# Using qualifier ions to improve ICP-MS data quality for waste water analysis

Application note

Environmental

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## Abstract

Researchers at a commercial environmental laboratory have developed an effective method for validating high throughput multi-element data from high matrix waste water samples. The method used an Agilent 7700x ICP-MS with High Matrix Introduction (HMI)[1] capability and third generation Collision Reaction Cell (CRC) operating in helium (He) mode. This simultaneously removes the polyatomic interferences from all isotopes of each analyte and gives access to secondary isotopes for many analytes. Simply checking the agreement between the results from the primary and secondary isotope provides a quick and easy means to confirm the accuracy of the analytical data. The new method was validated by analyzing approximately 6000 samples over a 21-week study period.

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**7800 ICP-MS**

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[1] The High Matrix Introduction System is patented by Agilent Technologies, US Patent number 7,671,329 B2

## Introduction

Commercial analytical service laboratories must meet strict client and ISO 17025 demands for data quality, while maintaining acceptable turnaround and profitability. Typical performance testing and quality control protocols are based largely on the analysis of periodic calibration checks, and reference samples or synthetic mixes that simulate the expected sample matrices to be analyzed. However, this approach does not confirm the actual analyte results measured in each of the unknown samples, and so may result in errors when sample matrices are variable. A technique that can validate the quality of the analytical results for each unknown sample, without adding significant cost or time provides a competitive advantage to the laboratory.

Eurofins Analytico, a branch of Eurofins Scientific, which is an international group of testing laboratories, uses a simple yet powerful method to confirm the routine multi-element results reported on their ICP-MS instruments. They have developed a method for secondary isotopes (or “qualifier” ions) as a fast quality check in their wastewater method using an Agilent 7700x ICP-MS. While the use of qualifier ions for quantitative confirmation is well established in organic mass spectrometry, the approach hasn’t been widely applied in conventional ICP-MS due to the presence of polyatomic interferences on secondary (and many primary) isotopes.

The Agilent 7700x/7800 ICP-MS use an Octopole Reaction System (ORS) cell operating in helium (He) mode to effectively remove the polyatomic interferences on both primary and secondary isotopes under the same cell conditions. This allows secondary isotopes to serve as qualifier ions for many elements, providing a fast and simple way to validate the analytical result. This method does not require any additional sample analysis or sample preparation for calibration or quality control.

### Effective Interference Removal

Agilent’s ORS collision cell is unique in operating effectively with He cell gas and Kinetic Energy Discrimination (KED) to remove spectral interferences caused by polyatomic ions. He mode on the ORS separates analyte ions from interfering polyatomic ions using the difference in ionic radius (polyatomic ions are always larger than monatomic analyte ions of the same mass), so the method is universal. As a result, HE mode works with all polyatomic ions, regardless of the sample matrix. This eliminates the need for interference correction equations, and the complicated matrix-, analyte- or isotope-specific optimization and method development characteristic of cells that use reactive gases. This makes He mode the most suitable CRC technique for the elimination of unpredictable interferences that arise in the analysis of complex and variable environmental samples such as wastewater. Figure 1 shows the results of preliminary interference tests investigating the applicability of the qualifier ion technique. A clean seawater matrix was diluted ten times to give a major element composition of approximately: Cl 2000 ppm, Na 1100 ppm, Mg 130 ppm, S 90 ppm, Ca 40 ppm, K 40 ppm, Br 7 ppm, and C 3 ppm. This solution was analyzed, and the apparent quantitative results measured at both the primary and secondary isotopes were examined.

Figure 1 demonstrates that He mode removed the matrix- based interferences effectively, reducing the quantitative error and enabling the use of all primary and secondary isotopes.

By contrast, the results for no gas mode showed that significant interferences were present on most primary and secondary isotopes of the analytes studied.

## Experimental

An Agilent 7700x ICP-MS, which includes the High Matrix Introduction (HMI) system, was used for this study. The fully integrated HMI provides plasma robustness through automated aerosol dilution and preset plasma conditions. For these high-matrix wastewater samples, maximum plasma robustness (Ultra Robust setting) was selected, along with mid-level aerosol dilution. The analytical conditions used for Analytico’s waste water method are shown in Table 1.

