Prodigy ICP

Application Note: # 1040

The Analysis of Brine and Related Chemicals by Inductively Coupled Plasma – Optical Emission Spectroscopy

INTRODUCTION

The determination of metal contaminates in brine is important to industries worldwide. Commercially processed brines are routinely used in the manufacturing of products ranging from raw materials such as Sodium, Magnesium, Chlorine and Bromine to finished products like table salt, road deicing salts and water softening products. In another example, sodium sulfate [produced from brine] is used in the preparation of pulp, paper, textiles and glass. The analysis of trace elements in brines and related chemicals is necessary to ensure the safety and efficacy of the processes in which they are used. Interestingly, brines are also used by the oil industry to heighten the recovery of oil from wells. In this case, brine is injected into a well to force residual oil from the well and because the brine is being put back into the earth it must be monitored for potential environmental contaminates.

In addition to their commercial usefulness, brines can be a source of environmental contamination. For example, brines leaching into drinking water supplies can contaminate them to the point the water cannot be consumed without pretreatment. In an ironic twist, the Aral Sea (once the forth-largest inland sea and now a fraction of its original size) has been identified as a source of salt contamination of both water and air as far away as the Himalayan Mountains. Apparently, the salt that was dissolved in the sea and is now present in large quantities on exposed seabed has become airborne in windstorms and distributed over thousands of miles of adjacent land.

When it comes to the chemical analysis of brines by ICP, there are two main challenges that need to be overcome. The first is that the high concentration of easily ionized alkali elements in the samples can affect the results for the other elements of interest. The second is that the high level of dissolved solids in the samples can clog sample introduction components, specifically nebulizers. To combat this challenge, dilutions of the samples and/or long rinse times are common in the analysis of brines.

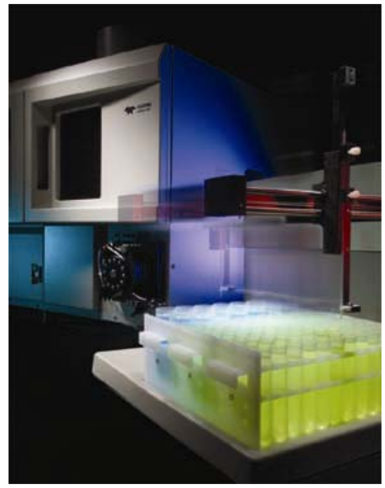
In this study 18 elements were measured in samples of Brine, $CaCl_2$, $FeCl_3$, HCl, NaOH and $NaClO_4$. For all samples except the HCL and NaOH, the Method of Standard Addition (MSA) was used. This was done because it was not possible to matrix match the remaining samples.

6 Wentworth Drive • Hudson, NH 03051 U.S.A.

Tel: 603 886 8400 • Fax: 603 886 9141 • www.leemanlabs.com

TELEDYNE LEEMAN LABS
A Teledyne Technologies Company

Instrument



A Prodigy High Dispersion Inductively Coupled Plasma (ICP) equipped with a dual view torch and an 88-position autosampler was used to generate the data for this application note.

The Prodigy is a compact bench-top simultaneous ICP-OES featuring an 800 mm focal length Echelle optical system coupled with a megapixel Large Format Programmable Array Detector (L-PAD). At 28 x 28 mm, the active area of the L-PAD is significantly larger than any other solid-state detector currently used for ICP-OES. This combination allows Prodigy to achieve significantly higher optical resolution than other solid-state detector based ICP systems. The detector also provides continuous wavelength coverage from 165 to 1100 nm permitting measurement over the entire ICP spectrum in a single reading without sacrificing wavelength range or resolution. This detector design is inherently anti-blooming and is capable of random access, non–destructive readout that results in a dynamic range of more than 6 orders of magnitude. For applications that require the measurement of chlorine, bromine or iodine an optional halogen detection system is available.

The Prodigy uses a 40.68 MHz free running, water-cooled oscillator, allowing it to handle even the most difficult sample matrices. A high sensitivity sample introduction system ensures that sufficient and steady emission signals are transmitted to the spectrometer. The torch and sample introduction system are uniquely integrated into the optical system through Prodigy's innovative Image Stabilization system, which treats the torch as an optical component by rigidly attaching it to the spectrometer.

The sample introduction system consists of a four-channel peristaltic pump, cyclonic spray chamber with a knockout tube, single piece quartz torch and a Glass Expansion SeaSpray AR30 Nebulizer. The specific operating conditions used in this work are described in **Table 1**.

