Elemental Scientific

U.S. EPA Method 200.7
SampleSense Enviro
PerkinElmer™ Avio™ 500 ICP

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Enhanced Automation using SampleSense Enviro and PerkinElmer Avio 500/550 Max ICP for U.S. EPA Method 200.7

Introduction

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

This work demonstrates the ability of the Elemental Scientific *FAST* system with revolutionary SampleSense Ultra-high throughput technology to meet the demanding requirements of U.S. EPA Method 200.7 and do it with sample-to-sample analysis times of 45 seconds or less. This is a productivity breakthrough for the high-throughput environmental laboratory.

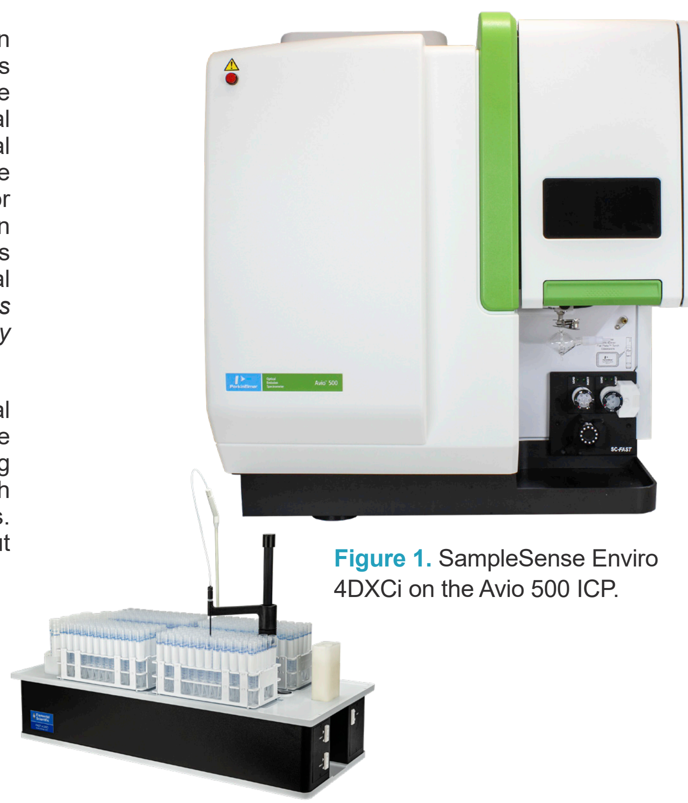


Figure 1. SampleSense Enviro 4DXCi on the Avio 500 ICP.

SampleSense Enviro

SampleSense *FAST* combines an auto-correcting DXCi autosampler and an inert sample valve. The SampleSense valve features integrated optical sensors that automatically detect the presence of a non-segmented liquid sample as it is quickly vacuum loaded into a sample loop. In a tightly-timed analytical sequence, the sensed sample is injected into the ICP, which is automatically triggered to acquire data. SampleSense Enviro further builds on SampleSense *FAST* by incorporating a vacuum-control valve (trapping valve) to minimize sample consumption. In addition to automatically sensing and injecting the sample, the SampleSense valve simultaneously switches the position of the trapping valve, shutting off the vacuum to conserve valuable sample. SampleSense also detects and reports sample loading failures. Unsensed samples – for example empty or capped tubes – are identified and logged, saving the operator the time and hassle of deciphering ICP data from non-sample events. These features eliminate all sample uptake method development including complicated uptake delays by the operator.

Features Include:

- Automatically goes to the correct sample tube every time – even when temporarily obstructed
- Eliminates all sample uptake method development – no uptake delays required
- Optimizes loading conditions for each sample matrix
- Allows sample loop sizes to be changed without method adjustments
- Automatically compensates for drift caused by kinked lines or partial blockages
- Provides positive confirmation of sample loading – if a sample fails to load for any reason, the failed sample is logged and the user is alerted
- Minimum sample consumption with vacuum control valve

Enhanced Washout with SampleSense Enviro

SampleSense Enviro optimizes the dual rinse of the DXCi autocorrecting autosampler by trapping the rinse solution from the first rinse station in the sample probe while the sample is analyzed, eliminating the need to dip into that rinse station after the analysis is complete. After analysis, the sample probe moves directly into the second rinse station when the trapping valve is opened, allowing the trapped dual rinse solutions – in series – to wash out the previous sample.