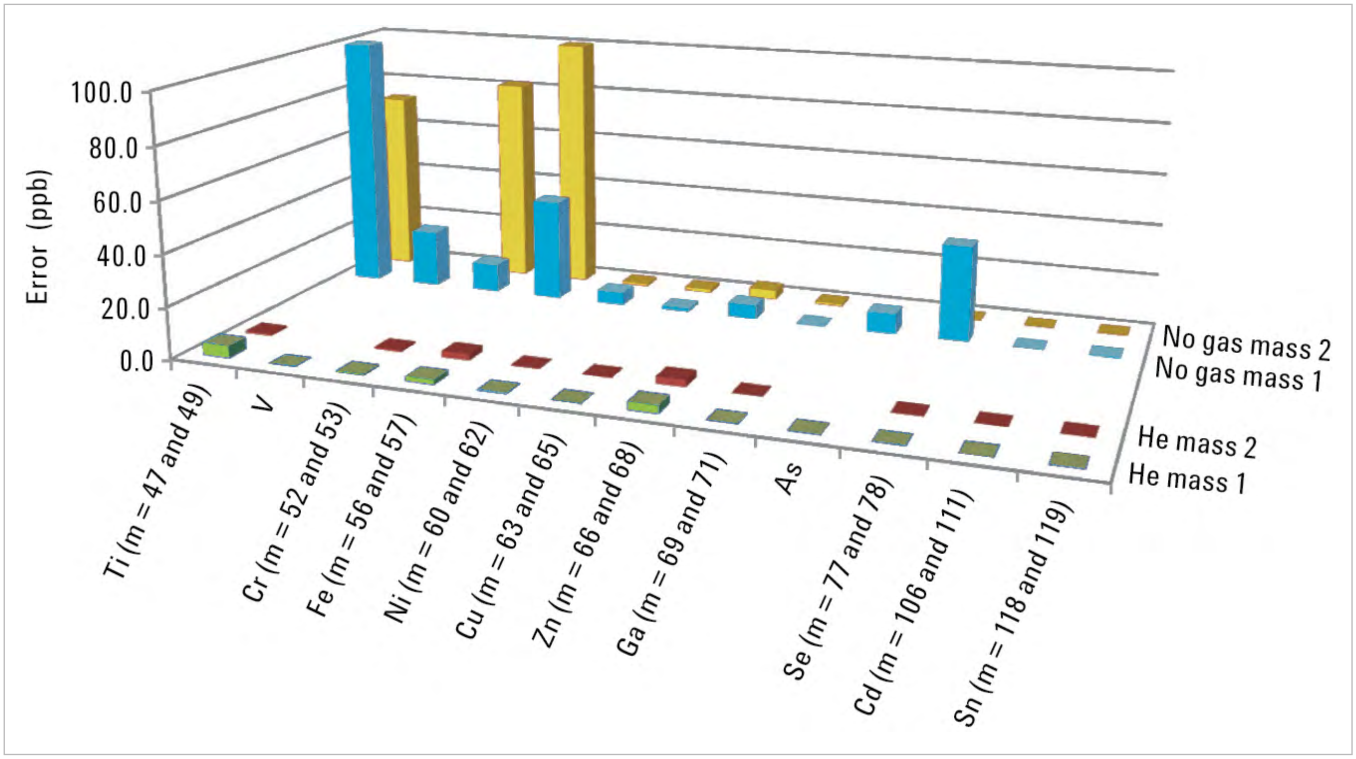

**Figure 1.** Quantification error in tenfold diluted seawater matrix. Apparent concentrations due to interferences are shown for two isotopes in both cell modes (no gas and He). V (51) and As (75) don't have secondary isotopes available.

Method validation for high throughput wastewater analysis consisted of:

- Analyte recoveries in a NaCl matrix
- Determination of method detection limits (MDL)
- Recovery and precision of low and high concentration spikes
- Accuracy and precision of measurement of certified reference materials (CRM)
- Accuracy and precision of continuing calibration blanks and calibration checks (CCB, CCV)
- Determination of linear dynamic range

For brevity, not all results from the method validation are presented in this application note.

Samples were prepared as follows: CRM samples were prepared by digesting 0.5 g sample plus 25 mL water with 2 mL $HNO_3$ and 6 mL HCl.

After digestion, samples were diluted to 50 mL with ultrapure water. Since the final acid concentration of the samples was quite high (4% $HNO_3$ and 12% HCl), an optional Ni plated sampling cone was fitted.

