mn	5000	0.954	0.038	0.04	0.05	0.5
Co	5000	0.94	0.041	0.022	0.02	0.2
Ni	5000	1.004	0.042	0.02	0.03	0.3
Cu	5000	0.922	0.048	0.002	0.02	0.2
Zn	20 000	0.953	0.036	0.015	0.08	0.8
As	20 000	3.731	0.128	0.043	0.04	0.4
Se	20 000	6.153	1.846	1.363	0.2	2
Mo	5000	3.175	0.082	0.126	0.01	0.1
Ag	500	0.799	0.042	0.015	0.02	0.2
Cd	5000	8.557	1.656	0.479	0.04	0.4
Sb	10 000	0.732	ND[a]	ND[a]	0.03	0.3
Ba	5000	1.538	0.088	0.067	0.06	0.6
Hg	20	0.662	0.08	0.02	0.01	0.1
Tl	5000	0.754	0.048	0.008	0.01	0.1
Pb	5000	0.838	0.046	0.015	0.01	0.1
Th	5000	0.802	0.039	0.005	0.002	0.02
U	5000	0.825	0.027	0.004	0.004	0.04

[a] ND: Not detected (concentration below the detection limit).

a combination of elements in the presence of a complicated matrix can cause precipitation and interference effects, thus reducing the linear range for a number of elements. The results of this study are based upon multi-element standards in a 3% nitric acid matrix. 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.

Results from the memory effects study are listed in Table 4. The results include the first 3 analysis cycles, along with the analyte concentrations in the high level standard. It can be seen that one or two cycles must be completed before several of the measured analytes are present at concentrations below 10 times the MDL. Furthermore, if compared to results published in a previous application note,[67] the rate at which analytes are washed out is slower with the FAST system present. These results indicate that the 5 s rinse is insufficient in washing out samples from the introduction system. The concentrations determined in this experiment are much higher than those encountered in typical water samples and the FAST method uses the rinse step to pump air through the probe tubing and sample loop. If one encounters particularly troublesome analytes or requires a faster washout, the insertion of a true rinse step should be considered. In this case, an acidic solution is flushed through the loop for several seconds before air is introduced. Note that the switching valve should remain in the "load" position to avoid introducing the rinsing solution into the instrument and potentially complicating future sample measurements.

The results for the analysis of the quality control sample, measured after every ten samples of local tap water, are plotted in Fig. 3. As the figure illustrates, the QC result was measured within ±10% of the true value, which is compliant with the requirement outlined in Method 200.8. For simplicity, a small number of elements that span across the entire mass range have been selected for illustration. The throughput with a FAST introduction system is roughly double that of a system using a conventional introduction system. The vertical line in Fig. 3 further illustrates this point by showing that the number of samples that are run in 10 h with conventional introduction systems, can be run in roughly 5.5 hours using the FAST system. The FAST system package for environmental analysis includes one 5 l rinse bottle. The FAST method includes a 4 s rinse step after every injection. This step was reduced to 2 s for all stability runs to provide enough rinsing solution for 10 h worth of samples. Though not shown, results from stability runs involving samples containing high dissolved solids indicated that the signal for the entire mass range fluctuates for the first hour of analysis. Therefore, it is recommended that the cones and lens be conditioned for a minimum of one hour prior to analysis, particularly when analyzing samples that contain high concentrations of total dissolved solids.

3.2.3 Validation. Method 200.8 specifies that the measured concentration of each analyte be within ±10% of the true (certified or spiked) concentration. The results for the analysis of the "Trace Metals in Drinking Water and Trace Elements in Water" samples are listed in Tables 5 and 6. For simplicity, data from the analysis of the interference check standard have been omitted. Results from the analysis of the interference check

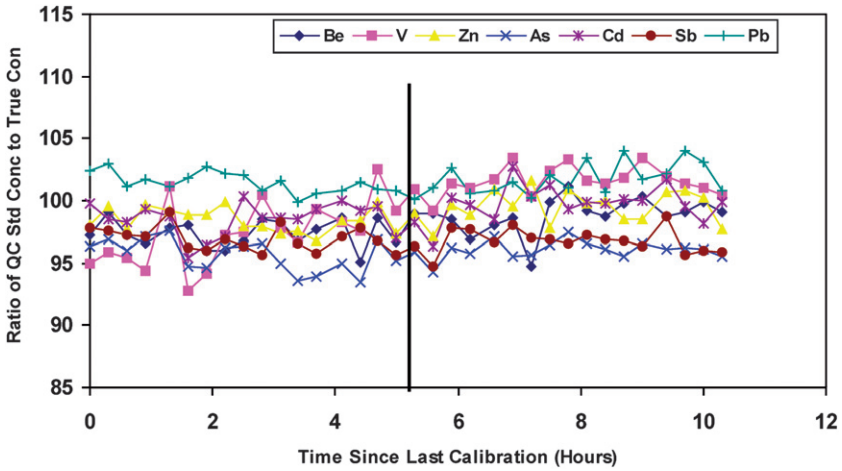

Fig. 3 Stability of a quality control sample over a 10 h period. The vertical line represents the number of samples that can be processed in 10 h using a conventional introduction system.

