

ICP - Mass Spectrometry

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The Analysis of Drinking Water Using Universal Collision-Reaction Gas Technology on the NexION 1000 ICP-MS

Introduction

Drinking water is sourced predominantly from rivers, lakes, or groundwater. Concentrations of elements in these waters can vary greatly according to the

underlying geology and type of anthropogenic activities affecting catchment areas.¹ Due to increasing urbanization, industrialization, mining, and farming practices within these areas, the need to monitor potable drinking water for hazardous components has increased in importance. Many countries have implemented stringent criteria (Table 1) which need to be met before waters can be distributed for human use and consumption.²⁻⁹ Such criteria require that analytical instrumentation be capable of reaching low detection limits so that trace concentrations of elements can be accurately and precisely quantified.

Table 1. Water regulations of different countries.

Element	Australia ² (µg/L)	Canada ³ (µg/L)	China ⁴ (µg/L)	EU ⁵ (µg/L)	India ⁶ (µg/L)	South Africa ⁷ (µg/L)	USA ⁸ (µg/L)	WHO ⁹ (µg/L)
Ag	100	---	50	---	100	---	100	---
Al	---	100*	200	200	30	150	200	100
As	7	10	10	10	10	10	10	10
B	4000	5000	500	1000	500	---	---	2400
Ba	700	1000	700	---	700	---	2000	1300
Be	---	---	2	---	---	---	4	---
Ca	---	---	---	---	75 000	32 000*	---	---
Cd	2	5	5	5	3	5	5	3
Cr	50	50	50	50	50	50	100	50
Cu	2000	1000*	1000	2000	50	1000	1300	2000
Fe	300*	300*	300	200	300	100	300	---
Hg	1	1	1	1	1	1	2	6
Mg	---	---	---	---	30 000	---	---	---
Mn	500 (100*)	50*	100	50	100	50	50	---
Mo	50	---	70	---	70	---	---	---
Na	180 000*	200 000*	200 000	200 000	---	100 000	---	---
Ni	20	---	20	20	20	---	---	70
Pb	10	10	10	10	10	10	15	10
Sb	3	6	5	5	---	---	6	20
Se	10	50	10	10	10	20	50	40
Tl	---	---	0.1	---	---	---	2	---
U	20	20	---	---	---	70	30	30
V	---	---	---	---	---	100	---	---
Zn	3000*	5000*	1000	---	5000	3000	5000	---

*Not regulated, but advised value for aesthetic reasons.

Over the past three decades, inductively coupled plasma mass spectrometry (ICP-MS) has gained acceptance as the technique of choice for trace metal analysis in drinking water. This is due to its wide linear dynamic range, ability to provide isotopic information, speed of analysis, and low detection limits. As with all analytical technologies, however, ICP-MS is not free from interferences. Plasma and matrix-based polyatomic interferences, such as ArAr^+ , ArO^+ , ArH^+ , and ArCl^+ , are inherent to ICP-MS and need to be accounted for through the use of correction equations, collision or reaction gases. Reaction gases can be extremely useful in the analysis of trace concentrations of analytes where the ratio of polyatomic interference to analyte signal exceeds four orders of magnitude. In contrast, the use of inert gases for overcoming interferences through kinetic energy discrimination (KED) can be a powerful tool when interferences are less significant.

Traditionally, ICP-MS instrumentation requires two or more gases to perform both collisions and reactions within a single sample analysis. In this work, collisions and reactions were performed using a single gas mixture on the NexION® 1000 ICP-MS. This unique approach empowers analytical laboratories to achieve high productivity, while at the same time exceeding the low detection limits required by the aforementioned regulations.²⁻⁹

