High-Speed Environmental Analysis Using the Agilent 7500cx with Integrated Sample Introduction System – Discrete Sampling (ISIS–DS)

Application Note

Environmental

Authors

Steve Wilbur
Agilent Technologies, Inc.
3380 146th Place SE, Suite 300,
Bellevue Washington, 98007
USA

Takeo Kuwabara and Tetsushi Sakai
Agilent Technologies
Tokyo Analytical Division
9-1 Takakura-cho, Hachioji
Tokyo 192-0033
Japan

Abstract

Agilent has further improved the sample throughput capabilities of its 7500cx ICP-MS with Octopole Reaction System (ORS) using a newly configured Integrated Sample Introduction System–Discrete Sampling (ISIS-DS) accessory, and helium collision mode. Employing this new methodology, a complete suite of 30 or more elements can be analyzed in compliance with USEPA criteria (spectrum mode, three replicates, and sub-ppb MDLs) in approximately 75 seconds, sample to sample, with excellent removal of polyatomic interferences. Performance data showing stability, interference control, accuracy, precision, and washout are presented. The new system is applicable to labs requiring extremely high sample throughput and with its low sample consumption of ~2.2 mL/sample, for applications where sample volume is limited.

Introduction

The Agilent Integrated Sample Introduction System (ISIS) has always permitted the highest sample throughput, using either high-speed uptake with constant flow nebulization or discrete sampling using a six-port valve and sample loop with time-resolved acquisition. In keeping with Agilent's continual focus on product enhancement, ISIS Discrete Sampling (ISIS-DS) has been reconfigured to further improve productivity. The resulting enhanced ISIS-DS sampling mode takes advantage of the ability of the 7500cx ICP-MS to analyze environmental samples using a single collision cell mode (He mode). This new mode of operation permits USEPA-compliant analysis (spectrum mode, three replicates, and sub-ppb MDLs) of a complete suite of 30 or more elements in approximately 75 seconds, sample to sample.

ISIS Configuration

Figure 1 shows the ISIS configuration used. It is a typical discrete sampling configuration with a couple of important modifications. Pump 1 (P1) is the large ISIS sample uptake peristaltic pump. Pump 2 (P2) is the standard 7500 nebulizer pump.

The ISIS uptake pump (P1), which is located downstream of the valve, draws the sample from the autosampler into the sample loop. As a result, the sample loaded in the sample loop is never exposed to peristaltic pump tubing, thereby eliminating a common source of contamination and carryover. This high-speed, high-capacity peristaltic pump is capable of rinsing and filling the sample loop in approximately 10 seconds when using the Cetac ASX-520 autosampler with the wide-bore 0.8 mm id probe. The other modification is the addition of the tee joint between the valve and nebulizer to allow the use of online internal standard addition. By minimizing both the length and diameter of the tubing between the valve and nebulizer, the time from rotation of the valve (sample injection) to the realization of a constant analyte signal is less than 15 seconds. A 300-µL loop is sufficient to allow more than 30 seconds of continuous spectrum mode acquisition. Larger loop sizes can be used to achieve any duration of acquisition required. After acquisition has completed, the valve returns to the load position, flushing any remaining sample to waste and rinsing the nebulizer and spray chamber with clean rinse solution. At this point, approximately 15 seconds is required for the signal to return to baseline in preparation for the next analysis (Figure 2).

