AN APPLICATION REPORT FROM
SPECTRO ANALYTICAL INSTRUMENTS

ICP-119

SPECTROGREEN

Analysis of 200 g/L NaCl-Solutions by ICP-OES with Single Radial and Dual-Side-On Interface Plasma Observation

Introduction

The electrolysis of NaCl using direct current is one of the basic processes in the chemical industry. In this chlor-alkaline electrolysis chlorine, caustic soda and hydrogen are produced simultaneously:

$$2\ H_2O + 2\ NaCl \rightarrow H_2 + 2\ NaOH + Cl_2$$

Chlorine is produced at the anode:

$$2\ Cl^- \rightarrow Cl_2 + 2e^-$$

At the cathode the reaction is:

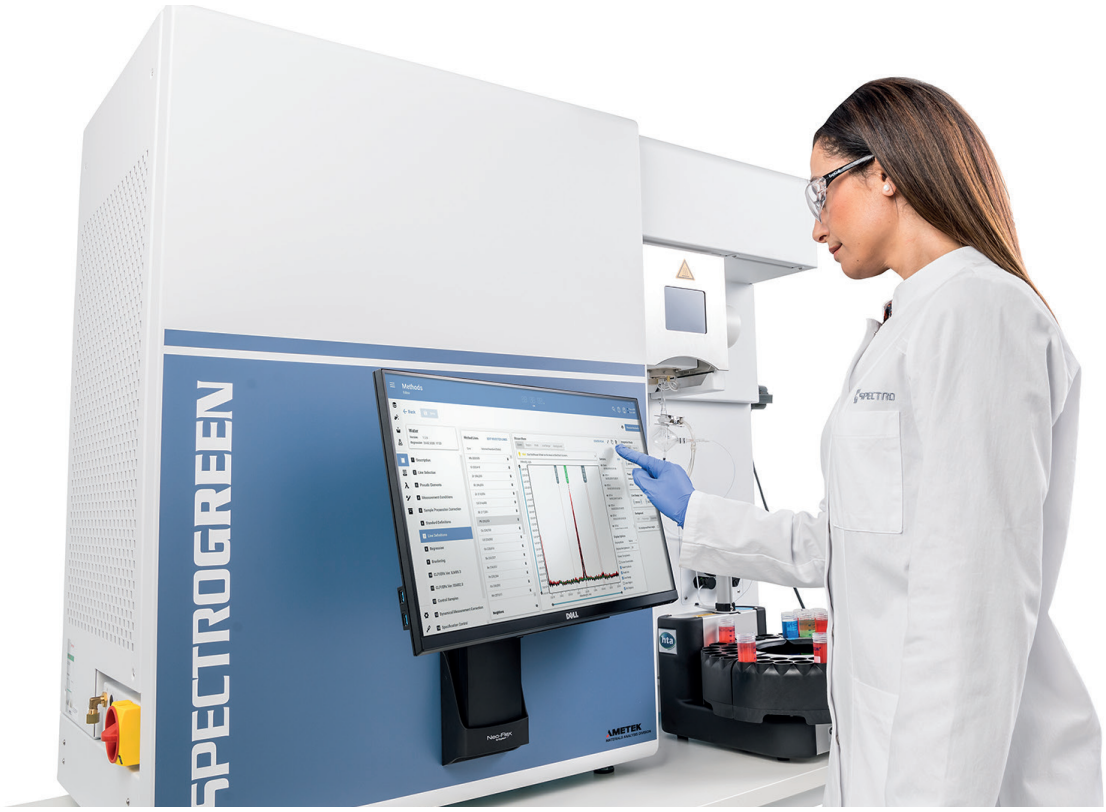
$$2\ H_2O \rightarrow H_2 + 2\ OH^-$$

Especially with modern membrane processes extremely low concentrations of Al, Ba, Ca, Mg and Sr at a µg/kg-level in the feed brine are required to protect the electrolysis cells. The limiting concentrations of impurities in NaCl for a selection of elements are given in Table 1.

Table 1: Typical feed brine purity requirements for the electrolysis of sodium chloride (selection)

Element	Limiting Value (µg/kg)	Typical Concentration (µg/kg)
Ca + Mg	20	2-3
Al	50	10-20
Ba	100	
I	100	< 50
Ni	10	
Hg	100	
Br	50000	
Sr	400	
Fe	50	
SiO_2	5000	
Sum: Cr, Mo, Cu, Co, Mn, Ni, Zn, Pb, As, Sb	200	

2 Analysis of 200 g/L NaCl-Solutions by ICP-OES with Single Radial and Dual-Side-On Interface Plasma Observation



The SPECTROGREEN with dual side-on and single radial plasma observation was investigated for the analysis of brines used for the electrolysis of alkaline chlorides. The trace elements were directly determined in 200 g/L NaCl solutions. With both techniques the required sensitivity for Ca, Mg, Sr, Ba, Al, Fe, Cu, Hg and P, needed to fulfill high purity specifications, can be achieved with one single method. Using the DSOI interface, the sensitivity could be increased by an average factor of 1.5 compared to single radial plasma observation.

