Fast Analysis of Environmental Samples using the Agilent 5110 ICP-OES and ESI prep*FAST*

Automated high-throughput method compliant with EPA Method 200.7

Author

Andrew Toms, Joel Uhlmeyer and Michael Plantz[1]

Neli Drvodelic[2]

[1]Elemental Scientific, Omaha, USA

[2]Agilent Technologies, Inc.

Introduction

Many regulatory agencies worldwide require the analysis of treated municipal wastewater, stormwater run-off, and industrial effluent. Analyzing these types of water samples ensures that outflows being discharged into natural bodies of water do not exceed local regulatory limits. One widely used method for testing outflows is Method 200.7 from the United States Environmental Protection Agency (EPA 200.7) (*1*). The method describes techniques for the collection, preservation, and analysis of wastewater, and other similar samples using Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES). Waste samples often contain high levels of metals and non-metals, in addition to dissolved and undissolved solids, which can be challenging for analysts and their instruments. Rapid sample throughput and accuracy of results can be harder to achieve with these types of samples due to a high concentration of interfering elements.

Agilent 5110 ICP-OES instruments can be used with Elemental Scientific's (ESI) prep*FAST* autodilution and sample preparation system. With integrated control of prep*FAST* via ICP Expert software that operates the ICP-OES instrument, the system provides a fully automated approach to EPA 200.7 compliant analysis. The benefits of autodilution include automated preparation of calibration standards, pre-emptive autodilution of samples, and fully integrated autodilution of overrange and ISTD out-of-range samples. The Agilent 5110 Synchronous Vertical Dual View (SVDV) ICP-OES is suited to the analysis of environmental samples, as the instrument captures the axial and radial views of the plasma in one measurement, delivering accurate results in the quickest time (*2*, *3*).

EPA Method 200.7 is a performance-based ICP-OES method that can be applied to the determination of over 30 elements in various matrices. In this study, an Agilent 5110 SVDV ICP-OES was coupled to an ESI prep*FAST* 2 autodilution system and ESI SC-DX autosampler (Figure 1). Several certified reference materials (CRM) were measured to test the accuracy and robustness of the instrumentation.

Experimental

Instrumentation

Figure 1. Agilent 5110 ICP-OES with ESI prep*FAST* system.

ICP-OES

All measurements were carried out using an Agilent 5110 SVDV ICP-OES with Dichroic Spectral Combiner (DSC) technology (*2*). The DSC improves analysis times by allowing a combination of axial and radial emission from the plasma to be synchronously directed into the polychromator, with all wavelengths being measured in a single reading. The 5110's vertical torch ensures robust measurements over extended periods for a range of water samples, especially sludge and trade waste samples that can be run using the 200.7 method. The outcome is a reduced number of sample or quality control (QC) sample reruns, resulting in higher sample throughput. The solid-state radio frequency (SSRF) system featured on the 5110 provides a reliable, robust, and maintenance free plasma suitable for handling complex samples such as sludges and wastewaters.

The instrument was fitted with a double-pass glass cyclonic spray chamber, standard Easy-fit 1.8 mm injector torch, and connected to a PFA-ST nebulizer that is included with the prep*FAST* system. Instrument operating conditions are listed in Table 1.

Table 1. 5110 SVDV ICP-OES operating parameters.

Parameter	Setting
Read time (s)	20
Replicates	3
Sample uptake delay (s)	1
Stabilization time (s)	20
Pump speed (rpm)	12
Rinse time (s)	1*
Fast pump (80 rpm)	No
Background correction	Off-peak
RF power (kW)	1.5
Nebulizer flow (L/min)	0.70
Plasma flow (L/min)	12.0
Aux flow (L/min)	1.00
Viewing height (mm)	15

**Rinse delay is controlled by the prepFAST.*

Autodilution and sample preparation system

The ESI prep*FAST* system consists of a dual-valve module that is located next to the nebulizer, and a syringe pump module that is located under the autosampler. The syringes deliver diluent and internal standard solutions, which are rapidly and precisely mixed with each sample. A dedicated rinse syringe provides rapid washout between samples, as shown in Figure 2 (lower schematic).