Experimental

Sample Preparation

Calibration standards were prepared in 2% HNO_3 (v/v) at the levels shown in Table 2. This concentration range aims to encompass the spread of target values set out by different drinking water quality standards (Table 1). A six-point calibration was used as this has been found to provide the least statistical

variance.¹⁰ However, it should be noted that this range could be reduced to meet the specific guideline that the end user is following. Internal standards were added to all standards and samples using online addition. Since activated carbon is an important additive in many water treatment processes, 1% isopropanol (IPA) was added into the internal standard to reduce the effect of carbon enhancement on Se and As, as recommended by the FDA.¹¹ Several internal standards were used so as to effectively cover the mass range and ionization potentials of the elements under investigation (Table 2). Concentrations of the internal standards differed from one another so as to account for variance in ionization potentials and isotopic abundances. To facilitate the washout of mercury (Hg), 200 µg/L of gold (Au) was added to all samples and standards, and all samples were acidified to 2% HNO_3 to preserve the elements in solution. The elemental isotopes and modes of analysis used in this method are listed in Table 3.

An initial calibration verification sample (ICV) and a standard reference material (SRM) were run prior to analysis to validate the calibration. The accuracy of this technique was demonstrated through the analysis of three certified reference materials (CRMs); namely 1640a Natural Water, 1643f Water (NIST™, Rockville, Maryland, USA), and Trace Metals in Water (High Purity Standards™, Charleston, South Carolina, USA), which were each run in triplicate. Additional measures of quality control include a continuing calibration verification standard (CCV) run every 10 samples, and a triplicate analysis of a spiked sample. Spike recoveries were not performed on Ca owing to its high levels in drinking water. All consumables utilized are summarized in the Consumables Used table at the end of this document.

Table 2. List of the relative concentrations of analytes in the calibration standards.

Analytes	Standard 1 (µg/L)	Standard 2 (µg/L)	Standard 3 (µg/L)	Standard 4 (µg/L)	Standard 5 (µg/L)	Standard 6 (µg/L)
Ag, As, Be, Cd, Co*, Se, Sb, Pb*, V, Tl	0.1	1	5	10	25	50
Cu, Zn	10	50	100	500	1000	5000
Al, B, Ba, Fe	10	50	100	300	600	1000
Mn, Mo, Ni, Cr, U	1	5	10	50	100	200
Hg, Th*	0.025	0.05	0.5	1	2.5	5
Na*, Mg*, K*, Ca*	50	100	1000	5000	10 000	20 000
Internal Standards	⁴⁵ Sc, ⁷¹ Ga, ⁷³ Ge, ¹¹⁵ In, ¹⁹³ Ir					

* Three Pb isotopes are monitored and summed as the natural abundance varies in nature

* Not required by many standards but included for informative value

Table 3. Recommended isotopes and mode of analysis for different elements.

Element	Recommended Isotope	Recommended Mode
Ag	107	Reaction
Al	27	Collision
As	75	Collision
B	11	Collision
Ba	137	Reaction
Be	9	Collision
Ca	44	Collision
Cd	111	Reaction
Co	59	Collision
Cr	52	Collision
Cu	65	Collision
Fe	56	Collision
Hg	202	Reaction
K	39	Collision
Mg	24	Collision
Mn	55	Collision
Mo	98	Collision
Na	23	Collision
Ni	60	Collision
Pb	206 + 207 + 208	Collision
Sb	121	Reaction
Se	78	Reaction
Tl	205	Collision
Th	232	Collision
U	238	Collision
V	51	Collision
Zn	66	Collision

Instrumentation

All analyses were performed with the NexION 1000 ICP-MS (PerkinElmer Inc., Shelton, Connecticut, USA) using the conditions shown in Table 4. The analysis was performed in Collision (KED) and Reaction (Dynamic Reaction Cell – DRC) modes using Universal Collision-Reaction Gas Technology. Selective bandpass mass filtering in Reaction mode also assists in reducing interferences, where ions outside of the *m/z* stability boundaries are rapidly ejected from the cell.¹² For this reason, the RPq was set to 0.45 and 0.65 for Collision and Reaction modes

respectively. A gas mixture of 7% H₂ in He (v/v) is effective in both Collision and Reaction modes, allowing for efficient and targeted interference removal. Moreover, in order to maintain productivity, all elements were analyzed with the gas, thereby eliminating the need to vent the cell during analysis. In Collision mode, polyatomic interferences are removed using the same gas mixture through collisions.

