

Reducing the Risk of Inaccurate Results When Quantifying Trace Elements in Seawater

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Introduction and Background

Monitoring elements at environmentally relevant concentrations in seawater is critical for developing accurate environmental assessments and evaluating the effectiveness of various pollution controls. Minute concentrations can have a significant impact on the health of the surrounding aquatic organisms, which has necessitated the advent of sophisticated analytical techniques. Inductively coupled plasma mass spectrometry (ICP-MS) is a powerful and efficient tool for the determination of low-level metals; however, the high salt

content of seawater can lead to inaccurate results. Numerous methods have been developed to mitigate the issues encountered when analyzing trace metals in seawater samples, but the limitations of the methods require multiple approaches to meet the data objectives of most projects. Selecting the most appropriate method depends on the chemical properties of the analyte of interest and the individual sample characteristics. Several method options, including the most recent developments are described here.



ICP-MS with Dilution

ICP-MS with Interface for High Matrix Samples

HGAAS/HGAFS

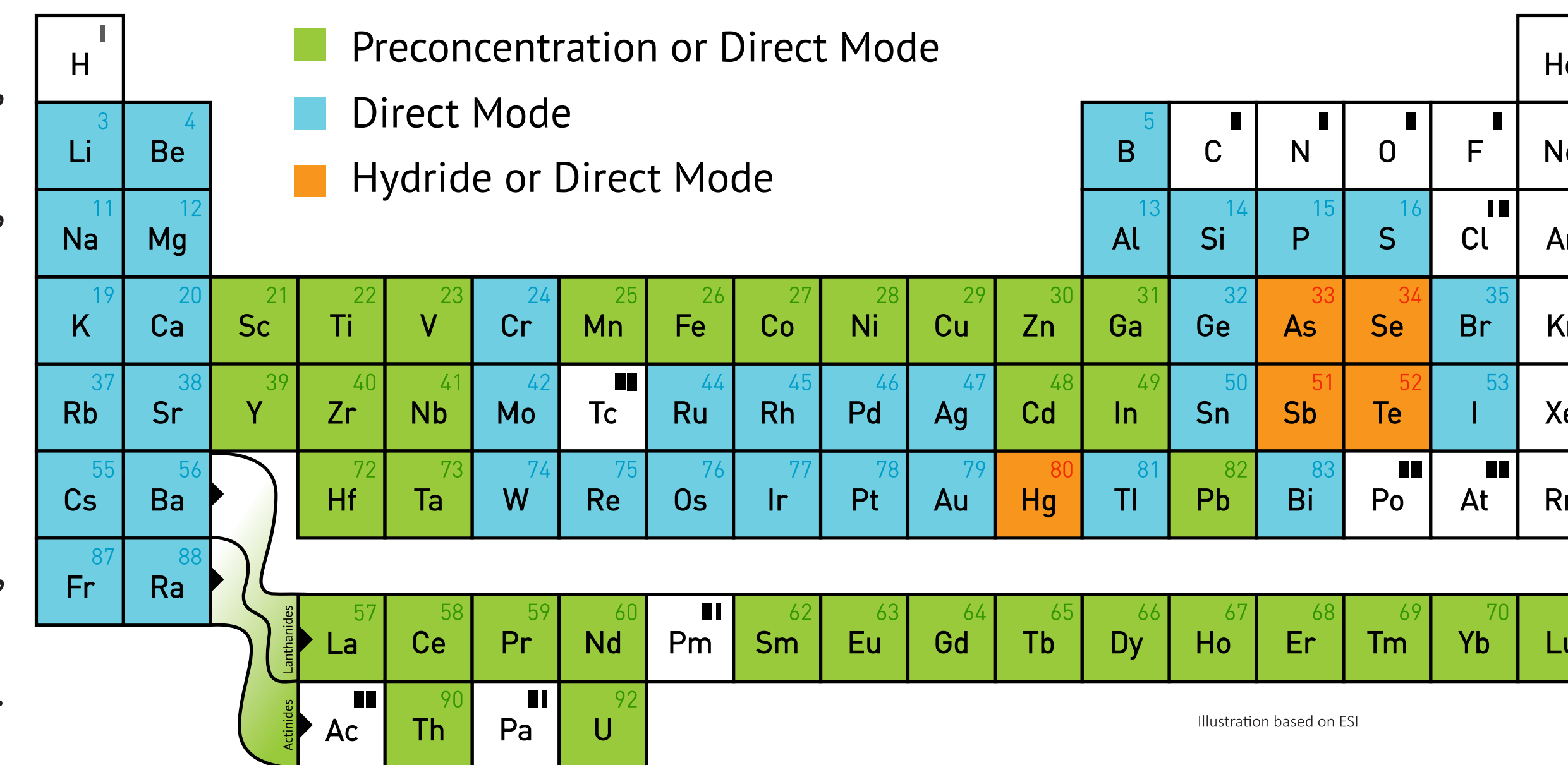
Reductive Precipitation and other Preconcentration Techniques/ICP-MS