Operating Parameters

Although Teledyne Leeman Labs generally recommends radial viewing for brine analysis, the lower limits of detection available with dual viewing were needed for some elements in the higher purity brines analyzed in this work. To avoid easily ionizable element interferences (EIEI) often seen with this type of matrix, radial view mode was used for those elements susceptible to EIEI effects (e.g. Na, K, Sr, etc.).

For each matrix analyzed, the wavelengths and background correction positions used are given in ***Tables 2 through 6***. Elements with the letter "r" after the wavelength were determined in the radial mode using a 5 second integration. (Elements determined radially are also displayed in bold text in the data tables.) The remaining elements were determined in the axial mode with a 30 second integration.

To prevent the torch from salting, a 120 second rinse time was used between samples. Again, an advantage of a dedicated radially viewed system for this application would be significantly higher tolerance to the high dissolved solid level.

For each wavelength, the Prodig*y* uses a 3 x 15 pixel subarray, which is centered on the wavelength of interest. Background correction points and the analytical peak have both position and width values within the subarray. In the table, the position value is designated by "x" in the column header, while "w" indicates the width. (Where w = 0, the background point was not used.) Pixels are numbered from left to right. The default position for the analytical peak is 7 with a width of 3. All data in the subarrays are collected simultaneously for each view. In addition, all pixel data are saved, permitting recalculation of results at a later time. ***Figure 1*** contains an example of the data contained in a subarray.

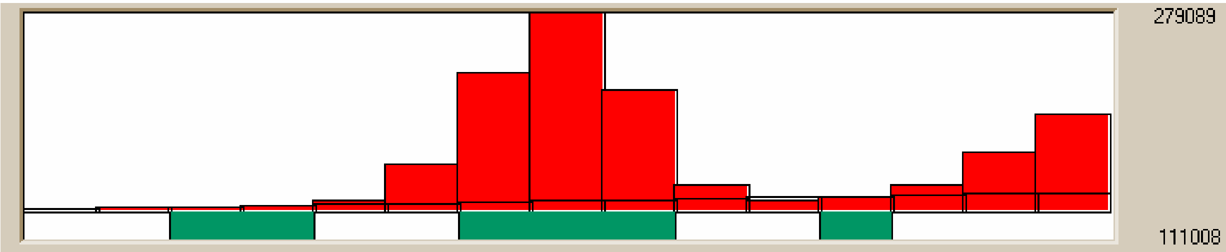


Figure 1. Sub-Array Data – Ca 317 nm line in the HC l Sample

Parameters	Setting	Part Number
RF Power	1.3 kW	
Torch Type	Dual View	120-00460-1
Coolant Flow	20 L/min	
Auxiliary Flow	0.0 L/m	
Nebulizer Pressure	34 psi	
Nebulizer Type	High Solids Concentric	120-00474-1
Spray Chamber	Cyclonic with Knock-Out	120-00461-1
Sample Uptake Rate	1.4 mL/min	
Sample Rinse Time	120 sec	

Table 1. ICP Operating Conditions

Line	BKG L X	BKG L W	PEAK X	PEAK W	BKG R X	BKG R W
Ca 393.366	2	3	7	3	12	2
Mg 279.553	1	3	7	3	12	2
Al 396.152	6	1	7	3	10	1
Si 251.611	2	3	7	3	13	1
Fe 259.940	6	1	7	3	10	1
Ba 455.403	3	1	7	3	15	1
Sr 407.771	1	1	7	3	12	1
Pb 220.353	1	0	7	3	10	1
Mn 257.610	2	2	7	3	13	3
Ni 221.648	2	1	7	3	14	1
Cr 267.716	2	1	7	3	11	1
As 189.042	3	0	7	3	10	1
Bi 223.061	4	1	7	3	15	1
Cd 214.441	3	1	7	3	11	1
Sn 189.991	2	1	7	3	11	1
V 292.401	6	1	7	3	10	1

Line	BKG L X	BKG L W	PEAK X	PEAK W	BKG R X	BKG R W
I 178.276	5	1	7	3	12	1
Zn 202.548	4	1	7	3	15	1

Table 2. Element Parameters for Brine Analysis

Line	BKG L X	BKG L W	PEAK X	PEAK W	BKG R X	BKG R W
Si 251.611	2	3	7	3	13	1
Fe 259.940	6	1	7	3	10	1
Ba 493.409	3	1	7	3	13	1
Sr 407.771 r	1	1	7	3	13	1
Pb 220.353	6	1	7	3	10	1
Mn 257.610	6	1	7	3	10	1
Ni 221.648	6	1	7	3	10	1
Cr 267.716	4	1	7	3	15	1
As 189.042	2	1	7	3	13	1
Cd 214.441	3	1	7	3	11	1
Sn 189.991	2	0	7	3	11	1
V 292.401	1	2	7	3	12	2
I 178.276	3	1	7	3	12	1
Zn 202.548	4	1	7	3	13	0
Na 588.995 r	4	1	7	3	14	1
Mg 279.078	1	1	7	3	15	1
Bi 223.061	4	1	7	3	13	0
Al 309.271	6	1	7	3	13	0

