APPLICATION NOTE

ICP-Optical Emission Spectroscopy

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Simultaneous Analysis of Hydride and Non-Hydride Elements in Drinking Water with Avio 550 Max ICP-OES and HydraMist Sample Introduction System

Introduction

Humans are primarily exposed to arsenic (As) through food and drinking water, which can occur through direct consumption of water, foods cooked in water, and beverages made from drinking water. Because of arsenic's toxicity to humans, the World Health Organization (WHO) has a recommended limit of 10 µg/L As in drinking water. However, this is a provisional limit because of the practical difficulties in removing As from drinking water. As a result, in areas where soup, rice, tea, and similar beverages and dishes are a dietary staple, exposure to arsenic is a great concern. The International Program on Chemical Safety (IPCS) concluded that long-term exposure to As in drinking water is related to an increased risk of cancer on the skin, lung, bladder and kidney, as well as skin changes such as hyperkeratosis and pigmentation.[1]

Arsenic measurements in drinking water are primarily carried out by ICP-MS due to its ability to accurately measure low concentrations. Measuring arsenic by ICP-OES may pose a challenge in drinking water due to the high excitation of arsenic and low As concentrations. The only way around this limitation is to use hydride generation, where As reacts on-line with a reducing agent (sodium borohydride) to form AsH_3, a gas phase species. Because AsH_3 is in the gas phase, desolvation is not necessary, meaning that all the plasma energy can go into exciting the As, resulting in higher sensitivity.[2,3]

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The limitation of hydride generation is that if samples need elements other than As measured, they must be run twice: once by hydride generation for As and once by conventional sample introduction for other elements.

However, the HydraMist sample introduction system (Glass Expansion, Port Melbourne, Victoria, Australia) circumvents this limitation. The HydraMist system combines both hydride and conventional nebulization in the same spray chamber, allowing the low-level measurement of hydride-forming elements (such as As, Hg, and Se) at the same time as other non-hydride-forming elements (i.e. Fe, Cd, Cu, Cr, Zn, etc.). When combined with PerkinElmer's fully simultaneous Avio® 550 Max ICP-OES, a complete elemental suite in drinking water can be measured.

This work describes drinking water analysis on the Avio 550 Max ICP-OES using the HydraMist sample introduction system.

Experimental

Samples and Sample Preparation

Method development and optimization of the experimental parameters were done with initial calibration verification (ICV) and Analytes B solutions, each of which was diluted 1000x (0.05 to 50 mL) in 1% HNO_3 (v/v). A mineral water purchased in a grocery store was used to evaluate the methodology and was prepared twice: the first preparation involved spiking with the hydride-forming elements (As, Se, Hg, Sb, and Bi) at 10 µg/L, and the second preparation was spiked with non-hydride-forming elements at 50 µg/L. Calibration standards were made in 1% HNO_3 (v/v) at the concentrations in Table 1.

Table 1. Calibration Standards.

Elements	Calibration Range (µg/L)
Ag, Al, Ba, Be, Bi, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Ni, Pb, Sr, Tl, V, Zn, Ge, Mo, Nb, Re, Ta, Ti, W, Zr	2, 5, 10, 20, 50, 100
Ca	5, 10, 20, 50, 100
As, Hg, Se, Sb, Bi	2, 5, 10
Si	20, 50, 100
P	50, 100

All samples, blanks, and standards underwent the following pre-reduction procedure: 25 mL of each solution was combined with 15 mL of concentrated hydrochloric acid in 50 mL DigiTUBE®s, capped, and heated at 70 °C for 30 minutes in a PerkinElmer SPB sample preparation block. The solutions were cooled to room temperature, then diluted to a final volume of 50 mL with deionized water.

Instrumental Parameters

All analyses were carried out on a fully simultaneous Avio 550 Max ICP-OES with the HydraMist sample introduction system to allow simultaneous analysis of hydride- and non-hydride-forming elements, as shown in Figure 1. All Avio 550 Max operating parameters are shown in Table 2, and the wavelengths used appear in Table 3. Multiple wavelengths for each of the hydride elements were monitored to confirm results. This did not add time to the analysis due to the true simultaneous nature of the Avio 550 Max system.