Table 5 Precision and recovery data for high purity "Trace Metals in Drinking Water" (CRM)

Analyte	Mass	Average measured concentration/ μg l^{-1}	Standard deviation/ μg l^{-1}	±Term[a]/ μg l^{-1}	%RSD/ μg l^{-1}	Certified value/μg l^{-1}	Ratio of measured to certified value	Spike level/μg l^{-1}	Average spike recovery (%)	Standard deviation of spike recovery/μg l^{-1}
Be	9	19.83	0.6	1.5	3.2	20	0.99	50	104.1	1.8
Na	23	5949	201	500	3.4	6000	0.99	—	—	—
Mg	24	9113	246	611	2.7	9000	1.01	—	—	—
Al	27	121.0	1.5	3.8	1.2	125	0.97	50	87.1	10.3
K	39	2588	82.4	205	3.2	2500	1.04	—	—	—
Ca	44	35 500	1135	2821	3.2	35 000	1.01	—	—	—
V	51	31.45	0.5	1.2	1.5	30	1.05	50	102.4	2.1
Cr	52	20.26	0.1	0.3	0.3	20	1.01	50	104.7	2.0
Mn	55	40.13	1.5	3.8	3.8	35	1.15	50	107.8	3.0
Co	59	24.14	0.6	1.5	2.3	25	0.97	50	106.7	4.0
Ni	60	58.75	3.0	7.5	5.1	60	0.98	50	99.2	7.5
Cu	63	20.17	0.04	0.1	0.2	20	1.01	50	105.1	2.5
Zn	66	72.61	1.3	3.2	1.7	70	1.04	50	96.2	0.4
As	75	82.43	0.7	1.7	0.8	80	1.03	50	100.9	4.2
Se	82	10.76	0.3	0.8	2.8	10	1.08	50	110.6	2.5
Mo	98	100.1	2.2	0.9	0.9	100	1.00	50	86.5	4.4
Ag	107	1.54	0.1	0.3	7.7	2.5	0.62	50	104.0	0.7
Cd	111	10.15	0.4	1.0	3.6	12	0.85	50	104.6	2.6
Sb	121	9.98	0.3	0.8	2.7	10	1.00	50	106.8	1.6
Ba	135	52.54	0.1	0.3	0.2	50	1.05	50	92.8	3.2
Tl	205	10.17	0.2	0.5	2.3	10	1.02	50	102.7	1.9
Pb	208	40.82	0.6	1.5	1.5	35	1.17	50	95.3	3.9
Th	232	ND[c]	—	—	—	NA[b]	—	50	104.6	1.8
U	238	10.32	0.2	0.5	1.7	10	1.03	50	104.7	1.1

[a] Error calculated based on a 95% confidence interval and 2 degrees of freedom. [b] NA: Not applicable. [c] ND: Not detected (concentration below the detection limit).

standard were compliant with EPA Method 200.8 guidelines, with the exception of those for Hg. The ratio between the measured and certified concentrations was slightly higher than 1.1; however, in the absence of errors associated with the certified concentrations in the interference check standard, it was not possible to determine whether the measured concentration was significantly different from the certified concentration, based on a 95% confidence interval.

Table 5 indicates that the relevant analytes were measured within ±10% of the High Purity certified concentrations, with the exception of Ag, Cd and Pb. When a ± term was calculated on the basis of a 95% confidence interval and 2 degrees of freedom, results indicate that 6 analytes were measured outside the acceptable range of concentrations. Since the certified values for this reference material do not have associated errors, it was not possible to determine whether the measured concentrations were statistically different from the certified concentrations. Results from spike recoveries indicate that all analytes were recovered within ± 10% of the spiked concentration, with the exception of Al and Mo.

