Direct, Rapid Analysis of Undiluted Seawater using ICP-MS with an Aerosol Dilution System

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Introduction

Trace and ultra-trace analysis of seawater is challenging as the matrix components are relatively high and required analytes low in concentration. The typical seawater matrix ranges between 2-3.5% Total Dissolved Solids (TDS) and all analytes of interest are in the order of µg l^{-1} to ng l^{-1}. This presents a challenge for ICP-MS as the TDS level is around 10-20x higher than compatible as it can induce spectroscopic and non-spectroscopic interferences.

Typical sample preparation approaches have included liquid-liquid extraction after APDC/DDDC complexation, solid phase extraction/matrix elimination and liquid dilution. Each methodology offers advantages and disadvantages – matrix elimination & preconcentration is time consuming and requires degree of expertise but can be useful to decrease detection limits. Dilution is very simple but requires greater instrumental sensitivity. Both of these approaches can still be compromised by contamination from the reagents or diluent used.

To simplify the analysis an ICP-MS system fitted with a High Matrix Introduction (HMI) system was used; this system uses "aerosol dilution" to reduce the matrix loading on the ICP-MS allowing the direct introduction of undiluted seawater. As throughput was also important, a loop injection system was used (Integrated Sample Introduction System - ISIS3) to inject a discrete sample plug into a flowing carrier stream.

Experimental

An Agilent 7800 ICP-MS with ISIS3 (Fig.1) was used for the analysis. This system incorporates HMI aerosol dilution and the ISIS3 was configured with a 300µl loop; sampling was performed by the Agilent SPS4 autosampler.

Fig 1. Agilent 7800 ICP-MS with ISIS3

The instrument was configured with the standard sample introduction system consisting of Micromist nebuliser, quartz spraychamber and 2.5mm id injector torch. The cones were standard Ni (with Ni-plated Cu core sampler base) and internal standards (Rh, Ir) were added online at a 1:1 ratio using 0.76mm id tubing for the ISTD and carrier.

Instrumental conditions are listed in Table 1 although the HMI conditions are set by autotune (this calibrates the plasma settings to the nebuliser, cones and torch). The analytes of interest (Ni, Cu, Zn, Cd & Pb) were all acquired under Helium Collision Mode to mitigate spectral interferences and simplify the methodology.

Table 1. Typical instrument parameters for HMI-8

Parameter	Value
Forward Power	1600W
Carrier Gas	~0.68 l min^{-1} (set by autotune)
Dilution Gas	~0.27 l min^{-1} (set by autotune)
Helium Cell Gas	5.0 ml min^{-1}
Energy Discrimination	5v
ISIS3 Loop size	300µl

Carrier solution was 2% HNO3/0.5%HCl (UpA Merck) and all solutions were prepared at the Environment Agency Starcross laboratory. Calibration and matrix blank solutions were prepared using trace element "free" seawater prepared by complexation on iminodiacetate functionalized polymer microbeads (CETAC).

Results and Discussion

Several seawater matrixes were tested including Quasimeme (estuarine and open ocean); an EA in-house AQC; natural open ocean & estuarine samples and spikes of each natural sample. These were measured (n=4) in random order against a single calibration regardless of salinity.

A blank seawater was also measured randomly throughout the run (n=40) in order to determine MDL's.
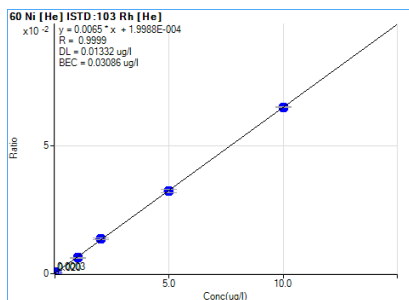

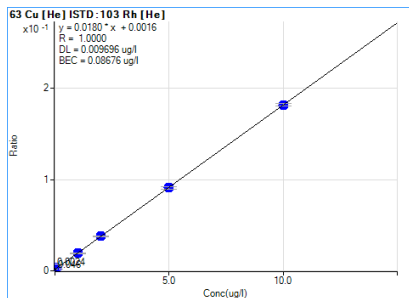**Fig 2. Nickel (⁶⁰Ni) calibration DL 0.013, MDL 0.036 µg l^{-1}**

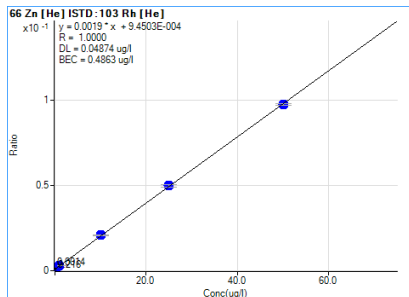**Fig 3. Copper (⁶³Cu) calibration DL 0.0096, MDL 0.055 µg l^{-1}**

