

ICP - Mass Spectrometry

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Advantages of a High Throughput Sample Introduction System in the Analysis of Drinking Waters Using ICP-MS (Method 200.8)

elements are mobilized into potable water sources, such as rivers, lakes and groundwater. As such, the concentrations of elements, which are known to elicit a toxicological response, are regulated throughout the world by international and national regulations, of which one of the most commonly used methods is the United States Environmental Protection Agency 200.8 (EPA 200.8). Since all drinking waters need to be tested prior to distribution to ensure fitness for consumption, this makes sample loads on water-testing laboratories high. In such settings, sample throughput is often hindered by the length of the uptake and washout times, and since lengthy run times cause an increase in the cost of analysis, the laboratory's overheads in routine testing can be very high.

Introduction

Water forms 80% of the human body and is essential to all life. Due to increasing pollution and land disturbance, vast quantities of potentially harmful

Where speed is a priority, sample-to-sample analysis time can be dramatically decreased through the implementation of selector valves and vacuum pumps, where a loop is filled with sample under vacuum and the sample is introduced to the plasma at a constant rate. This allows high sample throughput to be achieved since the time taken for the sample to enter the plasma is minimized. Therefore, a system in which the setup is fully integrated within the ICP-MS hardware and software would be highly beneficial and further enhance laboratory throughput.

In this work, we report the analysis of a number of water samples comprised of tap and natural waters in accordance with the EPA Method 200.8 using PerkinElmer's High Throughput System (HTS), which is fully-integrated with the NexION® ICP-MS using Syngistix™ for ICP-MS software.

Experimental

Sample Preparation

Tap and natural water samples were acidified (v/v) to 1% HNO₃ (67-70%, BDH Aristar® ULTRA, VWR, Mississauga, Ontario, Canada) to help keep the ions in solution. To facilitate the washout of Hg, 200 µg/L Au was added to all samples and standards, as well as the carrier, internal standard and rinse solutions. Calibration standards were prepared in 1% HNO₃ and 200 ppb Au at levels shown in Table 1, whereas the consumables used to perform this work are described in the table at the end of this document.

Internal standards were added online through the 7th port (central channel) of the HTS system's valve and were chosen to cover the complete mass range of the analytes, spanning the ionization efficiencies of the masses of interest. The concentrations of the internal standards were varied to account for differences in ionization potential, isotopic abundance and potential interferences.

Tap and natural water samples were analyzed in accordance with EPA 200.8 for 26 elements (Table 2) using inductively coupled plasma mass spectrometry (ICP-MS). Since the use of collision/reaction gases are prohibited by this method, mathematical correction equations were employed to address interferences as is allowed by EPA 200.8 (Table 2).

The accuracy of the calibration was validated through the implementation of an initial calibration verification standard (ICV) following the calibration. The method was validated through the analysis of three certified reference materials

(CRMs): Trace Metals in Drinking Water (High Purity Standards™, Charleston, South Carolina, USA), 1640a Natural Water and 1643f Water (NIST, Rockville, Maryland, USA). The robustness of the method was further validated through the implementation of low concentration and high concentration spikes (10 ppb and 50 ppb for all analytes specified in EPA 200.8, with the exception of Hg which was 0.5 and 1 ppb for the low concentration and high concentration spikes respectively) using a mixture of the analyte ions which covered the range of analytes typically found in drinking water.

Table 2. Recommended isotopes and mode of analysis for different elements.