Table 4. NexION 1000 ICP-MS instrument parameters.

Component/Parameter	Type/Value
Nebulizer	MEINHARD® plus Glass Type C
Spray Chamber	Glass Cyclonic
RF Power	1600 W
Injector	2.0 mm id quartz
Sweeps	20
Dwell Time	50 – 100 ms
Replicates	3
Mixing Tee	On-line addition of internal standard

Results and Discussion

Before the onset of any analysis, it is essential to validate the calibration. For this reason, an initial calibration verification standard (ICV: 50 ppb for all elements except Hg-5 ppb and Th-0.5 ppb) and a standard reference material (SRM: dilution of ICS18 to 20 ppb Se as a mid-range calibration check) were measured directly after the calibration standards and were in good agreement with the expected concentrations (Figure 1).

In order to assess the accuracy of the method, three certified reference materials were analyzed in triplicate; the averaged results are shown in Figure 2. All CRM concentrations were well within 10% of the certified values, demonstrating the accuracy of this methodology. Further quality control was performed using a triplicate analysis of a spiked tap water sample (Figure 3, spiked concentrations were 10 ppb for all elements except for Th and Hg which were 0.5 ppb), with the results showing that there is good recovery of the spikes, indicating that the method is appropriate over a large linear dynamic range.

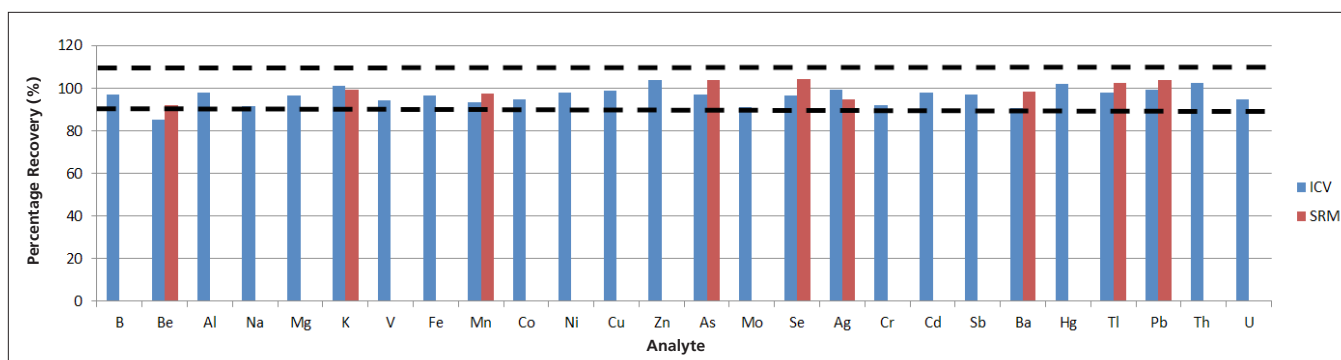


Figure 1. Percentage recovery (%) of the ICV and SRM standards prior to the onset of the analytical method.

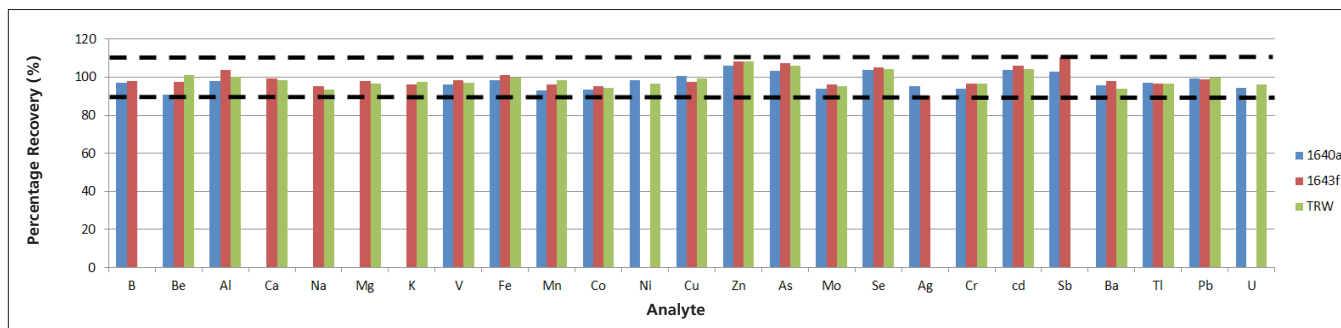


Figure 2. Recoveries of NIST 1640a, 1643f and Trace Metals in Water (TRW) certified reference material.