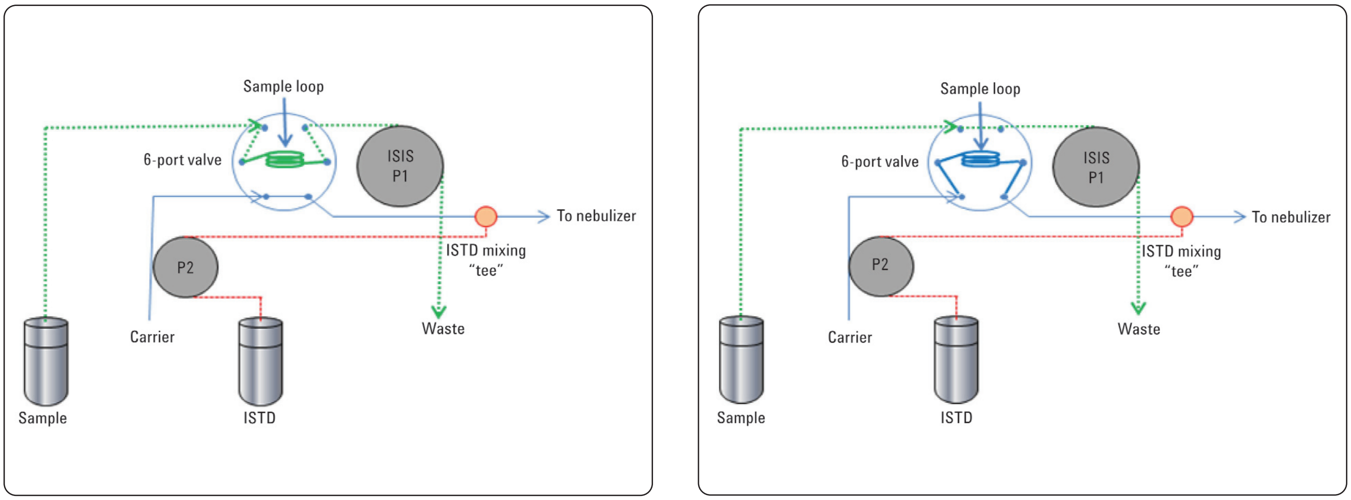

Figure 1. *ISIS-DS sampling with online internal standard configuration. Valve in "load" position on left and in "inject" position on right.*