This report describes the principle methodology for the analysis of brine solutions. Detection limits for the typical range of elements are presented.

Experimental

Instrumentation

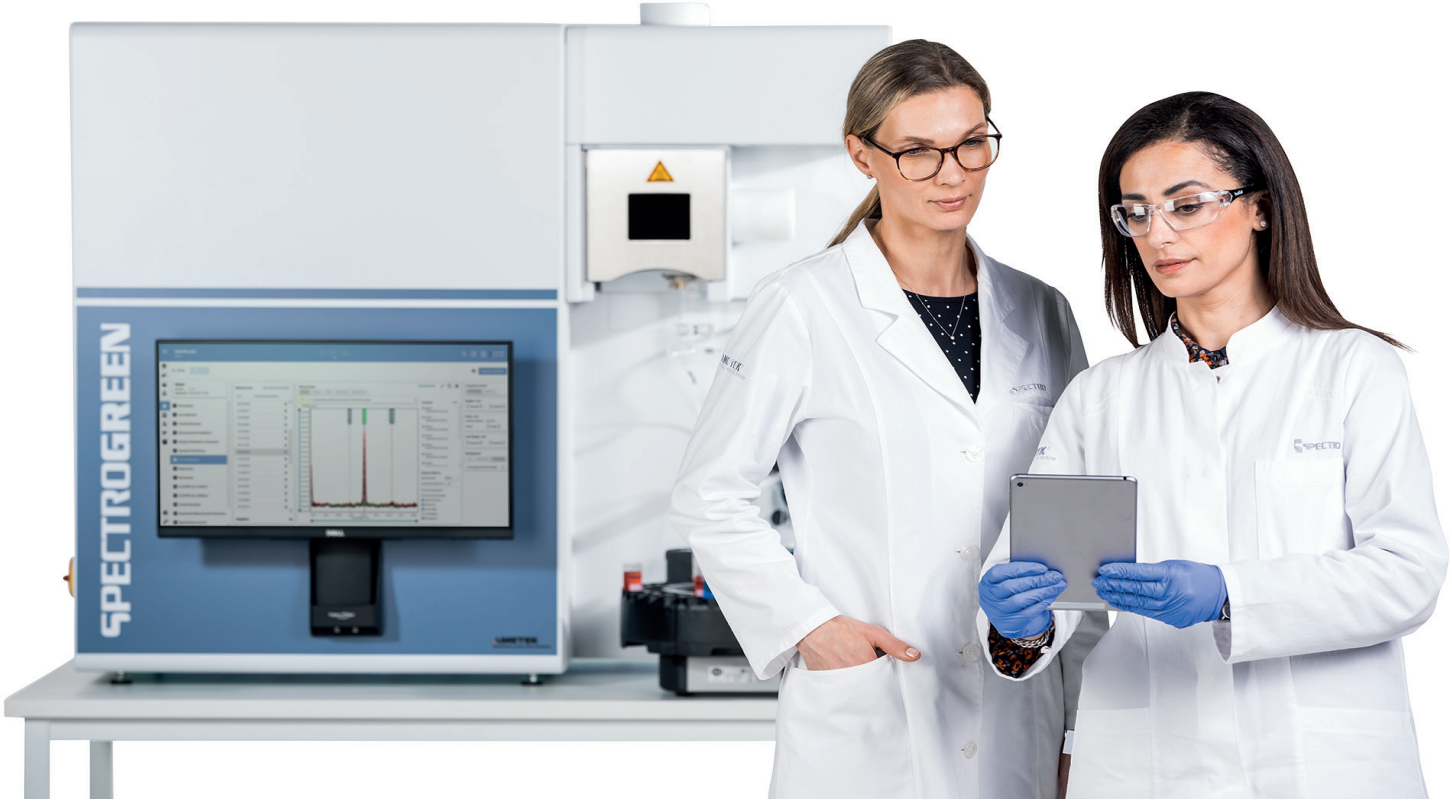
All measurements were performed with the SPECTROGREEN ICP optical emission spectrometer (SPECTRO Analytical Instruments, Kleve, Germany) with single radial and dual side-on plasma observation. The latter provides enhanced sensitivity compared to single radial plasma observation for many elements. In addition, it offers a high matrix compatibility, large linear dynamic range and excellent precision without the need to change the plasma observation mode during analysis. The SPECTROGREEN features a Paschen-Runge spectrometer mount, employing the proprietary Optimized Rowland Circle Alignment (ORCA polychromator) technique. Consisting of two hollow section cast shells, optimized small volume and 15 linear CMOS detectors, the wavelength range between 165 and 770 nm can be analyzed, allowing complete spectrum capture within 3 s. Due to the unique reprocessing capabilities of the system, a new measurement is not required even if additional elements or lines are to be determined at a later point in time.