Fast and efficient washout is achieved using this rinse trapping capability, facilitating high throughput and optimum washout.

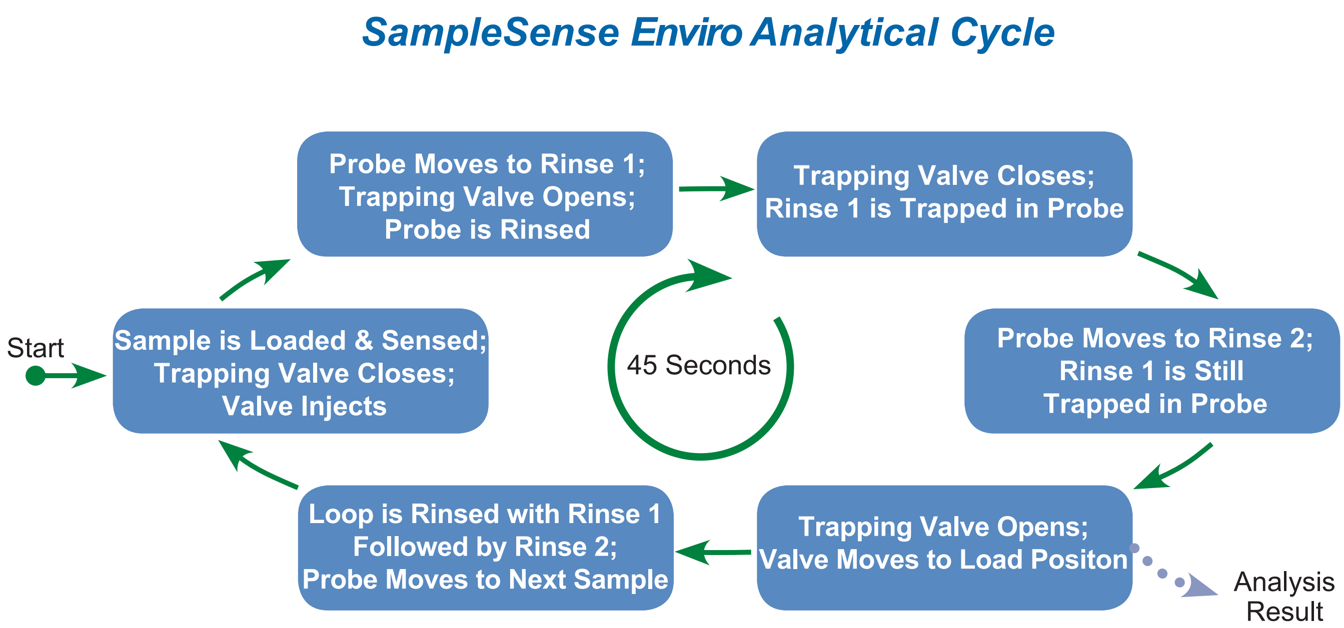


Figure 2. Analytical sequence using SampleSense Enviro.