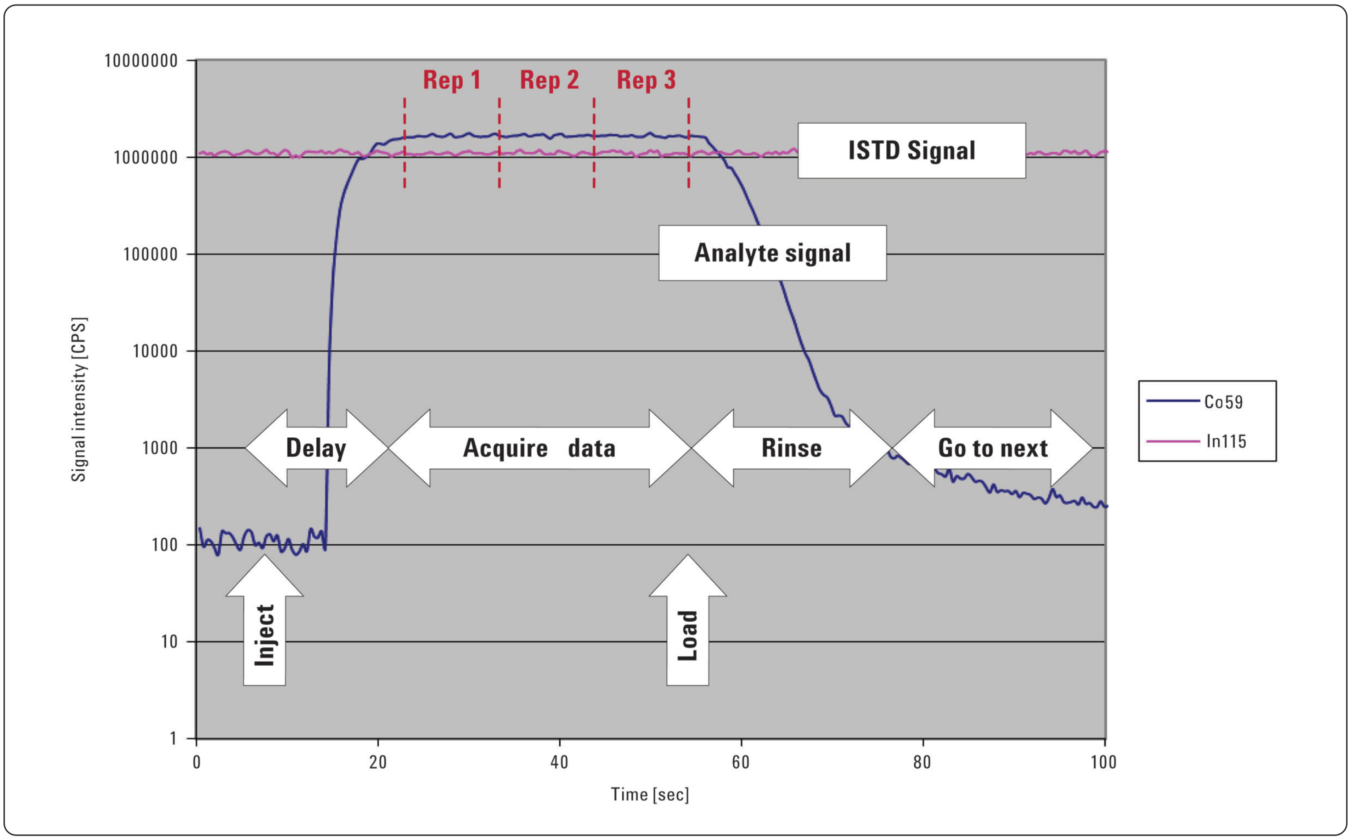

Figure 2. Analyte and internal standard profile during discrete sampling analysis (log scale for signal intensity). Time 0 – autosampler probe enters the sample and loop is loaded. Inject at 10 seconds, 15 seconds acquisition delay, 30 seconds acquisition, 10 seconds rinse, 10 seconds overhead. Total time is approximately 75 seconds.

Experimental

A sequence of 216 samples was analyzed in 4 hours 29 minutes using the new ISIS-DS sampling configuration depicted in Figure 1 and the acquisition conditions listed in Table 1. The 7500cx was operated in a single cell mode (He collision mode) resulting in both excellent removal of polyatomic interferences and very fast acquisitions since no cell gas switching or stabilization was required[1]. The sequence consisted of a single initial calibration at 0.1, 1, 10, and 100 ppb for all elements, followed by repeated (n = 26) analyses of a block of samples consisting of:

- 50 ppb calibration check (CCV)
- NIST 1643e water
- CCB (blank)
- USEPA Interference Check Solution – A (ICS-A)
- Blank
- USEPA ICS-AB (spiked with all analytes at 100 ppb to monitor carryover)
- Blank
- Blank

---

[1] This is a key benefit over reaction cell ICP-MS instruments that have to operate in multiple cell modes to cover all analytes. While it is possible to use multiple cell modes with discrete sampling, the resulting acquisition time is significantly lengthened, minimizing the benefits in terms of both run time and matrix exposure. If multiple cell modes are employed using the Agilent Octopole Reaction System, the small cell volume and very rapid gas switching reduce the cost in time and matrix exposure.

Table 1. ISIS/7500cx ICP-MS Acquisition Conditions for Spectrum Mode Discrete Sampling Analysis

Plasma	**Robust mode – 1550 watts**
Nebulizer	Glass concentric (standard)
Number of elements (including internal standards)	31
ORS mode	Helium - 4 mL/min (single mode)
Integration time per point	0.1 seconds (all elements)
Points per peak	1
Replicates	3
Total acquisition time (3 replicates)	29 seconds
Loop volume	300 µL
Loop rinse and fill time	10 seconds
Acquisition delay (after valve rotation to inject)	15 seconds
Steady state signal time (before valve rotation to fill again)	30 seconds

Results

Total Run Time and Sample Consumption

The resulting run-to-run time was measured at approximately 75 seconds per sample. Total sample consumption was determined by weighing each sample before and after analysis and was calculated to be 2.2 mL per sample per analysis. The method thus lends itself to samples in which the volume available for analysis is limited, and because small amounts are used, waste disposal costs are reduced. The small sample consumption also permits samples to be automatically reanalyzed by intelligent sequencing if needed from a 10-mL autosampler vial while allowing the ASX-520 to be configured for the maximum possible number of samples.