Table 3. Element Parameters for $CaCl_2$ Analysis

Element	LBG X	LBG W	PEAK X	PEAK W	RBG X	RBG W
Al 396.152	3	0	7	3	13	1
Si 251.611	2	3	7	3	13	1
Fe 259.940	3	0	7	3	13	1
Ba 493.409	1	3	7	3	13	3
Sr 407.771	5	1	7	3	10	1
Pb 220.353	1	1	7	3	11	1
Mn 257.610	6	1	7	3	10	1
Ni 221.648	1	1	7	3	13	1
Cr 267.716	4	1	7	3	12	1
As 189.042	1	1	7	3	10	1
Cd 214.441	3	1	7	3	15	1
Sn 189.991	2	0	7	3	12	1
V 292.401	1	1	7	3	11	1
I 178.276	2	1	7	3	13	1

Element	LBG X	LBG W	PEAK X	PEAK W	RBG X	RBG W
Zn 202.548	4	2	7	3	15	1
Mg 279.078	1	1	7	3	11	1
Bi 223.061	4	1	7	3	15	1
Ca 393.366	3	1	7	3	13	1

Table 4. Element Parameters for Hypochlorite Analysis

Element	LBG X	LBG W	PEAK X	PEAK W	RBG X	RBG W
Ca 317.933	3	2	7	3	12	1
Mg 279.553	1	3	7	3	13	3
Al 396.152	6	1	7	3	10	1
Si 251.611	2	3	7	3	15	1
Fe 259.940	6	1	7	3	10	1
Ba 455.403	3	1	7	3	10	1
Sr 407.771	6	1	7	3	10	1
Pb 220.353	6	1	7	3	10	1
Mn 257.610	6	1	7	3	10	1
Ni 221.648	3	1	7	3	10	1
Cr 267.716	4	1	7	3	10	1
As 189.042	3	0	7	3	10	1
Bi 223.061	3	1	7	3	15	1
Cd 214.441	3	1	7	3	10	1
Sn 189.991	3	1	7	3	12	1
V 292.401	6	1	7	3	10	1
I 178.276	3	1	7	3	12	1
Zn 202.548	4	2	7	3	15	1
Na 589.592	3	1	7	3	13	1

Table 5. Element Parameters for HCl and NaOH Analysis

Element	LBG X	LBG W	PEAK X	PEAK W	RBG X	RBG W
Mg 279.553	5	1	7	3	14	2
Al 396.152	3	0	7	3	15	1
Si 251.611	1	2	7	3	12	1
Ba 493.409	4	1	7	3	10	1
Sr 407.771	4	1	7	3	10	1
Pb 220.353	5	1	7	3	11	3
Mn 257.610	4	0	7	3	12	1
Ni 221.648	2	1	7	3	13	1
Cr 267.716	6	1	7	3	12	1
As 189.042	4	0	7	3	10	1
Cd 226.502	6	1	7	3	11	1
Sn 189.991	4	1	7	3	10	1
I 178.276	2	3	7	3	12	1

Element	LBG X	LBG W	PEAK X	PEAK W	RBG X	RBG W
Bi 223.061	3	1	7	3	10	1
Ca 393.366	6	1	7	3	15	1
Zn 206.200	1	1	7	3	15	1
Na 589.592	3	1	7	3	14	1
V 309.311	3	1	7	3	13	2

Table 6. Element Parameters for $FeCl_3$ Analysis

Calibration

For the brine, $CaCl_2$, Hypochlorite and $FeCl_3$ the method of standard additions (MSA) was performed by spiking each of the samples with 100 and 250 ppb of each of the analytes. The Prodigy software was then used to calculate the concentrations of the analytes in the unspiked samples. These data are listed in ***Tables 8 through 11***.

For the HCl and NaOH samples, calibration curves were created using the standard concentrations listed in ***Table 7***. A typical calibration curve is displayed in ***Figure 2***. These standards were made up in 10% HCl. Sc was used as an internal standard to correct for any viscosity differences. Each of samples was also spiked with 250 ppb of each analyte and the % Recovery was calculated. The results for these samples are in ***Tables 12 and 13***.

