

# High Throughput, Direct Analysis of Seawater using the Agilent 7800 ICP-MS with HMI for Aerosol Dilution

Environmental

## Authors

Shaun Fletcher<sup>1</sup> and Glenn Woods<sup>2</sup>

1. Environment Agency, Exeter, UK

2. Agilent Technologies, Stockport, UK



## Introduction

The Environment Agency (EA) is an executive nondepartmental public body that is sponsored by the UK government's Department for Environment, Food and Rural Affairs (DEFRA). Part of EA's remit is to safeguard the natural environment of England, protecting and improving the environment to create better places for people and wildlife. Similar Agencies perform equivalent functions in the other, devolved regions of the UK. The Agency also has a duty to manage and protect surface waters and groundwaters, including waters used for drinking water abstraction and aquaculture. This task involves the analysis of many varying water matrices.



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Some of the most challenging work undertaken in the EA laboratories is the determination of potentially toxic trace metals in saline and estuarine waters. This analysis helps ensure the safety of seafood derived from coastal and estuarine fishing and shell fisheries. The analysis is difficult due to the combination of the high and variable total dissolved solids (TDS) in solution, the potential spectral interferences that arise from the matrix, and the low detection limits that must be routinely achieved while operating at high sample throughput. Among the elements of interest are Ni, Cu, Zn, Cd and Pb, with required minimum reporting values of 0.3, 0.2, 0.4, 0.03 and 0.04 µg/L, respectively.

The existing method used for this application at the EA Starcross laboratory uses a suspended iminodiacetate reagent to perform the dual role of matrix elimination and analyte preconcentration, followed by analysis using Inductively Coupled Plasma Mass Spectrometry (ICP-MS). While the method achieves the required performance, the sample preparation stage requires expensive reagents, is time consuming, labor intensive, and needs to be carried out by a skilled analyst.

With the goal of simplifying the analysis, EA evaluated the latest generation of quadrupole ICP-MS. These instruments offer superior interference removal, lower detection limits, and significantly enhanced tolerance of high and variable matrices. The objective was to develop a robust and reliable method capable of directly analyzing saline and estuarine water samples, without requiring matrix elimination, preconcentration, or sample dilution before analysis. Improved efficiency had to be achieved without compromising data quality or degrading productivity.

## Experimental

### Instrumentation

An Agilent 7800 ICP-MS with the standard High Matrix Introduction (HMI) system and optional Agilent Integrated Sample Introduction System (ISIS 3) was used for the analysis. Sampling was performed by the Agilent SPS 4 autosampler.

The ICP-MS was configured with the standard sample introduction system consisting of a Micromist concentric nebulizer, quartz spray chamber, and quartz torch with 2.5 mm id injector. The cones were Ni (with a Ni-plated Cu-core sampler). The Agilent argon gas humidifier was also fitted to the carrier (nebulizer) gas to prevent salt build-up on the nebulizer. Internal standards (ISTD) Rh and Ir were added online at a 1:1 ratio using 0.76 mm id tubing for both the ISTD and carrier/sample streams.

Instrument operating conditions are listed in Table 1; the settings for HMI (shaded) were autotuned, based on the expected matrix level for the samples of interest. The five analytes of interest (Ni, Cu, Zn, Cd, and Pb) were all acquired in helium (He) collision mode. Employing a simple, single tune-step method, He mode reliably reduces or eliminates all common polyatomic interferences using kinetic energy discrimination (KED).

**Table 1.** ICP-MS operating parameters.

Parameter	Value
RF power (W)	1600
Sampling depth (mm)	10
Carrier gas (L/min)	0.68
Dilution gas (L/min)	0.27
Helium cell gas (mL/min)	5.0
Energy discrimination (V)	5
ISIS 3 loop size (µL)	300