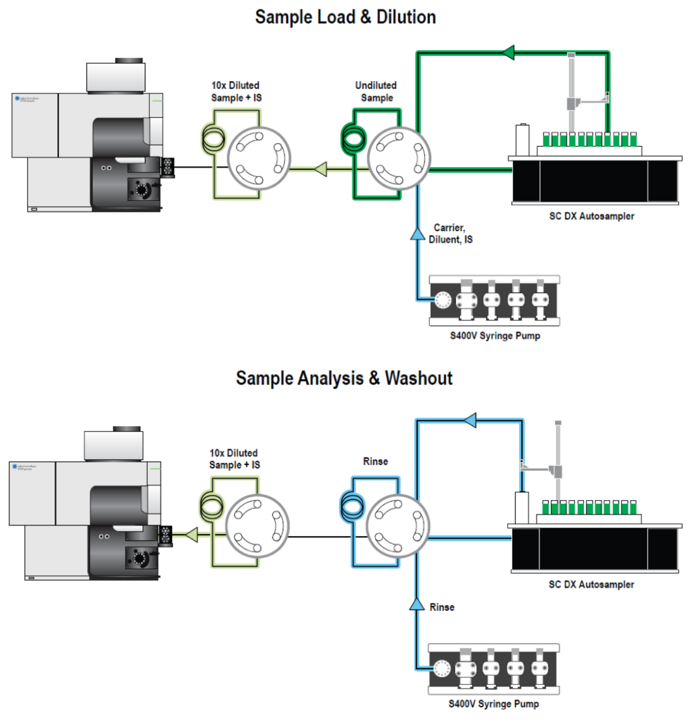


Figure 2. Schematic of prep*FAST* system loading and diluting a sample (top) before injection and rinse (bottom).

Samples are vacuum loaded into the dilution valve and then rapidly prepared and transferred to the analysis valve. The sample is then measured directly, while the sample probe and dilution valve are prewashed before the next sample. All dilution factors are automatically reflected in the reported results.

The prep*FAST* includes a dual rinse autosampler available in 2-, 4-, 8-, or 14-rack models to suit workload requirements. Unlike typical sample dilution, the prep*FAST* does not require a secondary sample container or volumetric dispensing tip. This reduces laboratory consumable costs and preparation time compared to manual preparation. Also, since the prep*FAST* only prepares the amount of solution required for the analysis, the amount of chemical waste generated is significantly reduced. In a typical application, every manually diluted sample generates an extra 10 mL of waste from a 15 mL diluted sample.

As a discrete sampling system, prep*FAST* significantly reduces the time for each sample analysis. Vacuum loading and syringe-driven rinse greatly reduce uptake and rinse-out delay times compared to a traditional autosampler. These features improve sample throughput and productivity while reducing operating costs.

Sample and standard preparation

The calibration standards were prepared from a single multi-element stock solution obtained from High-Purity Standards (Charleston, SC USA). Interference correction standards were prepared from individual single-element stock standards (High-Purity Standards). All standards were diluted into a mixture of 2% HNO_3 and 1% HCl (v/v).

River Sediment A and Soil B CRMs both from High Purity Standards and EP-H high-level drinking water CRM (SCP Science, Montreal, Québec, Canada) were analyzed to validate the analytical method.

The multi-element stock standard was placed in the autosampler standards' rack. Multiple dilutions of this standard were then automatically prepared inline and introduced to the 5110 ICP-OES by the prep*FAST* system. The calibration standard was analyzed at dilution factors of 50, 20, 10, 5, 2, and 1 (undiluted). If necessary, two separate stock standards at different concentrations can each be used to provide a calibration range covering more than four orders of magnitude.

The internal standard solution (ISTD), containing 5 ppm yttrium (Y) in 2% HNO_3 and 1% HCl, was automatically added inline to all solutions by the prep*FAST*.

Interference correction

Environmental samples often contain a wide range of elements at varying concentrations, so spectral interferences can occur. Inter Element Corrections (IEC) have been established as the preferred correction technique for these spectral interferences in labs running US EPA methods. In this study, IEC factors were set up using the Agilent ICP Expert software. Once the factors have been determined, they can be stored in a template and re-used in subsequent analyses. However, if accepted by local regulators, automated software correction techniques can be used, which eliminate the need for IECs.

Agilent provides two unique and powerful solutions to simplify interference correction: Fast Automated Curve-fitting Technique (FACT) and Fitted Background Correction (FBC). FACT is used for real-time spectral correction of complex samples and FBC is used for fast, accurate, and fully automated background correction (*4, 5*). In addition, the continuous wavelength coverage of the Agilent Vista Chip II CCD detector from 167 to 785 nm ensures a suitable, interference-free line can be found. There is no time penalty when adding additional wavelengths to the analysis.