SampleSense Enviro Flow Diagram

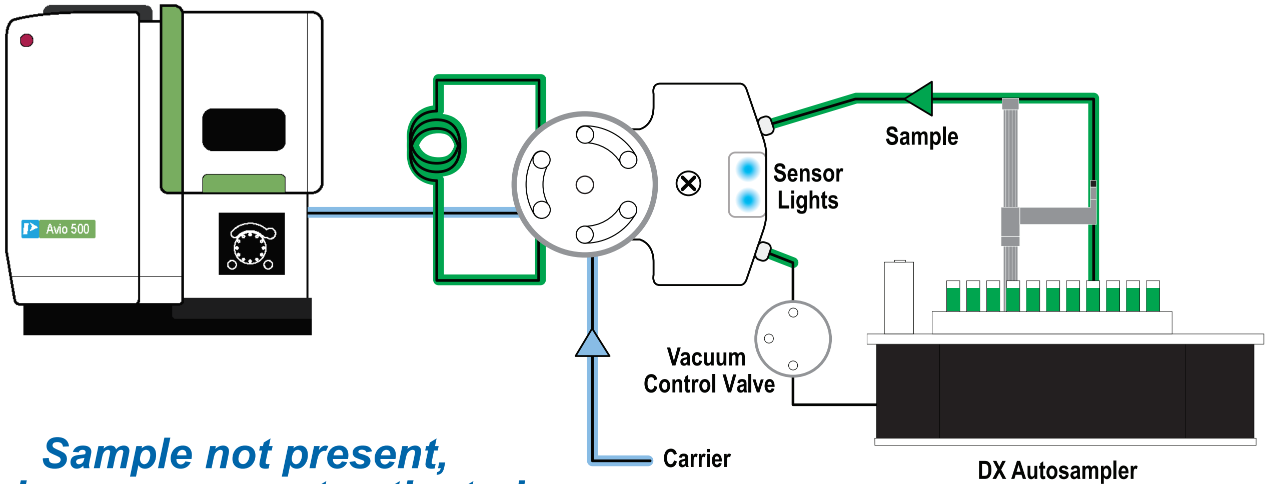


Figure 3. Flow diagram for SampleSense Enviro showing sensor actuation.

Sample not present, valve sensors not activated

Valve sensors activated, sample is sensed

Low Sample Consumption

SampleSense Enviro consumes < 2.5 mL of sample. The black line shows the original level of 6 mL extract. Post analysis, 3.5 mL of sample remains for a potential reanalysis.

Confirmation of Sample Loading with SampleSense

In addition to automatic sample loading, valve injection, and ICP triggering capabilities of SampleSense *FAST*, the optical sensors in the valve also provide positive confirmation to the laboratory that each sample is properly allocated into its vial, and subsequently loaded into the loop for analysis. If a sample container is either underfilled or empty, the SampleSense software will log the unsensed sample event and will not inject the contents of the sample loop. As additional confirmation of a missed sample in the raw ICP data, a marker component can be added to the carrier solution (see Figure 4). SampleSense automatically responds to any unsuccessful sample loading event by triggering the ICP to continue its analysis, without injecting the sample loop contents, resulting in the analysis of the marked carrier solution. The presence of this marker, at a high count rate in the ICP data, provides additional confirmation to the analyst that a sample was not introduced or loaded successfully.

