APPLICATION NOTE

ICP-Optical Emission Spectroscopy

AUTHORS

Ken Neubauer
PerkinElmer Inc.
Shelton, CT USA

Analysis of Desalination Discharge Brines for Pollutants Using the Avio 550 Max ICP-OES

Introduction

With climate change, access to fresh water is decreasing in many areas around the world. Combined with the continuing rise in global population, a shortage of potable water is imminent unless other sources of fresh water can be found. One way to increase amounts of potable water is through desalination of seawater, a technique which has been rapidly growing in importance. In 2019, there were about 16,000 desalination plants operating globally[1], with that number increasing yearly.

While several methods for desalination are available, the most used is reverse osmosis, a process which uses high pressure to force seawater through a membrane which separates minerals from the water, resulting in both fresh/potable water and a brine which contains the minerals removed from the seawater. The salinity of these brines is generally twice that of seawater (≈ 6% dissolved solids), and these brines are usually returned to the ocean. Over 142 million cubic meters of brine daily are returned to the ocean globally[1].

With so much brine being returned to oceans, its elemental content should be monitored for elements which may have been picked up during the desalination process and can have a negative impact on the aquatic environment. However, there are no international standards or regulations for monitoring elements in desalination discharge brines: elements and regulated levels vary widely and are set on a country or regional basis, as shown in Table 1 for four different areas. For example, boron (B), barium (Ba), and manganese (Mn) are only regulated in Singapore, but not Dubai or either facility in California; limits for other elements cover a broad range, such as silver (Ag), which varies by two orders of magnitude, and zinc (Zn), which varies by over one order of magnitude. Therefore, a variety of elements over a wide concentration range must be accurately measured.

Table 1: Regulated Elements and Discharge Limits in Various Locations.

Element	Singapore[2] (mg/L)	Dubai[3] (mg/L)	Huntington Beach[4], California (mg/L)	Carlsbad[5], California (mg/L)
Ag	0.1	0.005	0.11	0.156
Al	---	---	1.2	1.8
As	0.1	0.05	---	---
B	5	---	---	---
Ba	2	---	---	---
Cd	0.1	0.05	0.16	0.228
Cr	1	0.05	0.32	0.457
Cu	0.1	0.5	0.45	0.641
Fe	10	2	---	---
Hg	0.05	0.001	0.0064	0.00912
Mn	5	---	---	---
Ni	1	0.1	0.8	1.14
Pb	0.1	0.1	0.32	0.457
Se	0.5	0.02	---	3.42
Zn	1	0.1	3.1	4.39

[2] Discharge limits into watercourse
[3] Discharge limits to the marine environment
[4,5] Instantaneous maxima from NPDSE discharge permits

ICP-OES is an analytical technique which meets these requirements by providing multielemental analysis over a wide dynamic range. In addition, ICP-OES is highly tolerant to matrices, meaning that it can analyze these brines without dilution, which allows lower concentrations to be measured. The limitation of ICP-OES is sensitivity. For the regulated elements and levels in Table 1, ICP-OES can accurately measure these concentrations, apart from mercury (Hg) at concentrations less than 0.01 ppm. Accurate Hg analyses at these concentrations requires specialized techniques, such as hydride generation or dedicated mercury analyzers.

This work focuses on the analysis of environmentally important elements in desalination discharge brines using the Avio® 550 Max fully simultaneous ICP-OES.

Experimental

Samples and Sample Preparation

Six unknown desalination discharge brines were acquired and acidified to 1% HNO_3 (v/v). No other sample preparation was required. All measurements were made against external calibration standards at 0.1, 0.2, 0.4, and 1 ppm, prepared in 6% NaCl (w/v, 99.99% purity) to mimic the dissolved solid content of the brines. Although calibration standards could also have been prepared directly in the brines themselves and the method of additions used for calibration, preparing the standards in 6% NaCl proved simpler, as analyte concentrations in the brines did not have to be considered. Gallium (Ga) and yttrium (Y) were added to all blanks, standards, and samples.