Table 6 Precision and recovery data for NIST SRM 1643e "Trace Elements in Water"

Analyte	Mass	Average measured concentration/ μg l^{-1}	Standard deviation/ μg l^{-1}	±Term[a]/ μg l^{-1}	%RSD/ μg l^{-1}	Certified value/μg l^{-1}	Ratio of measured to certified value	Spike level/μg l^{-1}	Average spike recovery (%)	Standard deviation of spike recovery/ μg l^{-1}
Be	9	13.3	0.8	2.0	5.7	13.98 ± 0.17	0.95	50	98.9	2.4
Na	23	20 600	511	1270	2.5	20 740 ± 260	1.00	—	—	—
Mg	24	8173	361	897	4.4	8037 ± 98	1.02	—	—	—
Al	27	147	6.7	17	4.6	141.8 ± 8.6	1.04	50	84.3	11
K	39	2076	82	205	4.0	2034 ± 29	1.02	—	—	—
Ca	44	32 000	614	1526	1.9	32 300 ± 1100	0.99	—	—	—
V	51	37.9	0.8	2.0	2.1	37.86 ± 0.59	1.00	50	105.2	1.4
Cr	52	20.5	0.2	0.5	0.9	20.40 ± 0.24	1.00	50	106.7	3.4
Mn	55	37.3	0.7	1.7	1.8	38.97 ± 0.45	0.96	50	108.7	2.8
Co	59	25.8	0.3	0.8	1.0	27.06 ± 0.32	0.95	50	103.8	5.3
Ni	60	59.5	1.2	3.0	2.0	62.41 ± 0.69	0.95	50	100.2	4.5
Cu	63	22.2	0.8	2.0	3.7	22.76 ± 0.31	0.98	50	104.1	1.0
Zn	66	70.7	1.7	4.2	2.4	78.5 ± 2.2	0.90	50	97.1	1.4
As	75	55.4	0.9	2.2	1.5	60.45 ± 0.72	0.92	50	97.8	1.5
Se	82	10.4	0.2	0.5	1.5	11.97 ± 0.14	0.87	50	96.4	3.2
Mo	98	123	1.9	4.7	1.5	121.4 ± 1.3	1.01	50	84.8	7.6
Ag	107	0.2	0.1	0.3	32	1.062 ± 0.075	0.19	50	100.2	2.3
Cd	111	6.4	0.3	0.8	5.4	6.568 ± 0.073	0.97	50	100.4	0.2
Sb	121	57.8	1.4	3.5	2.4	58.30 ± 0.61	0.99	50	92.6	3.1
Ba	135	543.5	21	52	3.8	544.2 ± 5.8	1.00	50	—	—
Tl	205	7.4	0.05	0.1	0.6	7.445 ± 0.096	0.99	50	103.4	4.8
Pb	208	19.7	0.01	0.02	0.1	19.63 ± 0.21	1.00	50	96.9	4.0
Th	232	ND	—	—	—	n/a[b]	—	50	101.4	3.5
U	238	ND	—	—	—	n/a[b]	—	50	104.8	2.2

[a] Error calculated based on a 95% confidence interval and 2 degrees of freedom. [b] n/a = Not available.

Table 6 indicates that the measured concentrations for Se and Ag were outside the 10% range of certified NIST concentrations. When a more rigorous comparison is made, based on a 95% confidence interval, concentrations for Zn, As, Se and Ag fall outside the acceptable range of concentrations. Results from spike recoveries mimic those of the results from the analysis of the High Purity reference material in that only Al and Mo were determined below 90% of the expected concentrations.

Ag was measured below the certified concentration in each reference material; however, this was most likely due to precipitation out of the original stock solution. Ag was recovered within ±10% in all spiked samples, which further supports the hypothesis that Ag was lost due to problems with precipitation, not instrumentation.

Al was poorly recovered in spiked reference materials; however, this anomaly has been documented in the analysis of drinking water by ICP-MS.[67] The researchers in the previous study performed the analysis by conventional introduction, which indicates that the presence of the FAST system did not affect the recovery of this analyte.

Neither of the certified water samples contained Hg, so only spike recoveries could be calculated (results not shown). Results from the recovery studies indicate that Hg was consistently recovered above its expected concentration. The high recovery is most likely due to retention of Hg in the FAST valve. As stated previously, there is no true rinsing step in the FAST method. The sample loop is rinsed with the introduction of the next sample, which only adds to the retention problem if a series of samples all contain Hg. If samples are expected to have Hg present at concentrations higher than 1 μg l^{-1}, one should consider rinsing the sample loop with an acidic solution, such as 3% HCl, in between sample injections.

3.3 Application to water samples

Results for spike recoveries in local drinking water samples are listed in Table 7. All relevant analytes were recovered within ±10% of their spiked concentrations, with the exception of Al and Hg. As seen in the results from the certified reference materials, Al was recovered below 90% and Hg was recovered above 110% of the expected concentrations.

3.3 Approach to Hg retention

The online addition of gold in the internal standard solution reduced the retention of Hg for concentrations up to 1 μg l^{-1}; however, concentrations above 1 μg l^{-1} Hg resulted in carryover. The addition of gold to both the internal standard and carrier solutions offered no advantage over the addition of Au to the internal standard solution alone. Batchwise addition of Au to all standards and samples eliminated memory effects due to Hg retention; however, the addition of Au introduced HCl, which caused Ag to precipitate.

