

Agilent 7900 ICP-MS simplifies drinking water analysis

Application note

Environmental

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Introduction

Ensuring the quality of drinking water is a primary goal for public health bodies around the world. Most developed countries have enacted regulations and monitoring programs to ensure that the supply of drinking water is free from potentially harmful chemicals and organisms. The regulations typically include maximum allowable concentrations for a range of inorganic components. Trace metals are routinely monitored in both the treated water supplied to households, and the source water used for drinking water abstraction (from rivers, reservoirs, lakes, underground aquifers; and, in some regions, seawater used for desalination). With the large number of analytes that must be measured, the low concentrations at which many are regulated, and the extremely large sample numbers involved in national or regional water quality monitoring programs, the fast multielement technique of Inductively Coupled Plasma Mass Spectrometry (ICP-MS) is widely used for this application.



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The analytes and concentration levels at which the different elements are regulated in drinking water vary from country to country. Most regulations require that potentially toxic trace elements such as As, Cd, Hg, and Pb are controlled at low $\mu\text{g/L}$ (ppb) levels, while less harmful elements such as B, Fe, Cu, and Zn are controlled at 100s or even 1,000s of $\mu\text{g/L}$. Some major elements including Na and K are not subject to maximum allowable concentration limits, but may be routinely monitored in some regions. The World Health Organization (WHO) has published Guidelines for Drinking Water Quality (1996, 1998), which contain recommendations that have been adopted by many developed countries. In the US, drinking water quality is regulated by the United States Environmental Protection Agency (USEPA), as mandated under the Safe Drinking Water Act (SDWA) of 1974. In the European Union, drinking water quality is regulated by Council Directive 98/83/EC from 3 November 1998, and natural (source) water quality is controlled under the Water Framework Directive (2000/60/EC and amendments in 2008/32/EC). Drinking water in Japan is regulated under the Japan Water Supply Act, dating from 1957, and in China, the maximum allowable limits are defined in the Standards for Drinking Water Quality GB5749-2006.

Table 1 shows a summary of the drinking water analyte lists and maximum allowable concentrations for different regulations that apply worldwide or in specific countries or regions.

Typically, laboratories performing routine monitoring of drinking water quality have installed a range of analytical techniques to cover the full suite of elements and concentrations measured. Often this includes a combination of ICP-OES for rapid multi-element analysis in the ppm to ppb range, Graphite Furnace Atomic Absorption Spectrometry (GFAAS) for the lower concentration trace elements (ppb to high ppt levels), and Hydride Generation, Cold Vapor (CV) AAS or Atomic Fluorescence (AFS) for specific elements such as As, Se and Hg in the ppb to ppt range. However, the increasing demand for water quality testing and the introduction of more rigorous standards has meant that commercial and government testing laboratories have focused on improving detection limits, sample turnaround times and overall throughput. This has led to wider acceptance of ICP-MS for routine drinking water monitoring, with

the full suite of elements being determined in one measurement, rather than utilizing several separate techniques. This consolidation of instrumentation reduces reliance on single-element techniques and so allows drinking water laboratories to streamline their inorganic analysis workflow, greatly improving both the efficiency and cost-effectiveness of the analysis.

ICP-MS has long been valued for its low detection limits and wide elemental coverage. More recent developments have greatly extended the upper limit of the dynamic range (allowing routine measurement of major elements such as Na, K and Ca) and improved sample throughput, as well as addressing the issues of polyatomic interferences derived from components of the sample matrix and solution. The combination of these developments means that modern ICP-MS systems can operate as routine analytical tools for accurate, high throughput determination of all regulated elements in large scale drinking water monitoring programs.

The Agilent 7900 ICP-MS is the performance benchmark for routine environmental sample analysis, with superior matrix tolerance and advanced collision/reaction cell (CRC) technology to remove the polyatomic interferences that can affect some of the regulated trace elements, such as Cr, As, Se, and Cd, in drinking water. Agilent ICP-MS MassHunter software functionality provides simple autotuning functions, and a Method Wizard automates the method setup process, ensuring that any user can create optimized and reliable methods. For high-throughput laboratories, the optional Integrated Sample Introduction System (ISIS 3) uses discrete sampling to reduce sample run times to approximately 1 minute or less.