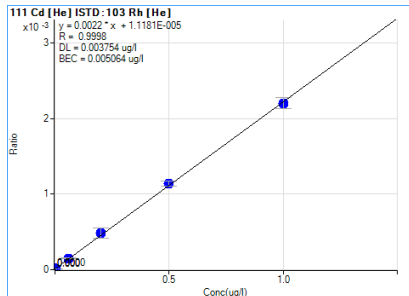**Fig 4. Zinc (⁶⁶Zn) calibration DL 0.049, MDL 0.22 µg l^{-1}**

Fig 5. Cadmium (¹¹¹Cd) calibration DL 0.0038, MDL 0.011 µg l^{-1}

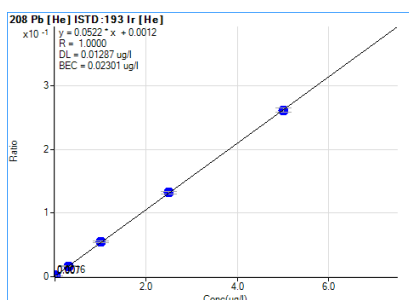**Fig 6. Lead (²⁰⁸Pb) calibration DL 0.013, MDL 0.022 µg l^{-1}**

Figures 2-6 show the calibrations for each analyte in the seawater matrix with its corresponding internal DL (3σ from the cal blank) and external MDL (from the 40 repeat measurements throughout the run).

Table 2. Mean data of the randomised 4 repeat measurements (µg l^{-1}) for each sample including the data acquired at the EA Starcross laboratory where appropriate

	60 Ni	63 Cu	66 Zn	111 Cd	208 Pb
AQC					
Mean	2.44	2.00	4.19	0.202	0.410
Expected	2.50	2.00	4.00	0.200	0.400
Quasimeme Estuarine					
Mean	1.22	5.19	15.54	0.271	1.62
Starcross	1.17	4.95	15.00	0.270	1.41
Assigned	1.14	4.83	14.80	0.260	1.51
Quasimeme Saline					
Mean	1.19	10.78	22.09	0.101	0.418
Starcross	1.14	10.40	21.10	0.095	0.380
Assigned	1.04	10.00	20.70	0.098	0.410
Saline					
Mean	1.13	0.91	2.52	0.021	0.081
Saline Spike					
Mean	8.21	8.09	39.01	0.732	3.64
Recovery	101.13	102.55	104.27	101.65	101.79
Estuarine					
Mean	0.73	1.87	1.17	0.02	0.02
Estuarine Spike					
Mean	7.78	9.02	36.64	0.716	3.52
Recovery	100.66	102.13	101.33	99.56	99.82
Standard 4					
Mean	10.20	10.21	51.29	1.03	5.08
Expected	10.00	10.00	50.00	1.00	5.00

Sample-to-sample run times were approximately 60s including a multi-chemistry rinse (base, mixed acid and sample acid equivalent) and loop/valve rinse.

Internal Standard drift (Fig. 7) throughout the run was minimal indicating the excellent matrix tolerance afforded by HMI and loop injection – the effect of the lighter matrix samples (estuarine) on internal standards can be seen but was not particularly pronounced and recovered immediately afterwards.
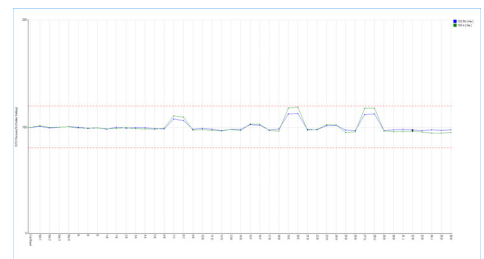

Fig 7. Internal Standard recovery over the undiluted seawater run – virtually no drift was experienced

Conclusions

The Agilent 7800 ICP-MS with High Matrix Introduction system offers the ability to directly analyse samples with matrix levels over 10x above the normal limits for ICP-MS, when combined with loop injection, this provides a very rapid and simple means of measuring ultratrace elemental concentrations without the complication of advanced sample preparation methodologies.

Using a simple aerosol-phase "dilution" also reduces the likelihood of sample contamination from reagents or preparation methodologies.

The overall sample-to-analysis time is significantly shortened due to the rapid throughput of loop injection and lack of sample preparation needed. The system proved fit for purpose for routine, direct measurement of seawater.