Table 2: Avio 550 Max ICP-OES Instrumental Parameters.

Component / Parameter	Description / Value
Sample Uptake Rate	0.5 mL/min
Nebulizer	SeaSpray
Spray Chamber	Baffled glass cyclonic
Injector	2.0 mm id alumina
Torch	Quartz
RF Power	1500 W
Plasma Flow	12 L/min
Auxiliary Flow	0.4 L/min
Nebulizer Flow	0.65 L/min
Argon Humidifier	Elegra
Torch Position	-3
Integration	Auto
Read Times	1 - 10 sec
Replicates	3
Sample Uptake Tubing	Green/orange (0.38 mm id), PVC
Drain Tubing	Gray/gray (1.30 mm id), Santoprene

Instrumental Parameters

All analyses were performed on an Avio 550 Max fully simultaneous ICP-OES (PerkinElmer Inc., Shelton, Connecticut, USA) using the parameters in Table 2 and the analytes, wavelengths, and plasma views in Table 3. To promote robustness and minimize the chance of nebulizer and injector clogging, a SeaSpray nebulizer was used in conjunction with an argon humidifier. An auxiliary flow of 0.40 L/min raised the plasma above the injector, which further minimized salt deposition. In addition, a sample uptake rate of 0.5 mL/min reduced sample loading in the plasma, minimizing matrix-induced plasma effects. The Avio Max family of ICP-OES instruments also incorporates PlasmaShear™ technology[6], where a stream of air removes the top of the plasma, eliminating matrix deposition on the spectrometer entrance window and the need for orifices, which must be maintained.

A quartz torch was used, along with a higher plasma flow of 12 L/min to extend the torch lifetime due to the harsh sample matrix which devitrifies the quartz. As an option, a ceramic torch could be used, which removes the possibility of devitrification, allowing lower plasma gas flows to be used.

Results and Discussion

Due to the matrix composition of the brines, the choice of wavelength, plasma view, and internal standard was critical to attaining accurate, consistent results. Atom lines produced more consistent, accurate results and were selected when available. Barium (Ba), iron (Fe), and manganese (Mn) only have ion lines available for their top five preferred wavelengths; while lead (Pb) has atom lines available, they do not provide enough sensitivity, so the more sensitive ion line was selected for analysis.

Matrix-induced plasma effects are minimized when viewing the plasma in radial mode, which was selected for most analytes. However, since sensitivity is also reduced in radial mode, axial mode was used for those elements where additional sensitivity was required. The dual-view capability of the Avio 550 Max ICP-OES allows both axial and radial views to be measured in the same method, with a switching time of 1 second. This dual view flexibility within a method was important for attaining accurate, repeatable results.

Table 3: Elements, Wavelengths, and Plasma Views.

Element	Wavelength (nm)	Atom or Ion	Plasma View	Internal Standard
Ag	338.290	Atom	Axial	Ga 417.211
Al	396.153	Atom	Radial	Y 317.029
As	188.982	Atom	Radial	Ga 417.211
B	249.775	Atom	Radial	Y 317.029
Ba	233.351	Ion	Radial	Y 317.029
Cd	228.800	Atom	Axial	Ga 417.211
Cr	357.863	Atom	Axial	Ga 417.211
Cu	327.400	Atom	Axial	Ga 417.211
Fe	259.943	Ion	Radial	Y 317.029
Mn	257.614	Ion	Radial	Y 317.029
Ni	232.004	Atom	Radial	Ga 417.211
Pb	220.356	Ion	Radial	Y 317.029
Se	196.030	Atom	Axial	Y 317.029
Zn	213.859	Atom	Axial	Ga 417.211

Finally, the selection of an internal standard was crucial for obtaining accurate, reproducible results. Although Y is a commonly used internal standard for most elements in ICP-OES, it was found to behave differently in the plasma than some of the analytes in the brine matrix. As a result, Ga was also used as an internal standard for some elements. In general, elements that produced ionic emissions worked better with Y as an internal standard since it also has an ionic transition, while elements with atomic emissions produced better results with Ga as an internal standard, which also emits as an atom.