Analyte	Recommended Isotope	Correction Equation
Ag	107	
Al	27	
As	75	-3.127 * [ArCl77 - (0.815 * Se82)]
Ba	137	
Be	9	
Ca*	43	
Cd	111	-1.073 * [MoO108 - (0.712 * Pd106)]
Co	59	
Cr	52	
Cu	63	
Fe*	54	- 0.0282 * Cr52
Hg	202	
K*	39	
Mg*	24	
Mn	55	
Mo	98	- 0.1096 * Ru101
Na*	23	
Ni	60	
Pb#	206 + 207 + 208	+ 1 * Pb206 + 1 * Pb207
Sb	121	
Se	82	
Tl	205	
Th	232	
U	238	
V	51	-3.127 * [ClO53 - (0.013 * Cr52)]
Zn	66	

*Not required by EPA 200.8, but included for informative value

#Three isotopes should be monitored and summed

Table 1. Concentrations of calibration standards and internal standards used during analysis.

Analytes	Standard 1	Standard 2	Standard 3	Standard 4	Standard 5
Ag, Al, As, Ba, Be, Cd, Co, Cr, Cu, Fe*, Mn, Mo, Ni, Pb, Sb, Se, Th, Tl, U, V, Zn	1	5	10	50	100
Hg	0.05	0.1	0.5	1	2.5
Ca*, K, Mg*, Na*	50	100	1000	5000	10 000
Au	200	200	200	200	200
Internal Standards	⁷¹ Ga, ⁷² Ge, ¹⁰³ Rh, ¹⁵⁹ Tb				

*Not required by EPA 200.8, but included for informative value

Instrumentation

All analyses were performed using a NexION® ICP-MS (PerkinElmer Inc., Shelton, Connecticut, USA) equipped with a fully integrated HTS (PerkinElmer Inc.) using the components and parameters defined in Table 3.

Table 3. Component and parameters list for ICP-MS analysis.

Component/Parameter	Type/Value
Nebulizer	MEINHARD® plus Glass Type C
Spray Chamber	Glass Cyclonic at room temperature
Sample Uptake Rate	300 µL/min
RF Power	1600 W
Injector	2.0 mm I.D. quartz
Sweeps	20
Dwell Time	15-100 ms (analyte dependent)
Replicates	3

The analysis of easily-ionizable, high isotopic abundance analytes such as Na and K (isotopic abundances of 100% and 93% respectively) can be challenging in drinking water samples. This is because concentrations may be high and can result in a decrease in the detector life for ICP-MS systems when the ion beam signal is measured at full strength. In such a scenario, analysts can benefit from the Extended Dynamic Range functionality (EDR) of the NexION ICP-MS. Having a quadrupole ion guide as its universal cell, which can double as a collision/reaction cell for other applications, allows for the active adjustment of the transmission of ions through the quadrupole cell per isotope. This attenuates the analyte signals which are present in high abundance (Figure 1) before detection, extending the dynamic range by up to 12 orders of magnitude while preserving detector lifetime. When analyzing low concentration analytes, ion transmission is maximized, allowing low concentration analytes to be detected with ease. All of this can be performed in a single analytical method and run.

Results and Discussion

All samples were analyzed for 27 analytes using a NexION ICP-MS. Sample-to-sample times were proven to be 3-5x faster than normal analysis times using the fully integrated HTS system, saving on the time and cost of analysis.

Short-term precision was evaluated by running 10 repeat injections of a sample spanning the low, mid and high mass ranges and was determined to be <1.5 % for all analytes except Hg, which was just over 2%. These findings demonstrate that the amount of variance between replicate measurements is negligible and is unaffected by the HTS system. Water samples could be observed in the plasma within 9 seconds from the immersion of the sample probe in the sample (Figure 2), demonstrating that the sample is in the plasma and stable within a very short time when compared to standard uptake methods.

Figure 3 shows the instrument detection limits for the integrated HTS and ICP-MS system using 1% HNO₃ plotted against those specified by EPA 200.8. The observed concentrations were significantly lower than those reported in the EPA document, showing that the metal-free fluid path of the HTS system does not have any significant effect on the detection limits which are more than adequate to meet the needs of this application.