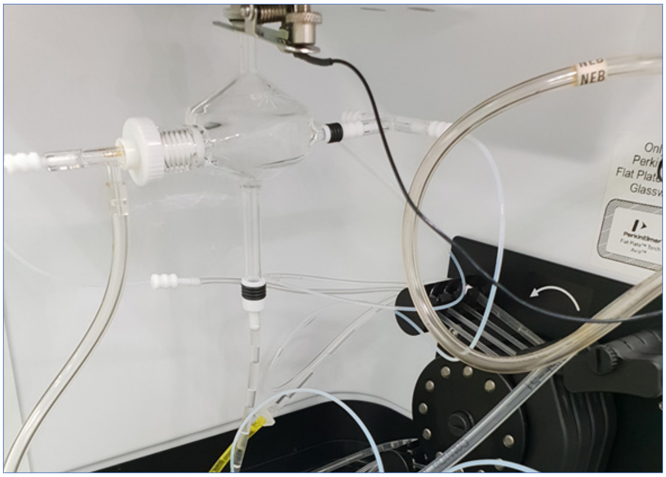

Figure 1. HydraMist sample introduction system connected to an Avio 550 Max ICP-OES.

Table 2. Avio 550 Max ICP-OES Operating Parameters.

Parameter	Value
Nebulizer	SeaSpray (2 mL/min)
Spray Chamber	HydraMist
RF Power	1500 W
Injector	2.0 mm Alumina
Plasma Flow	12 L/min
Auxiliary Flow	0.2 L/min
Nebulizer Flow	0.55 L/min
Torch Position	-3
Sample Uptake Rate	1 mL/min
Replicates	3
Plasma View	Axial
Integration	Auto
Read Time Range	Min = 2s; Max = 10s
Sample Line Pump Tubing	White/White
$NaBH_4$/NaOH Reductant Line Pump Tubing	Black/Black
Drain Line Pump Tubing	Black/White

Table 3. Analytes and Wavelengths.

Element	Wavelength (nm)
Ag	328.068
Al	396.153
As	188.979, 193.696, 197.197
Ba	233.527
Be	313.107
Bi	233.061, 190.171, 306.766
Cd	228.802
Co	228.616
Cr	267.716
Cu	327.393
Fe	238.204
Ga	294.364
Ge	209.426
Hg	253.652, 194.168
K	766.490
Mn	257.610
Mo	202.031
Nb	309.418
Ni	231.604
Pb	220.353
Re	197.248
Se	196.026, 203.985
Sb	206.836, 217.582
Ti	334.940
V	290.880
W	207.912
Zn	206.200
Zr	343.823

Results and Discussion

To evaluate the effectiveness of the HydraMist system to enhance the sensitivity of hydride-forming elements, the sensitivities of arsenic (As) and selenium (Se) were compared between conventional sample introduction (i.e. pneumatic nebulization, cyclonic spray chamber) and the HydraMist. As shown in Figure 2, the sensitivities of a 5 µg/L As and Se standard with the HydraMist are significantly higher than those of a 50 µg/L standard with conventional sample introduction, demonstrating the ability of the HydraMist to significantly enhance sensitivities of hydride-forming elements.

With the effectiveness of the HydraMist established for increasing the sensitivity of hydride-forming elements, calibration standards were run simultaneously for both hydride- and non-hydride-forming elements. Calibration correlation coefficients of >0.999 were achieved easily for all elements, as shown in Figures 3 and 4 for hydride- and selected non-hydride-forming elements, respectively.