When the brines were measured, only five elements were detected, as shown in Figure 1; all other elements were not detected. Compared to the regulated levels from Table 1, only boron (B) exceeds a regulated level (Singapore) in all the brines, while copper (Cu) in Brine 2 exceeds all the regulated levels. Silver (Ag), manganese (Mn), and zinc (Zn) are below all regulated limits in all the brines, while Mn was not detected in Brines 5 or 6, and Cu was not detected in Brine 5.

Detection limits were determined for Brines 1 and 5 (since they were the cleanest) using the Detection Limits function in Syngistix™ for ICP software as three times the standard deviation of 10 replicate measurements of the brines made against the calibration curve. As shown in Figure 2, the detection limits are lower than all the regulations (apart from the regulated levels of selenium (Se) in Dubai), demonstrating that the Avio 550 Max ICP-OES can be used to measure elements at their regulated limits.

The accuracy of the methodology was determined through spike recovery studies, where one of the brines was spiked with all analytes at different concentrations, based on the regulated levels in Dubai, Singapore, and Carlsbad (as displayed in Table 4):

- Low: Dubai and half of the Singapore regulated concentrations
- Medium: Singapore regulated concentrations
- High: Carlsbad concentrations

Since not all elements are regulated in all regions, not all elements had four spike recoveries measured.

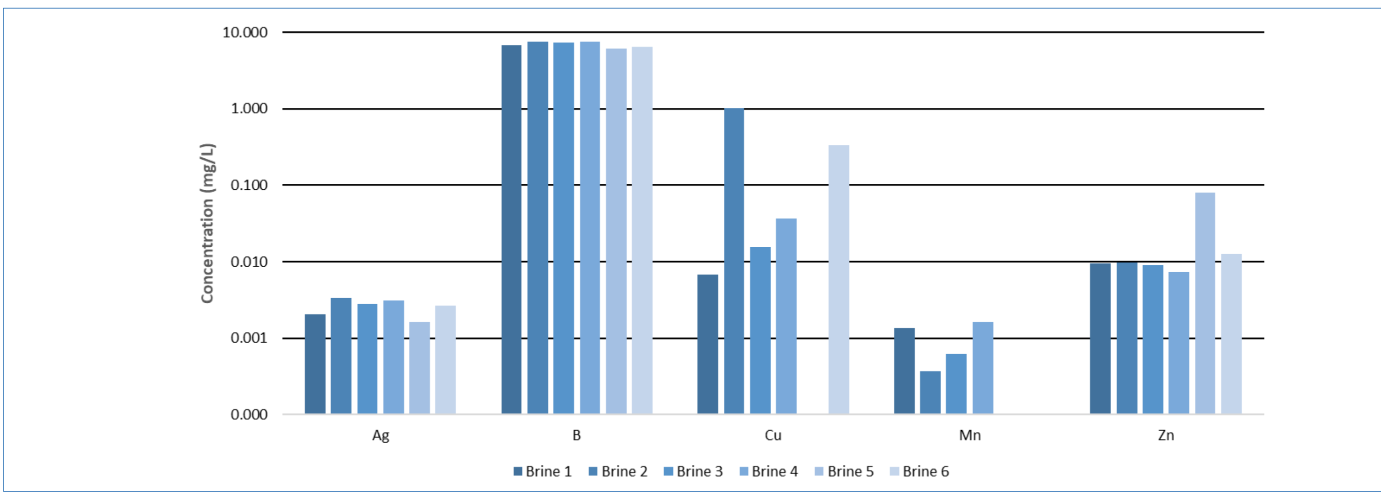

Figure 1. Elements detected in the six desalination discharge brines. All other elements were not detected in any of the brines.