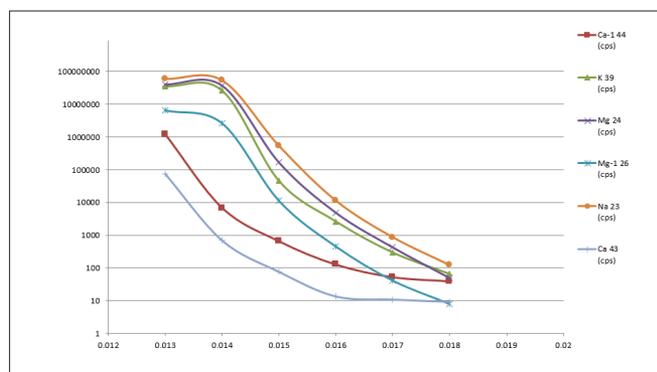


Figure 1. Effect of EDR on signal of analytes which are easily ionizable.

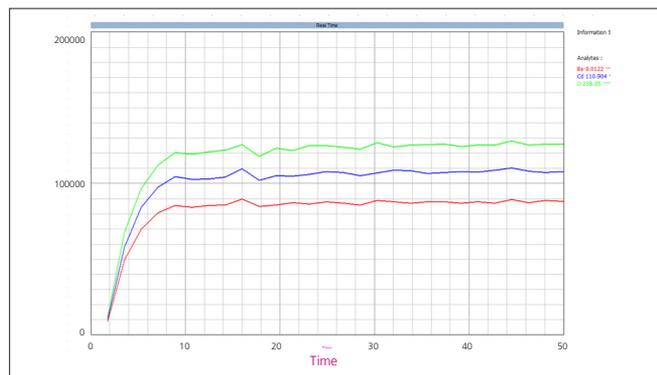


Figure 2. Sample introduction into the plasma in less than 10 seconds.

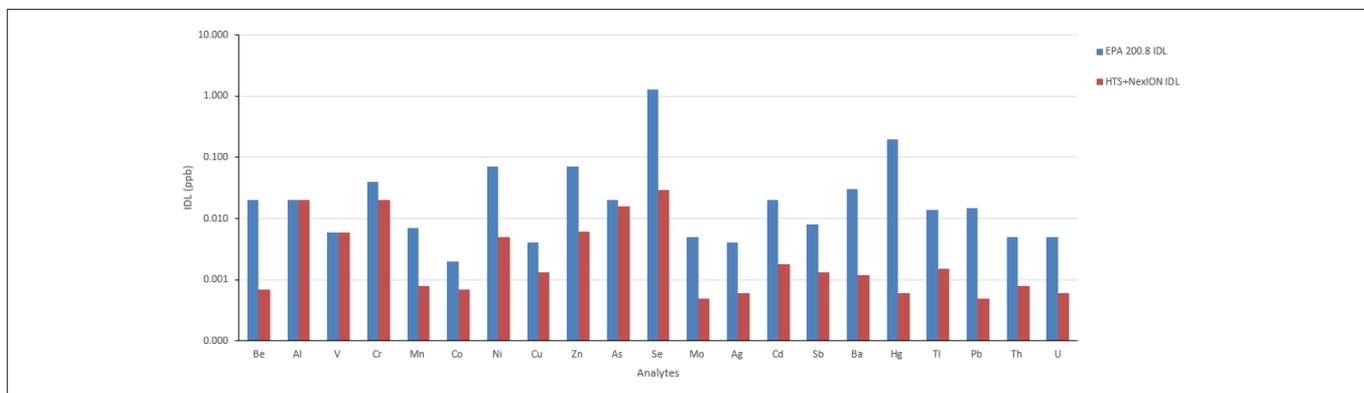


Figure 3. Detection limits using HTS system compared to those reported in the EPA 200.8.

The calibration was appropriately validated using an initial calibration verification standard (ICV), which was measured after the calibration standards and was found to be in good agreement with the expected concentrations (Figure 4). Further quality control involving five replicate analyses of a low- and high-spiked water sample showed that there was a good recovery of all analyte spikes. This demonstrates the applicability of the method over a large linear range and its robustness, further validating the analytical method (Figure 4).