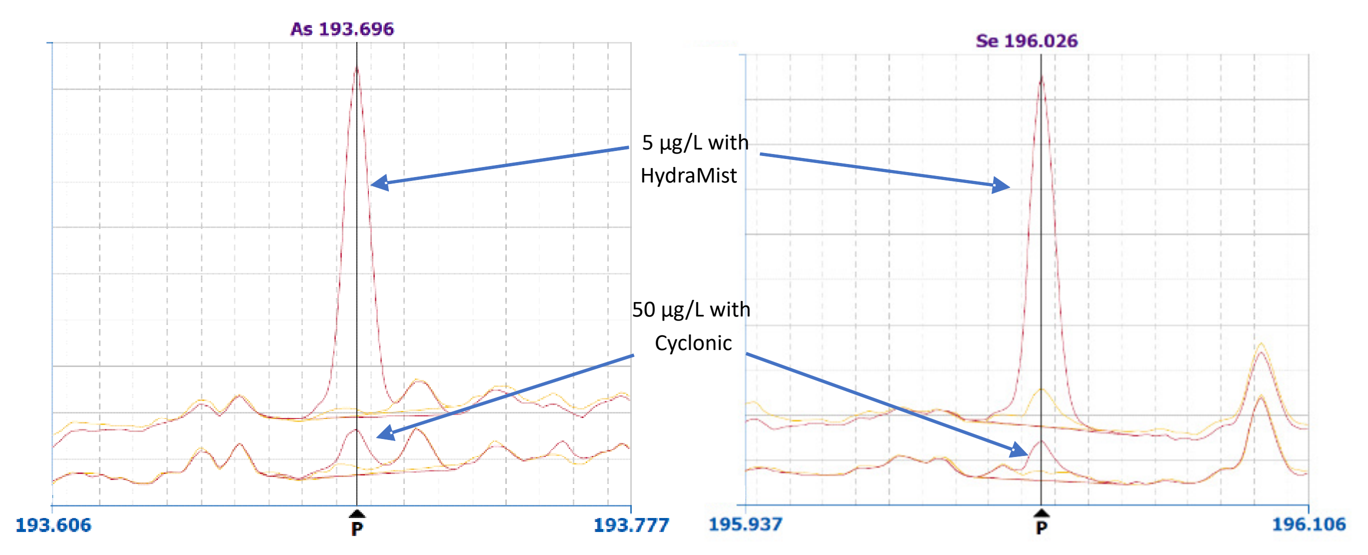

Figure 2. Comparison of arsenic and selenium sensitivities with conventional sample introduction and hydride generation with the HydraMist sample introduction system.

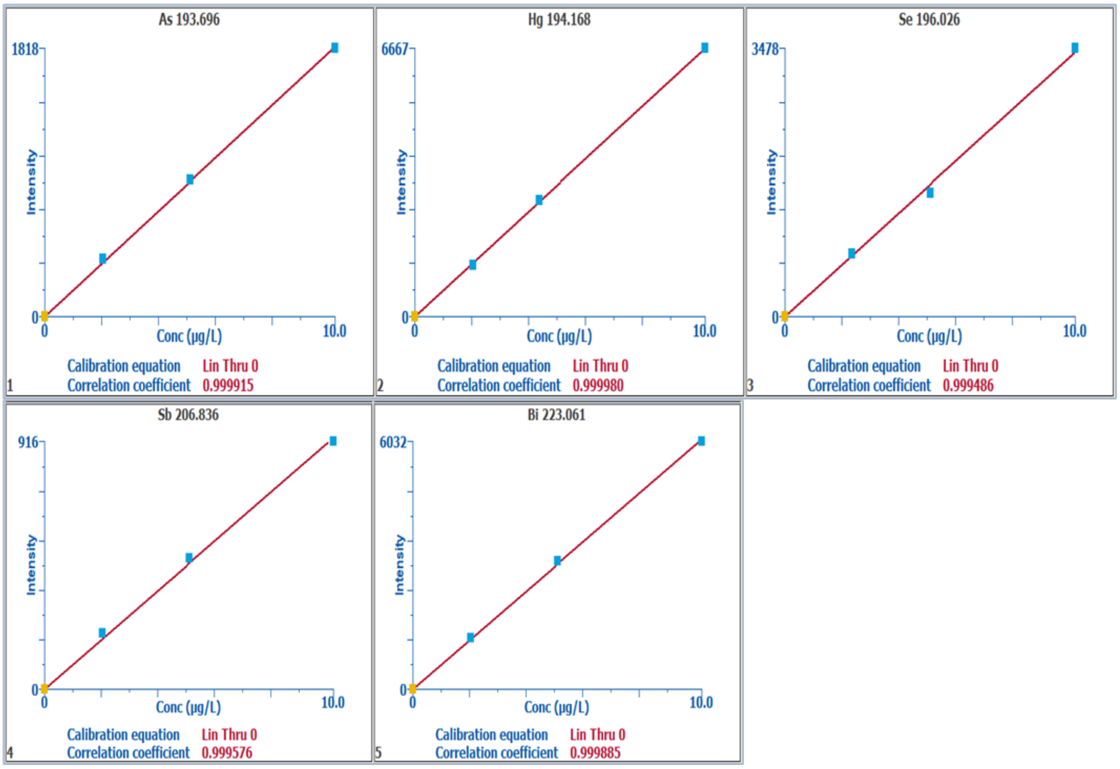

Figure 3. Calibration curves for hydride-forming elements.

