

Analysis of Trace Elements in Seawater Using the Thermo Scientific iCAP 7000 Series ICP-OES Duo

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Key Words

pergo Argon Nebulizer Gas Humidifier, seawater, trace elements

Goal

This application note demonstrates the analysis of trace elements in seawater by ICP-OES. The analysis is simplified by the addition of an argon humidifier, allowing stability over extended periods of time. The addition of the argon humidifier does not degrade the detection limits in this challenging matrix, with sub-ppb detection limits being achieved.

Introduction

Seawater is a complex mixture, consisting of water, dissolved salts and gases as well as inorganic and organic materials. On average the salinity of the seawater is 3.5% (35 grams of salt per kilogram). Sodium chloride (NaCl) is the main salt in seawater which mainly contains Na⁺, K⁺, Ca²⁺, Mg²⁺ cations and Cl⁻, SO₄²⁻ anions in high concentrations. Inorganic carbon, bromine, boron, strontium and fluoride are found in lower concentrations.

The chemical composition of the oceans has been influenced both globally and locally by human activities. Industrial pollution, oil and gas exploration, continuous and uncontrolled use of fertilizers in combination with climate change, and the rise in the atmospheric CO₂ have resulted in a change in the elemental mixture in seawater. Concentrations of trace elements such as lead, which naturally occur in water, have risen in recent decades and will continue rising, making efficient elemental analysis of seawater essential for environmental monitoring.

Instrumentation

The Thermo Scientific™ iCAP™ 7000 Series ICP-OES employs a high-resolution echelle spectrometer with a highly advanced charge injection device (CID) detector. Improvements in CID technology enable a greater photosensitive area, allowing the new CID detector to provide higher sensitivity and lower noise levels than any of the detectors previously employed. For this analysis, a Duo model was chosen as it enables maximum sensitivity in axial viewing mode while maintaining exceptional matrix tolerance using radial view. Table 1 summarizes the parameters that applied to the iCAP 7600 ICP-OES Duo for this analysis. Additionally, a Burgener Mira Mist nebulizer was used to minimize salt deposition in the nebulizer tip.

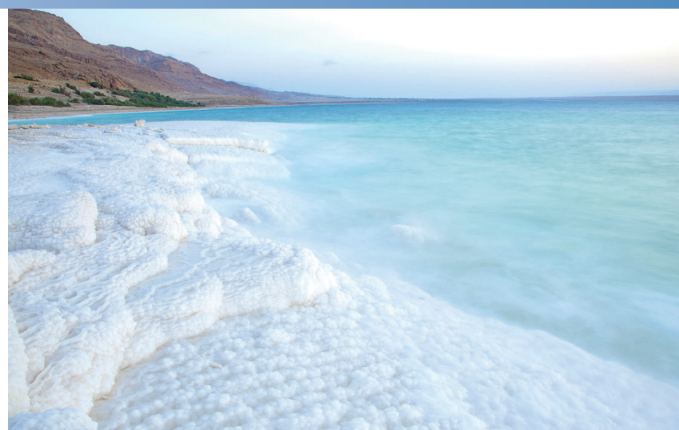


Table 1. Instrument Parameters

Instrument Parameter	Setting
Pump Tubing	White/white tygon sample Blue/yellow tygon drain
Pump Speed	50 rpm
Flush Pump Speed	100 rpm
Nebulizer Gas Flow	0.55 L/min
Auxiliary Gas Flow	0.5 L/min
Coolant Gas Flow	12L/min
RF Power	1250 W
Torch	EMT
Torch Orientation	Axial
Centre Tube	2 mm
Nebulizer	Burgener Mira Mist®
Spray Chamber	Glass Cyclonic
Data acquisition Mode	Speed
High/Low Integration Time	15/5 s
Replicates	3
Software	Thermo Scientific Qtegra ISDS

Argon Humidifier

The analysis of salt-containing samples is a challenge for ICP-OES. Salt tends to be deposited in the nebulizer tip, changing the nebulization efficiency, resulting in signal drift and high RSDs.

To allow efficient analysis of salt-containing samples as well as to overcome any challenges associated with such analysis, the iCAP 7000 Series ICP-OES uses the optional *pergo* Argon Nebulizer Gas Humidifier (Elemental Scientific) (Figure 1) which is designed for the analysis of solid containing samples and can be used for ICP-OES analyses. The humidifier employs a Nafion tubing that has the ability to permeate water vapour through its membrane, humidifying the argon gas used for the nebulizer. The water prevents salt accumulating in the nebulizer, allowing for uninterrupted analysis and operation with no maintenance for extended periods of time. The principle of operation of the humidifier is shown in Figure 2.



