

The accurate quantification of low-ppt hexavalent chromium in water.

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1 Introduction

Chromium has a number of industrial applications which can result in its intentional or unintentional release into surface- and ground- waters. The basic pH and high oxygen content which many of these waters possess may promote the formation of Cr VI. This form of chromium is carcinogenic and can result in acute and chronically toxic health effects in humans. For this reason, many national and regional water standards aim to lower the maximum permissible levels of total chromium and hexavalent chromium in potable waters.¹

In California, for example the OEHHA, established a Public Health Goal (PHG) of 0.02 ppb for Cr VI and a maximum contaminant level of 10 ppb in 2014. Although the MCL became “no longer in effect” in 2017, the PHG still stands.² Around the world, other global regulatory bodies are expected to implement similar limits.

This work reports a method for the measurement of low-ppt concentrations of Cr VI in twelve water samples using the NexSAR HPLC-ICP-MS Speciation Solution.

Key Features

- Completely metal-free fluid path- NexSAR Inert HPLC
- Robust and versatile NexION ICP-MS with ability to use pure reaction gases such as NH₃ for comprehensive interference removal
- Controlled reactions in the Universal cell



NexSAR™ Speciation Solution comprised of the NexSAR™ Inert HPLC and the NexION® ICP-MS



Inert, metal-free binary pump

- Completely metal-free and inert fluid path does not contribute towards Cr baseline=better LODs and LOQ.
- Post-seal wash reduces seal wear and tear, downtime and service needs.

2 Methodology

Since a neutral pH has been shown to promote the stability of chromium species when complexed with EDTA, the mobile phase was prepared at pH 7.³ Drinking water samples (12 samples) were collected from various sources and filtered using 0.45 µm hydrophilic PTFE syringe filters. After filtration, samples were diluted (1:1) in mobile phase (Table 1) and allowed to complex for three hours at room temperature (22 °C) before analysis.

All analyses were performed using a NexSAR Inert HPLC System (PerkinElmer, Inc., Shelton, Connecticut, USA) comprised of the NexSAR 200 Inert HPLC Pump, Cooled Inert Autosampler, Solvent Tray and Degasser, Column Oven and Inert Switching Valve coupled to a NexION® ICP-MS. Analysis and post-analysis processing were performed using Clarity™ Chromatography Software. Details pertaining to the HPLC and ICP-MS conditions are shown in Table 1.

Calibration standards (0.005-10 ppb, n=8) were prepared in the mobile phase where the concentrations were chosen to cover the range between the PHG and the maximum contaminant level (MCL) for Cr VI as set by the State of California in 2014. In the absence of a CRM, validation of the method was achieved through the implementation of a low-level and high-level sample spike (0.05 ppb and 1 ppb Cr VI respectively), addressing the range of Cr VI typically found in potable waters.

Table 1 HPLC and ICP-MS parameters

Parameter	Value
Chromatography	Ion exchange chromatography
Mobile Phase	Ion-exchange reagent, pH 7.0
Flow rate	1.5 mL/min
Separation Scheme	Isocratic
Injection volume	200 µL, full loop
Nebulizer	MEINHARD® plus Glass Type C
Spray Chamber	Glass cyclonic
RF power	1600 W
Injector	2.0 mm ID Quartz
Mode	Reaction mode, NH ₃ , 0.5 mL/min
RPq	0.8

3 Results and Discussion

As can be seen in Figure 1, a 0.005 ppb (5 ppt) Cr VI standard was easily distinguished from the baseline, providing a S/N of 4, an LOD of 3.8 ppt and an LOQ of 12.5 ppt. This outstanding LOD is important, especially when compared to HPLC systems with metal fluid paths which can only deliver LODs >50 ppt.

The ultra-low LOD and LOQ of this method can be attributed to the metal-free fluid path of the NexSAR Speciation System, allowing concentrations much lower than the California PHG² to be quantified with confidence.

Although not of interest in this study, Cr III is also shown in Figure 1 for reference to demonstrate that the baseline separation of Cr III and Cr VI has been achieved.