The method used two cell gas modes: He and hydrogen ($H_2$) mode. $H_2$ was needed for low level analysis of sulfur in the method. Sulfur is a difficult element for ICP-MS because of its high ionization potential and intense interference from polyatomic ions such as $O_2^+$. Though xenon cell gas has been widely used for sulfur analysis, $H_2$ also gives good performance by allowing sulfur to be detected as the reaction product, $SH^+$.

He mode was operated in both conventional KED mode and high energy mode which offers enhanced sensitivity for selenium. $H_2$ mode was also operated in two modes, because the measurement of sulfur at SH requires that energy discrimination be turned off to allow transmission of the SH polyatomic for measurement.

In Table 2, all measured isotopes are shown. As illustrated, most of the elements measured have at least two isotopes available; the primary isotope used for quantification and a second isotope for use as a qualifier. All isotopes except those underlined were analyzed using He mode. Underlined isotopes were analyzed using $H_2$ mode.

| **Equipment** | | | | |
|---|---|---|---|---|
| Nebulizer | Mira Mist nebulizer - PTFE (Agilent G3161-80000) | | | |
| Sampler/skimmer | Ni plated sampler (Agilent G3280-67061)/Ni skimmer | | | |
| ISTD | $^{6}$Li, $^{45}$Sc, $^{103}$Rh and $^{193}$Ir added 1:1 to sample via online ISTD kit | | | |
| **Plasma setting** | **Ultra Robust/Mid-level Aerosol Dilution** | | | |
| Forward power | 1600 W | | | |
| Carrier gas | 0.6 L/min | | | |
| Dilution gas | 0.4 L/min | | | |
| Extract 1 | 0 V | | | |
| **Parameter** | **He Mode** | **He Mode (high energy)** | **$H_2$ Mode** | **$H_2$ Mode (sulphur)** |
| Cell gas flow (mL/min) | 4.3 | 10 | 6 | 8 |
| KED (V) | 3 | 4 | 3 | 0 |

## Results

Table 2 summarizes the MDL and reference sample (BCR-145R- sewage sludge, FeNeLab - Dutch soil) results obtained during the method validation.

The MDLs were calculated using a synthetic digested wastewater (a digested clean water sample was used to calculate the MDLs for the matrix elements), spiked at a low level (a few times the required MDL concentration), measured on 10 different days, over a period of 30 days. MDLs (3 sigma of the 10 replicates) for all elements met the required reporting limits despite the high matrix. Quantification results of two CRMs are shown for both the primary ion (isotope 1) and qualifier ion (isotope 2).

Relative Percentage Difference (RPD) values in the table show the difference between the quantitative results reported from the primary and qualifier ions. If the RPD exceeds ±20%, the analyst is automatically alerted. In this way, both human and analytical errors are detected and can be corrected. For example, while the quantified concentration using the primary ion shows good recovery for almost all certified elements, the RPD exceeded the ±20% criteria for Ce in both CRMs and Ti in BCR-145R. These differences were not, however, due to residual polyatomic interferences, but the fact that the secondary isotopes of both elements ($^{142}$Ce and $^{48}$Ti) suffer from direct isobaric interferences from another element ($^{142}$Nd and $^{48}$Ca, respectively). This illustrates the importance of isotope selection when considering choices for secondary or qualifier ions in ICP-MS. While He mode has been demonstrated to remove polyatomic interferences effectively, it cannot remove isobaric (same-mass) overlaps from an isotope of another element. In this case, $^{49}$Ti might be another option as a secondary isotope for Ti analysis.

While the CCV/CCB test showed good stability during the method validation, long term stability throughout routine analysis of real samples is also essential. Figures 2 and 3 show the internal standard (ISTD) stability in real sample sequences. Figure 2 shows the normalized internal standard recoveries compared to the calibration blank for a single sequence consisting of 160 high-matrix wastewater samples. Figure 3 shows the raw internal standard response at the end of each day's sequence over the course of the 21-week study period. During this period, nearly 6000 samples were analyzed. These plots demonstrate the excellent robustness provided by the HMI and the exceptional stability of the Agilent 7700x ICP-MS, despite the high matrix and high acid concentrations. This exceptional matrix tolerance and stability contributes significantly to the laboratory's productivity by minimizing both recalibration overhead and maintenance downtime.