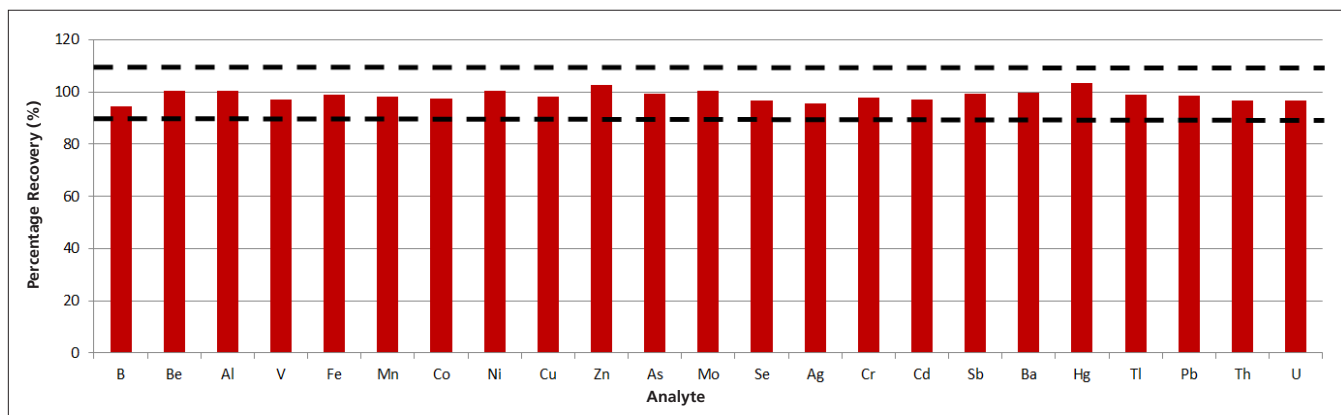


Figure 3. Averaged percentage recovery of spike recoveries for elements spiked into tap water.

After the accuracy of the method was established, stability was evaluated using a single calibration at the start of the analysis and by measuring a CCV every 10 samples over 13 hours (Figure 4). The CCV was found to have good stability over this period without any need to recalibrate. Figure 5 illustrates the method detection limits (determined as 3 times the standard deviation of 10 replicates of a blank sample), and compares these values to the lowest permissible limits for potable drinking

water (TWQG) as outlined in Table 1. Notable detection limits within these results can be found for V, Co, Mo, Se, Ag, Hg, Ba, and Pb, which were lower than 10 ppt, and Cd, Sb, Tl, Th, and U, which were lower than 1 ppt. The MDLs shown here demonstrate that the concentrations of metals and metalloids in natural drinking waters can be easily assessed using Universal Collision-Reaction Gas Technology on the NexION 1000 ICP-MS.