Marked Carrier Used to Identify Non-sample Event

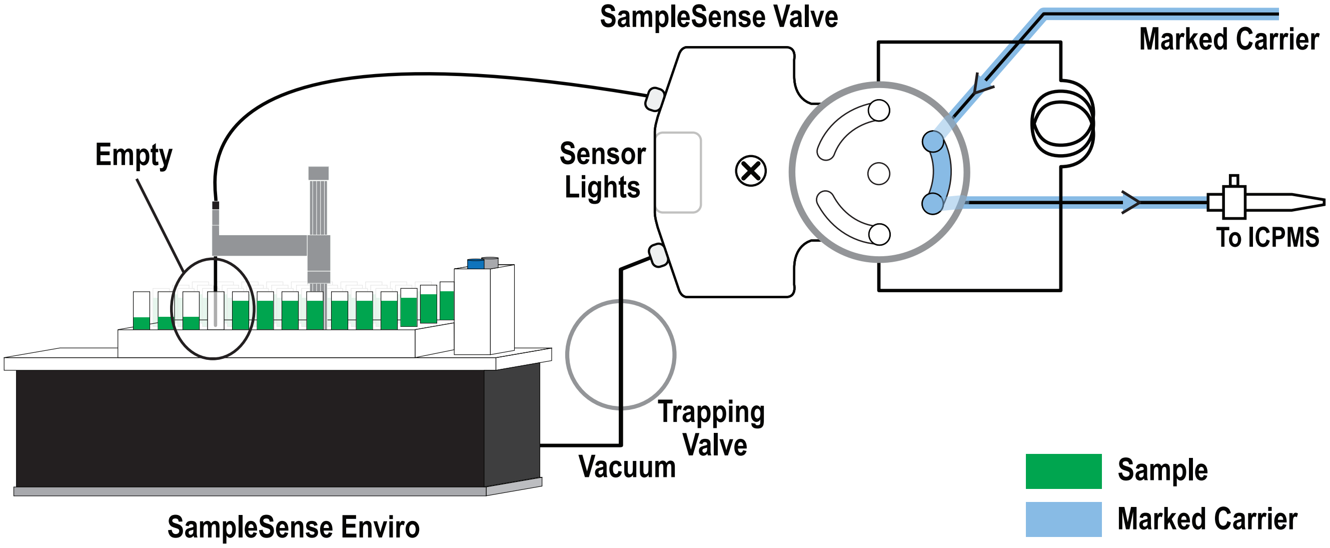


Figure 4. A carrier marker is an element present in the carrier solution that provides verification in the raw data of any non-sample event, such as an empty or underfilled sample. If a sample is not successfully loaded, the SampleSense valve will trigger analysis of the marked carrier solution, providing a noticeably higher count rate for the marker element.

Missing Samples Detected

This table demonstrates the automatic missed sample logging capabilities provided by the SampleSense Enviro sensors. Empty sample vials were placed in the first three sample racks at positions 45 and 90. SampleSense identified the missing samples and provides this information in the software log shown here.

Message

Unsensed Samples

	SC Rack Number	SC Vial Number	Instrument Rack	Instrument Vial	Time
▸	1	45	1	45	20190813 9:05:00
	1	90	1	90	20190813 9:09:34
	2	45	2	45	20190813 9:14:08
	2	90	2	90	20190813 9:18:42
	3	45	3	45	20190813 9:23:16
	3	90	3	90	20190813 9:27:50

Instrument Conditions

The *FAST* system was configured with a 1.5 mL sample loop and automatically triggered the Avio 500 analysis after the sample was loaded. The SampleSense automated sample detection and injection capabilities, combined with the trigger functionality of the ICP, greatly simplified method development as all uptake and stabilization delays in the PerkinElmer Syngistix™ software were set to "0". Total sample consumption from each vial was less than 3 mL, leaving sufficient sample volume for reanalysis, if necessary. An overview of the *FAST* operation is depicted in Figure 2.

The sample introduction system included a *pergo* 500 argon humidifier to improve both short and long-term stability. *pergo* optimizes performance of concentric nebulizers by utilizing a reservoir to perfuse water vapor into the nebulizer gas stream. By increasing humidity in the argon nebulizer gas, *pergo* continually dissolves micro-crystal droplets in the nebulizer tip to reduce long-term drift, extend length of analytical runs, while improving RSDs and stability. The instrument conditions are summarized in Table 1.

The instrument was calibrated using a blank and 4 levels of calibration standards prepared from PerkinElmer Calibration Standards for Method 200.7 (N9307107). The trace elements were calibrated at 0.1, 0.5, 1, and 2 mg/L. Phosphorus was calibrated at 2.5, 5, and 10 mg/L. Aluminum and lithium were calibrated at 2.5, 12.5, 25, and 50 mg/L, while the levels of the major elements were calibrated at 5, 25, 50, and 100 mg/L, respectively.

Table 1. Instrument analysis settings.

Parameter	Value
Nebulizer	PFA ST 3-90
Spray Chamber	Unbaffled Quartz Cyclonic
Sample Flow Rate	1 mL/min
RF Power	1500 W
Torch/Injector	ESI One-piece Quartz Ziptorch with 2 mm id injector
Argon Humidifier	*pergo* 500
Nebulizer Gas Flow	0.6 L/min
Auxiliary Gas Flow	0.2 L/min
Plasma Gas Flow	8 L/min
Sample Uptake Tubing	Black/Black PVC (0.76 mm id), Flared
Drain Tubing	Grey/Grey Santoprene (1.14 mm id)
Integration Time	0.2-5 s
Replicates	3

Table 2. Wavelengths and elements monitored in this work. All elements determined in Axial viewing mode unless designated by (R) indicating Radial viewing was used.