The 7900 ICP-MS includes a 4th generation CRC, the Octopole Reaction System (ORS⁴), which provides optimized operating conditions for helium (He) collision mode. The small cell volume and octopole ion guide deliver superior interference removal using kinetic energy discrimination (KED), while maintaining high ion transmission when using an inert cell gas.

He mode is simple and universal, and is accepted as the preferred method for removing multiple, unknown polyatomic interferences in high or variable sample matrices. The ORS⁴ in He mode enables the 7900 ICP-MS to remove all common polyatomic interferences under a single set of conditions, without requiring sample-specific user setup, and without the need for any mathematical interference corrections. The result is easier set-up, lower detection limits, faster analysis, and improved accuracy. Even elements such as Fe and Se, which are affected by higher intensity plasma-based

interferences (ArO^+ on Fe^+ at m/z 56 and Ar_2^+ on Se^+ at m/z 78) can now be determined at low levels in He mode, with detection limits in the ng/L (ppt) range.

For high matrix sample analysis such as seawater and saline ground water, the 7900 ICP-MS can also be fitted with the Ultra High Matrix Introduction (UHMI) option to extend the matrix tolerance to 25 % total dissolved solids (TDS), a level more than 100 times higher than the accepted maximum salt limit for conventional ICP-MS of 0.2 % or 2,000 ppm [1].

Table 1. Worldwide drinking water regulated analytes and maximum allowable concentrations, with 3.14 sigma method detection limits (MDLs¹) for the Agilent 7900 ICP-MS. All data are shown in µg/L (ppb) for ease of comparison.

Analyte	Typical Agilent 7900 ICP-MS Isotope	WHO Guidelines for drinking water quality (µg/L)	USEPA SDWA Maximum Contaminant Level (MCL) (µg/L)	EC Drinking Water Directive 98/83/EC (µg/L)	Japan drinking water quality standards (µg/L)	China standards for drinking water GB 5749-2006 (µg/L)	Agilent 7900 ICP-MS MDL ¹ (µg/L)
Aluminum (Al)	27	-	50 - 200*	200*	200	200	0.007
Antimony (Sb)	121	20	6	5	15*	5*	0.004
Arsenic (As)	75	10**	10	10	10	10	0.008
Barium (Ba)	137	700	2,000	-	-	700*	0.007
Beryllium (Be)	9	-	4	-	-	2*	0.005
Boron (B)	10	500**	-	1,000	1,000	500*	0.005
Cadmium (Cd)	111	3	5	5	10	5	0.003
Chromium (Cr)	52	50**	100	50	50 as Cr (VI)	50 as Cr (VI)	0.004
Copper (Cu)	63	2,000	1,000*	2,000	1,000	1,000	0.005
Iron (Fe)	56	-	300*	200*	300	300	0.004
Lead (Pb)	208 ^{††}	10	15	10	10	10	0.002
Manganese (Mn)	55	400	50*	50*	50	100	0.009
Mercury (Hg)	202	6	2	1	0.5	1	0.001
Molybdenum (Mo)	95	70	-	-	70**	70*	0.006
Nickel (Ni)	60	70	-	20	10*	20*	0.010
Selenium (Se)	78	10	50	10	10	10	0.015
Silver (Ag)	107	-	100*	-	-	50*	0.002
Sodium (Na)	23	-	-	200 mg/L*	200 mg/L	200 mg/L*	0.047
Thallium (Tl)	205	-	2	-	-	0.1*	0.002
Uranium (U)	238	15**	30	-	2*	-	0.002
Zinc (Zn)	66	-	5,000*	-	1,000	1,000	0.011

* Secondary standard, indicative parameter or limited testing requirement

**Provisional guideline value

¹MDL calculated according to USEPA Method 200.8

^{††}Pb data is based on the sum of the 208, 207 and 206 isotopes

Experimental

The Agilent 7900 ICP-MS was used for the analysis of a range of analytes including all those elements listed in worldwide drinking water quality regulations. The General Purpose plasma mode was used, derived from the preset method for drinking water analysis which is included in the ICP-MS MassHunter software. Conditioning of the cones was performed by running a series of solutions comparable to the sample type of interest, after which the instrument was optimized using the autotune function of the ICP-MS MassHunter software, giving the operating conditions shown in Table 2. No gas mode and He modes are autotuned independently, but very few of the instrument parameters change their values, apart from the cell gas flow and cell voltages. The cell gas flow and energy discrimination values are defined in the Preset Method, so no further tuning was required. Table 2 illustrates the consistency of the tuning conditions for different cell modes, which contributes to the ease of use of

the 7900 ICP-MS. This is an important consideration in routine laboratories where each analytical technique may be used by several operators with different levels of experience.