**Table 2.** MDL and CRM Test Results

| | Measured isotope (m/z) | | MDL | Reporting Limit | FeNeLab "Dutch Soil" | | | | | BCR-145R "Sewage Sludge" | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Measured | | | | | Measured | | | |
| | #1 | #2 | µg/L | µg/L | Certified mg/kg | #1 mg/kg | #2 mg/kg | Recovery % | RPD% | Certified mg/kg | #1 mg/kg | #2 mg/kg | Recovery % | RPD% |
| Be | 9 | | 0.8 | 1 | 1.52 | 1.68 | | 110 | | | 0.41 | | | |
| B | 11 | 10 | 25.6 | 60 | 35.10 | | | | | | 18.72 | | | |
| Na | 23 | | 120 | 200 | 316 | 325 | | 103 | | | 652 | | | |
| Mg | 24 | 26 | 30 | 100 | 9400 | 9147 | 9427 | 97 | 3.1 | | 5316 | 5473 | | 3.0 |
| Al | 27 | | 50 | 100 | 25600 | 28424 | | 111 | | | 21484 | | | |
| P | 31 | | 30 | 50 | 2520 | 2451 | | 97 | | | 11804 | | | |
| S | 34 | 33 | 570 | 1000 | 1230 | 911 | 1004 | 82 | –9.2 | | 12329 | 11977 | | 2.9 |
| K | 39 | | 180 | 200 | 5250 | 6417 | | 122 | | | 1363 | | | |
| Ca | 40 | 44 | 170 | 200 | 36500 | 34516 | 34385 | 95 | –0.4 | | 43499 | 43319 | | –0.4 |
| Ti | 47 | 48 | 10.0 | 20 | 504.79 | 556.35 | | 10.2 | | | 204.64 | 268.13 | | 31.0 |
| V | 51 | | 2.8 | 10 | 55.8 | 64.03 | | 115 | | | 28.82 | | | |
| Cr | 52 | 53 | 1.9 | 5 | 180 | 193.66 | 191.91 | 108 | –0.9 | 300 | 289.57 | 289.94 | 97 | 0.1 |
| Fe | 56 | 54 | 40.0 | 50 | 35.54 | 35.25 | 35.80 | 99 | 1.6 | | 12.85 | 13.36 | | –3.9 |
| Mn | 55 | | 0.004 | 20 | 1.05 | 1.03 | | 99 | | 0.145 | 0.14 | | 96 | |
| Ni | 60 | 61 | 2.0 | 5 | 54.0 | 56.81 | 57.00 | 105 | 0.3 | 251 | 224.33 | 220.81 | 89 | –1.6 |
| Co | 59 | | 2.0 | 10 | 18.4 | 19.03 | | 103 | | 5.3 | 4.83 | | 91 | |
| Cu | 63 | 65 | 1.0 | 5 | 153 | 151.27 | 151.56 | 99 | 0.2 | 707 | 652.40 | 646.36 | 92 | –0.9 |
| Zn | 66 | 68 | 6.0 | 10 | 1020 | 1019.1 | 1028.8 | 100 | 1.0 | 2140 | 1963.8 | 2002.1 | 92 | 1.9 |
| As | 75 | | 1.7 | 2 | 41.6 | 44.62 | | 107 | | | 8.01 | | | |
| Se | 78 | 77 | 1.8 | 2 | 1.71 | 1.80 | 1.74 | 105 | –3.3 | | 6.08 | 6.36 | | 4.6 |
| Sr | 88 | 86 | 3.6 | 10 | 129 | 139.35 | 139.88 | 108 | 0.4 | | 295.02 | 294.20 | | –0.3 |
| Mo | 95 | 98 | 0.002 | 10 | 0.0014 | 0.0014 | 0.0014 | 100 | 0.0 | | 0.01 | 0.01 | | 0.3 |
| Ag | 107 | 109 | 0.4 | 2 | 2.75 | 3.06 | 3.04 | 111 | –0.6 | | 13.39 | 13.48 | | 0.6 |
| Cd | 114 | 111 | 0.3 | 0.4 | 8.24 | 8.30 | 8.33 | 101 | –0.3 | 3.43 | 3.10 | 3.18 | 93 | –2.4 |
| Sn | 118 | 120 | 1.8 | 10 | 22.2 | 24.32 | 24.35 | 110 | 0.1 | | 58.22 | 59.18 | | –0.1 |
| Sb | 121 | 123 | 1.4 | 2 | 3.28 | 2.56 | 2.63 | 78 | 2.8 | | 12.00 | 12.03 | | 0.3 |
| Te | 125 | 126 | 0.9 | 1 | | 0.29 | | | | | 0.06 | | | |
| Ba | 135 | 137 | 4.5 | 10 | 797 | 857.95 | 858.54 | 108 | 0.1 | | 2446.6 | 2450.4 | | 0.2 |
| Ce | 140 | 142 | 3.6 | 10 | | 46.96 | 89.62 | | 90.9 | | 9.94 | 18.90 | | 90.1 |
| Hg | 201 | 200 | 0.1 | 0.1 | 3.81 | 3.67 | 3.68 | 96 | 0.4 | 1.99 | 1.83 | 1.85 | 92 | 1.2 |
| Tl | 205 | 203 | 3.1 | 10 | 1.10 | 1.25 | 1.21 | 114 | –3.2 | | 0.16 | 0.15 | | –2.1 |
| Pb | 208 | 206 | 2.7 | 5 | 282 | 295.52 | 291.08 | 105 | –1.5 | 282 | 262.46 | 256.17 | 93 | –2.4 |