Element	Wavelength Measured (nm)
Ag	328.066
Al	394.400 (R)
As	188.979
As	193.965
B	249.675
Ba	493.401 (R)
Be	313.044
Ca	315.886 (R)
Cd	214.440
Ce	413.761
Co	228.614
Cr	205.558
Cu	324.753
Fe	259.939
K	766.488
Li	670.778
Mg	285.209 (R)
Mn	257.608
Mo	203.844
Na	589.599 (R)
Ni	231.604
P	178.223
Pb	220.351
Sb	206.833
Se	196.025
Si	251.608
Sn	189.927
Sr	421.549 (R)
Ti	334.938
Tl	190.806
V	292.400
Zn	213.856
Y (IS)	371.029
Sc (IS)	361.383 (R)
Tm (CM)	346.220

Y and Sc were used as Internal Standards; Tm was used as a Carrier Marker.

Results and Discussion

The Avio 500 was tuned according to the manufacturer's recommendations for environmental analysis. The analytical sequence was configured to follow the protocols defined in the U.S. EPA Method 200.7. The selected reference materials were analyzed in a repeating sequence over several hours to evaluate long-term method stability. The sample-to-sample time during this experiment – including three replicates in both axial and radial views – was 45 seconds. The percent recoveries for two of the quality control samples, TM-C and TM-D, are shown below in Figure 5. All elements were recovered with acceptable (±10%) recovery. The internal standard recoveries, using the calibration blank as a reference, were very stable and drifted less than 10% as illustrated in Figure 6 – a benefit of using the *pergo* 500 for this application.

Table 3. Analytical Sequence of repeated QC samples and reference materials. The analytical sequence performed in this study utilized the QC and sample list shown in the table below. After performing the calibration, the required calibration checks and QC samples in the order shown.

Sample Name	Sample Type
CCB	Continuing Check Blank
TMDW	Trace Metals in Drinking Water
QCP-TMS	Wastewater CRM
QCP-MTL	Potable Water CRM
QCS (IV)	Quality Control Standard
TM-C	Tracemetals in Wastewater
TM-D	Tracemetals in Wastewater

