

Trace contaminant analysis in brine using a Thermo Scientific iCAP 6000 Series Duo ICP-OES

James Hannan, Thermo Scientific, Cambridge, UK
Eivind Rosland, Research Scientist, Borregaard, Sarpsborg, Norway

Key Words

iCAP 6000 Series, Brine, Trace level impurity, Short/Long term stability, Customer Case Study

Benefits in Brief:

- Trace contaminant analyses in 10% brine
- Bespoke sample introduction system for easy analysis of high solids samples
- Analyst-definable background and integration points for best sensitivity without the use of interference correction
- Unique ability to switch internal standard on/off per element before or after the analysis
- Robust, swing frequency RF for trace analysis in the presence of heavy matrices

Introduction

The determination of trace contaminants in brines is of interest to the manufacturer of chlorine and caustic soda as its use is employed across many industrial sectors including food, petrochemical and metallurgical production. The production of brine has modernized in recent years from using mercury cell electrolysis to a cleaner and more environmentally friendly membrane cell technology. This involves the electrolysis of brine - aqueous sodium chloride (NaCl) - in a membrane cell. Saturated brine is passed into the first chamber of the cell where the chloride ions are oxidized at the anode to chlorine and at the cathode, water is reduced to hydrogen gas, releasing hydroxide ions into the solution. The non-permeable ion exchange membrane at the center of the cell allows the sodium ions (Na⁺) to pass to the second chamber where they react with the hydroxide ions to produce caustic soda (NaOH). A membrane cell is used to prevent the reaction between the chlorine and hydroxide ions. In this process, the presence of trace metals have considerable impact on the lifetime and performance of the ion exchange membrane cell, which is why the analysis of these elements is essential in the chlor-alkali process. From this point, sampling is typically done before the column, between (if more than one is employed) and after the second column. This tests the performance of the columns as well as the final output, so is useful for preventative maintenance and quality control.



The analysis of high salt matrices by optical ICP can be difficult as a dedicated radial system is best suited to the matrix, but the trace level impurities require the sensitivity of an axially mounted system. Common problems with the analysis of brines on an axial system are;

- Matrix-matching issues – it is difficult and expensive to source high purity sodium chloride (NaCl) for calibration standards
- Sample transport effects – when sampling raw and purified brines and also when using aqueous standards to calibrate, there are considerable differences in viscosity which cause differential sample transport and nebulization efficiencies and can bring about reactions in the plasma
- Salting and clogging – the nebulizer and centre tube can be prone to salt deposition from continuous aspiration of heavy brine solutions
- Dilution and loss of sensitivity – most axial systems will not cope with 30% NaCl for a long period of time. As a result of this, samples will need to be diluted, which degrades the detection limits in an already challenging matrix

These problems can be overcome with relative ease with the use of modern ICP instruments which enable internal standard addition (which will compensate for transport effects) and the use of high solids sample introduction kits and argon humidifiers to reduce the clogging of the system during analyses. Even with these problems solved, the issue of sensitivity still remains – a dual view instrument which can view both axially and radially will go some way to increasing the sensitivity where it is required, but when solutions are diluted (normally to 10-15% NaCl) – the system must be sensitive enough to ‘see’ at these low levels and resolve the peaks in the matrix. This often requires that only the axial view is used for the analysis.

Instrumentation and method development

A Thermo Scientific iCAP 6500 Duo ICP was chosen for this analysis, although the Thermo Scientific iCAP 6300 ICP Duo with nebulizer mass-flow control may be used as an alternative model configuration. A high solids kit (p/n 8423 120 51831) and an argon humidifier (p/n 8423 120 52081) were fitted to help with the handling of the high dissolved salt content of the samples.

Axial view was chosen for all elements due to the trace levels required. The system parameters (shown below in Table 1) were optimized with a 10% NaCl solution spiked at 500 ppb, using the Optimize Source function, which automatically optimizes pump speed, nebulizer gas flow, auxiliary gas flow, coolant gas flow and RF power for the Best Signal, Best SBR or Best DL. Best DL was chosen for this method.