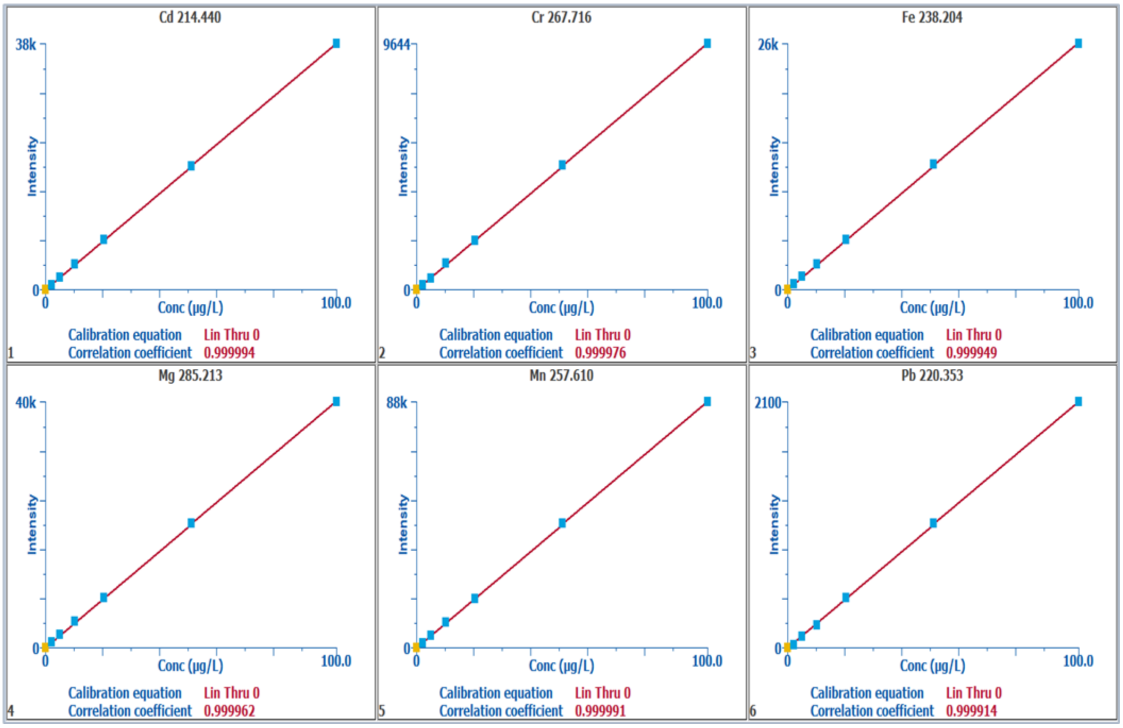

Figure 4. Calibration curves of representative non-hydride-forming elements.

After establishing calibration curves, the accuracy of the methodology was assessed by analyzing both the ICV and Analytes B solutions. The analyte concentrations of these two solutions are shown in Table 4, after the sample preparation procedure. As shown in Figures 5 and 6, all analytes in both solutions recovered within 10% of their true values, despite the wide concentration ranges, verifying the accuracy of the methodology. It should be noted that although sodium (Na) and thallium (Tl) were present in these solutions, neither of these elements were measured. One of the limitations of the HydraMist system is that Na cannot be measured due to the extremely high Na background, resulting from the $NaBH_4$ being pumped into the spray chamber to enable hydride formation. After dilution and sample preparation, the concentration of Tl is below the detection limit of ICP-OES.

Table 4: Analytes and Concentrations in the ICV and Analytes B Solutions after Sample Preparation.