Figure 5 shows the average recoveries of five repeat injections of the CRM materials and demonstrates that most analyte recoveries were within 10% of the certified value of the CRM for NIST 1643e, NIST 1643f and Trace Metals in Water with the exception of Se which was at 89 and 88% for 1640a and 1643f respectively, further validating the analytical accuracy of the method.

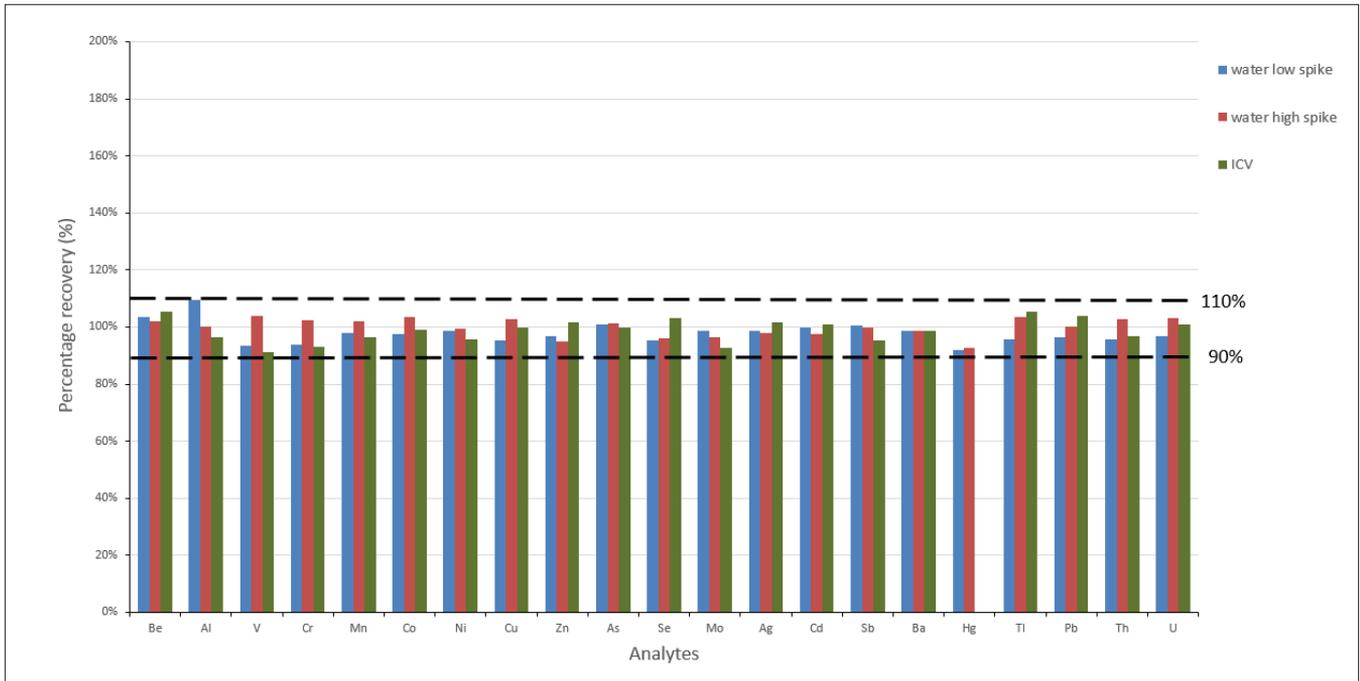


Figure 4. Initial calibration standard, low and high concentration spike recoveries.