Table 1: Instrument Parameters

Parameter	Setting
Pump tubing	Tygon orange/white sample White/white drain
Pump rate	50 rpm
Nebulizer	Aerosalt
Argon humidifier	Yes
Nebulizer gas flow	0.6 L/min
Spraychamber	Baffled Cyclonic
Centre tube	2 mm
Torch orientation	Duo (axial view)
RF forward power	1350 W
Coolant gas flow	12 L/min
Auxiliary gas flow	1 L/min
Integration time	5 seconds High/Low for Method 1 15 seconds High/Low for Method 2

Sample and calibration preparation

2 sources of brine were used for these studies which were procured from European brine manufacturers - Brine 1 was 10% brine from a food production factory, and Brine 2 was a 30% solution from an industrial chemical producer. Brine 2 was diluted 3X with deionized water to a 10% mixture. In the absence of a brine certified reference material (CRM), Brine 1 was spiked with 50 ppb of all elements to check the analyte recoveries in the matrix.

A calibration was prepared in deionized water at 0, 50 and 250 ppb for all elements (see Table 2 below). An yttrium internal standard was employed with a final concentration value of 1 ppm at the plasma. This was added online using the internal standards mixing kit (p/n 8423 120 51551).

Table 2: Analyte, plasma view and internal standard wavelengths

Element & Wavelength	View	Internal Standard Reference Line
Al 167.079 nm	Axial	Y 224.306 nm
Ba 455.403 nm	Axial	Y 324.228 nm
Ca 393.366 nm	Axial	Y 324.228 nm
Cu 324.754 nm	Axial	Y 324.228 nm
Fe 259.940 nm	Axial	Y 324.228 nm
Mg 279.553 nm	Axial	Y 324.228 nm
Mn 257.610 nm	Axial	Y 324.228 nm
Mo 202.030 nm	Axial	Y 224.306 nm
Ni 231.604 nm	Axial	Y 324.228 nm
P 177.495 nm	Axial	Y 224.306 nm
Pb 220.353 nm	Axial	Y 224.306 nm
Si 251.611 nm	Axial	Y 324.228 nm
Sr 407.771 nm	Axial	Y 324.228 nm
Ti 334.941 nm	Axial	Y 324.228 nm
V 292.402 nm	Axial	Y 324.228 nm
W 207.911 nm	Axial	Y 224.306 nm
Zn 202.548 nm	Axial	Y 224.306 nm

Analyses and results

Two methods were created – Method 1 was a fast screening method to mimic the analysis performed at Borregaard, Norway (see Customer Case Study on page 4). Method 2 used a longer integration time to improve detection limits, and to test the robustness of the sample introduction system over long periods of analysis and verify analytical performance in terms of sample recoveries.

Method 1 was analyzed with 20 samples and 2 calibrations (one after each 10 samples as shown in Figure 1). The entire run was completed in less than 1 hour without the requirement to perform user maintenance on the sample introduction system.

Method 2 was setup to acquire data in the format of 3 replicates of 30 seconds (15 for UV and 15 for VIS) and was applied to 100 samples (in the same analysis pattern as per Method 1 and Figure 1). Samples were analyzed over 2 days with the largest run consisting of 3 calibrations and 30 samples – this run took 2 hours and 30 minutes to

complete without the requirement to any perform user maintenance on the sample introduction system components.

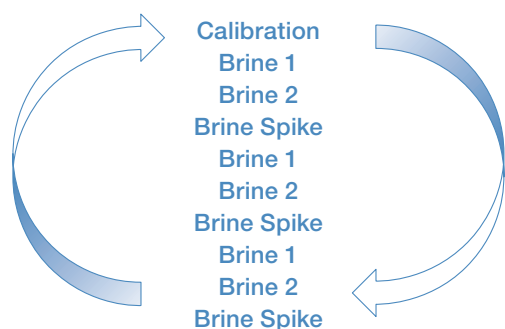


Figure 1: Analyses pattern for Methods 1 and 2

The results for Brines 1 and 2 were quite different, which is indicative of local procedures and plant treatments employed at the different sources and also their intended final use in different industries.