4. Conclusions

The FAST system has been shown to produce results that meet the requirements outlined in U.S. EPA Method 200.8. In addition, the FAST system significantly decreases the cost per sample

Table 7 Spike recoveries for local drinking water (LDW)

Analyte	Mass	LDW concentration/μg l^{-1}	Low spike level/μg l^{-1}	Low spike results/μg l^{-1}	Low spike recovery (%)	High spike level/μg l^{-1}	High spike results/μg l^{-1}	High spike recovery (%)
Be	9	ND[a]	10	9.82	98.2	50	49.52	99.0
Na	23	13 700	—	—	—	—	—	—
Mg	24	2129	—		—	—	—	—
Al	27	13.62	10	8.87	88.7	50	48.39	96.8
K	39	1612	—	—	—	—	—	—
Ca	44	13 200	—	—	—	—	—	—
V	51	0.26	10	10.49	104.9	50	52.28	104.6
Cr	52	0.15	10	10.43	104.3	50	52.56	105.1
Mn	55	3.82	10	10.55	105.5	50	52.10	104.2
Fe	57	4.83	—	—	—	—	—	—
Co	59	0.01	10	10.71	107.1	50	53.06	106.1
Ni	60	0.98	10	10.72	107.2	50	52.70	105.4
Cu	63	348.0	—	—	—	—	—	—
Zn	66	217.4	—	—	—	—	—	—
As	75	0.20	10	10.60	106.0	50	52.30	104.6
Se	82	0.31	10	10.46	104.6	50	51.92	103.8
Mo	98	ND[a]	10	10.74	107.4	50	52.82	105.6
Ag	107	ND[a]	10	10.24	102.4	50	50.27	100.5
Cd	111	ND[a]	10	10.65	106.5	50	52.30	105.4
Sb	121	ND[a]	10	10.69	106.9	50	52.67	105.3
Ba	135	8.87	10	10.15	101.5	50	50.99	102.0
Hg	202	0.44	1	1.52	151.9	4	7.37	184.2
Tl	205	0.046	10	10.50	105.0	50	51.93	103.9
Pb	208	0.38	10	10.47	104.7	50	52.32	104.6
Th	232	ND[a]	10	10.81	108.1	50	53.32	106.6
U	238	ND[a]	10	10.76	107.6	50	53.36	106.7

[a] ND: Not detected (concentration below the detection limit).

analysis. The online addition of internal standards helps to simplify sample preparation and reduces the potential for dilution and sample preparation errors and sample contamination. When used in conjunction with the SC autosampler, the FAST system provides a rugged, automated sample introduction system that can significantly increase the efficiency of routine sample analysis, resulting in higher laboratory productivity.

The FAST system has been designed to increase throughput and to decrease sample carryover as compared to conventional ICP-MS sample introduction. Carrier and internal standard solutions provide a continuous flow of solution to the nebulizer, which allows sample uptake and stabilization to take place more rapidly. Furthermore, during analysis the FAST system rinses the autosampler probe and moves it to the next sample vial. The FAST system thus completes the analysis of a sample (following Method 200.8 protocol) in 90 s (sample to sample), about half the time needed to perform the same analysis with conventional sample introduction. Increasing the sample throughput increases productivity and lowers costs, both labor- and instrument-related.

As the sample solution is not in contact with the peristaltic pump tubing, washout times and memory effects are decreased. Furthermore, an additional length of tubing that delivers the carrier solution provides a source of pulse damping, which reduces pump roller noise.[70] Though a longer length of tubing is used, no additional memory effects are observed because the sample is contained within the sample loop and loop itself is made of chemically resistant Teflon®. As the volume of sample introduced into the nebulizer is decreased, the amount of salt that is deposited on the cones is also decreased. The FAST system uses a total flow rate between 400 and 500 μl min^{-1}, much lower than flow rates used with conventional introduction systems. These lower pump flow rates, combined with the shorter analysis time, reduce the amount of salt deposition on the cones, reagent consumption, and waste production, all of which lower maintenance operational costs.

In addition to higher throughput and reduced memory effects, the FAST system allows for the online addition of internal standards, simplifying sample preparation and decreasing the opportunities for contamination.

Retention of Hg is an ongoing research issue. Experiments in which gold is added batchwise to standards and samples significantly reduced Hg retention; however, the addition of Au introduces HCl, which causes Ag to rapidly precipitate. It should be noted that many laboratories analyze Hg-containing samples separately and will continue to do so even if a protocol is developed that allows for relatively high concentrations of Hg to be determined along with the suite of elements outlined in Method 200.8. With that in mind, the FAST system and the method outlined in this work are suitable to rapidly screen for samples that contain measurable concentrations of Hg.

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