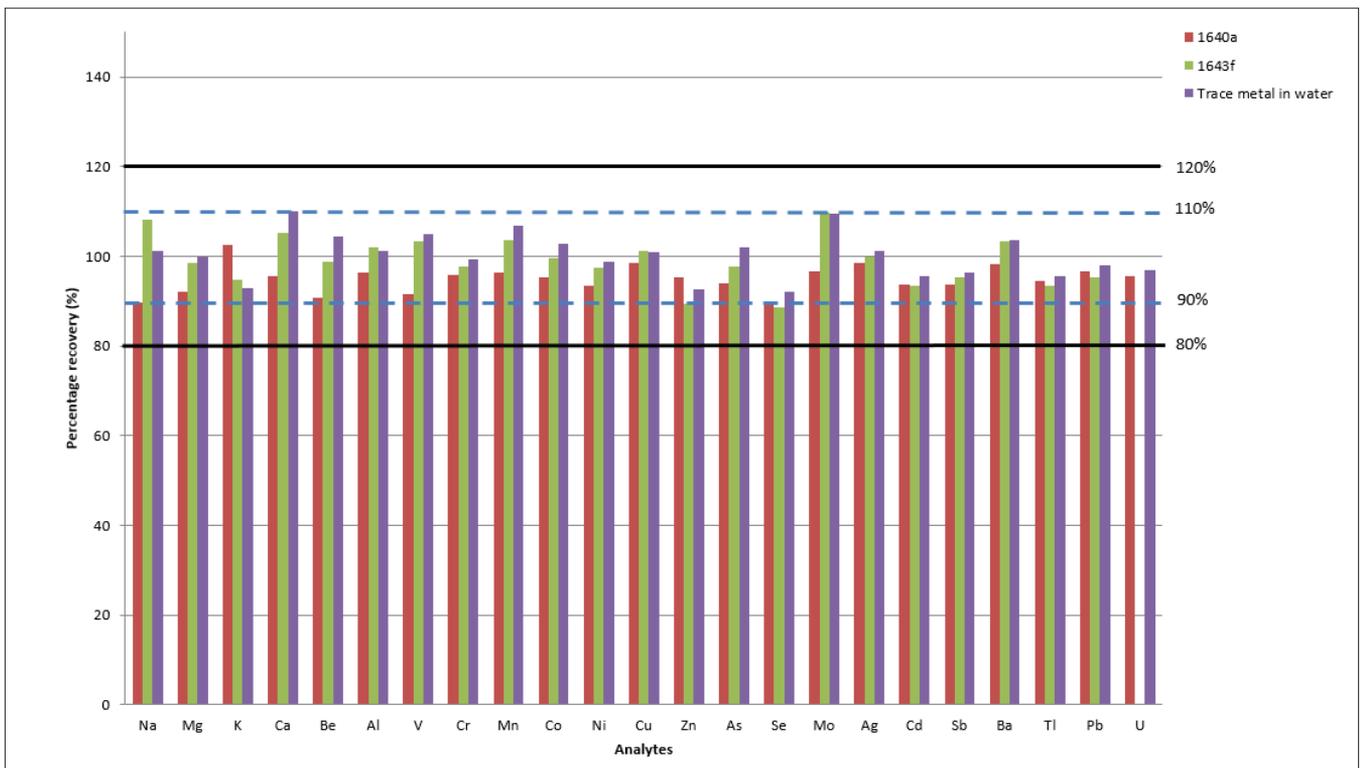


Figure 5. Certified reference material recoveries.

Stability of the method was evaluated by running a continuing calibration standard (CCV) every 10 samples and internal standards in every sample over 8 hours, which is the period of a typical work shift (Figure 6). The CCV was found to have excellent stability ($<10\%$ RSD) over the analysis period without the need to recalibrate, showing the ability of the system to deliver reliable, consistent and accurate results over the long

sample run times which most high-throughput laboratories require. It can also be seen from Figure 7 that the internal standard did not deviate more than $\pm 15\%$ over the period of 8 hours and was well within the limits of 60-125% recovery as is allowed by EPA 200.8. This demonstrates the suitability of the HTS system for its application in the routine analysis of trace metals and metalloids in tap and natural water samples.