The averaged results from the 100 samples of Brines 1 and 2, analyzed with Method 2, are presented in Table 3. Results for Brine 2 were multiplied by 3 to correct for the dilution factor applied.

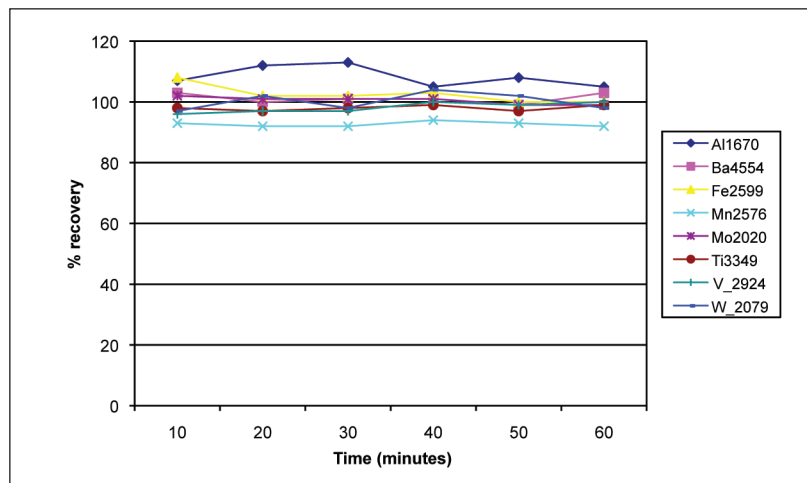
Table 3: Averaged results for Brine 1 and 2 using Method 2. All units are in ppb ($\mu\text{g/L}$).

Element & Wavelength	Brine 1	Brine 2
Al 167.079 nm	7.12	2.18
Ba 455.403 nm	0.54	0.40
Ca 393.366 nm	OR	1.2
Cu 324.754 nm	1.41	<DL
Fe 259.940 nm	35.23	60.94
Mg 279.553 nm	2.1	0.9
Mn 257.610 nm	0.12	<DL
Mo 202.030 nm	0.48	1.67
Ni 231.604 nm	0.90	1.26
P 177.495 nm	5.25	OR
Pb 220.353 nm	1.92	3.52
Si 251.611 nm	94.64	OR
Sr 407.771 nm	20.87	0.49
Ti 334.941 nm	0.26	0.38
V 292.402 nm	0.76	2.84
W 207.911 nm	2.42	5.27
Zn 202.548 nm	1.00	0.16

Key: <DL = Below detection limit; OR = Over calibration range (250ppb)

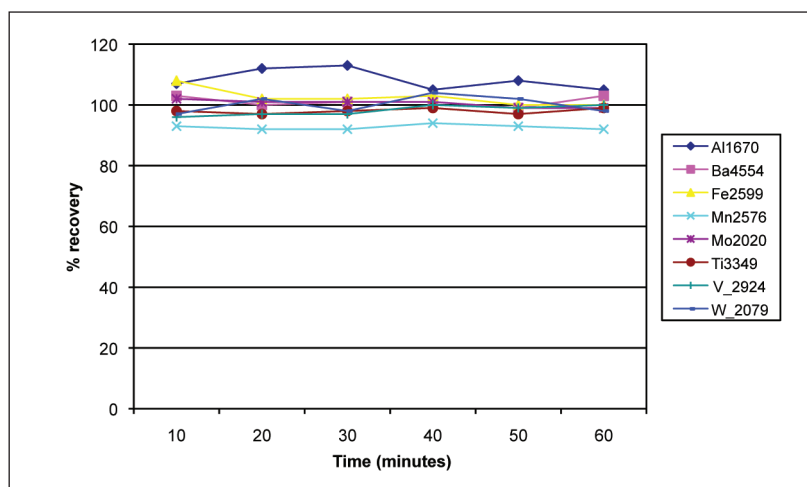
Recoveries and short/long term precision