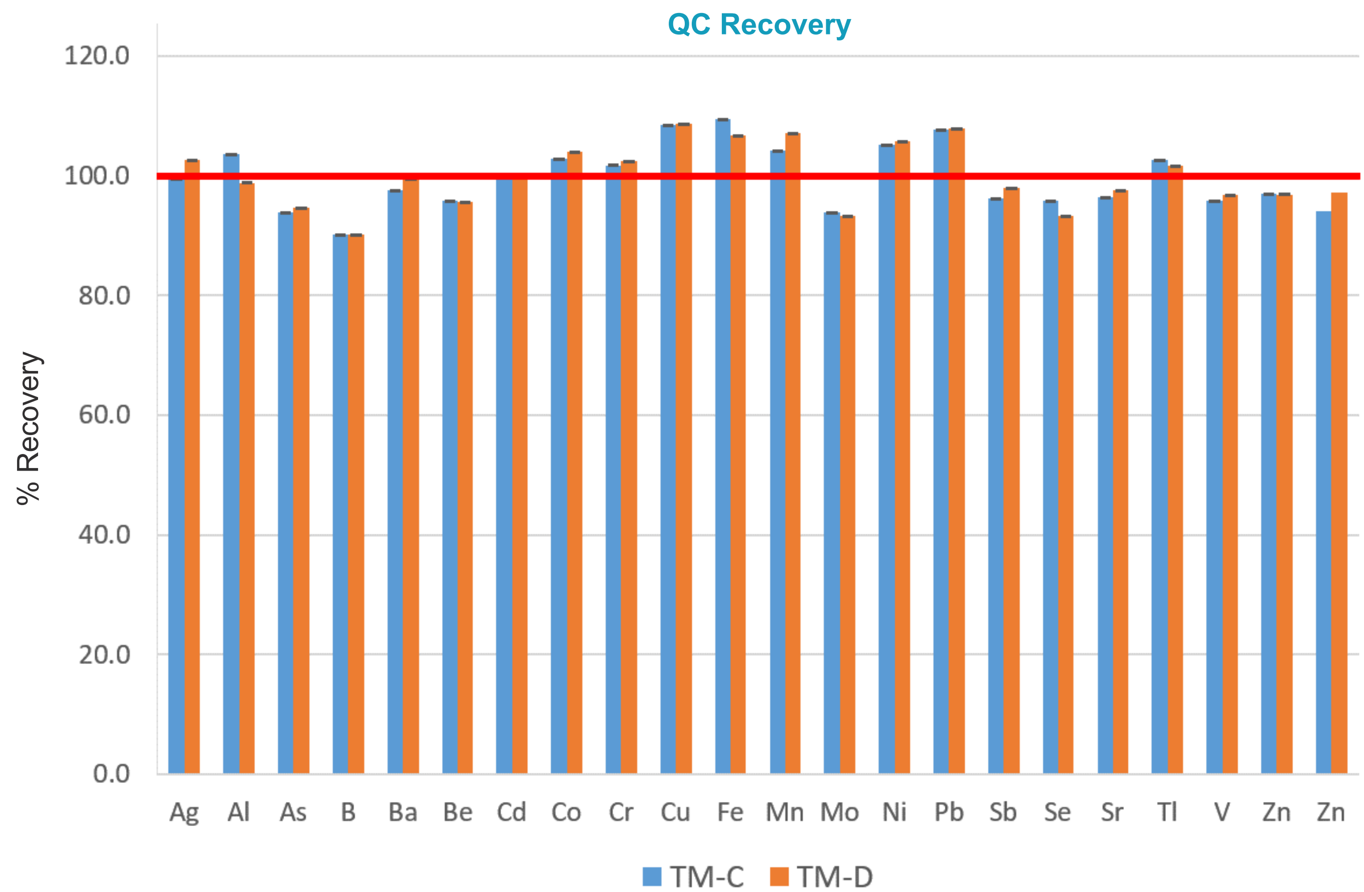


Figure 5. Recoveries of selected quality control samples.