Element	ICV (µg/L)	Analytes B (µg/L)
Ag	5	10
Al	100	---
As	5	5
Ba	100	25
Be	2.5	25
Ca	250	---
Cd	2.5	50
Co	25	25
Cr	5	25
Cu	12.5	25
Fe	50	---
K	250	---
Mg	250	---
Mn	7.5	25
Ni	20	50
Pb	1.5	2.5
Sb	30	30
Se	2.5	2.5
Tl	5	5
V	25	25
Zn	10	50

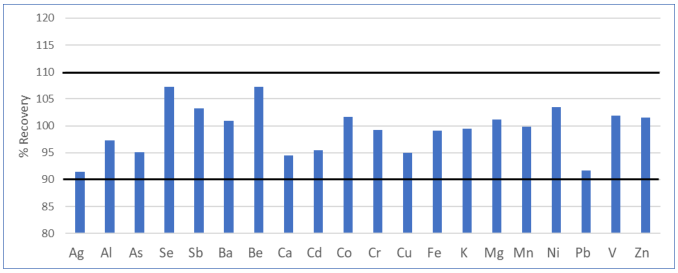

Figure 5. Analyte recoveries in ICV solution.

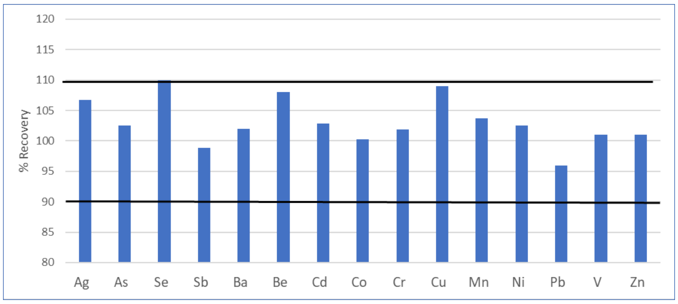

Figure 6. Analyte recoveries in Analytes B solution.

To evaluate the effect of matrices, a commercial mineral water was spiked with 10 µg/L of the hydride-forming elements and 50 µg/L of the non-hydride-forming elements and measured against the calibration curves. As shown in Figures 7 and 8, all of the analytes recover within 10% of their true values, despite having high concentrations of Na, Mg, Ca, and K, demonstrating the robustness of the methodology in the presence of high mineral concentrations. For the hydride-forming elements, multiple wavelengths of each element were measured to confirm the results.

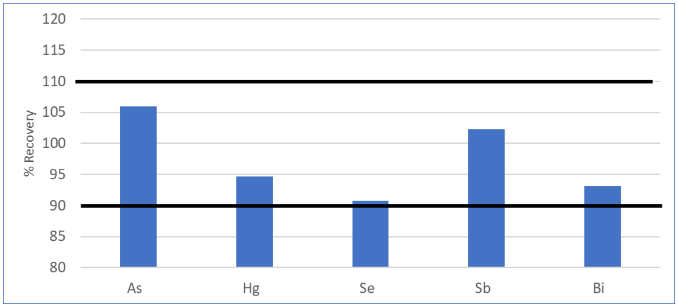

Figure 7. 10 µg/L spike recoveries for hydride-forming elements in mineral water.

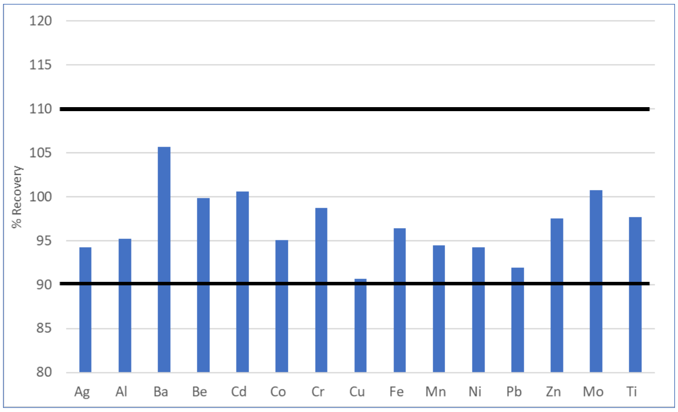

Figure 8. 50 µg/L spike recoveries for non-hydride-forming elements in mineral water.

With the accuracy of the methodology established, stability was assessed on a separate run by measuring 20 samples of a 50 µg/L standard. Figures 9 and 10 show concentration variations of <2% over the run, demonstrating the stability of the system, while simultaneously measuring both hydride- and non-hydride-forming elements.