HMI conditions (shaded parameters) were automatically optimized during startup

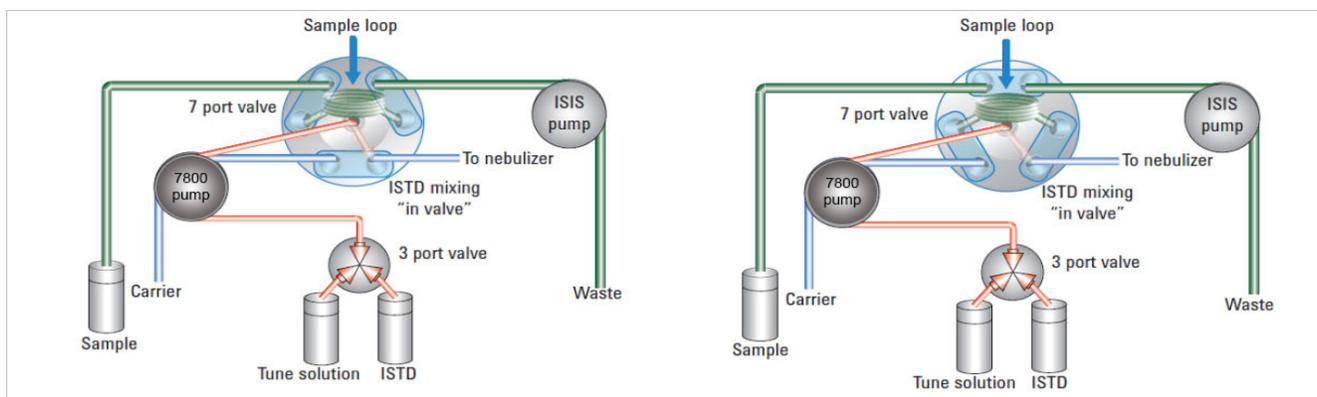
### Reagents and samples

Trace element free seawater was prepared by complexation on iminodiacetate functionalized polymer microbeads (CETAC). The seawater was then used to prepare calibration, QC and matrix blank solutions. All solutions were prepared at the Environment Agency Starcross laboratory. The ISIS 3 carrier solution was 2% HNO<sub>3</sub>/0.5% HCl (UpA Merck).

### New ICP-MS method and workflow

In developing the new ICP-MS method, various seawater samples were analyzed using the 7800 ICP-MS. The 7800's HMI system uses "aerosol dilution" to reduce the matrix loading on the ICP-MS, allowing the direct introduction of high matrix samples, such as seawater. As sample throughput was also an important factor, the 7800 was fitted with an ISIS 3 loop injection system. ISIS 3 injects a discrete volume or "plug" of the sample into a flowing carrier stream, allowing sample run times to be reduced to approximately 1 minute.

The ISIS 3 further improves matrix tolerance by minimizing the period that the ICP-MS instrument's sample introduction, plasma and interface are exposed to the sample matrix during each measurement. Figure 1 shows the basic operation of the system.



**Figure 1.** Overview of ISIS 3 loop injection system operation. Valve in load position (left) and inject position (right)

A wide range of matrix-based polyatomic interferences can hinder the measurement of many analytes when analyzing saline waters by ICP-MS. Examples include:  $^{44}\text{Ca}^{16}\text{O}$  on  $^{60}\text{Ni}$ ;  $^{23}\text{Na}^{40}\text{Ar}$  on  $^{63}\text{Cu}$ ;  $^{95}\text{Mo}^{16}\text{O}$  on  $^{111}\text{Cd}$ . To provide effective attenuation of these polyatomic ions, the 7800 includes an Octopole Reaction System (ORS<sup>4</sup>) cell that is optimized for operation in helium (He) collision mode. He mode provides the simplicity of a single tune-step method and delivers reliable and accurate quantitation of a wide range of elements. As well as reducing method complexity, the use of He collision mode eliminates the element-by-element and sample-by-sample optimization that is often required in quadrupole ICP-MS methods that use reactive cell gases.

The 7800 – including HMI settings and ISIS 3 program – is fully controlled by Agilent ICP-MS MassHunter software. MassHunter provides simple, consistent autotuning, and automated method setup using Agilent’s proprietary MassHunter Method Wizard.

## Results and Discussion

Several seawater matrices were tested including: Quasimeme interlaboratory performance test samples (estuarine and open ocean); an EA in-house Analytical Quality Control (AQC) sample; natural open ocean and estuarine water samples; and spikes of each natural sample. All these varied sample matrices were measured (n=4) in random order, regardless of salinity,

against a single multi-element calibration set. The blank seawater was also repeated randomly throughout the run (n=40) to determine method detection limits (MDLs).

Figure 2 shows the calibration curves for each analyte in the clean seawater matrix. Corresponding internal DLs ( $3\sigma$  of the calibration blank; n=3) and external MDLs (from the 40 blank seawater measurements throughout the run) are shown in Table 2.

**Table 2.** Detection Limits and Method Detection Limits for  $^{60}\text{Ni}$ ,  $^{63}\text{Cu}$ ,  $^{66}\text{Zn}$ ,  $^{111}\text{Cd}$ , and  $^{208}\text{Pb}$ .