The calibration standards were prepared in an acid matrix of 1 % HNO₃ and 0.5 % HCl to ensure the stability of the elements Ag, Sb, and Hg. Historically, HCl has been avoided in the preparation of samples for ICP-MS, due to the formation of Cl based interferences on As, Se, Cr and V. However, the ORS⁴ in He mode is able to remove these interferences to background levels, allowing all interfered elements to be measured reliably in a single cell gas mode, and eliminating the need for hydrogen or other reactive gases. Typically, uninterfered low-mass elements are measured in no gas mode, but the superior sensitivity of the 7900 ICP-MS allows even these analytes to be measured in He mode if a single mode analysis is required to maximize sample throughput.

Table 2. Agilent 7900 ICP-MS autotuned operating conditions for drinking water analysis.

	No gas mode	He mode	High energy He mode
Plasma mode	General Purpose		
Extract 2 (V)	-150		
Omega bias (V)	-80		
Omega lens (V)	8.8		
Deflect lens (V)	13.4	0	-74.6
Energy discrimination (V)	5		7
Cell gas flow rate (mL/min)	0.0	4.3	10

Note: Other operating parameters were predefined in the Preset Method or set by autotune.

Results and discussion

Representative calibration curves for several trace elements are shown in Figure 1 and Figure 2. Figure 1 shows the calibrations for V and As, both of which are subject to polyatomic overlap in chloride matrices (ClO^+ on V^+ at m/z 51, and ArCl^+ on As^+ at m/z 75). The low ng/L (ppt) instrument detection limits (IDLs) for V and As displayed in the calibrations in Figure 1 demonstrate the efficient removal of the Cl-based interferences in He mode on the 7900 ICP-MS. These interferences are difficult to remove by other cell modes, typically requiring highly reactive cell gases such as NH_3 or O_2 , which are not suitable for multi-element analysis.

Figure 2 shows the calibrations for the trace elements Cd and Hg, which are controlled at the lowest maximum allowable concentrations in most drinking water regulations. These elements are often measured in no gas mode to maximize sensitivity, but both can suffer from polyatomic overlaps in some natural matrices (from MoO^+ on Cd^+ at m/z 111 and WO^+ on Hg^+ at m/z 202), so it is beneficial to measure them in He mode if sensitivity can be maintained. The 7900 ICP-MS uses a redesigned interface vacuum configuration, new ion lens, and high gain orthogonal detector system (ODS) to deliver increased sensitivity and lower backgrounds, allowing low detection limits to be achieved in combination with He mode. The single-ppt or sub-ppt IDLs for both elements (shown in Figure 2) demonstrate the excellent sensitivity and low background achieved for these trace analytes in He mode on the 7900 ICP-MS.