Figure 1. The *pergo* - Argon Nebulizer Gas Humidifier (Elemental Scientific)

The *pergo* Argon Nebulizer Gas Humidifier is user-friendly; the water reservoir at atmospheric pressure provides the necessary safety for extended analytical runs, unlike other argon humidifiers which run at elevated pressures. It is easy to use and maintain with any iCAP 7000 Series ICP-OES instrument, enabling improved detection limits and long-term stability when high TDS samples are analyzed.

Materials and Methods

Reagents

- 69% HNO₃ trace metal grade (Fisher Scientific).
- Single element standards (1000 mg/l for Al, As, Ba, Be, Cd, Cr, Co, Cu, Fe, Pb, Mn, Mo, Ni, Ag, Tl, Sn, Ti, V, Zn (Fisher Scientific). Ge (265.118 nm and 219.871 nm the wavelengths used for the visible and the UV range respectively) was selected as internal standard.

Certified Reference Materials

- Sea salt (ASTM International 1141-98).
- Fortified water-reference material (LGC Standard).

Samples

The simulated seawater used for this analysis was made by dissolving 41.953 grams of the ASTM International 1141-98 sea salt in 1 litre of deionised water. After mixing the pH was adjusted to 8.2 using a 0.1n NaOH solution. The same quantities were used when sea salt was dissolved in fortified water. For the analysis 50 ml aliquots were used. The ASTM International 1141-98 sea salt composition is summarized in Table 2. At all times the *pergo* Argon Nebulizer Gas Humidifier was used.

Table 2. The ASTM International 1141-98 Sea Salt composition

Substance	Composition (%)
NaCl	58.490
MgCl ₂ - 6H ₂ O	26.460
Na ₂ SO ₄	9.750
CaCl ₂	2.765
KCL	1.645
NaHCO ₃	0.477
KBr	0.238
H ₃ BO ₃	0.071
SrCl ₂ - 6H ₂ O	0.095
NaF	0.007

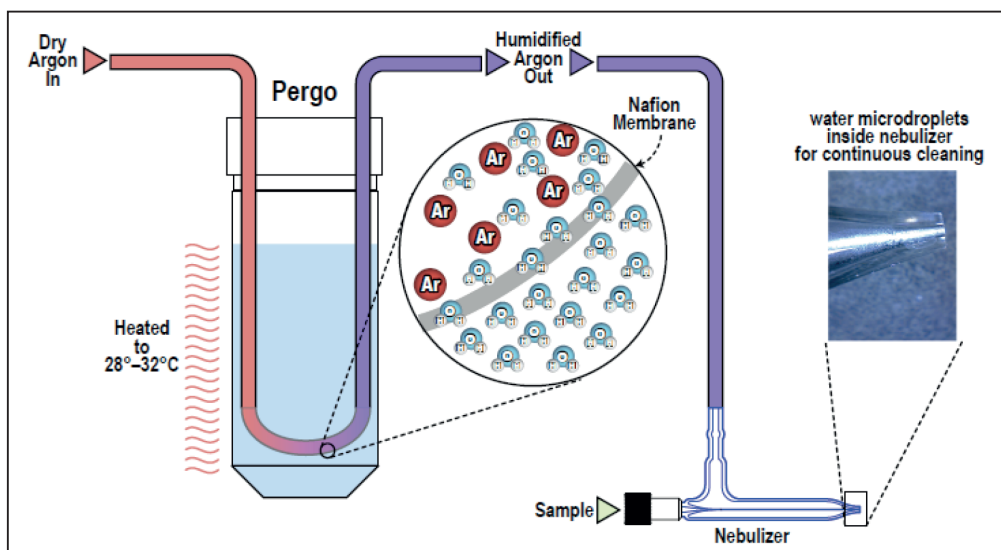


Figure 2. The principle of operation of the *pergo* Argon Nebulizer Humidifier (courtesy of Elemental Scientific)

Standard Preparation

High purity standards were used to prepare the calibrations standards for this analysis. The standards were prepared in 2% (v/v) HNO_3 at element concentrations to cover the required range for each element (i.e. 50, 100, 200, 500 $\mu\text{g/l}$). Standards were made in seawater. However, since the percentage (%) recovery used against the reference material was also assessed, another set of standards was made at the same concentrations, this time in deionised water.