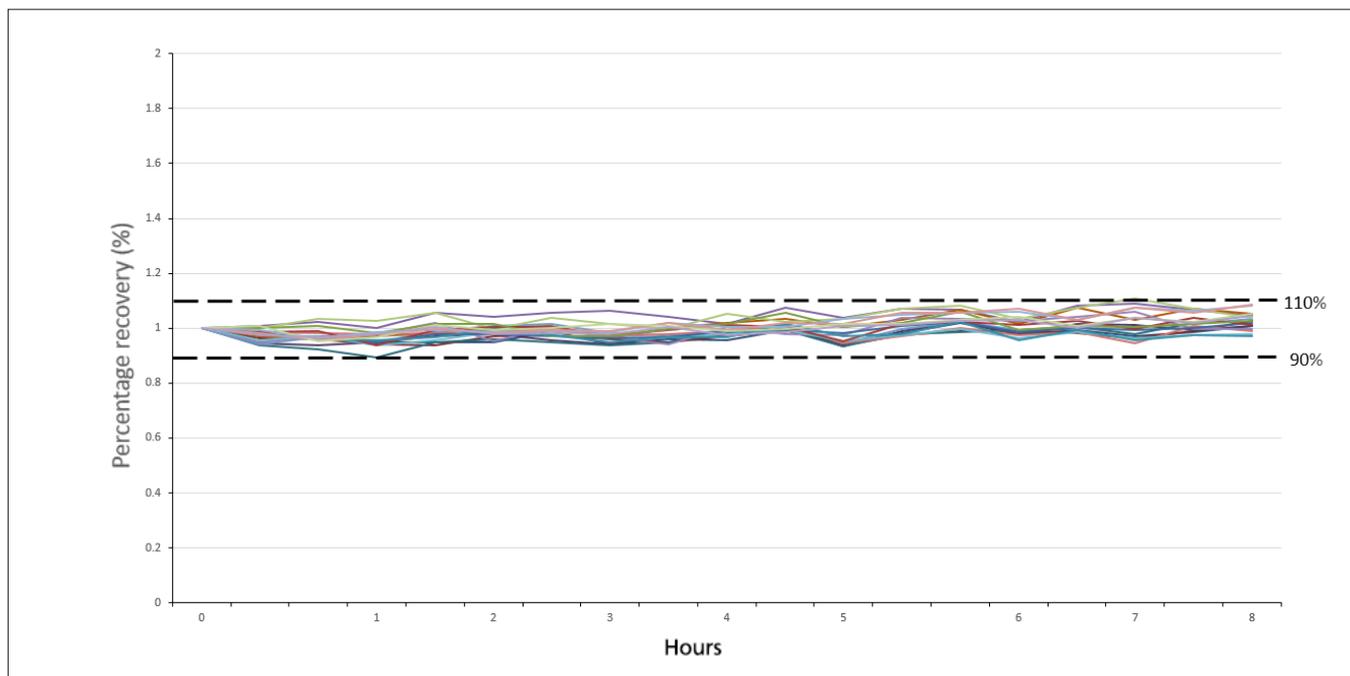


Figure 6. Percentage recovery of the continuing calibration verification standard over a period of 8 hours.