Stability

Long-term stability was monitored using internal standards. The abstracted internal standard data are illustrated in Figure 3, and show no downward drift, even after repeated (52 total) injections of ICS-A and ICS-AB. Only ^{6}Li demonstrated matrix suppression greater than 10% in the highest matrix samples, otherwise internal standard recoveries were within ~ ± 10% for the entire sequence. Calibration stability was monitored by measuring a 50-ppb CCV once in each 8-sample block (Figure 4). USEPA limits for CCV recovery are ± 10%. No CCV failures occurred; in fact, nearly all CCV recoveries were within ± 5% for the entire sequence.

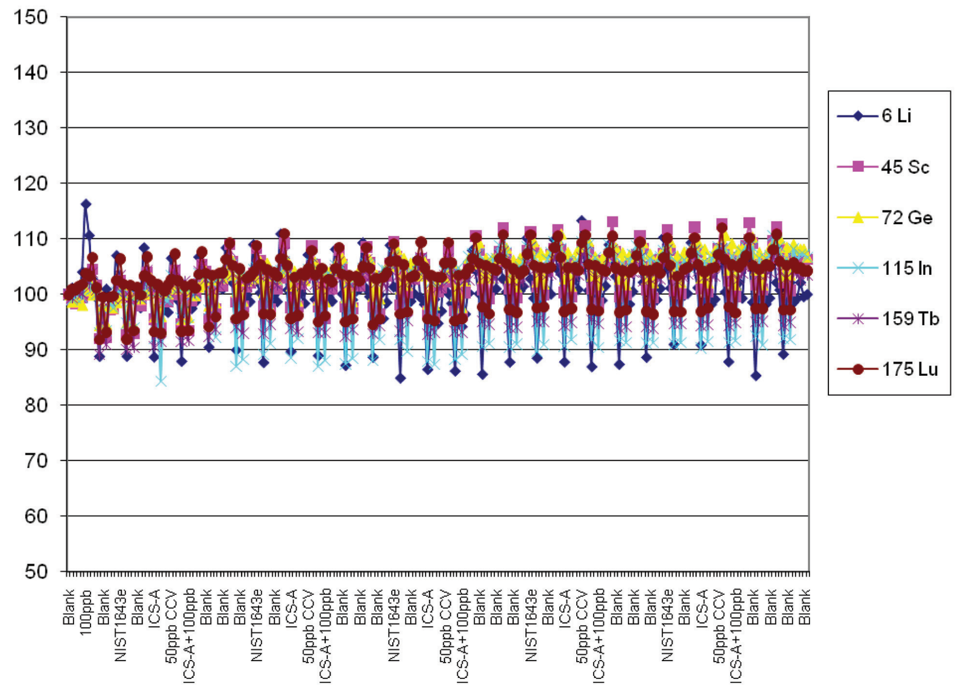

Figure 3. Internal standard recoveries compared to calibration blank for all 216 samples.