Column Chelation/ICP-MS

Column Separation/ICP-MS

An Overview of Common Methods of Analysis

ICP-MS methods using direct analysis are widely available and automated, providing a cost-effective option for trace metals analysis; however, seawater contains elevated concentrations of total dissolved solids, requiring significant dilution to ensure optimal instrument performance. Using high dilution factors can attenuate matrix issues, but there are still interfering ions present that affect the data quality. Also, the resulting elevated detection limits often cannot support the data objectives for water quality monitoring programs such as the Clean Water Act¹. Several instrument manufacturers have developed a front-end interface for ICP-MS instruments that utilizes an in-line gaseous dilution for aqueous samples, but these methods may not be sufficient to support low-level detection limit requirements.



Several methods have been developed that utilize reaction-based chemistry (e.g., hydride generation, chelation, coprecipitation) to remove the target elements from the matrix prior to analysis. Trace-level detection limits have been achieved with these methods, though the chemical properties of each element often necessitate multiple sample preparation approaches for the same sample. The convoluted chemistry required to obtain meaningful data is associated with a high probability of bias. Additionally, these methods are typically very labor intensive, which is reflected in the available turn-around times and costs.

Column chelation is a preconcentration option that can be automated and does not require complex sample preparation, which makes it an appealing solution for seawater analysis. Column chelation methods are also less prone to the issues encountered with reaction-chemistry methods, such as poor accuracy and reproducibility. However, this technique is prone to matrix effects if dissolved organic matter is present in the samples at levels significantly higher than what is found in typical seawater samples. An experienced analyst will be able to recognize this limitation and resolve the issue with minimal investigation. The list of elements appropriate for analysis by column chelation ICP-MS includes many of the cationic transition metals and rare earth elements, but most anionic metals (such as arsenic, chromium, and selenium) cannot be supported by this method.

Waters with High Organic Content (0.7 mg/L humic acid)							
Results in µg/L (ppb)							
Analyte	Detection Limit (1x)	Dilution Factor			Effect of Dilution on Concentration	RPD between 5x-25x	RPD between 25x-50x
		50x	25x	5x			
Cd	0.005	1.92	1.91	2.61	Decrease	31%	1%
Co	0.010	3.07	2.97	3.82	Decrease	25%	3%
Cu	0.010	57.8	56.8	81.5	Decrease	36%	2%
Mn	0.010	67.0	66.8	82.4	Decrease	21%	0%
Ni	0.005	14.1	14.1	20.1	Decrease	35%	0%
Pb	0.005	5.51	5.55	4.48	Increase	21%	1%
V	0.005	7.34	7.30	7.25	None	1%	1%
Zn	0.060	85.1	84.5	113	Decrease	29%	1%

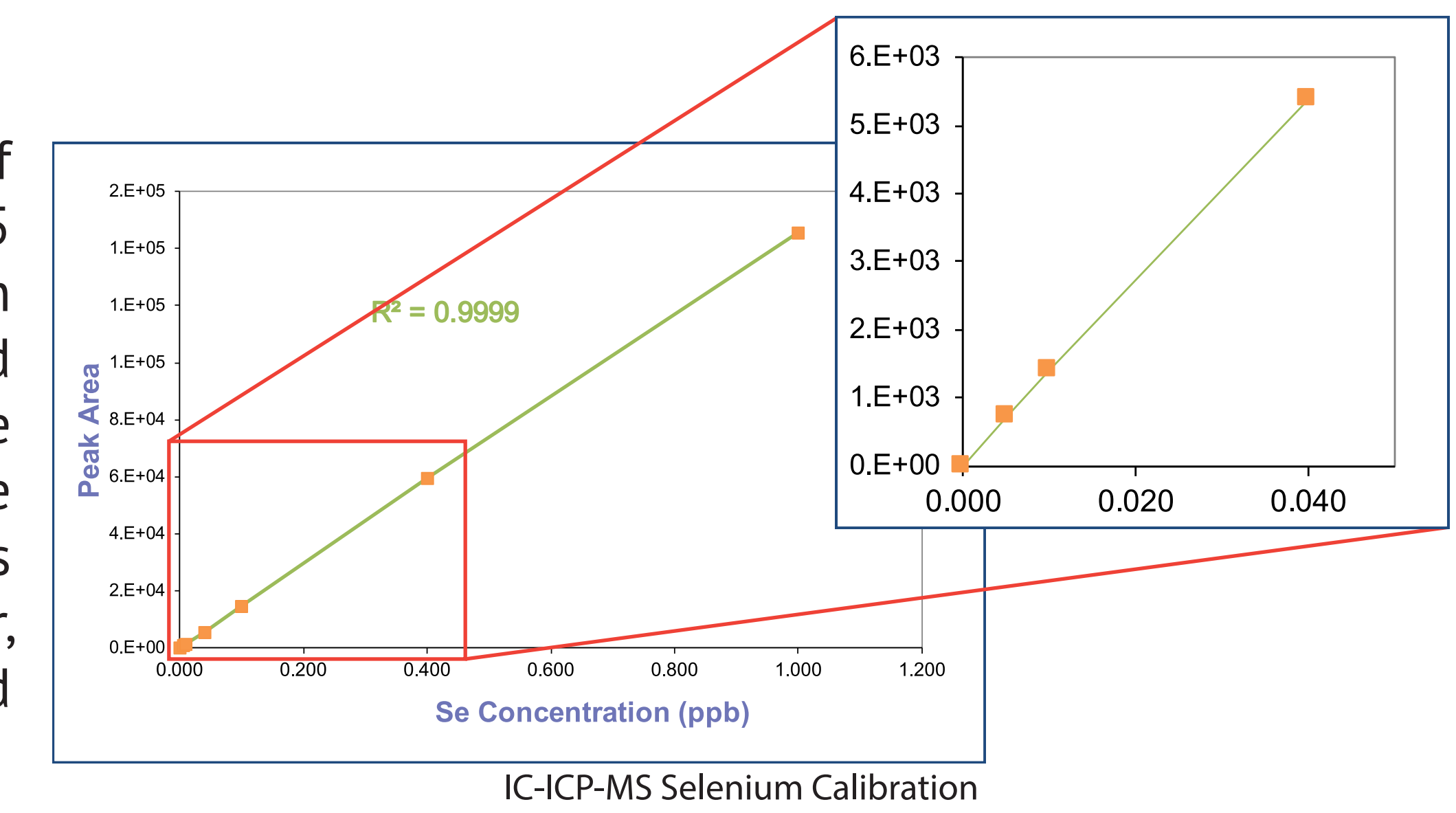
Typical Method Detection Limits (µg/L)