Element	DL (µg/L)	MDL (µg/L)
$^{60}\text{Ni}$	0.013	0.036
$^{63}\text{Cu}$	0.0096	0.055
$^{66}\text{Zn}$	0.049	0.22
$^{111}\text{Cd}$	0.0038	0.011
$^{208}\text{Pb}$	0.013	0.022

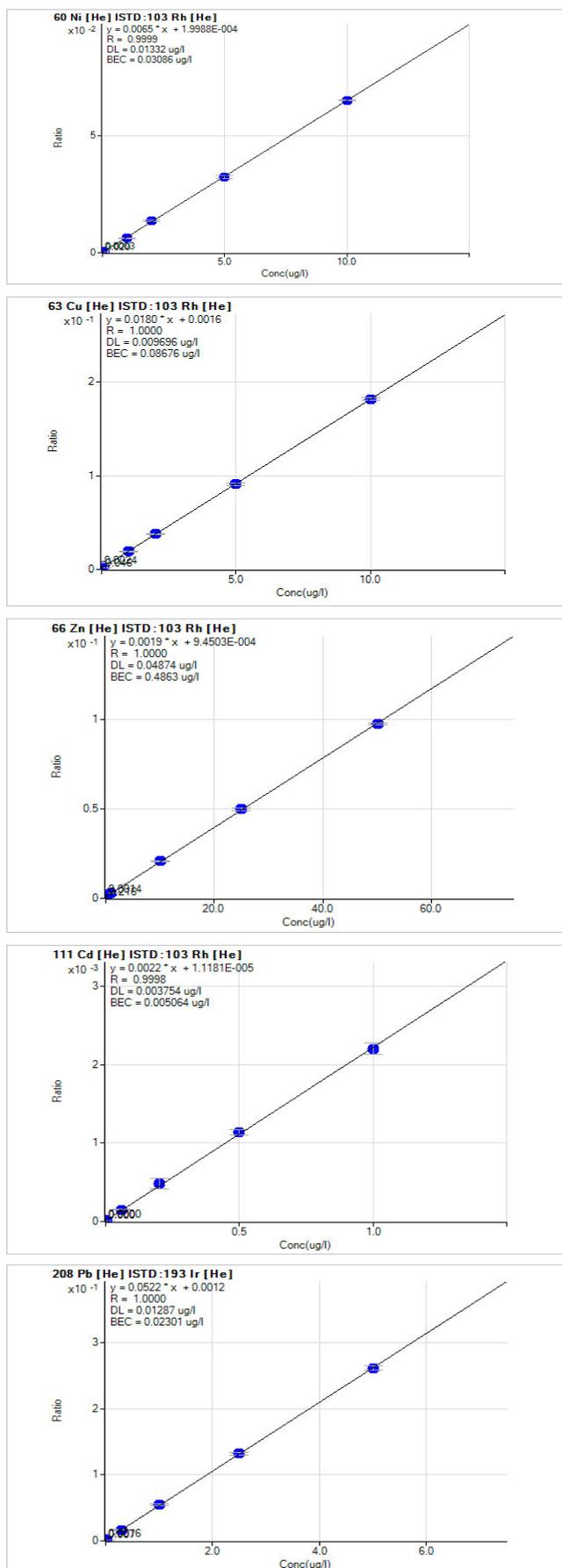


Figure 2. Calibration curves for  $^{60}\text{Ni}$ ,  $^{63}\text{Cu}$ ,  $^{66}\text{Zn}$ ,  $^{111}\text{Cd}$ , and  $^{208}\text{Pb}$

The results for the various seawater samples are given in Table 3. The mean results are in good agreement with the expected or assigned values where provided. Good agreement was also achieved between the mean results obtained using the 7800 and the results obtained at EA Starcross laboratory, which were obtained using the existing ICP-MS method. Using the 7800 ICP-MS direct analysis method, excellent spike recoveries were achieved for all five elements in the spiked seawater and estuarine samples. Recoveries were within  $\pm 2\%$  for most elements and within  $\pm 5\%$  for all elements.

Table 3. Mean concentrations ( $\mu\text{g/L}$ ) of the randomized four repeat measurements for each sample, including comparison with the data acquired at the EA Starcross laboratory, where appropriate.

Sample		$^{60}\text{Ni}$	$^{63}\text{Cu}$	$^{66}\text{Zn}$	$^{111}\text{Cd}$	$^{208}\text{Pb}$
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
Quasimeme Saline	Assigned	1.14	4.83	14.80	0.260	1.51
	Mean	1.19	10.78	22.09	0.101	0.418
	*Starcross	1.14	10.40	21.10	0.095	0.380
Saline	Assigned	1.04	10.00	20.70	0.098	0.410
	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

\*Results obtained using EA's current method of matrix elimination and preconcentration of samples followed by analysis using ICP-MS

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

Figure 3 shows that the ISTD drift throughout the run was minimal, demonstrating the excellent matrix tolerance afforded by HMI and loop injection using ISIS 3. The high matrix level of seawater has an impact on the physical processes of sample uptake, nebulization and aerosol transport, as well as plasma effects such as ionization suppression. However, the superior robustness provided by the 7800 with HMI means that suppression effects are minimized. This performance characteristic can be seen from the small impact that the variable sample matrices had on the



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