MDLs shown were calculated from 3-sigma of a low level spiked sample based on the primary isotope (mass 1) of each element. # 1 - *m/z* of primary isotope, # 2 - *m/z* of qualifier isotope. Underlined isotopes analyzed in $H_2$ mode, all other isotopes analyzed using He mode.

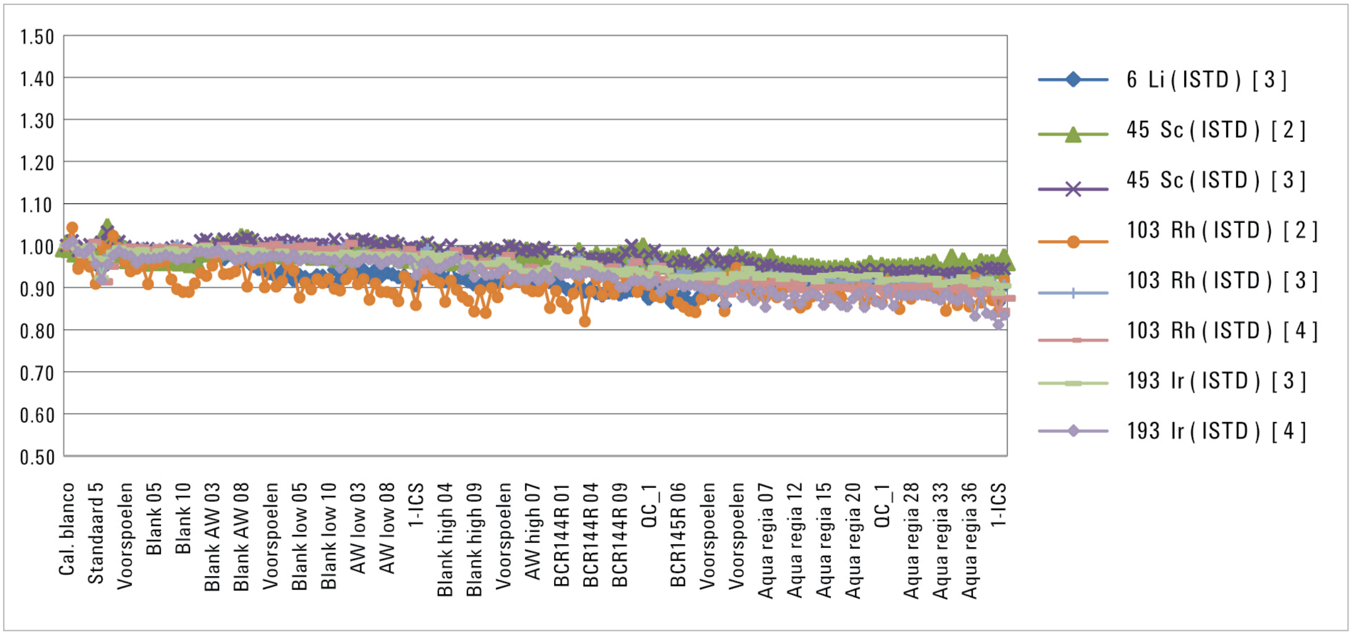

**Figure 2.** Normalized internal standard stability over a single sequence of 160 high matrix wastewater samples. Not all samples are labeled due to space restrictions.