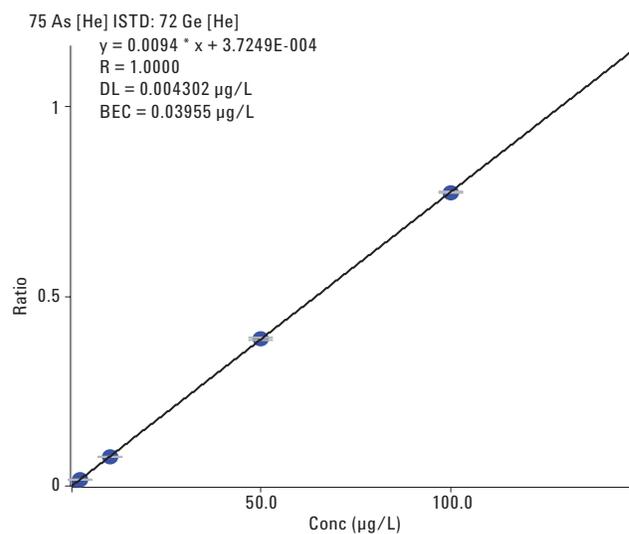
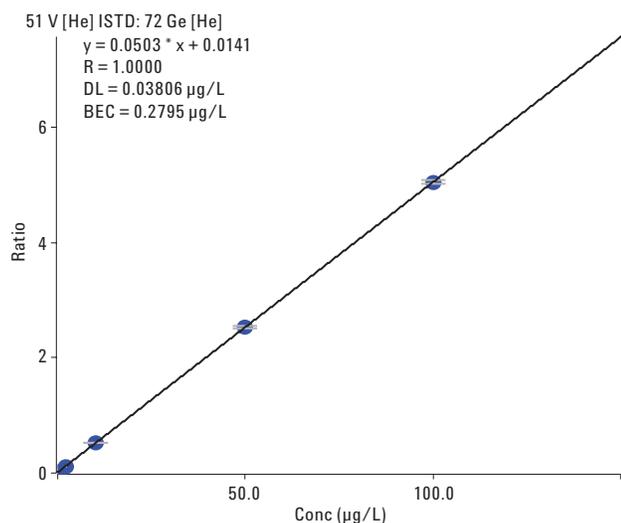


Figure 1. Calibration curves for V and As in He mode, showing reduction of Cl interferences for drinking water method. All standards contain 1 % HNO_3 and 0.5 % HCl.

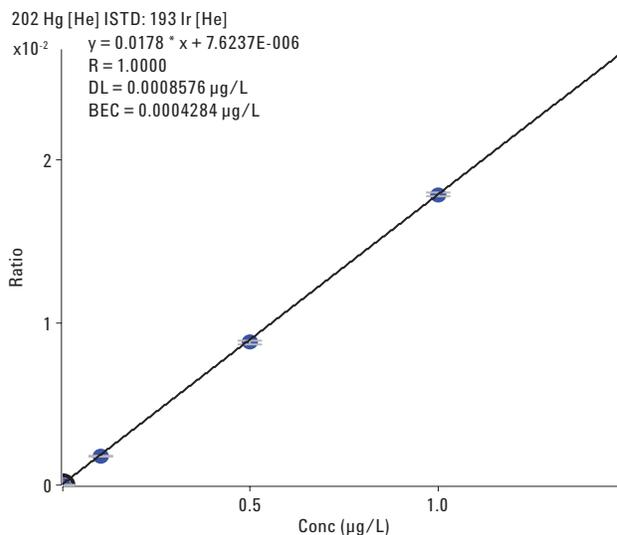
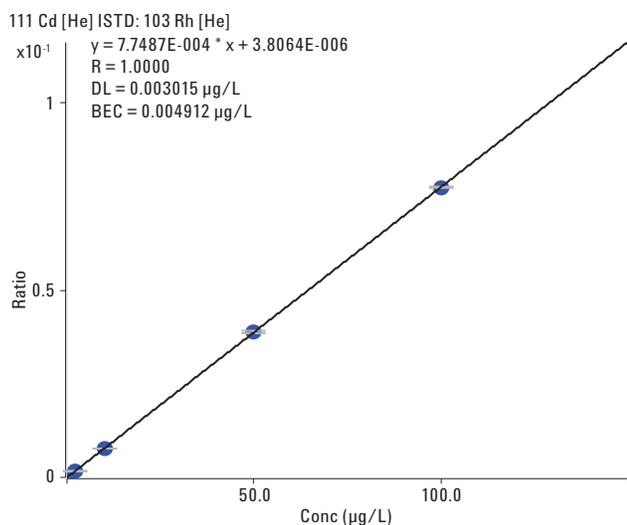


Figure 2. Calibration curves for low level elements Cd and Hg with drinking water method, illustrating single- or sub-ppt instrumental DLs in He mode and excellent precision and linearity at low concentrations.

Typical 7900 ICP-MS method detection limits (MDLs) in $\mu\text{g/L}$ (ppb) for all regulated elements in drinking water are shown in Table 1. These MDLs were not generated under highly optimized conditions, but using the default robust plasma conditions obtained by the Autotune routine ($\text{CeO}^+/\text{Ce}^+ \sim 1\%$), as used for routine sample analysis. MDLs were calculated from the 3.14 sigma method (3.14 times the standard deviation of seven separate measurements of a water blank fortified at a level of 3–5 times the estimated MDL), in accordance with USEPA Method 200.8 requirements.