The spiked samples were analyzed repeatedly with Methods 1 and 2 in order to determine the stability of the instrument over an extended period - 60 minutes for Method 1 and 150 minutes for Method 2. The short term precision averaged at <2 % RSD for Method 1 and <1 % RSD for Method 2 across all elements. The graphs below present a selection of the elements from both methods with their respective recoveries. It is worth noting that the integration time was not a significant factor in recoveries as both methods produced comparable data in the first hour. Graph 1 shows the data from Method 1 was excellent with +/- 5% accuracy realized for all elements except aluminium (which was still within +/- 15%).



Graph 1: Analytical stability over 1 hour in 10% brine at 50 ppb

Using Method 2 (recoveries in Graph 2) – no significant degradation in analyte signals was observed after 2 hours and 30 minutes of analysis, proving the outstanding long-term stability and robust sample introduction of the instrumentation. All elements showed +/- 15% accuracy with most (Al, Mn and Mo excepted) within +/-10%.



Graph 2: Analytical stability in 10% brine during a 2 hour and 30 minute analysis period

Detection limit study

A detection limit study was undertaken using a broad suite of elements and multiple wavelengths are reported for each element to highlight those which provide the optimum analytical performance. Both Brine 1 and 2 were analyzed using 10 replicates of 15 seconds (15 UV/ 15 VIS). The detection limits in Table 6 were obtained by multiplying the standard deviation of these brine sample measurements by 3.

Note: Detection limits were calculated without the use of an internal standard in order to account for all measurement noise, giving a conservative detection limit evaluation.

Table 6: Detection limit study using Method 2 parameters (15 second integration). All units are in ppb ($\mu\text{g/L}$).

Element & Wavelength	Brine 1	Brine 2
Al 167.079 nm	1.52	0.9477
Ba 233.527 nm	0.518	0.8414
Ba 455.403 nm	0.1491	0.5177
Ca 393.366 nm	OR	0.3
Cu 224.700 nm	5.286	15.25
Cu 324.754 nm	0.6757	5.401
Cu 327.396 nm	1.436	6.247
Fe 238.204 nm	4.884	2.599
Fe 239.562 nm	4.961	3.11
Fe 259.940 nm	4.568	2.124
Mg 279.553 nm	0.219	0.624
Mn 257.610 nm	0.449	1.331
Mo 202.030 nm	1.064	5.152
Ni 221.647 nm	25.93	4.044
Ni 231.604 nm	2.133	10.3
P 177.495 nm	43.73	39.13
P 178.284 nm	29.15	14.57
Pb 220.353 nm	21.57	20.17
Si 251.611 nm	10.87	9.497
Si 288.158 nm	6.352	25.45
Sr 407.771 nm	2.362	0.0772
Sr 421.552 nm	2.407	0.3328
Ti 334.941 nm	0.2921	0.7672
V 292.402 nm	0.4615	3.532
V 309.311 nm	0.2996	2.92
W 207.911 nm	9.196	12.98
W 224.875 nm	7.003	15.71
W 239.709 nm	13.56	76.26
Zn 202.548 nm	0.6126	1.208
Zn 213.856 nm	0.695	0.873

Key: OR = Over calibration range (250ppb)

Table 7, shows the detection limit data from clean water to 10% brine in comparison with the 10% Brine detection limit data (Brine 2) as shown above in Table 6. Detection limits shown for the clean water matrix are derived using the same analytical approach as the data derived in Table 6.

Table 7: Detection Limit comparison of clean water and brine 2, with typical maximum concentrations for pure brine (30%). * The most critical elements are Ca and Mg, which must not have a combined concentration value of more than 20 ppb in 30% purified NaCl. All units in this table are ppb ($\mu\text{g/L}$).