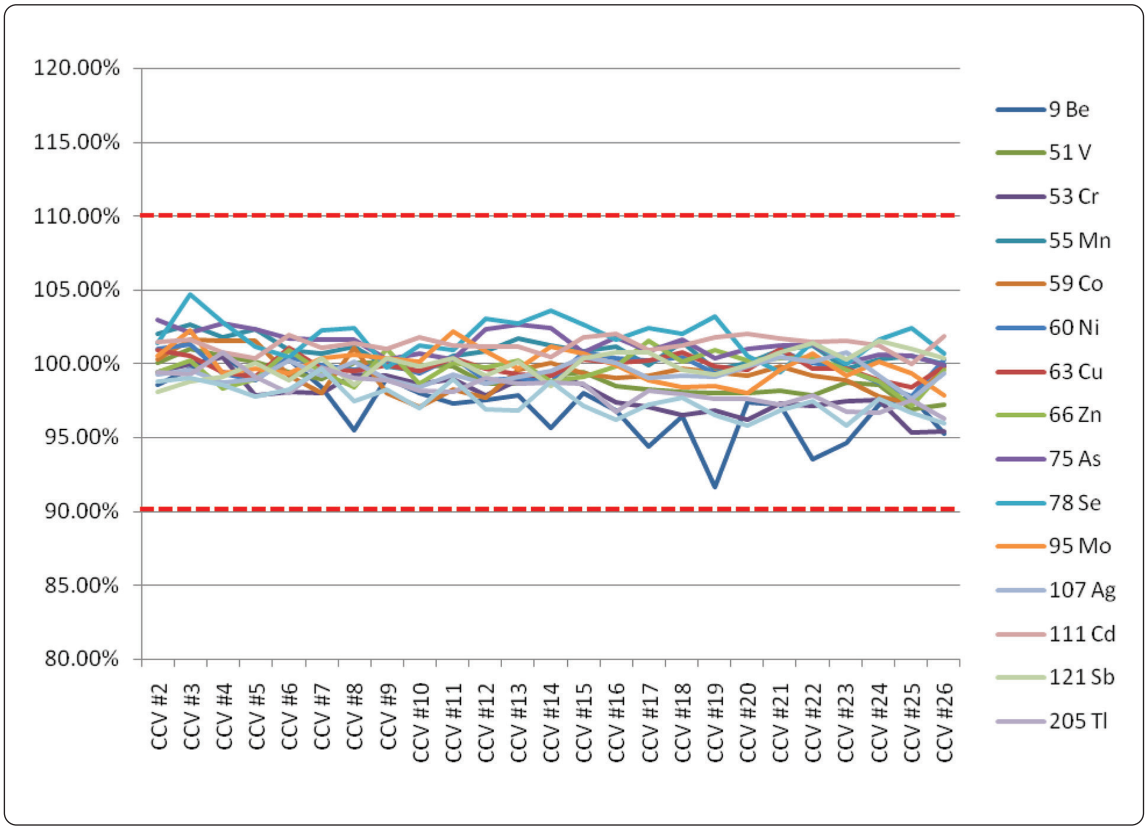

Figure 4. CCV recoveries (50 ppb) for entire sequence. USEPA limits for CCV recoveries in both Method 200.8 and 6020 are ± 10% (shown in red).

Accuracy

Long-term accuracy and precision were also determined through repeated analysis of NIST 1643e Certified Reference Water (n = 26). Results are tabulated in Table 2, showing recoveries within ± 10% or better of certified values and relative standard deviations near 1% for most elements. Be and Se had higher %RSDs due to the short integration times used and slightly lower count rates for these elements in He mode. Longer integration times can be used if higher counts or better precision are required for these elements. When ultimate DLs for Se are required (low ppt), H_2 mode is recommended. Due to the fast switching time of the ORS, Se can be measured in H_2 mode with only ~30 seconds added to the sample to sample run time.

Table 2. Precision (%RSD) and Mean Recovery of NIST 1643e Water for 26 Separate Analyses

Mass/ element	Mean measured value (µg/L)	RSD (%)	Certified value (µg/L)	Mean recovery (%)
9 Be	13.8	2.5	14.0	101.0
23 Na	22689.2	2.0	20740.0	109.4
24 Mg	7300.3	2.1	8037.0	90.8
27 Al	142.3	3.3	141.8	100.4
39 K	1837.8	1.1	2034.0	90.4
43 Ca	32170.1	0.7	32300.0	99.6
51 V	37.8	1.1	37.9	99.8
53 Cr	19.2	1.7	20.4	93.9
55 Mn	38.0	0.9	39.0	97.6
56 Fe	98.1	3.9	98.1	100.0
59 Co	28.8	0.7	27.1	106.4
60 Ni	59.2	0.8	62.4	94.9
63 Cu	23.2	0.8	22.8	101.9
66 Zn	70.0	0.5	78.5	89.2
75 As	54.3	0.9	60.5	89.8
78 Se	10.0	3.4	12.0	83.2
95 Mo	121.7	1.1	121.4	100.3
107 Ag	1.1	1.4	1.1	101.1
111 Cd	6.2	0.8	6.6	94.3
121 Sb	59.5	0.9	58.3	102.0
205 Tl	7.4	0.8	7.4	100.0
208 Pb	19.6	0.9	19.6	99.7

Table 3. Washout Performance (Mean value of 26 ICS-AB spikes [100 ppb], each immediately followed by two consecutive blanks. Percent reduction calculated as 1-([mean Blank]/[mean ICS-AB]) in percentage.)