The optic is hermetically sealed and filled with argon, continuously circulated through a filter, which absorbs oxygen, water vapor and other species. High optical transmission in the UV is achieved, allowing the determination of non-metals as well as the use of prominent and interference free lines in this region.

An air-cooled, 27.12 MHz, free running type LDMOS ICP-generator is installed, which ensures excellent stability of the forward power even in the case of rapidly changing sample loads. All relevant ICP operating parameters are software controlled, allowing easy selection of the optimum operating conditions.
For sample introduction, a Cross Flow nebulizer, a Scott type spray chamber and an argon humidifier were used. The ICP operating conditions are given in Table 2.

Table 2: Typical ICP operating conditions for Dual-Side-On Interface and Single Radial Interface

	Dual-Side-On Interface	Side-On Interface
Power	1150 W	1400 W
Observation Mode	Dual-Side-On	Single Radial
Coolant flow	14.0 L/min	
Auxiliary flow	2.0 L/min	
Nebulizer flow	0.90 L/min	0.85 L/min
Plasma Torch	Quartz, fixed, 3.0 mm Injector tube	
Spray Chamber	Double pass (Scott type)	
Nebulizer	Cross Flow	
Sample aspiration rate	2 mL/min	
Replicate read time	57 s per replicate	



Calibration

The standards were prepared with a matrix concentration of 200 g/L NaCl of "suprapure" quality [1]. For calibration, a commercially available multi-element standard [2] was used. All standards were acidified with 1% HNO_3 (v/v) [3] and 2 mg/L Sc [4] was added as an internal standard to all solutions. The concentrations of the resulting calibration standards are given in the following table 3.

Table 3: Calibration standards

Element	Std.1 [mg/L]	Std.2 [mg/L]	Std.3 [mg/L]	Std.4 [mg/L]
Al	0	0.1	0.5	2
As	0	0.1	0.5	2
B	0	0.1	0.5	2
Ba	0	0.1	0.5	2
Be	0	0.1	0.5	2
Ca	0	0.1	0.5	2
Cd	0	0.1	0.5	2
Co	0	0.1	0.5	2
Cr	0	0.1	0.5	2
Cu	0	0.1	0.5	2
Fe	0	0.1	0.5	2
Hg	0	0.1	0.5	2
K	0	0.5	2.5	10
Li	0	0.1	0.5	2

Element	Std.1 [mg/L]	Std.2 [mg/L]	Std.3 [mg/L]	Std.4 [mg/L]
Mg	0	0.1	0.5	2
Mn	0	0.1	0.5	2
Mo	0	0.1	0.5	2
Ni	0	0.1	0.5	2
P	0	0.5	2.5	10
Pb	0	0.1	0.5	2
Sc	2	2	2	2
Si	0	0.1	0.5	2
Sn	0	0.1	0.5	2
Sr	0	0.1	0.5	2
Tl	0	0.1	0.5	2
V	0	0.1	0.5	2
Zn	0	0.1	0.5	2

Results

Table 4 shows the selected wavelengths and the limits of detection (LOD) achieved. The LODs were calculated according to the equation [5]:

$$LOD = 3\ RSD_b\ c/\ 100\ SBR$$

Where:

RSD_b: - relative standard deviation of 10 replicates of the blank (in %)