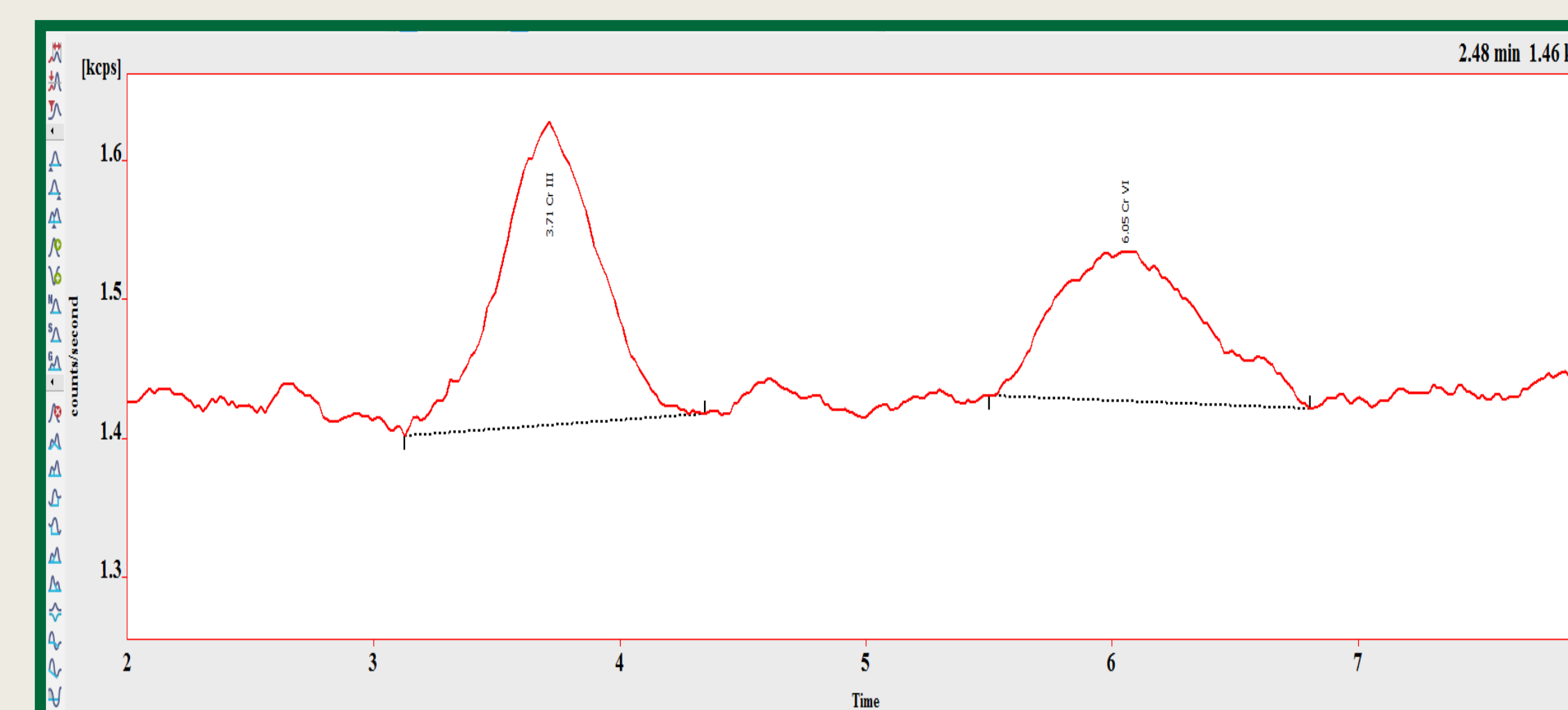


Figure 1 Chromatogram of 0.005 ppb (5 ppt) standard of Cr III and Cr VI in mobile phase without blank subtraction.

The calibration standards had a correlation coefficient of 0.99999 for Cr VI, showing good linearity across the range for the PHG and MCLs.² As can be seen in Figure 2, the calibration standards all have the same retention time, regardless of the concentration. This speaks further to the importance of consistent pump flows and the importance of a column oven in such applications.