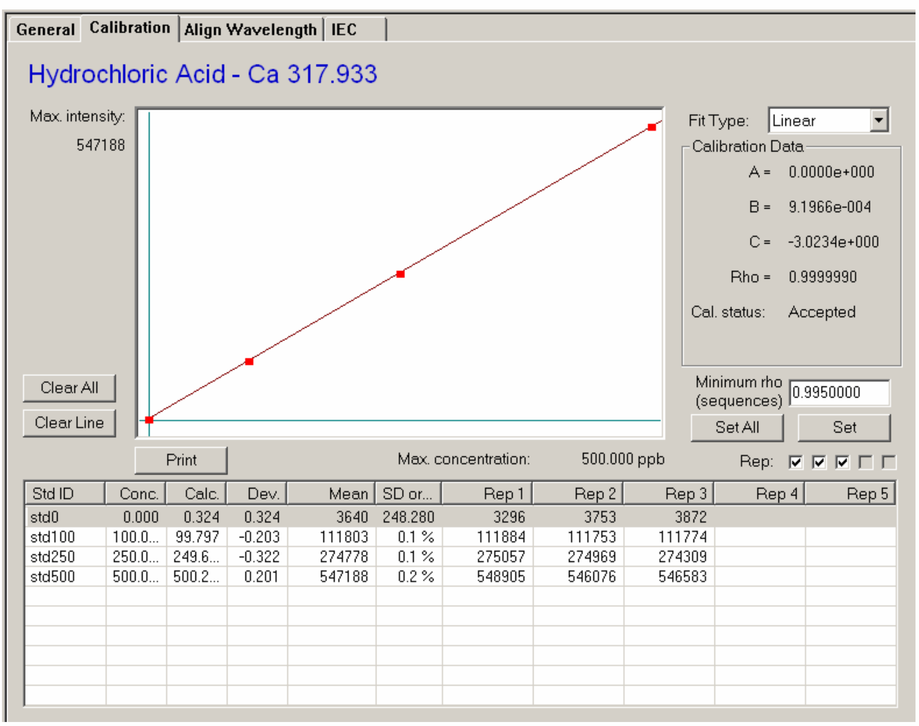


Figure 2. Ca Calibration Curve for HCl and NaOH Samples

Element	std0	std1	std2	std3
Ca 317.933	0	100	250	500
Mg 279.553	0	100	250	500
Al 396.152	0	100	250	500
Si 251.611	0	100	250	500
Fe 259.940	0	100	250	500
Ba 455.403	0	100	250	500
Sr 407.771	0	100	250	500
Pb 220.353	0	100	250	500
Mn 257.610	0	100	250	500
Ni 221.648	0	100	250	500
Cr 267.716	0	100	250	500
As 189.042	0	100	250	500
Bi 223.061	0	100	250	500
Cd 214.441	0	100	250	500
Sn 189.991	0	100	250	500
V 292.401	0	100	250	500
I 178.276	0	100	250	500
Zn 202.548	0	100	250	500
Na 589.592	0	100	250	500

Table 7. Calibration Standards for the HCl and NaOH Samples (ppb)

Results

The results of all the sample analyses are contained in ***Tables 8 through 13***. The concentrations listed are those in the samples as analyzed and do not reflect any dilutions.

Spike recoveries were excellent, ranging from approximately 85 – 111%.

Brine	Primary	Ultra	
Ca 393.366	190.5	6.926	ppb
Mg 279.553	4.155	0.005	ppb
Al 396.152	ND	ND	ppb
Si 251.611	514.4	579.9	ppb
Fe 259.940	ND	0.994	ppb
Ba 455.403	3.772	2.742	ppb
Sr 407.771	48.92	1.732	ppb
Pb 220.353	43.63	72.63	ppb
Mn 257.610	0.382	2.902	ppb
Ni 221.648	7.726	13.60	ppb
Cr 267.716	ND	1.925	ppb
As 189.042	ND	ND	ppb
Bi 223.061	6.868	10.31	ppb
Cd 214.441	6.625	7.421	ppb
Sn 189.991	8.866	17.11	ppb
V 292.401	5.169	5.524	ppb
I 178.276	49.69	91.37	ppb
Zn 202.548	0.485	2.034	ppb