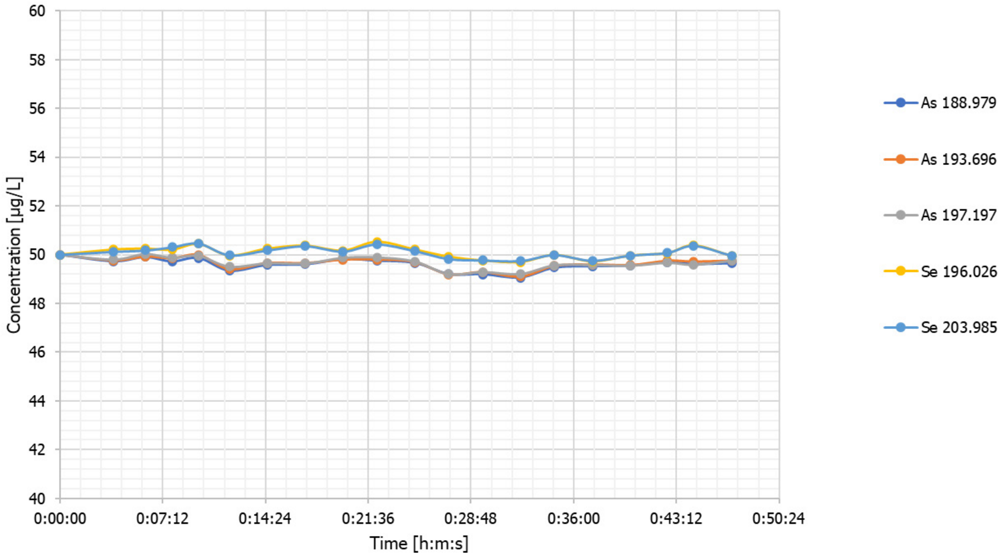

Figure 9. Concentrations of As and Se from 20 consecutive measurements of a 50 µg/L standard.

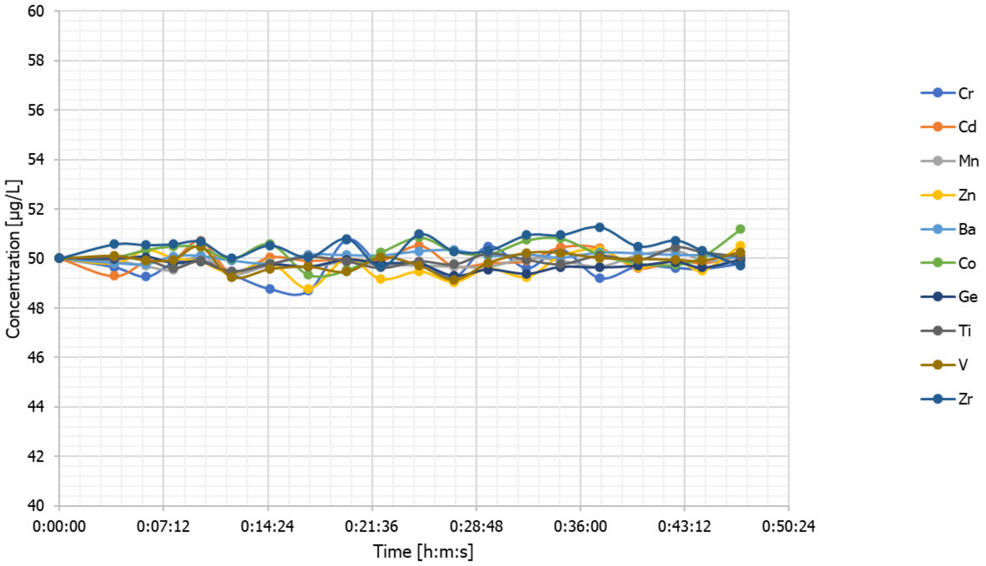

Figure 10. Concentrations of non-hydride-forming elements from 20 consecutive measurements of a 50 µg/L standard.

Finally, instrument detection limits (IDLs) were determined by measuring the calibration blank 10 times and multiplying the standard deviations of the resulting concentrations by three. The resulting IDLs are plotted in Figure 11, along with the WHO guidelines for drinking water.[4] The IDLs for hydride-forming elements (As, Se, Hg, Sb) show significant improvement compared to conventional sample introduction, falling 20-100x below the WHO guideline values. While ICP-OES with conventional sample introduction may not be able to satisfy WHO guideline values for drinking water testing, the incorporation of the HydraMist sample introduction system could reverse this restriction.