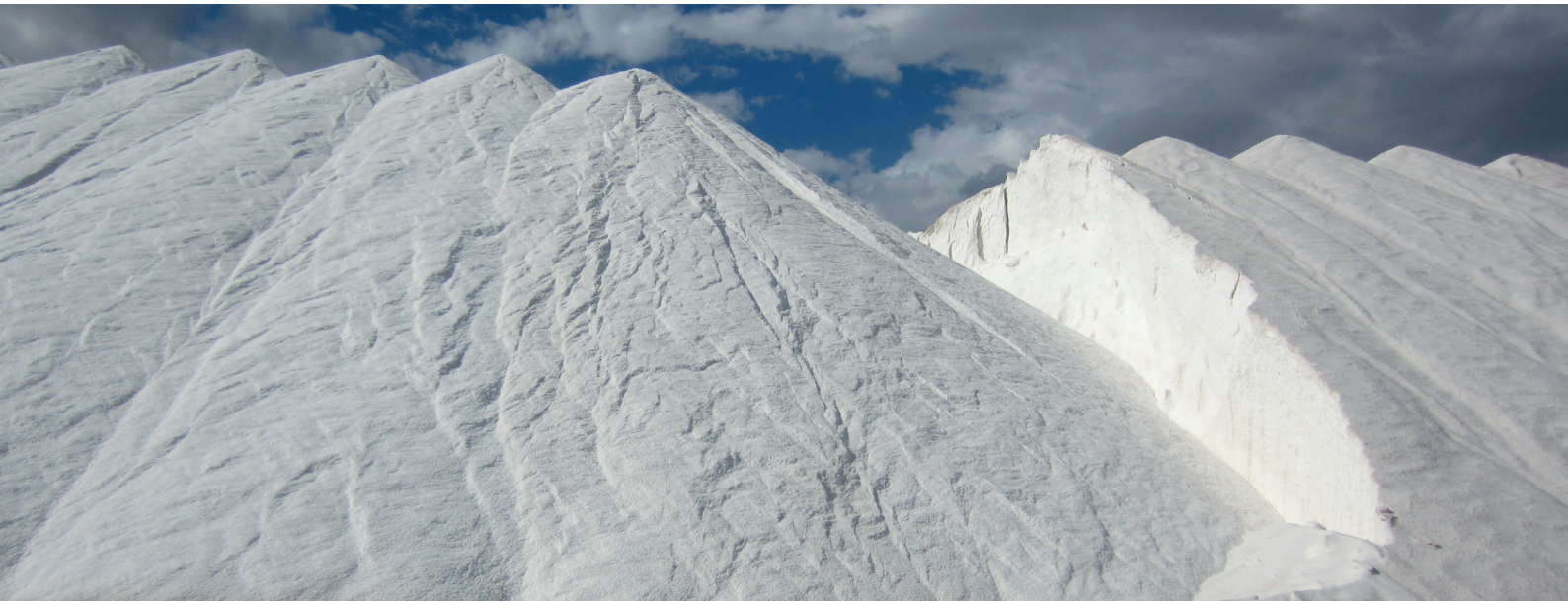
c: - concentration of the standard

SBR: - signal to background ratio

Table 4: Typical Limits of Detection (LOD) for the selected lines with Single Radial and Dual-Side-On plasma observation.

Element	λ [nm]	LOD (3σ) [µg/L] Dual-Side-On	LOD (3σ) [µg/L] Single Radial
Al	167.078	0.3	0.3
As	189.042	4.5	6.5
B	182.641	1.0	1.5
Ba	455.404	0.4	0.6
Be	313.042	0.2	0.3
Ca	393.336	0.15	0.2
Cd	214.438	0.4	0.45
Cd	226.502	0.7	0.9
Co	228.616	1.4	1.8
Cr	267.716	1.7	2.3
Cu	324.754	1.6	4.0
Fe	259.941	1.3	1.8
Hg	184.950	1.5	2.8
K	766.491	39	75

Element	λ [nm]	LOD (3σ) [µg/L] Dual-Side-On	LOD (3σ) [µg/L] Single Radial
Li	670.780	1.0	3.5
Mg	279.553	0.08	0.1
Mn	257.611	0.2	0.3
Mo	202.095	1.5	1.8
Ni	231.604	2.4	3.0
P	177.495	4.0	7.0
P	178.287	6.0	8.0
Pb	220.353	9.0	13
Si	251.612	3.0	4.5
Sn	189.991	2.5	3.5
Sr	407.771	0.1	0.2
Tl	190.864	7.0	8.0
V	311.071	3.5	4.0
Zn	213.856	0.2	0.35



Conclusions

The SPECTROGREEN with dual-side-on interface or single radial plasma observation offers a simple, fast, accurate, precise and cost-efficient method for the analysis of brine solutions. Using the DSOI interface, the sensitivity could be increased by an average factor 1.5 of compared to single radial plasma observation. In combination with an autosampler, the SPECTROGREEN can be fully automated. Independent from the number of lines and elements an analysis (including three replicates and pre-flush) can be performed in less than four minutes.

References

[1] NaCl Suprapur®, Merck, Darmstadt, Germany
[2] Bernd Kraft GmbH, Duisburg, Germany
[3] HNO_3 Suprapur®, 65%, Merck, Darmstadt, Germany
[5] Inorganic Ventures, Christiansburg VA, USA
[4] P. W. J. M. Boumans, Spectrochim. Acta 46B, 431 (1991)

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