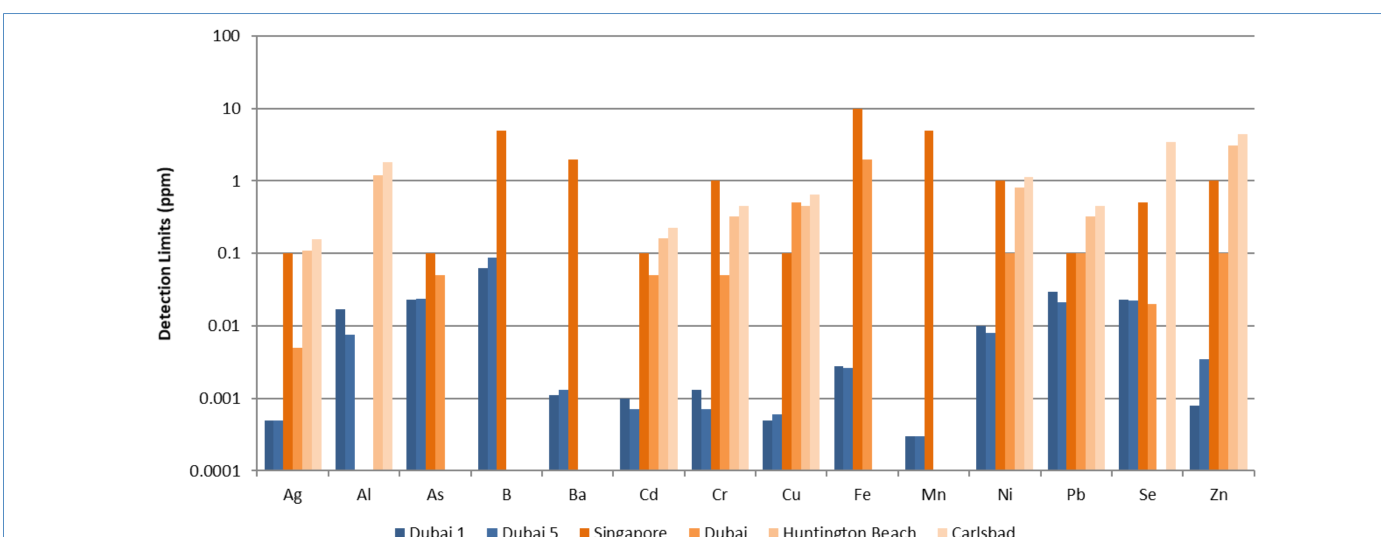

Figure 2. Detection limits (blue) determined in two desalination brines compared to regulated levels (orange; not all elements are regulated in all areas).

Table 4: Spike Concentrations in Desalination Brine.

Element	Dubai Spike (mg/L)	Half Singapore Spike (mg/L)	Singapore Spike (mg/L)	Carlsbad Spike (mg/L)
Ag	0.005	0.05	0.10	0.15
Al	---	0.25	0.50	1.8
As	0.05	0.05	0.10	---
B	---	2.50	5.00	---
Ba	---	1.00	2.00	---
Cd	0.05	0.05	0.10	0.22
Cr	0.05	0.50	1.00	0.45
Cu	0.50	0.05	0.10	0.64
Fe	2.00	5.00	10.00	---
Mn	---	2.50	5.00	---
Ni	0.10	0.50	1.00	1.10
Pb	0.10	0.05	0.10	0.45
Se	0.02	0.25	0.50	3.4
Zn	0.10	0.50	1.00	4.3

Figure 3 shows that all of the analytes at the four different spike levels recover within 10% of their true values, thereby validating the accuracy of the methodology.

The stability of the methodology was evaluated by repeatedly analyzing one of the brine samples for 4.5 hours (with a 90 second wash between samples) and monitoring the internal standard signal. As shown in Figure 4, the internal standard response varied by less than 10% over the 4.5 hours while switching between axial and radial views for each sample. This stability results from the robust sample introduction and plasma conditions as well as PlasmaShear technology, which prevents matrix buildup on the interface.