15 second detection limit comparison

Element & Wavelength	Clean water	Brine 2	Typical Maximum Values for Purified 30% Brine
Al 167.079 nm	0.12	0.9477	100
Ba 455.403 nm	0.03	0.5177	200
Ca 393.366 nm	0.003	0.3	5-20*
Cu 324.754 nm	0.39	5.401	–
Fe 259.940 nm	0.25	2.124	200
Mg 279.553 nm	0.006	0.624	0-10*
Mn 257.610 nm	0.07	1.331	10
Mo 202.030 nm	0.38	5.152	–
Ni 221.647 nm	0.14	4.044	10
P 177.495 nm	1.55	39.13	–
Pb 220.353 nm	1.06	20.17	10
Si 251.611 nm	0.87	9.497	5000 (as SiO_2)
Sr 407.771 nm	0.01	0.0772	50
Ti 334.941 nm	0.30	0.7672	–
V 292.402 nm	0.23	3.532	–
W 207.911 nm	0.83	12.98	–
Zn 202.548 nm	0.09	1.208	–

Customer case study

Borregaard is a Norwegian company, established in 1889 in the southeastern town of Sarpsborg in Østfold county. Its main products were traditionally pulp and paper, although the company now produces chemicals based on timber as a raw material. After acquisition in 1986, Borregaard is today part of the chemical division of the Orkla Group. The company's core business is based on a Biorefinery that manufactures products based on the different components in wood. Borregaard also produces caustic soda, hydrochloric acid and bleaching chemicals for internal use and for sale to external customers. Their old mercury cell electrolysis plant was replaced by a modern environmentally friendly membrane cell electrolysis plant, with the caustic soda produced being used in Borregaard's own factories, while the chlorine is processed to hydrochloric acid.

It is in this process that Borregaard uses an iCAP 6000 Series Duo for the analysis of the NaCl produced on site. One of the critical parameters of this process is the purity of the feed brine, with respect to the concentrations of Ca and Mg. The sum of these two elements must be less than 20 µg/L in 30 % NaCl. The raw brine is purified in two ion exchange columns, and an analysis is carried out to measure the impurities before, between and after these columns once a day. The routine analysis comprises approximately ten solutions included calibration standards, samples and control samples. Using a high solids kit and argon humidifier, the samples are analyzed from the factory line, so a fast turnaround is required. Consequently, their method uses only a 5 second integration time as this enables rapid screening and feedback to the factory. The iCAP 6000 Series instrument parameters used for brine analysis at Borregaard are shown in Table 8 for reference.

Detection limits obtained by Eivind Rosland of Borregaard are presented in Table 9. This data was achieved using the 3x standard deviation method using 5 second integration times and 3 replicate measurements per sample. The method did not use an internal standard. 22 samples derived from two brine sources were analyzed over a 3-day period and the average was calculated (the results are shown in Table 9). Both brine solutions were 15% w/v NaCl; sample (*bl*) is a Merck Suprapure 30% NaCl solution and sample (*etter*) is the in-house Borregaard NaCl solution from their factory which is sampled after the solution passes through the two ion exchange membranes - "etter" being the Norwegian for "after".

Looking at the detection limits in Table 9, it can be seen that the critical elements - calcium and magnesium, which cannot have a combined concentration value in excess of 20 ppb are both well within range for both the in-house and the external brine sample detection limit, which will allow for their easy analysis below these required levels. The in-house Borregaard sample is considerably contaminated with Sulfur, which is not a critical element in this process, although overall the two contamination of the two brines is low, assuring the quality of the brine produced on site and its accurate determination in this method and by comparison.

Table 8: Instrument parameters for Borregaard brine method

Parameter	Setting
Pump tubing	Tygon orange/white sample White/white drain
Pump rate	50 rpm
Nebulizer	Aerosalt
Argon Humidifier	Yes
Nebulizer gas flow	0.57 L/min
Spraychamber	Cyclonic
Centre tube	2 mm
Torch orientation	Duo (axial view)
RF forward power	1350 W
Coolant gas flow	12 L/min
Auxiliary gas flow	1 L/min
Integration time	5 seconds High/Low

Conclusions

The analysis of challenging sample matrices such as brines can be achieved easily using the Thermo Scientific iCAP 6000 Series ICP-OES through its outstanding robustness and elegant sample introduction. This enables long term analyses without loss of sensitivity or clogging of the system. It is clear that significant benefits in terms of detection limits can be realized by using a longer integration times, but this must be weighed against the requirement for fast analysis.