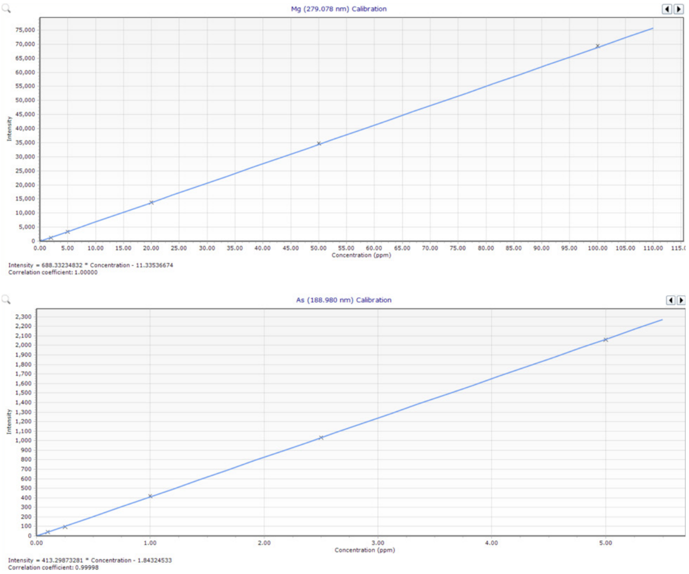
Intelligent autodilution

The prep*FAST* system performs automated dilution of samples that exceed QC parameters. The accuracy and effectiveness of this approach are demonstrated using challenging samples. When out-of-range limits are exceeded, the ICP-Expert software calculates the appropriate dilution factor needed to bring the out-of-range analytes within the calibration range. This information is sent to the prep*FAST*. In a real-time update to the sample list, the sample is added at the end of the current sequence list. The sample is then re-analyzed with the calculated dilution factor. No analyst interaction is required, providing significant labor savings and improving sample result acceptance rates.

Results and discussion

Autocalibration

Representative calibration curves for a major (Mg) and a trace element (As) are shown in Figure 3. The minimum linearity threshold for all calibrations was a correlation coefficient of ≥ 0.9995. All the calibration points were derived from a single multi-element standard placed on the autosampler standards' rack.



Intensity = 688.33234832 * Concentration - 11.33536674
Correlation coefficient: 1.00000

Intensity = 413.29873281 * Concentration - 1.84324533
Correlation coefficient: 0.99998

Figure 3. Calibration curves for Mg and As.

Expansion of linear dynamic range

The prep*FAST* system allows the ICP Expert software to automatically compensate for errors in the reported results. Errors can be caused by signal suppression effects in the plasma when samples with different matrices are analyzed. Figure 4 shows the measurements of several replicates of a simulated river sediment CRM (River Sediment A). The original (undiluted) analysis results showed that 1200 mg/L Fe was 'non-linear' at high signal levels due to self-absorption by nearly 50%, while good recoveries were achieved for 1 µg/L Cu. Following automatic dilution, the recovery for both analytes was excellent. The diluted analysis was performed without any input from the analyst.

Figure 4 also shows that the effective linear dynamic range (LDR) of the method can be extended well above the highest calibration standard. Extending the LDR ensures that the correct results will be obtained after prescriptive autodilution provided by the prep*FAST*.

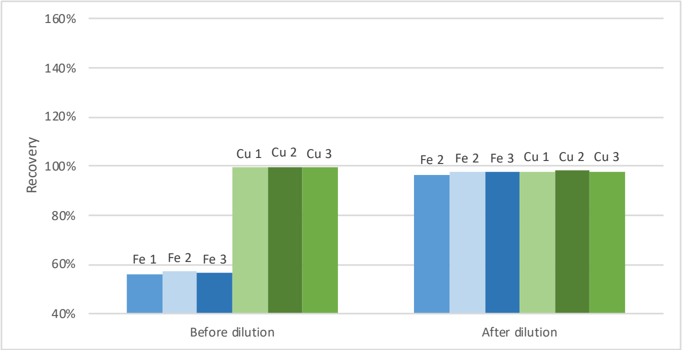


Figure 4. Improved recovery of high-level analytes through automated dilution.

High matrix samples

A simulated digested soil CRM (Soil B) was run to demonstrate the accuracy of the prep*FAST* for a high matrix environmental sample when diluted by up to two orders of magnitude. The results for the undiluted sample show a lower recovery for Al (700 µg/L) compared to V (0.8 µg/L), as shown in Figure 5. However, when diluted 24x, 47x, and 94x, accurate results were obtained for both major and trace components of the sample.