Method Development

Method development and analysis were performed using the Thermo Scientific™ Qtegra™ software. In order to evaluate the efficiency of the method, the percentage (%) recovery using fortified water was initially performed. Then the sea salt-fortified water mix was used to assess the % recovery, having the seawater as a matrix and the fortified water as a matrix spike. More than one wavelength was chosen for each element, always using the axial viewing. The sub-arrays for each wavelength were examined in each case and the most appropriate wavelength was chosen for each element, based on the presence of interferences, calibration curve, readback of standards and the required linearity for the element. The sub-array plot of each element can be easily manipulated in the Qtegra software, allowing the analyst to select the optimum peak integration and background correction points.

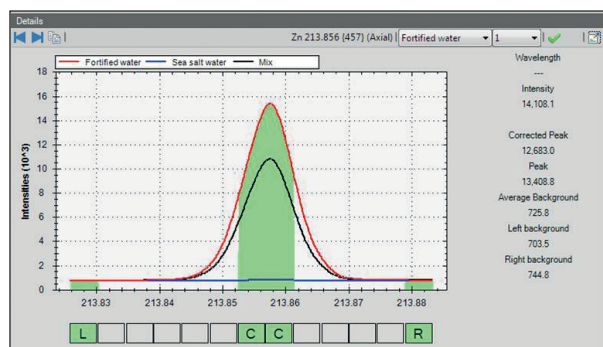


Figure 3. Sub-array plot for Zn 213.856 nm as displayed by the Qtegra software, showing background correction areas

Results

When the recovery of the reference material was calculated, the instrument was calibrated using the standards previously described in deionised water. For the rest of the experiments the instrument was calibrated using the standards in seawater. A linear fit was applied to all elements. An example calibration generated by the Qtegra software is shown in Figure 4. Values and percentage recoveries from measuring the reference material (fortified water) as well as from measuring the sea salt-fortified water mix are shown in Table 3. The recovery of the sea salt-fortified water mix was assessed by the MXS (Matrix spike) Quality Test available in the Qtegra software. Method detection limits (MDLs), were established by analyzing the blank (sea salt dissolved in deionised water) acid matched calibration, using a ten-replicate analysis and multiplying the standard deviation by three (3) (shown in Table 4). Additionally, the stability of the mixture sea salt-fortified water was evaluated over time, for a period of more than three hours. The graph (figure 5) summarizes the stability over time evaluation.

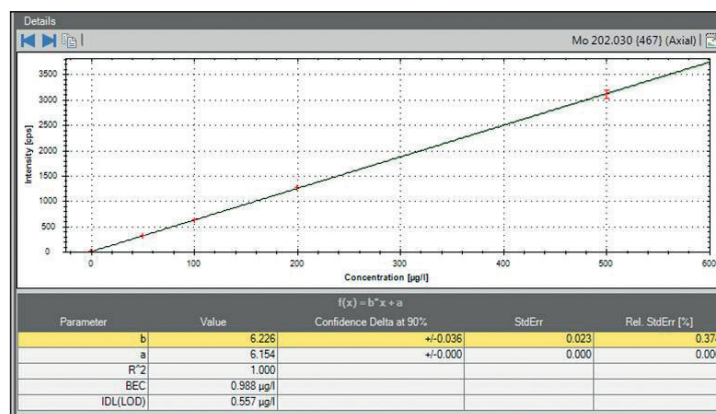


Figure 4. Calibration Curve for Mo 202.030 nm as displayed by the Qtegra software

Table 3. Percentage (%) recovery of the reference material and seawater, calculated without further correction for the uncertainty associated with that value.