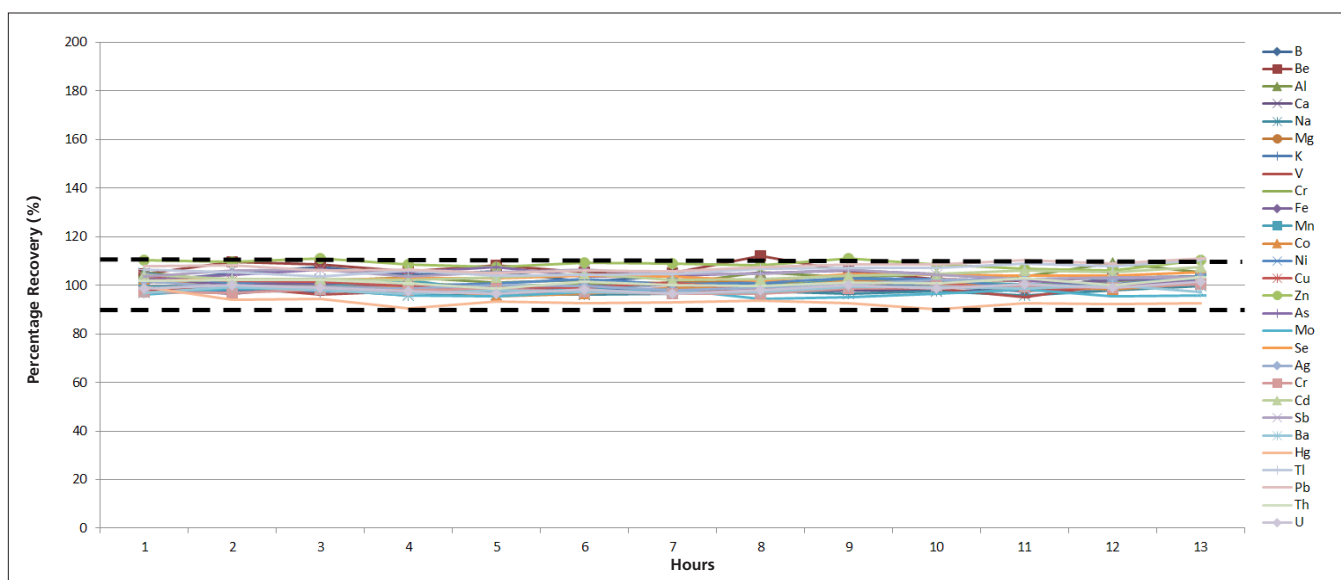


Figure 4. Continuing calibration verification standards evaluated every 10 samples over a period of 13 hours without recalibration.

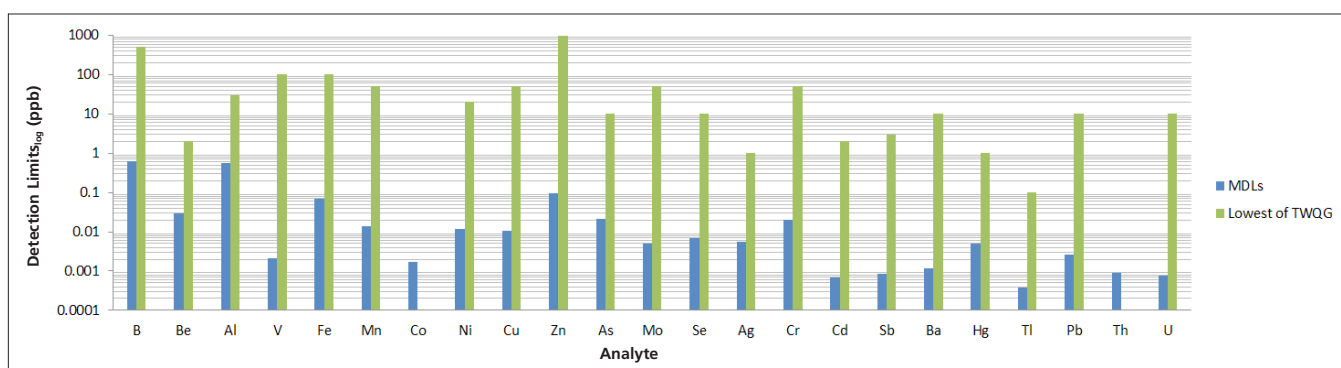


Figure 5. MDLs compared to the lowest concentrations for the global TWQG for metals using universal gas in Collision and Reaction modes using NexION 1000 ICP-MS.