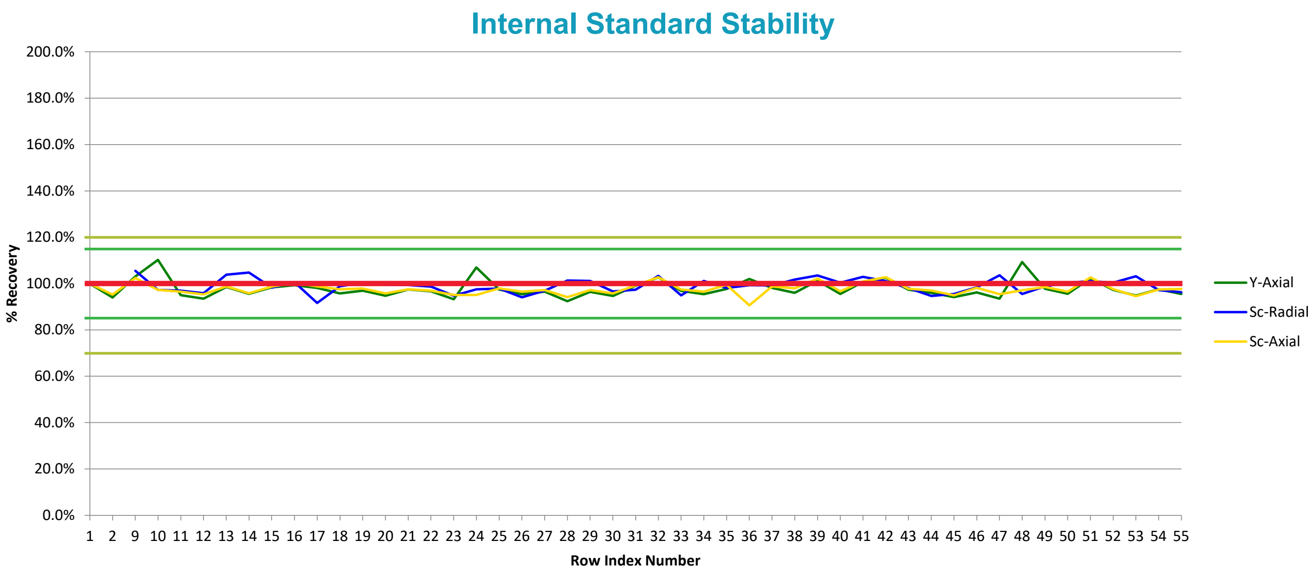


Figure 6. The graph above shows excellent stability and recovery over 55 samples. Outlier recoveries remained well within ± 15% (inner green lines) and easily within the allowable range of 70-120% (outer green lines).

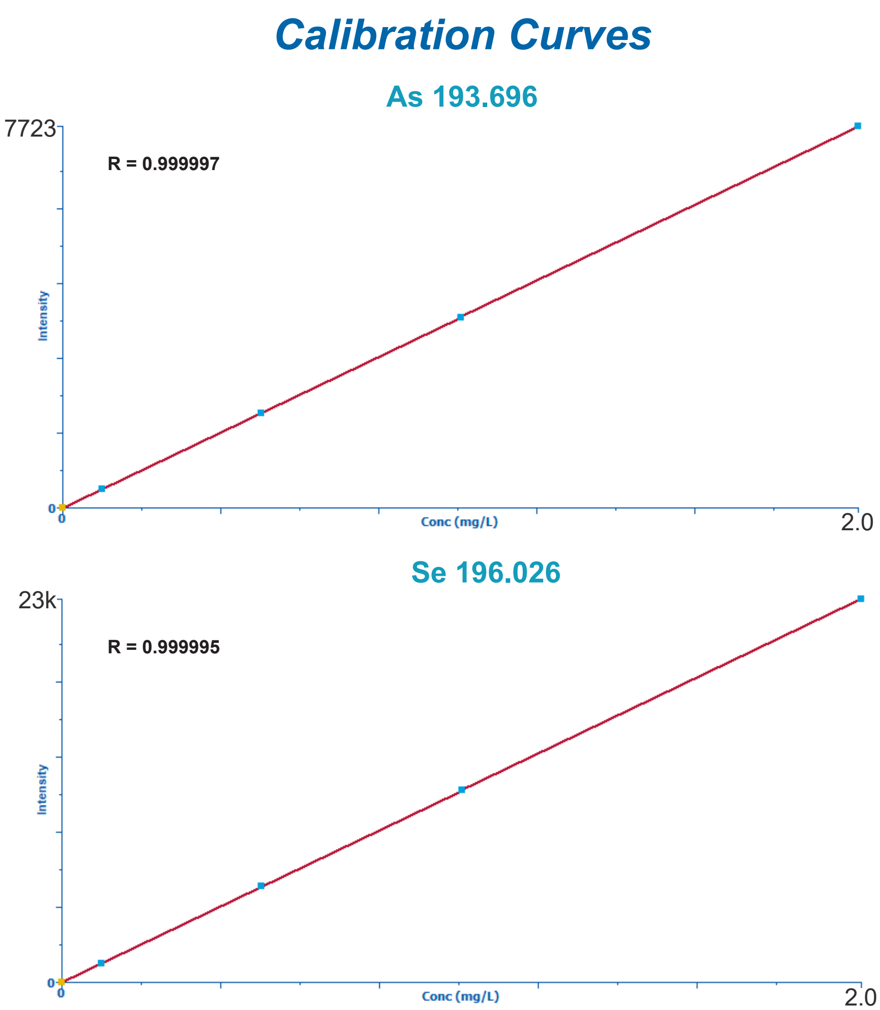


Table 4. Detection Limits and Calibration Linearity. Summary of estimated detection limits, calculated as 3*standard deviation of 10 blank measurements, and calibration linearity, shown by the calibration coefficient, R.