Element	Wavelength (nm)	Reference Value (µg/L)	±2s	Measured Fortified Water (µg/L)	% Recovery	Measured Seawater (µg/L)	% Recovery
Ag	328.068	20.60	1.80	17.75	86.16	18.00	94.60
Al	167.079	310.00	24.90	293.74	94.75	311.52	107.70
As	189.042	25.40	3.30	27.22	107.15	30.98	127.50
Ba	455.403	148.00	10.70	136.56	92.27	141.92	96.00
Be	234.861	17.60	1.60	17.99	102.20	16.94	96.20
Cd	226.502	90.90	8.10	85.47	94.02	87.21	96.10
Cr	267.716	165.00	11.50	155.98	94.53	161.96	98.70
Co	228.616	136.00	9.10	126.19	92.79	133.47	98.20
Cu	324.754	197.00	15.00	183.62	93.21	190.11	97.40
Fe	259.940	412.00	38.30	395.08	95.89	416.46	112.80
Pb	220.784	358.00	28.70	340.62	95.14	362.11	100.90
Mn	257.610	198.00	14.70	182.27	92.06	191.30	92.70
Mo	202.030	207.00	15.00	206.27	99.65	215.66	104.10
Ni	231.604	274.00	20.00	257.02	93.80	273.55	96.90
Sn	189.989	19.80	2.90	18.79	94.90	26.94	139.90
Ti	323.452	120.00	7.60	115.00	95.84	118.74	100.10
Tl	190.856	18.30	1.70	15.29	83.52	17.07	91.10
V	292.402	145.00	11.20	166.51	114.83	165.30	114.21
Zn	213.856	263.00	25.30	264.87	100.71	256.87	98.59

Table 4. Method detection limits derived from acid matched blank

Element	Wavelength (nm)	DL (µg/L)	Element	Wavelength (nm)	DL (µg/L)
Ag	328.068	1.131	Pb	220.784	2.046
Al	167.079	1.857	Mn	257.610	0.357
As	189.042	3.369	Mo	202.030	0.537
Ba	455.403	0.552	Ni	231.604	0.627
Be	234.861	0.087	Sn	189.989	2.580
Cd	226.502	0.147	Ti	323.452	0.762
Cr	267.716	0.942	Tl	190.856	2.811
Co	228.616	0.528	V	292.402	0.987
Cu	324.754	0.816	Zn	213.856	0.507
Fe	259.940	7.5			

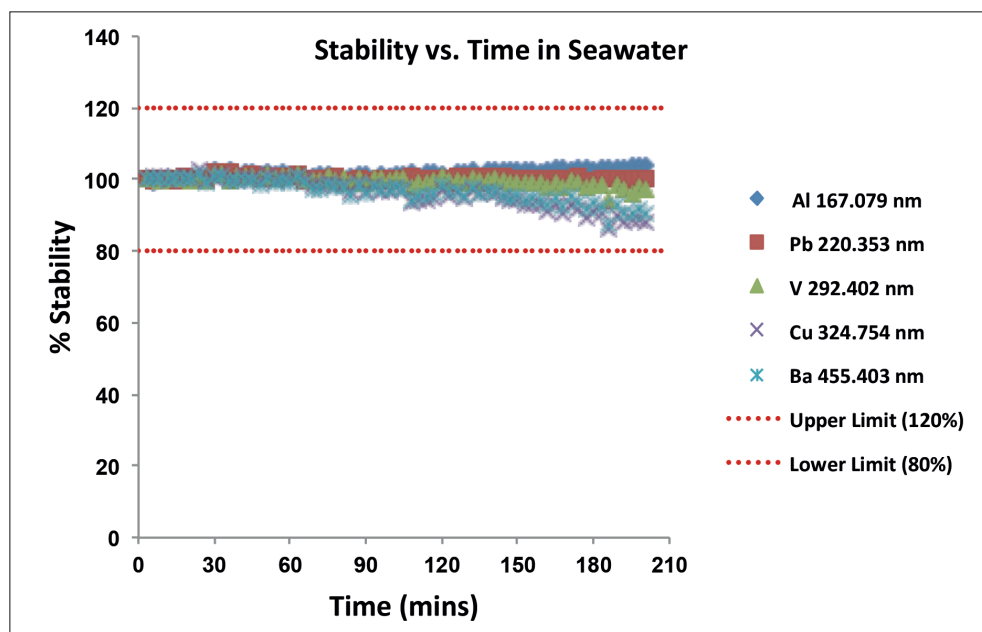


Figure 5. Stability over time of the sea salt-fortified water mixture. All elements are within the $\pm 20\%$

Conclusions

It was clearly shown that the iCAP 7600 ICP-OES along with the *pergo* argon humidifier, enables accurate analysis of seawater or high salt-containing samples over a long period of time, without any problems. Exceptionally precise results were obtained regarding the recovery while the MDLs were the lowest possible for this application. The latest generation design CID detector that the iCAP 7600 ICP-OES utilizes, provides higher sensitivity and lower noise allowing the optimum signal to be selected at the same time, and the signal to noise ratio to be as high as possible, even in a demanding applications such as this.

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