Analyte	50x Manual Dilution ICP-MS	Agilent ICP-QQQ-MS Using HMI	Reductive Precipitation ICP-MS	Column Chelation ICP-MS	Column Separation ICP-MS
Ag	0.30	0.060	0.017	-	-
As	0.35	0.060	0.034	-	0.005
Be	0.50	0.10	0.006	-	-
Cd	0.20	0.040	0.004	0.004	-
Co	0.35	0.040	0.043	0.003	-
Cr	1.3	0.25	0.040	-	0.005
Cu	1.1	0.22	0.030	0.015	-
Fe	14	2.8	-	0.040	-
Mn	2.1	0.22	-	0.005	-
Ni	1.2	0.23	0.040	0.013	-
Pb	0.25	0.050	0.005	0.003	-
Se	0.55	0.11	0.083	-	0.005
Tl	0.80	0.13	0.004	-	-
V	0.60	0.12	0.030	0.020	-
Zn	6.0	1.2	0.35	0.015	-

Seawater contains metals at extremely low concentrations combined with a high salt content. Choosing an appropriate method for trace metals analysis in saline matrices requires consideration of the target group of elements and data quality objectives.

The Solution for Ultra-Trace Arsenic, Chromium, and Selenium

Brooks Applied Labs recently unveiled a new method for the quantitation of arsenic, chromium, and selenium in saline waters at concentrations as low as 5 ng/L (parts-per-trillion). This is an automated, in-line method that utilizes ion chromatography to separate out the target metals from alkali earth metals and their conjunctive anions in natural aquatic systems. The method has undergone validation confirming all molecular forms of arsenic, chromium, and selenium are captured and measured. This new capacity to support ultra-trace detection limits for elements predominately existing as anions in saline waters (such as seawater, brackish waters, and brines) will support discharge requirements and investigations for estuaries, bays, near shore and open ocean, and saline lakes.



Method Efficacy for Column Separation (results & spike concentrations in µg/L)

Sample ID	Concentration	Duplicate	RPD (%)	Se(IV) Spike	Recovery (%)	Se(VI) Spike	Recovery (%)
1702025-01	0.518	0.523	0.9	2	84	2	88
1702025-02	0.368	0.374	1.6	-	-	10	95
1702025-04	0.358	0.384	7.0	-	-	10	95

Conclusion

Methods for obtaining meaningful and accurate data for low-level trace elements in seawater and other saline matrices have been challenged by labor-intensive sample preparation methods, uncooperative sample chemistries, and limitations on the list of applicable analytes. However, advances in technology have now led to a combination of methods that can avoid those issues and quantify low-level anions and cations in seawater matrices with improved accuracy, precision, and throughput. Although there is no single analytical or preparatory approach that will cover the periodic table, column chelation (transition metal cations and REEs) or ion chromatographic separation (arsenic, chromium, and selenium) are excellent, cost-effective options for reliable ultra-trace metals data from seawater and other saline matrices.

References

¹ Environmental Protection Agency (1997), Office of Water, Office of Science and Technology, Engineering and Analysis Division (4303), Method 1640 Determination of Trace Elements in Water by Preconcentration and Inductively Coupled Plasma-Mass Spectrometry.