Application Note

Brine analysis with the ULTIMA 2 ICP-AES

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1 Introduction

Salt is popular due to its use in cooking but there are many other applications using salt as a brine which is a saturated solution of salt, i.e., a solution containing 20 to 30% sodium chloride. The food industry uses brines for food preservation in both human and animal nutrition. However, the food industry represents only 30% of the worldwide salt consumption. The chemical industry consumes 60% of the salt production, using it mainly as brine to produce chemicals such as chlorine, caustic soda and soda ash in the chlor-alkali industry and to produce pure metals such as Sodium and Magnesium. The petrochemical industry also makes use of brines for well drilling muds to inhibit fermentation, increase density and to stabilize drilling in rock salt formations. The last 10% of salt production is used for road de-icing, water treatment and other smaller applications.

Production of salt is mainly done by solar evaporation of seawater or inland brines (solar salt) and by mining rock salt deposits (rock salt called Halite). Annual production is exceeds 250 million metric tons and is increasing, due to the growing demand from the Chinese chemical industry. Since salt's value increases with purity, industrial production is focussed on making the purest sodium chloride possible.

Analysis of traces elements is then essential for salt production and it has to be done on brines to allow the determination of low concentrations. It is also a major issue for the use of brines in the food industry to ensure that no heavy metals are present and for the chemical production to avoid any contamination in production of chemicals that may result in lethal consequences. For example, excessive magnesium content in the salt brine of electrolytic cells will cause hydrogen evolution on the anode and hydrogen mixed with chlorine form an explosive mixture causing damage to the equipment and release of chlorine that is very toxic and dangerous to the environment.

This application note will describe the analysis of brines using the ULTIMA 2 ICP-AES, that is ideal for brine analysis as it does not require dilution of the samples and it allows the analysis of many elements with low detection limits.

2 Sample preparation

Samples are prepared by dissolution of NaCl in water to obtain a final concentration of 250 g/L. To enhance the reliability of the analysis, the method of standard additions is used.

Using standard addition allows working in the matrix, eliminating any bias due to matrix effects that may occur in the plasma, due to the difference of composition between standards and samples. Moreover, this method eliminates the need to use high purity reagents that may not be pure enough for the analysis.

Due to the absence of reference materials, spikes are done on a brine sample, using multi-element solution standards, to evaluate the stability and the accuracy of the method.

3 Operating conditions

The characteristics of the ULTIMA 2 used for this study are given in Table 1.

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Table 1: Specification of the ULTIMA 2 ICP Spectrometer

Parameter	Specification
Optical mounting	Czerny Turner
Focal length	1 m
Far UV option	Yes
Gratings: number of grooves per mm	2400 g/mm
Resolution	5 pm 120-320 nm 10 pm 320-800 nm
Thermoregulation	32 +/- 0.1 °C
Type of generator	40.68 MHz Solid state, water-cooled
Torch	Vertical Radial view with Total Plasma View*

* Total Plasma View measurement of the whole Normal Analytical Zone of the plasma for enhanced sensitivity

Table 2: Specification of the sample introduction system

Parameter	Specification
Nebulizer	Concentric K3 nebuliser
Spray chamber	Cyclonic glass spray chamber
Sample uptake	1 mL/min
Argon humidifier	Yes
Injector tube diameter	3 mm
Pump tubing	Black-black pump tubing for sample Grey-grey pump tubing for drain

A concentric K3 nebuliser associated with a cyclonic glass spray chamber is used in combination with the patented argon humidifier that uses membrane technology for unmatched efficiency. The concentric K3 nebulizer allows a good stability in the aerosol creation and the cyclonic spray chamber leads to improved detection limits compared to double pass spray chambers.

The ULTIMA 2 is equipped with a unique fully demountable torch, 3 mm i.d. alumina injector and the HORIBA Jobin Yvon patented sheath gas device. The 3 mm i.d. injector increases the residence time of the sample in the plasma leading to enhanced sensitivity and reduced matrix effects, while the sheath gas reduces the contact between the injector and the sample, eliminating deposit issues and memory effects.

The plasma parameters and gas flows are optimized for the best sensitivity along with long term stability and are given in Table 3.

Table 3: Operating conditions of the spectrometer

Parameter	Specification
RF generator power	1200 W
Plasma gas	14 L/min
Auxiliary gas	0.8 L/min
Sheath gas	0.3 L/min
Nebulizer flow	0.8 L/min

All measurements are performed using a 20/15 µm slit combination with integration time ranging from 3 to 10 seconds according to the element.