Drinking water may be considered a low-matrix sample type, but some bottled mineral waters contain several 100s or even 1,000s of mg/L (ppm) TDS. In this work, we used two mineral waters with more typical TDS levels of approximately 350 ppm (MW1) and 100 ppm (MW2). These samples were measured repeatedly both with and without a spike, interspersed with Certified Reference Material NIST 1643e Trace Elements in Water, and QC samples (CCV and CCB). The sequence consisting of mineral waters, NIST 1643e reference water and QC samples was analyzed continuously for more than 12 hours.

Continuing Calibration Verification (CCV) recoveries for all the regulated analytes measured periodically during the entire sequence are plotted in Figure 3. All CCV recoveries were within the $\pm 10\%$ limits defined in EPA method 200.8.

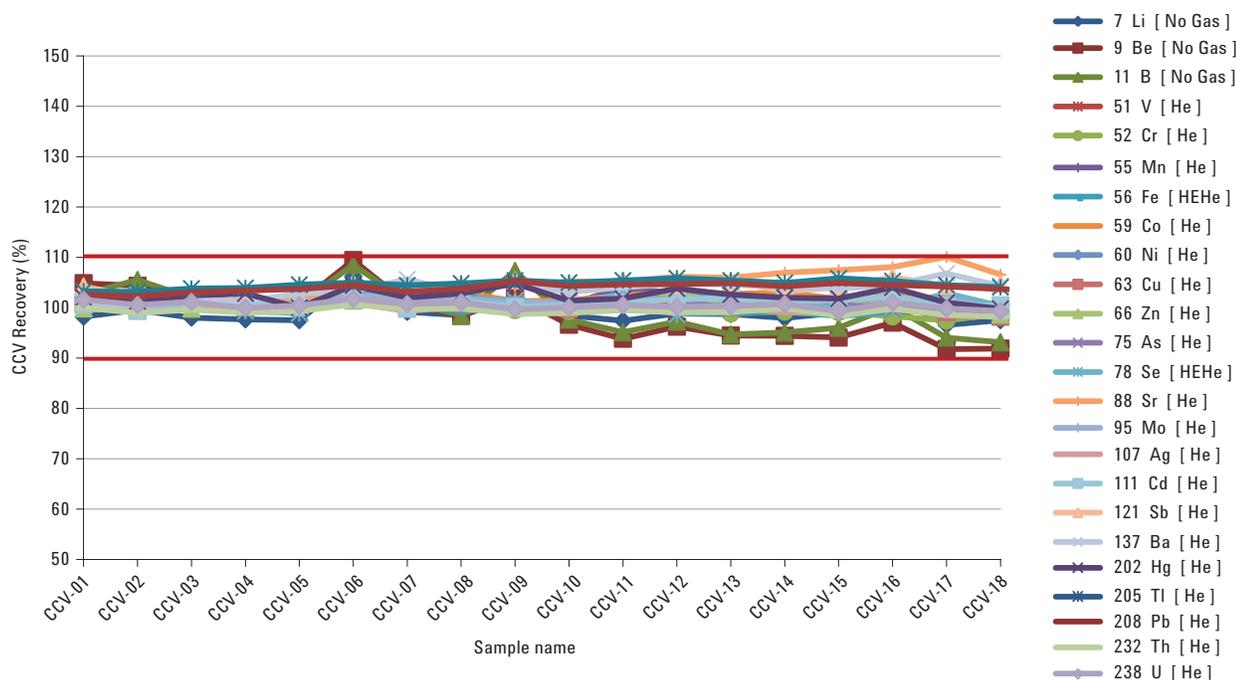


Figure 3. CCV recoveries (20 $\mu\text{g/L}$ except Hg: 0.5 $\mu\text{g/L}$) for the 12 hour sequence. The red lines show the $\pm 10\%$ control limits.