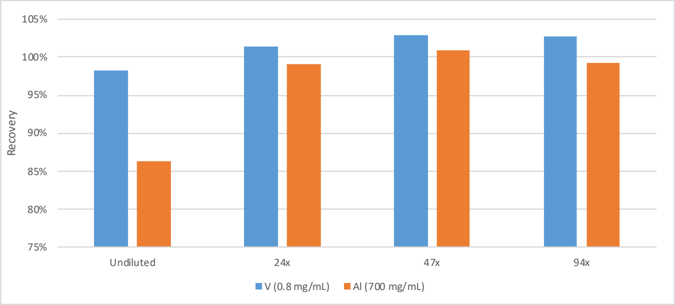


Figure 5. Accuracy of results across a wide range of dilutions.

Internal standards

The analyst specifies the required QC limits for internal standards (ISTDs) in the “Autodilutor” page of the ICP Expert software. If any sample falls outside the limits, it will be automatically diluted and rerun. To simulate a sample containing a natural concentration of yttrium, a known standard solution (which would have a known amount of ISTD automatically added by the prep*FAST* during the analysis) was spiked with an extra 1 ppm of yttrium. This concentration was enough to cause it to deliberately fail the ISTD control limits set in the ICP Expert software. The recovery results of the ISTD out-of-range test are shown in Figure 6. Initially, both yttrium lines, which were measured as internal standards, failed. The concentrations of all the other analytes were well below their true values due to the excessive internal standard correction being applied. Following autodilution and re-analysis, the ISTD recoveries for yttrium were within normal limits, and the suppression of the results for the other analytes was eliminated.

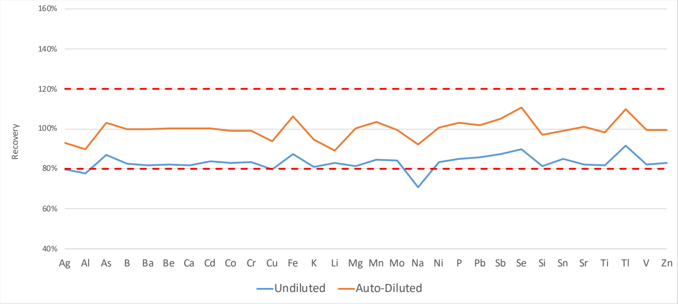


Figure 6. Recovery of results in a known standard before and after autodilution due to internal standard failure.

QC recovery tests

A Continuing Calibration Verification (CCV) solution (O2SI/LGC, Charleston, SC, USA) for all analytes was automatically measured every 10 samples during the 6 h 45 min sequence. The elemental concentrations of this CCV were selected to be at a midpoint of the calibration range for all analytes. The QC stability plot in Figure 7 shows the recovery of all elements over the six-hour period to be within the ±10 % limits defined in EPA method 200.7 (Table 2). The relative standard deviation (%RSD) was less than 1.5% for all elements except Si with 4.3% RSD. The results demonstrate the excellent robustness and precision of the 5110 SVDV ICP-OES over the extended run.

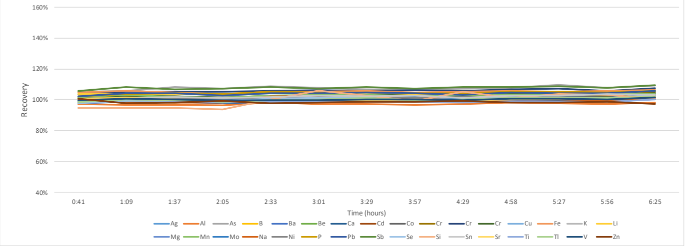


Figure 7. CCV recoveries of all analytes measured every 10 samples over six hours.

Table 2. CCV recovery test results.

Element and Wavelength (nm)	CCV Concentration (mg/L)	Average CCV Recovery (%)
Ag 328.068	0.05	100
Al 308.215	10	97
As 188.980	0.5	107
B 249.772	0.5	100
Ba 493.408	0.5	99
Be 313.042	0.5	99
Ca 315.887	10	99
Cd 226.502	0.5	100
Co 228.615	0.5	101
Cr 267.716	0.5	103
Cu 324.754	0.5	101
Fe 259.940	0.5	105
K 766.491	10	101
Li 670.783	0.5	104
Mg 279.078	10	99
Mn 257.610	0.5	103
Mo 203.846	0.5	101
Na 589.592	10	100
Ni 231.604	0.5	101
P 214.914	10	104
Pb 220.353	0.5	104
Sb 206.834	0.5	108
Se 196.026	0.5	100
Si 251.611	10	100
Sn 189.925	0.5	102
Sr 421.552	0.5	100
Ti 334.941	0.5	99
Tl 190.794	0.5	100
V 292.401	0.5	100
Zn 213.857	0.5	99

Matrix spike recovery

Multiple CRMs were evaluated to determine the accuracy and reproducibility of the method. In this example, a drinking water matrix EP-H CRM was used as a performance test sample for the matrix spike recovery test. The CRM, which contained all elements apart from Ag, was spiked to illustrate recovery at multiple dilutions. Figure 8 shows the results following three replicate analyses of the original (spiked) sample of EP-H, and three analyses of the spiked sample after it was diluted at two different levels. The EPA limits for a matrix spike test of ± 30% (Method 200.7 v4.4 section 9.4.3) are also shown in Figure 8. The recoveries obtained were excellent, even after autodilution and re-analysis at lower concentration levels.