Similarly, the use of an internal standard offers enhanced stability to long term analyses by correcting for any dynamic drift on the system. However, as seen in the Borregaard case study, for small batches of samples, excellent detection limits can be realized without the use of internal standardization for fast, accurate analyses.

Acknowledgements

Kind thanks to Eivind Rosland of Borregaard, Sarpsborg, Norway for providing information and data for the Customer Case Study section.

Table 9: Borregaard method detection limits for their in-house fast screening method. All units are ppb ($\mu\text{g/L}$).

Element & Wavelength	(bl)	(etter)
Al 396.152 nm	10	10
Ba 455.403 nm	3	3
Ca 393.366 nm	2	1
Ca 396.847 nm	2	1
Cd 226.502 nm	0.3	0.4
Cd 228.802 nm	0.6	0.8
Co 228.616 nm	1	0.8
Cr 267.716 nm	1	1
Cu 224.700 nm	4	5
Cu 324.754 nm	1	1
Cu 327.396 nm	3	3
Fe 238.204 nm	1	2
Fe 239.562 nm	2	2
Fe 259.940 nm	1	2
Mg 279.553 nm	0.1	0.1
Mg 280.270 nm	0.2	0.2
Mn 257.610 nm	0.2	0.3
Mo 202.030 nm	2	1
Ni 221.647 nm	1	1
Ni 231.604 nm	2	2
P 177.495 nm	8	10
P 178.284 nm	10	20
Pb 220.353 nm	6	6
S 180.731 nm	200	102000
S 182.034 nm	200	73000
S 182.624 nm	200	51000
Si 251.611 nm	7	20
Sr 407.771 nm	0.1	0.1
Sr 421.552 nm	0.1	0.1
Ti 334.941 nm	0.6	0.6
V 292.402 nm	1	1
V 309.311 nm	0.8	1
W 207.911 nm	6	6
W 224.875 nm	7	10
W 239.709 nm	20	20
Zn 202.548 nm	0.4	0.5
Zn 213.856 nm	0.5	0.4

www.thermoscientific.com

©2012 Thermo Fisher Scientific Inc. All rights reserved. ISO is a trademark of the International Standards Organization. All other trademarks are the property of Thermo Fisher Scientific Inc. and its subsidiaries. This information is presented as an example of the capabilities of Thermo Fisher Scientific Inc. products. It is not intended to encourage use of these products in any manners that might infringe the intellectual property rights of others. Specifications, terms and pricing are subject to change. Not all products are available in all countries. Please consult your local sales representative for details.



Thermo Electron Manufacturing Ltd
(Cambridge) is ISO Certified.

Africa-Other +27 11 570 1840
Australia +61 3 9757 4300
Austria +43 1 333 50 34 0
Belgium +32 53 73 42 41
Canada +1 800 530 8447
China +86 10 8419 3588
Denmark +45 70 23 62 60
Europe-Other +43 1 333 50 34 0
Finland/Norway/Sweden
+46 8 556 468 00
France +33 1 60 92 48 00
Germany +49 6103 408 1014
India +91 22 6742 9434
Italy +39 02 950 591

Japan +81 45 453 9100
Latin America +1 561 688 8700
Middle East +43 1 333 50 34 0
Netherlands +31 76 579 55 55
New Zealand +64 9 980 6700
Russia/CIS +43 1 333 50 34 0
South Africa +27 11 570 1840
Spain +34 914 845 965
Switzerland +41 61 716 77 00
UK +44 1442 233555
USA +1 800 532 4752

AN40986_E 06/12C

Thermo
SCIENTIFIC
Part of Thermo Fisher Scientific