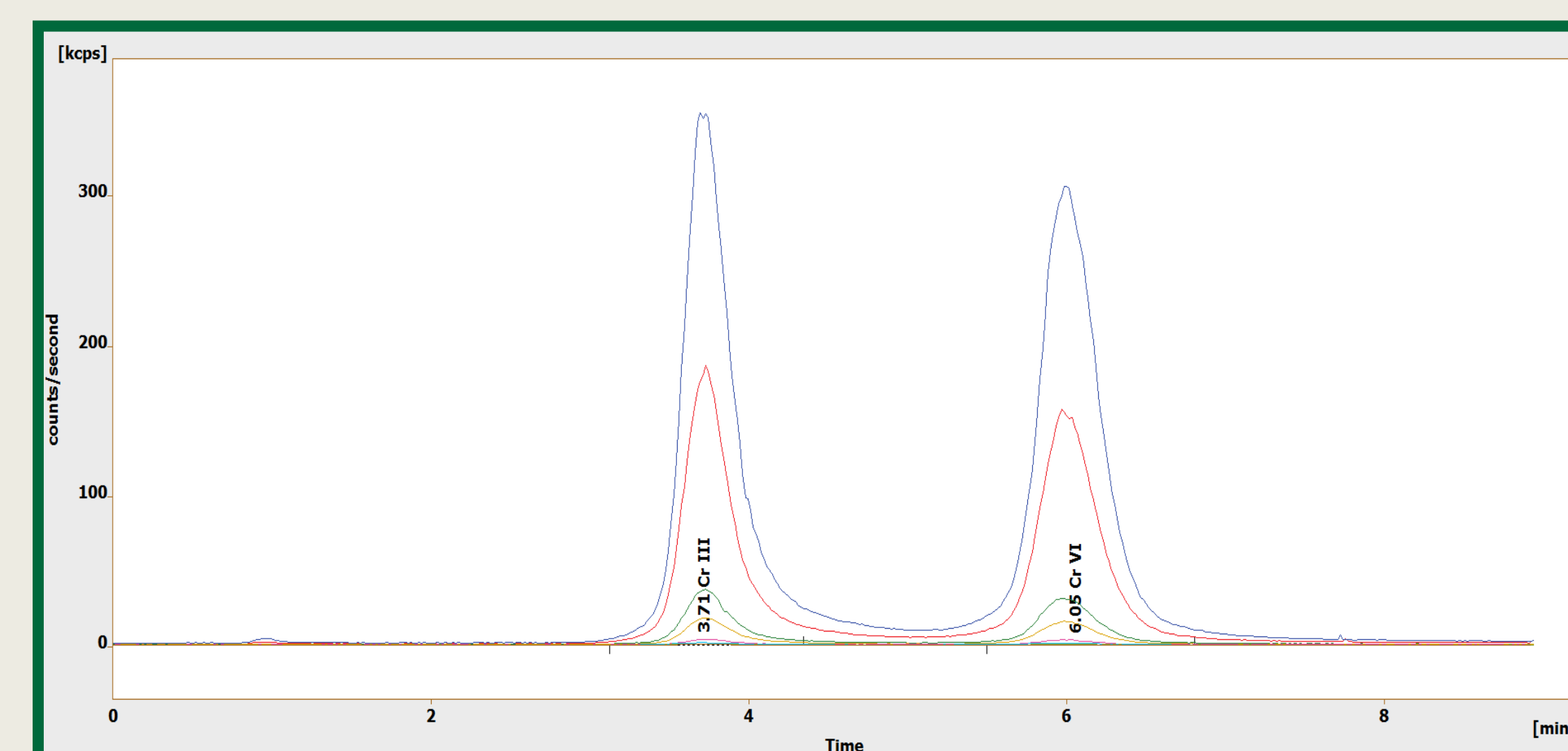


Figure 2 Overlay of calibration standards (0.005 – 10 ppb, blank subtracted) in the mobile phase at pH 7.0.

Spiked water samples were prepared and analyzed in order to assess the impact of the matrix upon analytical accuracy. The spike recoveries of Cr VI in the different sample matrices were excellent, ranging between 96% and 99% for the groundwater sample, 92% and 106% for the tap water sample, and 98% and 97% for the spring water sample for the low- and high-concentration spikes respectively. These results prove the accuracy of the method across a wider linear dynamic range which allows the PHG and MCL to be considered. Moreover, the applicability of this method for the quantitation of Cr VI in a wide range of potable drinking waters is also demonstrated.

As can be seen in Figure 3, all samples had concentrations of Cr VI <0.12 ppb (120 ppt). The findings are outlined as follows:

- The highest concentrations were found in three of the four spring water samples which were evaluated;
- The groundwater samples were all below the detection limits of the method (BD);

- Tap water samples had the second highest concentrations of Cr VI, where the filtered tap water sample had lower concentrations of Cr VI than the other tap water samples.

All samples except for the groundwater samples exceeded the PHG for California but were below the MCL according to the regulation set in 2014 (10 ppb for Cr VI) and below the current 50 ppb total Cr concentration limit for this state.