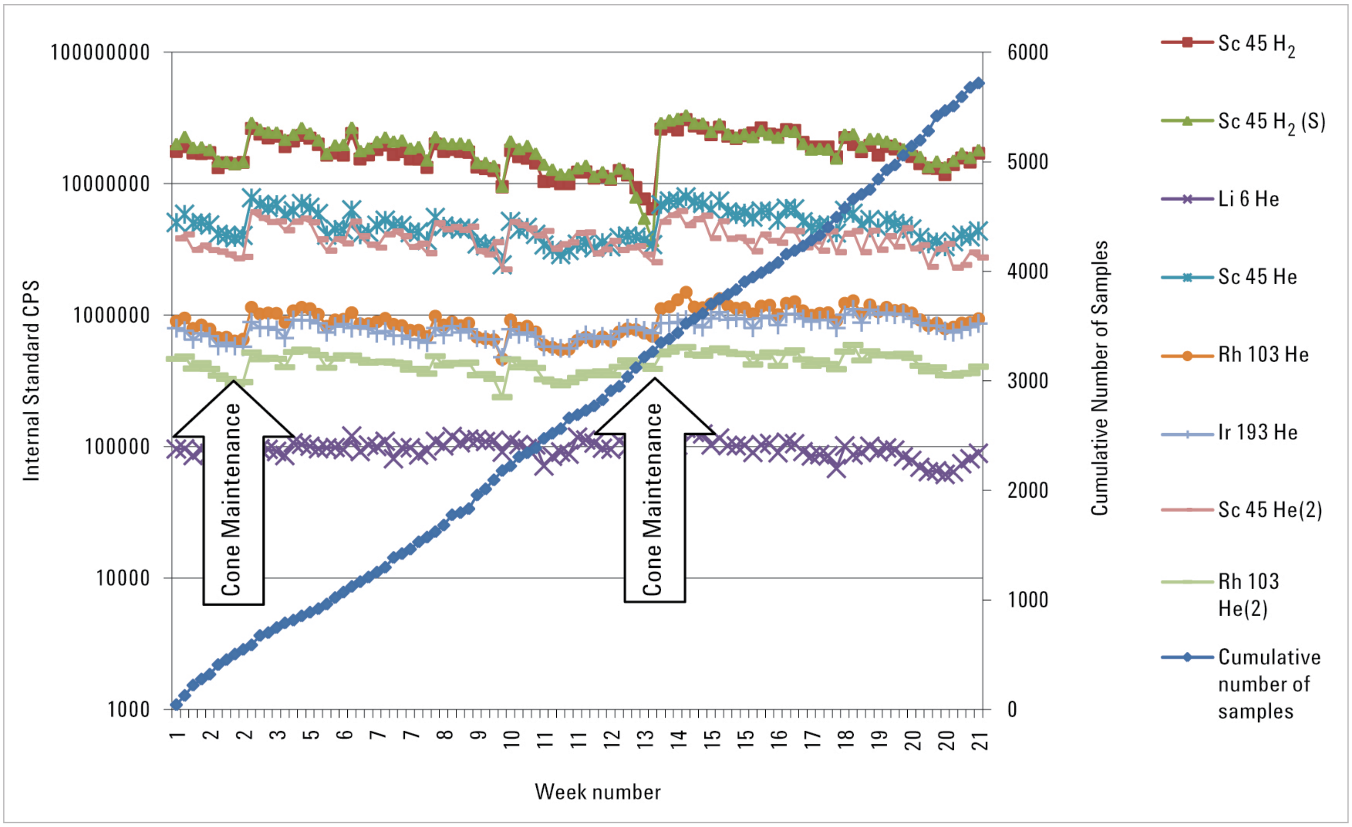

**Figure 3.** Internal standard signal at the end of sequences run each day over 21 weeks, demonstrating excellent stability throughout the analysis of nearly 6000 real samples. Individual days of the week are not shown due to space restrictions. Samples were analyzed five days per week.

## Conclusions

The Agilent 7700x/7800 ICP-MS with HMI provides a stable, sensitive, robust method for the analysis of long sequences of high-matrix environmental samples such as wastewaters.

Simple, universal He mode reliably removes polyatomic interferences on all analyte isotopes. It ensures accurate quantification across variable and complex sample matrices, and makes available secondary (qualifier) isotopes for many analyte elements. This allows users to confirm their measurements by comparing the primary and qualifier ion results, giving a quick, simple, and reliable method for validating the accuracy of the analysis. In addition, the method does not incur additional QC costs or sample analysis overheads.

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**7800 ICP-MS**

Results presented in this document were obtained using the 7700x, but performance is also verified for the 7800 ICP-MS.

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