4 Analytical results

A pure grade NaCl blank at 250 g/L was used to evaluate the detection limits. This blank was analyzed 10 times after calibration and the detection limit is defined as follows:

DL=3 x S_B, where DL is the detection limit in µg/L and S_B is the standard deviation, in µg/L, of the 10 measurements of the blank.

A sample was also analyzed and spiked to evaluate the ability of the ULTIMA 2 to give reliable results without any bias. The stability was evaluated by a 5 hour analysis without any recalibration or internal standard.

4.1 Detection limits

The detection limits, calculated according to the formula already described, are given in Table 4. Due to the difficulty to obtain a pure blank for Ca, Mg, Sr, K, Si and Ba, the detection limits obtained for these elements are not as low as can be expected.

Table 4: Detection limits in µg/L estimated on a 250 g/L NaCl blank.

Element	Wavelength (nm)	LOD (µg/L)	Element	Wavelength (nm)	LOD (µg/L)
Al	167.020	0.98	Mg	279.553	0.16
Al	396.152	2.3	Mn	257.610	0.17
As	189.042	2.9	Mo	202.030	1.4
B	249.773	2	Ni	221.647	1.6
Ba	455.403	0.10	P	178.229	2.6
Be	313.042	0.24	Pb	220.353	6.3
Ca	396.847	0.15	Si	251.611	7
Cd	228.802	0.24	Si	212.412	8
Co	228.616	1.3	Si	288.458	12
Cr	205.552	0.98	Sn	189.989	2.5
Cr	267.716	1.1	Sr	407.771	0.21
Cu	324.754	0.48	Ti	337.280	0.78
Fe	259.940	0.87	Tl	190.864	5.1
K	766.490	40	V	292.402	1.2
Li	670.784	2	Zn	213.856	0.15

The detection limits are excellent for all the elements and quite close to those obtained in water even for difficult elementas such as As, Pb, Sn, Tl. This is due to the radial viewing mode of the plasma and to the 3 mm i.d. injector that reduce the matrix effects observed in the plasma.

Table 5: Results of the quantitative analysis for unspiked, spiked samples and recoveries

Element		Brine sample		Brine sample + spike (100 µg/L)			
		Conc (mg/L)	RSD (%)	Conc (mg/L)	RSD (%)	Expected Conc (mg/L)	Recovery (%)
Al	167.020	0.234	1.0	0.338	0.4	0.334	101
Al	396.152	0.274	1.4	0.368	2.1	0.374	98
As	189.042	0.028	7.5	0.120	3.5	0.128	94
B	208.959	6.61	0.5				
B	249.773	6.72	0.5				
Ba	455.403	0.059	0.3	0.154	0..3	0.159	97
Be	313.042	0.0011	4.0	0.097	0.7	0.101	96
Ca	317.933	13.6	0.6				
Cd	228.802	< 0.0002		0.102	0.6	0.100	102
Co	228.616	< 0.0013		0.097	0.8	0.100	97
Cr	267.716	< 0.0011		0.098	1.2	0.100	98
Cu	324.754	< 0.0005		0.103	1.0	0.100	103
Fe	259.940	0.002	6.5	0.104	0.9	0.102	102
K	766.490	19.35	1.4				
Li	670.784	0.210	1.6	0.304	1.0	0.310	98
Mg	280.270	0.018	1.2	0.125	0.6	0.118	106
Mn	257.610	< 0.0002		0.095	0.4	0.100	95
Mo	202.030	< 0.0014		0.104	0.9	0.100	104
Ni	221.647	< 0.0016		0.096	0.9	0.100	96
P	178.229	0.067	3.8	0.175	1.4	0.167	105
Pb	220.353	< 0.006		0.095	2.6	0.100	95
Si	212.412	5.85	1.5				
Si	251.611	5.87	0.8				
Si	288.158	5.8	0.4				
Sn	189.989	0.013	12.8	0.120	1.9	0.113	106
Sr	407.771	0.154	0.4	0.250	0.2	0.254	98
Ti	337.280	0.003	8	0.101	0.3	0.103	98
Tl	190.864	< 0.005		0.095	2.6	0.100	95
V	292.402	0.004	6.3	0.102	1.3	0.104	98
Zn	206.200	0.004	2.3	0.107	0.7	0.104	103
Zn	213.856	0.006	0.7	0.102	0.4	0.106	97

4.2 Sample analysis

A brine sample and the same sample spiked with 100 µg/L of a multi-element solution were analyzed. Results of the quantitative analysis for both the unspiked and the spiked samples as well as recoveries obtained on the spiked sample are given in Table 5.
Elements with concentrations much higher than the spike were not determined as the variation of concentration was not significant.