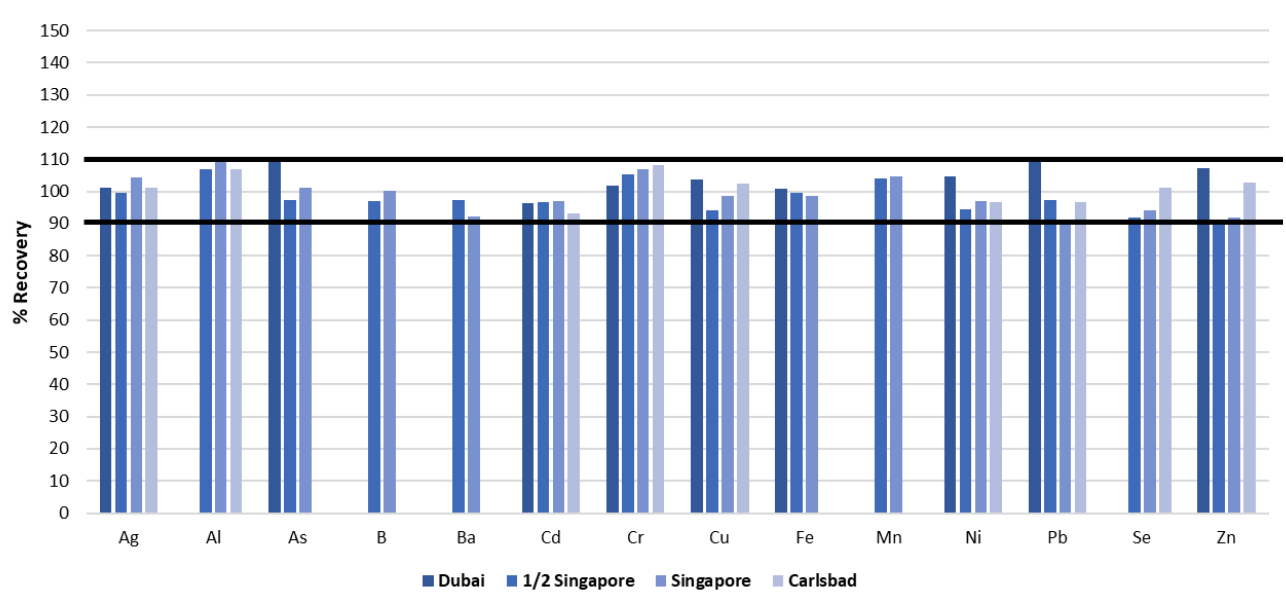

Figure 3. Spike recovery results.