Element	Detection Limit	Correlation Coefficient (R)
Ag	1.5 ppb	0.999834
As	5.7 ppb	0.999997
Be	1.5 ppb	0.999956
Cd	0.9 ppb	0.999905
Cr	1.1 ppb	0.999913
Mo	3.5 ppb	0.999979
Pb	1.5 ppb	0.999832
Se	5.6 ppb	0.999995
Tl	3.4 ppb	0.999732
Zn	1.7 ppb	0.999954

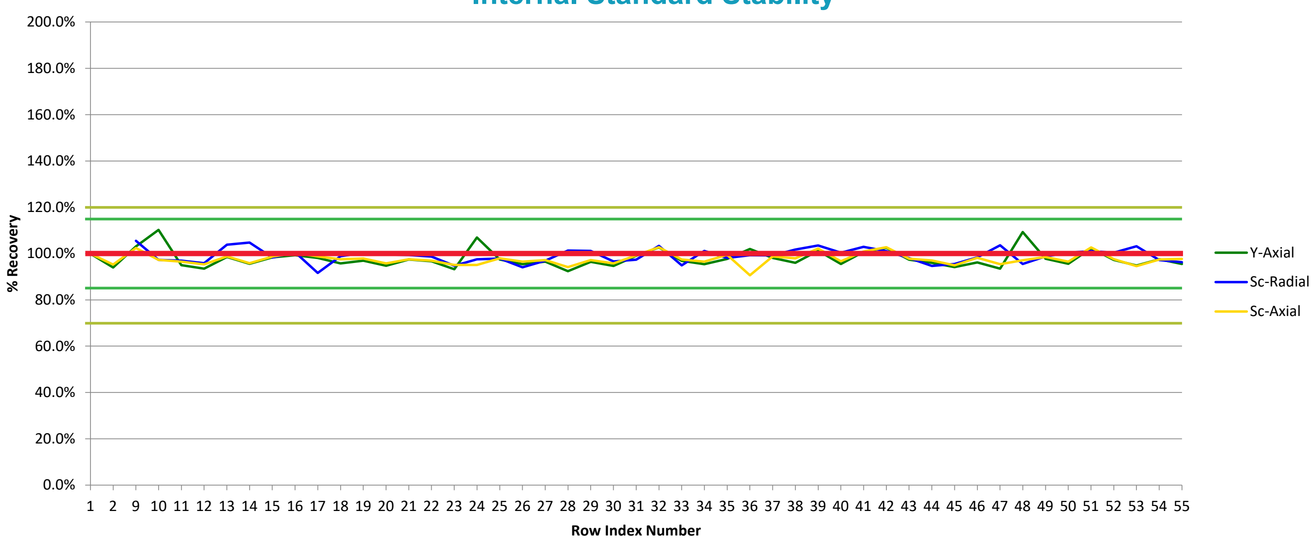
Conclusions

With the aid of an advanced, automated valve injection sample introduction system – SampleSense Enviro – optimized analysis of environmental waters by ICP in high throughput situations has been achieved.

Trace metals were quickly and efficiently determined – saving over 10 seconds per sample when compared to other high-throughput systems – in part due to built-in optical sensors on the SampleSense valve for sample loading which eliminates method customization and the need to adjust timing parameters for variable sample viscosity. Time was also saved during the washout of sample introduction components with a novel rinse-trapping valve. The DXCi autocorrecting autosampler assisted in also maximizing laboratory productivity and reducing needless sampling errors. In addition to the reduction in time, reliability, stability and accuracy remained well within the regulated parameters based on certified samples that were analyzed in both axial and radial views.

SampleSense Enviro has thus been proven to improve analytical efficiency in a production laboratory environment by maximizing throughput, and minimizing and flagging sampling errors while providing a higher level of data authentication and reliability for results.

Internal Standard Stability



Excellent stability and recovery over 55 samples.
Easily within the allowable range of 70-120%