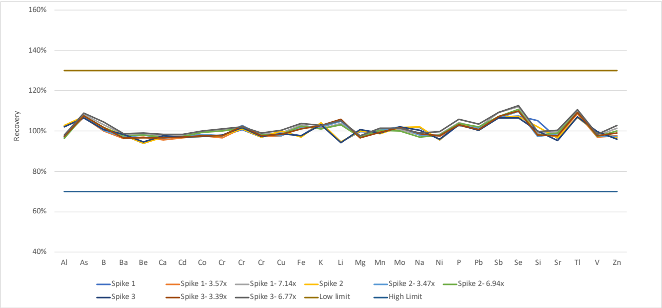


Figure 8. Accuracy of spike recoveries of a drinking water matrix proficiency test sample.

Table 3. Method detection limits (µg/L) per US EPA Method 200.7 guidelines.

Element and Wavelength (nm)	MDL (µg/L)	Element and Wavelength (nm)	MDL (µg/L)
Ag 328.068	0.72	Mn 257.610	0.23
Al 308.215	7.73	Mo 203.846	1.53
As 188.980	4.61	Na 589.592	5.92
B 249.772	0.23	Ni 231.604	1.04
Ba 493.408	0.27	P 214.914	22.31
Be 313.042	0.27	Pb 220.353	3.26
Ca 315.887	5.49	Sb 206.834	2.57
Cd 226.502	0.39	Se 196.026	6.71
Co 228.615	0.75	Si 251.611	9.01
Cr 267.716	0.44	Sn 189.925	2.12
Cu 324.754	0.34	Sr 421.552	0.21
Fe 259.940	3.37	Ti 334.941	0.45
K 766.491	27.01	Tl 190.794	5.06
Li 670.783	0.17	V 292.401	0.39
Mg 279.078	6.78	Zn 213.857	9.94

Method detection limits

The method detection limit (MDL) of each element was determined according to the procedure outlined in US EPA Method 200.7 Rev. 5 (40 CFR, part 136 Appendix B, Section 9.2.1). A standard solution containing analytes at a concentration of 2 to 5 times the estimated instrument detection limit (IDL) was measured 10 times on three non-consecutive days. The Student t-test was applied to the data reported in Table 3.

Conclusion

The Agilent 5110 SVDV ICP-OES is an ideal instrument to meet the productivity demands of environmental labs working to EPA 200.7 methodology. Integrating an ESI prep*FAST* 2 autodilution and sampling system to the 5110 SVDV ICP-OES offers many benefits for the high throughput analysis of challenging environmental samples, including:

- Autocalibration: automated, real-time preparation of calibration standards from a single stock solution located in the autosampler rack. The prep*FAST* 2 can dilute a calibration stock standard by up to a factor of 200, resulting in a highly accurate multilevel calibration.
- Prescriptive autodilution: the analyst specifies the required dilution factor for each sample ahead of time in the Sequence page of the ICP Expert worksheet software. The prep*FAST* dilutes the sample accordingly, directly from the original sample tube on the autosampler. Significant savings are realized through a reduction in both analyst time and required laboratory glassware usage and cleaning.
- Intelligent autodilution: defined acceptance windows for calibration ranges and internal standard performance allows the system to automatically respond to out-of-control conditions with automatic dilutions. Autodilution significantly reduces required re-analysis, speeding up the recording of reportable results.
- All dilutions of standards and samples are automatically documented within the instrument software, which eliminates the need for external record-keeping of manual dilutions.
- Reduction of waste: the prep*FAST* prepares the diluted standards and samples inline at the time of analysis. This approach eliminates the need to manually prepare and then dispose of the excess volume that is not used.
- Autodilution with prep*FAST* also reduces the risk of contamination from the laboratory environment and human error.
- Generally, the rapid sample uptake and washout performance of prep*FAST* leads to a 20–30% reduction in total analysis time, which results in less argon gas consumption and lower electrical power usage.

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Note: the ESI prep*FAST* autodilution system can be used with Agilent 5100 and 5110 ICP-OES instruments running ICP Expert version 7.4 (or later version) software.

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