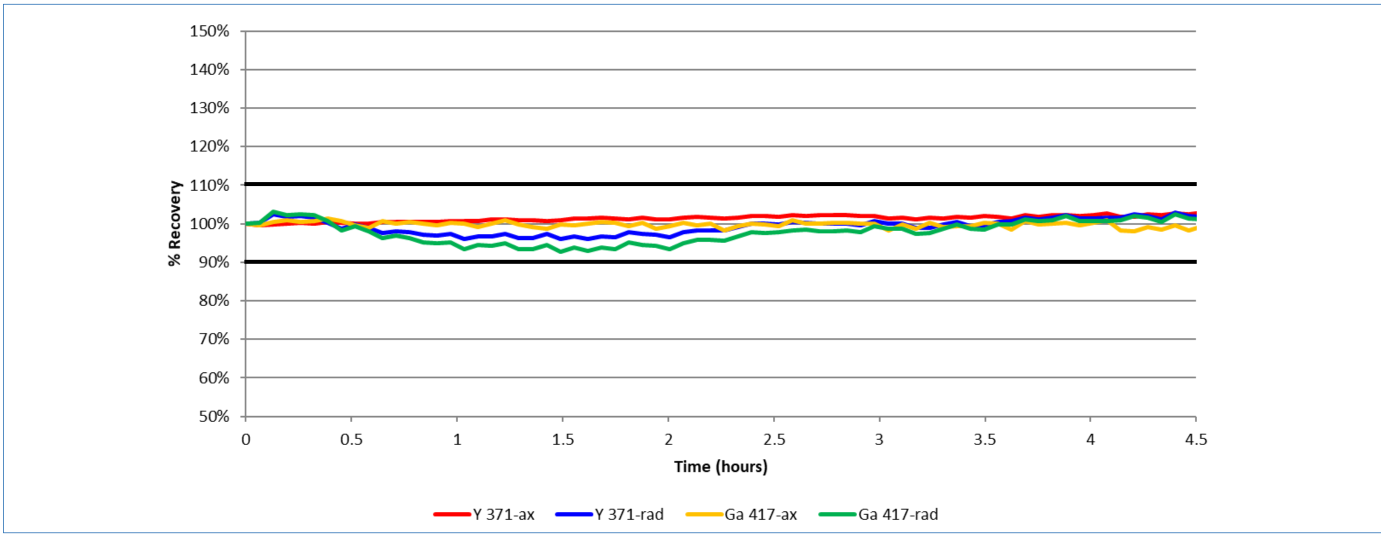

Figure 4. Internal standard response over 4.5 hours of running a desalination brine sample. All values were normalized to the first reading.

Conclusion

This work demonstrates the ability of the Avio 550 Max fully simultaneous ICP-OES to measure elements of environmental importance in desalination discharge brines, taking advantage of the Avio's dual view capability and PlasmaShear technology to attain accurate, stable results. Because of the Avio's matrix tolerance, the brines were run undiluted with no pre-treatment other than acidification, allowing lower concentrations to be measured.

References

1. "UN Warns of Rising Levels of Toxic Brine as Desalination Plants Meet Growing Water Needs", United Nations University, 2019, https://unu.edu/media-relations/releases/un-warns-of-rising-levels-of-toxic-brine.html.
2. "Allowable Limits for Trade Effluent Discharge to Watercourse or Controlled Watercourse", Singapore National Environment Agency, NEA | Allowable Limits for Trade Effluent Discharge to Watercourse or Controlled Watercourse.
3. "Discharge Limits to the Marine Environment", Dubai Electric and Water Authority, 2021.
4. "Waste Discharge Requirements for Poseidon Resources (Surfside) L.L.C. Huntington Beach Desalination Facility Orange County", Order R8-2021-0011, NPDSE No. CA8000403, California Regional Water Quality Control Board, Santa Ana Region.
5. "Waste Discharge Requirements for the Poseidon Resources (Channelside) LP Claude "Bud" Lewis Carlsbad Desalination Plant Discharge to the Pacific Ocean", Order R9-2019-0003, NPDSE No. CA 019223, California Regional Water Quality Control Board, San Diego Region.
6. "The Advantages of PerkinElmer's PlasmaShear Technology for ICP-OES", Technical Note, PerkinElmer Inc., 2020.

Consumables Used

Component / Description	Part Number
SeaSpray Nebulizer	N0811306
Elegra Argon Humidifier	N0781598
Sample Uptake Tubing, Orange/ Green (0.38 mm id), PVC, Flared	N0777042
Drain Tubing, Gray/Gray (1.30 mm id) Santoprene	N0777444
U.S. EPA Method 200.7 Standards Kit	N9300297
Gallium Standard, 1000 ppm	N9303772 (125 mL) N9300119 (500 mL)
Autosampler Tubes, qty 500	B0193233 (15 mL) B0193234 (50 mL)

PerkinElmer, Inc.
940 Winter Street
Waltham, MA 02451 USA
P: (800) 762-4000 or
(+1) 203-925-4602
www.perkinelmer.com

876116 PKI