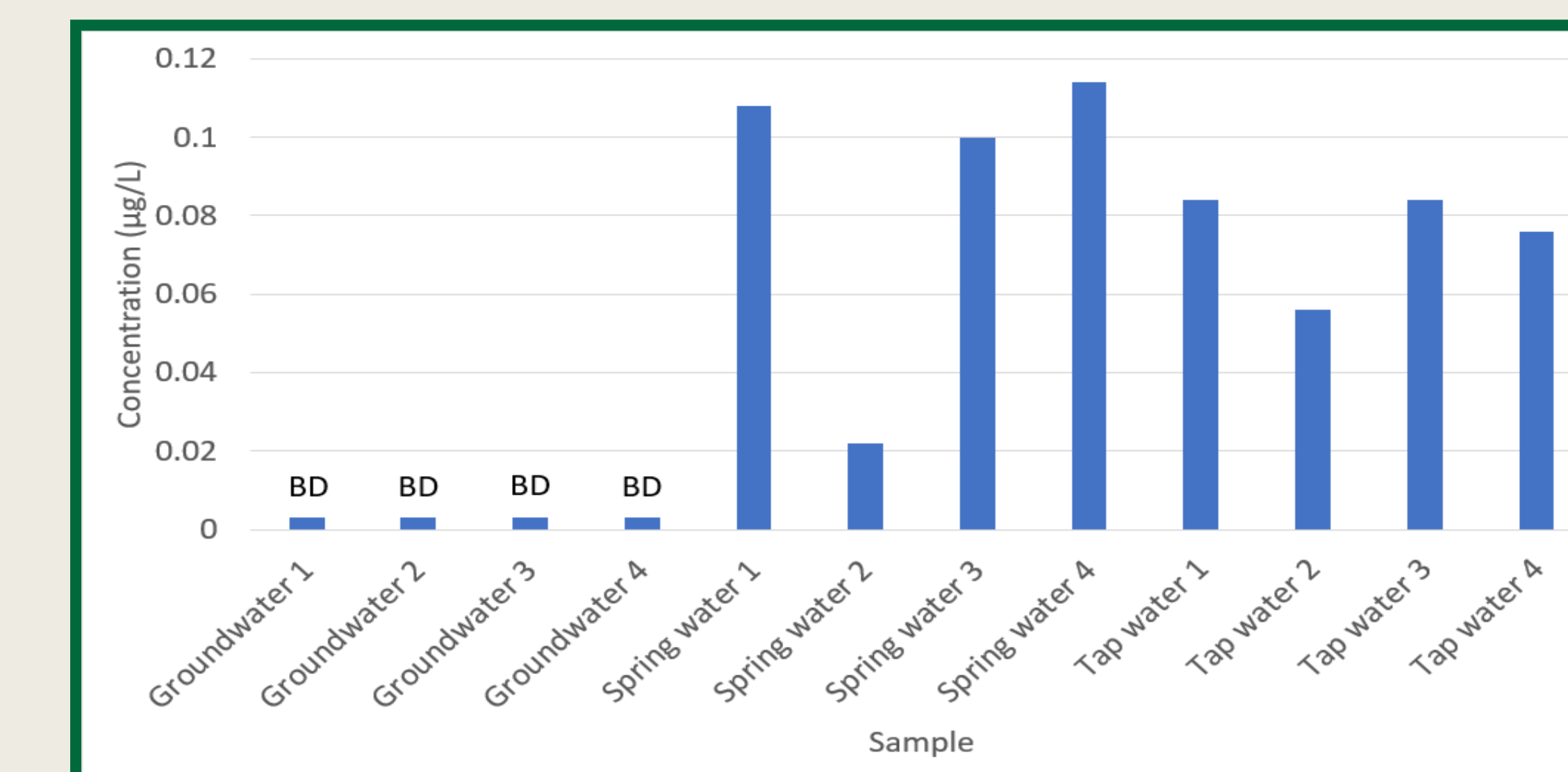


Figure 4 Hexavalent chromium concentrations potable water where concentrations below the LOD are shown by 'BD'.

4 Conclusion

In this study we presented a method for the low-ppt detection and accurate quantification of hexavalent chromium in potable waters in less than eight minutes. Hexavalent chromium could be observed in all samples with the exception of groundwater, which had come from a pristine location.

An LOD of 3.8 ppt was obtained, providing an LOQ of 12.5 ppt. This ensured that concentrations below the PHG could be quantified with confidence.

These low LODs were made possible by two factors:

1. The inert and metal-free fluid path of the NexSAR Inert HPLC which ensured that there was no undue elevation of the chromatographic baseline for Cr.
2. NexION ICP-MS' Universal Cell Technology™ with pure ammonia gas. UCT is the only cell to create controlled reactions, rapidly ejecting interfering ions and reaction byproducts from the cell before they have a chance to react and form new interferences.

References

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2. https://www.waterboards.ca.gov/drinking_water/certlic/drinkingwater/Chromium6.html
3. doi.org/10.1093/chromsci/32.11.524