The RSD obtained, even on low concentrations, as well as the excellent recoveries on the 100 µg/L spiked sample, illustrate the excellent sensitivity, robustness and short-term stability of the ULTIMA 2.

4.3 Stability test

A stability test was performed on a 250 g/L NaCl blank spiked with 200 µg/L of a multi-element solution. The test was performed without internal standard or recalibration over 5 hours. The graphic of the normalized intensities is given in Figure 1. The RSD obtained is less than 1.5%, showing the excellent long-term stability of the ULTIMA 2 thanks to the vertical torch, the 3 mm i.d. injector and the original sheath gas device.

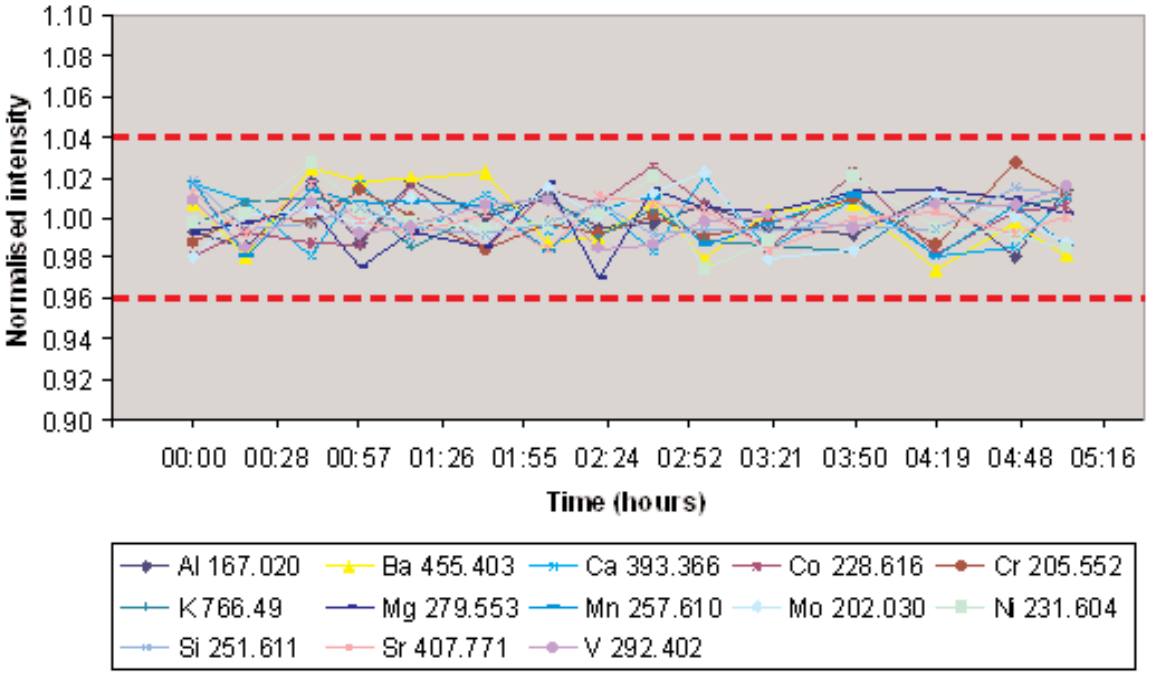

Figure 1. Stability test on a 250 g/L NaCl sample over 5 hours.

5. Conclusions

The analysis of brines can be easily performed using the ULTIMA 2. Low detection limits are obtained due to the ability of the system to perform the analysis without any dilution thanks to the 3 mm i.d. injector associated with radial viewing and the Total Plasma view that minimize matrix effects and enhance sensitivity. The sheath gas device allows perfect short and long-term stability of the system for routine analysis, without any internal standard, recalibration, or drift correction procedure. Good long term stability allows the use of the best plasma parameters and integration times for enhanced performance.