Table 8. Brine Sample Results - Method of Standard Additions

CaCl2		
Si 251.611	10.05	ppb
Fe 259.940	5.114	ppb
Ba 493.409	174.8	ppb
Sr 407.771 r	0.104	ppm
Pb 220.353	21.46	ppb
Mn 257.610	5.784	ppb
Ni 221.648	ND	ppb
Cr 267.716	8.594	ppb
As 189.042	ND	ppb
Cd 214.441	9.173	ppb
Sn 189.991	5.066	ppb
V 292.401	15.10	ppb
I 178.276	ND	ppb
Zn 202.548	11.27	ppb
Na 588.995 r	225.9	ppm
Mg 279.078	48.27	ppm
Bi 223.061	159.8	ppb
Al 309.271	ND	ppb

Table 9. $CaCl_2$ Sample Result - Method of Standard Additions

Hypochlorite		
Al 396.152	50.93	ppb
Si 251.611	276.5	ppb
Fe 259.940	104.4	ppb
Ba 493.409	ND	ppb
Sr 407.771	2.099	ppb
Pb 220.353	19.73	ppb
Mn 257.610	3.904	ppb
Ni 221.648	8.306	ppb
Cr 267.716	23.06	ppb
As 189.042	ND	ppb
Cd 214.441	3.771	ppb
Sn 189.991	26.46	ppb
V 292.401	1.440	ppb
I 178.276	28.40	ppb
Zn 202.548	0.783	ppb
Mg 279.078	0.001	ppb
Bi 223.061	149.2	ppb
Ca 393.366	200.3	ppb

Table 10. Hypochlorite Sample Results - Method of Standard Additions

$FeCl_3$		
Mg 279.553	491.8	ppb
Al 396.152	4336	ppb
Si 251.611	2379	ppb
Ba 493.409	50.2	ppb
Sr 407.771	19.3	ppb
Pb 220.353	647.1	ppb
Mn 257.610	52.48	ppm
Ni 221.648	1585	ppb
Cr 267.716	2139	ppb
As 189.042	4.743	ppb
Cd 226.502	672.7	ppb
Sn 189.991	97.19	ppb
I 178.276	244.5	ppb
Ca 393.366	3171	ppb
Zn 206.200	245.2	ppb
V 309.311	791.4	ppb
Bi 223.061	57.6	ppb
Na 589.592	1324	ppb

Table 11. FeCl3 Sample Results - Method of Standard Additions

HCL	Unspiked	Spiked	% recovery
Ca 317.933	128.1	365.3	94.9
Mg 279.553	5.118	244.8	95.9
Al 396.152	3.490	231.9	91.4
Si 251.611	54.16	294.7	96.2
Fe 259.940	ND	243.0	99.8
Ba 455.403	4.323	256.2	100.7
Sr 407.771	0.175	254.1	101.6
Pb 220.353	6.677	250.8	97.7
Mn 257.610	0.148	241.5	96.5
Ni 221.648	ND	238.6	96.0
Cr 267.716	0.961	243.7	97.1
As 189.042	3.054	238.1	94.0
Bi 223.061	26.55	232.5	82.4
Cd 214.441	0.016	245.7	98.3
Sn 189.991	1.695	239.5	95.1
V 292.401	0.169	245.3	98.1
I 178.276	25.62	252.3	90.7
Zn 202.548	1.200	240.5	95.7
Na 589.592	177.6	416.2	95.4

Table 12. HCl Sample Results, ppb

NaOH	Unspiked	Spiked	% recovery
Ca 317.933	86.19	339.6	101.4
Mg 279.553	7.88	248.5	96.3
Al 396.152	22.46	304.9	113.0
Si 251.611	45.64	323.7	111.2
Fe 259.940	25.10	270.2	98.0
Ba 455.403	0.69	214.2	85.4
Sr 407.771	0.27	221.0	88.3
Pb 220.353	0.52	222.6	88.8
Mn 257.610	1.63	234.0	93.0
Ni 221.648	ND	220.8	88.9
Cr 267.716	4.21	243.1	95.6
As 189.042	ND	272.0	109.0
Bi 223.061	29.78	288.7	103.6
Cd 214.441	-0.01	236.6	94.6
Sn 189.991	-0.55	230.0	92.2
V 292.401	-0.29	249.9	100.1
I 178.276	-9.75	236.5	98.5
Zn 202.548	6.45	237.6	92.4

Table 13. NaOH Sample Results, ppb

Conclusion

The data presented in this report illustrate the ability of the Leeman Labs *Prodigy* High Dispersion ICP to provide accurate analyses of a variety of chemicals typically encountered in Brine applications.

The high solids sample introduction system performs without any clogging of the torch or nebulizer.

The image stabilized plasma and the simultaneous data collection of both peak and background data combine to provide exceptionally precise and stable results.