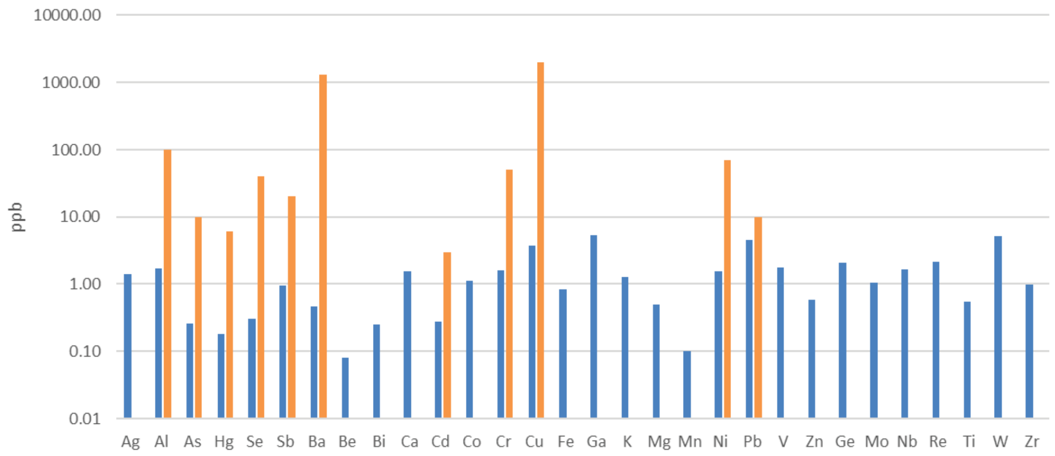

Figure 11. Measured detection limits (blue) compared to World Health Organization guideline values (orange).

Conclusion

This work has demonstrated the ability of the Avio 550 Max fully simultaneous ICP-OES to provide accurate, stable, low-level simultaneous analyses of hydride- and non-hydride-forming elements using the HydraMist sample introduction system. The HydraMist system incorporates simultaneous introduction of hydride- and non-hydride-forming elements, allowing lower concentrations of difficult-to-measure elements, such as arsenic, mercury, and selenium, to be measured without compromising the ability to measure non-hydride-forming elements. Combined with the exceptional optical throughput and excellent resolution of the Avio 550 Max ICP-OES, World Health Organization requirements for drinking water are met for challenging elements, like arsenic and mercury. This combination provides efficient and accurate analyses for routine laboratory testing.

Experimental

1. “Environmental Health Criteria 224: Arsenic and Arsenic Compounds”, World Health Organization, 2001.
2. “Continuous Flow Hydride Generation Using the Optima ICP”, Field Application Report, PerkinElmer, 2004.
3. “Determination of Arsenic and Selenium in Drinking Water by ICP-OES with Continuous Flow Hydride Generation using a Single Pre-Reduction Procedure”, Application Note, PerkinElmer, 2021.
4. “Guidelines for Drinking-Water Quality: Fourth Edition Incorporating the First Addendum”, World Health Organization, 2017.

Consumables Used

Component	Part Number
ICV Solution: Ag, Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Sb, Se, Tl, V, Zn	N9303953 (125 mL)
Analytes B Solution: Ag, As, Ba, Be, Cd, Co, Cr, Cu, Mn, Ni, Pb, Sb, Se, Tl, V, Zn	N9300227 (125 mL)
DigiTUBEs with Caps (750)	N9308037 (125 mL)
Multielement Calibration Standard 3, 10 µg/L	N9300235 (125 mL)
Multielement Calibration Standard 5, 10 µg/L	N9300233 (125mL)
Mercury Standard, 1000 µg/L	N9300174 (125 mL)
Antimony Standard, 1000 µg/L	N9300207 (125 mL)
SeaSpray Nebulizer	N0811305
Black/Black (0.76 mm id) Peristaltic Pump Tubing, Flared, PVC	N0777043
Black/White (3.18 mm id) Peristaltic Pump Tubing, PVC	N8122012

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