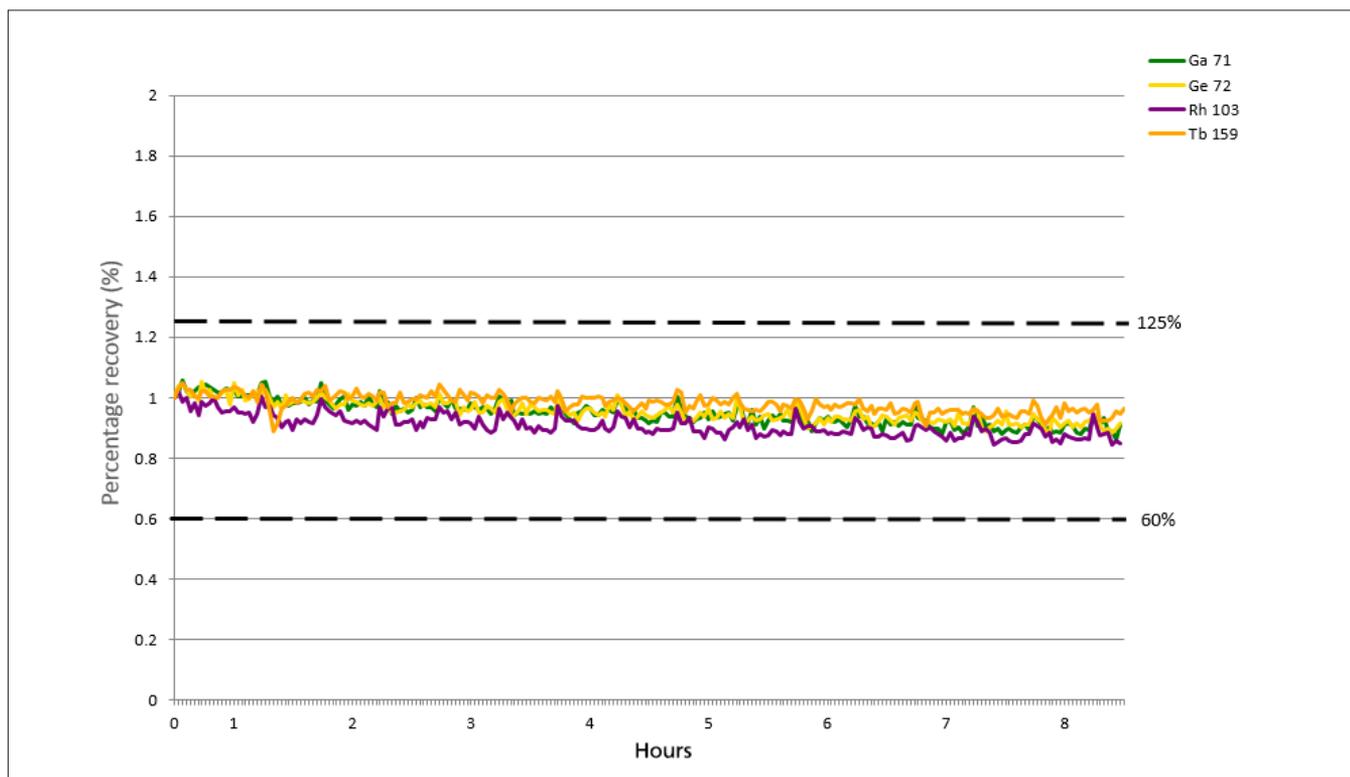


Figure 7. Internal standard over a period of 8 hours.

Conclusion

In this study, a high throughput method evaluating 27 analytes in drinking water following EPA 200.8 was presented. Through the use of the HTS system fully integrated with the NexION ICP-MS, sample analysis was dramatically reduced by 3-5 times without compromising detection limits, accuracy or the repeatability of the analysis. With excellent precision, the long-term stability of the system was found to fall within 10% for all analytes, as was determined using a CCV over an 8-hour analytical run. These results demonstrate the suitability of this system for high throughput laboratories, dramatically reducing the cost and time of analysis.

Accessories and Consumables Used

Component	Part Number
PerkinElmer HTS System	N8150141
Instrument Calibration Standard 2	N9301721
Environmental Standard Mix B, Th, U	N9307807
Environmental Standard Mix Ca, K, Mg, Na	N9307805
Mercury Standard	N9300253
Ga Standard	N9303772
Ge Standard	N9303739
Rh Standard	N9303749
Tb Standard	N9303778
Au Standard	N9303759
Autosampler Tubes	N0776118 (15 mL) N0776116 (50 mL)