Mass/ element	ICS-AB spike Mean	Blank 1 Mean	Percent reduction Mean	Blank 2 Mean	Percent reduction Mean
9 Be	94.9315	0.0199	99.979	0.0097	99.990
23 Na	96707.6923	19.6032	99.980	13.5090	99.986
24 Mg	79238.8462	14.2332	99.982	9.8046	99.988
27 Al	75758.0769	11.7913	99.984	7.8004	99.990
39 K	82694.2308	17.6441	99.979	13.2657	99.984
43 Ca	9092.8462	1.4105	99.984	0.9697	99.989
53 Cr	95.7327	0.0419	99.956	0.0441	99.954
55 Mn	94.8977	0.0132	99.986	0.0069	99.993
56 Fe	77021.9231	12.5122	99.984	8.0837	99.990
57 Fe	75266.5385	12.0863	99.984	7.7304	99.990
59 Co	106.8577	0.0140	99.987	0.0092	99.991
60 Ni	101.3692	–0.0161	100.016	–0.0129	100.013
63 Cu	98.5700	0.0163	99.984	0.0043	99.996
66 Zn	99.9350	0.0055	99.994	0.0011	99.999
75 As	95.8615	0.0290	99.970	0.0171	99.982
78 Se	94.0162	0.0841	99.911	0.0428	99.955
95 Mo	1862.3077	1.4281	99.923	0.6278	99.966
107 Ag	96.8769	0.0181	99.981	0.0098	99.990
111 Cd	104.0538	0.0134	99.987	0.0084	99.992
121 Sb	109.1346	0.2629	99.759	0.1077	99.901
205 Tl	93.4731	0.0339	99.964	0.0131	99.986
208 Pb	92.4704	–0.0175	100.019	–0.0241	100.026

Washout

Washout is always a concern in high sample throughput applications, particularly when analyzing high-matrix, variable samples. In order to evaluate the washout for each element, two sequential blank samples were measured immediately after each spiked ICS-AB sample. The spiked ICS-AB contained 100 ppb of all calibrated elements, plus very high concentrations of Na, Mg, Al, K, and Fe. Memory effects were determined by measuring the blank immediately following the ICS-AB. Any subsequent carryover was measured in the second blank (Table 2). In all cases, greater than 3 orders of magnitude reduction (> 99.9%) was achieved before the first blank, even for the high-concentration matrix elements. The second blank showed nearly no additional reduction, indicating that essentially complete washout was achieved during the configured sample uptake and rinse-out steps of the analysis. Even "sticky" elements, such as Mo, Sb, and Tl, demonstrated the same high degree of washout. This level of washout is comparable to or better than standard peristaltic pumped systems using much longer rinse times.

Conclusions

The results of this simple experiment illustrate that discrete sampling in spectrum mode (as opposed to time-resolved mode) using the Agilent Integrated Sample Introduction System can achieve extremely high sample throughput for typical environmental analyses using USEPA criteria. These data highlight that this novel method, using ISIS, easily exceeds the demanding USEPA requirements for stability, interference control, accuracy, precision, and washout.

The ISIS-DS system offers several advantages over other discrete sampling systems: Full integration into the ICP-MS mainframe, fully integrated software, compatibility with the industry standard ASX 520 autosampler, no vacuum pump and associated pump valve to wear and replace, very low sample consumption (~2.2 mL/sample), and the flexibility to use the ISIS for other supported sample-introduction tasks, such as constant-flow nebulization, autodilution, or hydride generation.

For More Information

For more information on our products and services, visit our Web site at www.agilent.com/chem.

www.agilent.com/chem

Printed in the USA
March 11, 2009
5990-3678EN

Agilent Technologies