Table 3 lists the analyte and method information, recoveries and relative standard deviations (% RSD) for the 40 separate measurements of NIST 1643e, which were included in the sequence. The data in Table 3 includes several additional elements that have certified values in NIST 1643e and are often monitored in drinking water, even though they are not included in drinking water regulations. The recoveries for all elements were within $\pm 10\%$ of the certified values, and most elements were within $\pm 5\%$. For most elements, the stability was better than 2% RSD throughout the 12 hour sequence, demonstrating the suitability of the 7900 ICP-MS for routine measurement of large batches of drinking water samples.

Table 3. Analytes, masses, cell modes, internal standards (ISTD), quantitative results, and recoveries for NIST 1643e, measured 40 times throughout the 12 hour sequence.

Element	Mass	Cell mode	ISTD	Measured conc. (µg/L, n=40)	RSD (%)	Certified conc. (µg/L)	± (µg/L)	Recovery (%)
Li	7	No gas	Li6	17.01	3.2	17.4	1.7	97.8
Be	9	No gas	Li6	12.98	6.0	13.98	0.17	92.9
B	11	No gas	Li6	142.6	5.4	157.9	3.9	90.3
Na	23	No gas	Sc	19767	3.6	20740	260	95.3
Mg	24	No gas	Sc	7935	3.5	8037	98	98.7
Al	27	No gas	Sc	142.3	3.5	141.8	8.6	100.3
K	39	He	Sc	2004	0.5	2034	29	98.6
Ca	44	He	Sc	31859	0.5	32300	1100	98.6
V	51	He	Ge	37.51	1.0	37.86	0.59	99.1
Cr	52	He	Ge	20.09	1.5	20.4	0.24	98.5
Mn	55	He	Ge	37.86	0.8	38.97	0.45	97.2
Fe	56	HE He	Ge	95.58	0.9	98.1	1.4	97.4
Co	59	He	Rh	26.27	0.6	27.06	0.32	97.1
Ni	60	He	Rh	59.62	0.8	62.41	0.69	95.5
Cu	63	He	Rh	21.26	0.8	22.76	0.31	93.4
Zn	66	He	Rh	73.18	0.7	78.5	2.2	93.2
As	75	He	Ge	58.06	0.9	60.45	0.72	96.1
Se	78	HE He	Ge	11.22	2.0	11.97	0.14	93.7
Sr	88	He	Rh	326.1	1.7	323.1	3.6	100.9
Mo	95	He	Rh	122.3	0.6	121.4	1.3	100.7
Ag	107	He	Rh	0.99	1.2	1.062	0.075	92.9
Cd	111	He	Rh	6.22	0.9	6.568	0.073	94.8
Sb	121	He	Tb	57.10	0.7	58.3	0.61	97.9
Ba	137	He	Tb	514.4	1.0	544.2	5.8	94.5
Tl	205	He	Ir	7.48	1.2	7.445	0.096	100.5
Pb	208	He	Ir	19.09	0.9	19.63	0.21	97.2

Conclusions

The Agilent 7900 ICP-MS is capable of measuring all required elements in drinking waters, easily meeting the detection limit and recovery requirements defined in worldwide drinking water quality regulations. The significantly improved sensitivity and lower background of the 7900 ICP-MS means that He mode can be applied to a wider range of elements including ppt level analytes such as Cd and Hg, which can therefore benefit from simple and reliable interference removal in routine analysis. Using He mode eliminates the need for reactive cell gases and interference equations, both of which make method development more complex, and can lead to inaccurate data when unexpected matrix elements are present. The 7900 ICP-MS with He mode provides absolute confidence in data quality with significantly improved ease-of-use and productivity.

The 7900 ICP-MS has the largest operating dynamic range of any quadrupole ICP-MS at more than 10 orders of magnitude, while the optional UHMI system enables the same instrument to be used for very high matrix samples containing up to 25 % total dissolved solids. Furthermore, the cell gas modes and instrument method settings used for drinking water analysis can also be applied to more complex environmental samples such as soils and sludges, eliminating the need for the sample specific optimizations which are required on instruments that must use reactive cell gases for adequate control of interferences.

Reference

1. Wim Proper, Ed McCurdy and Junichi Takahashi, Performance of the Agilent 7900 ICP-MS with UHMI for high salt matrix analysis, Agilent publication **2014**, 5991-4257EN.

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