Conclusion

The NexION 1000 ICP-MS has been shown to exceed expectations for the low detection limit requirements found in potable drinking water standards from around the world through its use of a single, universal Collision-Reaction gas. Its efficacy was especially notable in the analysis of trace concentrations of ^{78}Se with MDLs lower than 10 ppt, which is often considered challenging due to its low ionization efficiency and low natural abundance. The accuracy and robustness of this method has been validated through the analysis of certified reference materials and spiked tap water samples, respectively, while the stability was demonstrated over 13 hours using a single calibration. The NexION 1000 ICP-MS, with its unique Universal Collision-Reaction Gas Technology, allows for the best of both worlds by promoting productivity while still achieving low ppt detection limits as is required by many high-throughput laboratories.

Consumables Used

Component	Description	Part Number
Sample Uptake and Internal Standard Tubing	Green/Orange (0.38 mm id), Flared, PVC, 12 Per Package	N8152403 (Standard Peristaltic Pump)
Spray Chamber Drain Tubing	Gray/Gray Santoprene (1.30 mm id), 12 Per Package	N8152415 (Standard Peristaltic Pump)
Mercury Standard	10 mg/L Hg – 125 mL	N9300253
Environmental Standard Mix 2	1000 mg/L Na, Mg, K, Ca – 125 mL	N9307805
Internal Standard Mix	100 mg/L Sc, 50 mg/L Ge, 1 mg/L In, Rh, Tb – 125 mL	N9308592
Interference Check Solution 18	20000 mg/L K, 1000 mg/L As, Pb, Tl, 500 mg/L Se, 300 mg/L Ag, Ba, Cd, Co, Cr, Cu, Ni, V, Zn	N9300205
Gallium Standard	1000 mg/L – 125 mL	N9303772
Gold Standard	1000 mg/L – 125 mL	N9303759
Autosampler Tubes	Metal-free, Racked, White Caps, 500 Per Package	N0776118 (15 mL) N0776116 (50 mL)
Internal Standard Addition T	0.5 mm ID, (10/32") Fittings	N8152386
Internal Standard Probe	Carbon Fiber Support	N8152452

Please note that the calibration standards were made up from individual standard solutions so as to address the range of concentrations set out by the various target water quality guidelines. For more targeted applications, the multi-element solution (20 mg/L Ag, Al, As, Ba, Be, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sb, Se, Th, Ti, U, V, Zn: N9303816) and single-element solutions Fe (1000 mg/L: N9304237) and B (1000 mg/L: N9304210) could be used.

References

1. Adomako D et al. 2008. Environ. Monit. Assess. 141:165–175.
2. National Health and Medical Research Council. 2004. Australian Drinking Water Guidelines 6th Ed., Australia.
3. Health Canada. 2017. Guidelines for Canadian Drinking Water Quality Summary Table. Water and Air Quality Bureau, Healthy Environments and Consumer Safety Branch, Health Canada, Ottawa, Ontario.
4. Ministry of Health of China. 2007. Standards for Drinking Water, National Standard of the People's Republic of China, China.
5. EU's drinking water standards. 1998. Quality of water intended for human consumption. <http://www.lenntech.com/applications/drinking/standards/eu-s-drinking-water-standards.htm#ixzz4tEtNMQzP>. Accessed on 20 September 2017.
6. Bureau of Indian Standards. 2012. Indian Standard—Drinking Water-Specification 2nd Edition, New Delhi, India.
7. Department of Water Affairs and Forestry. 1996. South African Water Quality Guidelines 2nd Edition, Volume 1.
8. United States Environmental Protection Agency. 2009. National Primary Drinking Water Regulations. Report no. EPA 816-F-09-004. <https://www.epa.gov/ground-water-and-drinking-water/national-primary-drinking-water-regulations#Inorganic> Accessed on 20 September 2017.
9. World Health Organization. 2017. Guidelines for Drinking-Water Quality 4th Edition.
10. Ellison, S., Barwick, V., Duguid Farrant, T. (2009). Practical statistics for the analytical scientist, a bench guide. 2nd Edition. RSC Publishing. 25-172.
11. FDA. 2015. Elemental Analysis Manual for Food and Related Products Chapter 4.7 pp 1-24.
12. Thomas R. Practical Guide to ICP-MS: A tutorial for beginners. 3rd Ed. pp 81.