FIELD APPLICATION REPORT

ICP-Optical Emission Spectroscopy

Author

Dan Jones
PerkinElmer, Inc.
710 Bridgeport Avenue
Shelton, CT 06484

Contributor

Nathan Saetveit
Elemental Scientific, Inc.
2440 Cuming Street
Omaha, NE 68131

The Analysis of Ultra Pure Brine Using the Optima 7300 DV and a Trace Impurity Pre-concentration System

Introduction

Membrane cell electrolysis has been used in the production of sodium hydroxide and chlorine gas from ultra pure brines since the 1970s. It has since become the most common chlor-alkali process. The process involves an anode and a cathode that are separated by an ion permeable membrane. The brine is split into its Na^+ ions, which are permeable to the membrane, pass through the membrane and form a sodium hydroxide solution. The Cl^- ions, which are not permeable to the membrane, are then oxidized into chlorine gas on the other side of the membrane. The chlorine gas and hydroxide solution are then collected, purified and stored.

Brine contaminants, such as Mg, Fe, Mn, Ca, Al, Ba and Sr, can poison the membrane cell rendering the process inefficient or not functional. Accurate determinations for these impurities are essential to plant process control.

Experimental

Ultra pure brine was supplied by a membrane chlor-alkali plant for analysis. Samples were analyzed at their facility using the existing Optima™ ICP-OES fitted with an ESI duo FAST sample introduction system. Results were compared to those obtained using standard sample introduction following the traditional dilution protocol previously established by the laboratory.

PerkinElmer®
For the Better

Instrumentation

The PerkinElmer® Optima 7300 DV simultaneous ICP optical emission spectrometer was equipped with the ESI duo FAST system. The Optima 7300 DV is a dual-view system allowing for the best possible detection limits in the axial mode and the longest linear range in the radial mode. This process of analyzing brines involves separating the analytes from the NaCl matrix. In order to accomplish this separation, the normal sample introduction system was replaced with an ESI trace impurity pre-concentration sample introduction system called a duo FAST system. This unique sample introduction system consists of a high purity autosampler with a dual-flowing rinse station, two high purity fluoropolymer injection valves, a chelation column, a high efficiency nebulizer, an o-ring free spray chamber, and a sapphire injector.

The PerkinElmer WinLab32™ software is integrated with the ESI duo FAST system for complete control of all parameters necessary for the automated analysis of metal contaminants in brine and other high salt solutions. During the analysis, a sequence of events automatically occurs. First, a finite amount of sample is drawn through the pre-concentration column. In the pre-concentration column, the analyte collects on the substrate. The column is then washed to remove any excess NaCl matrix. Next, an acidic solution elutes the analytes from the column and is aspirated into the plasma. The column is then automatically cleaned in preparation for the next sample.

The operating parameters of the plasma were optimized for robust conditions to obtain the best possible detection limits. Axial viewing was used with RF power set at 1500 watts. The sample volume is controlled by the size of an injection loop on one of the valves. A very small amount is needed to obtain accurate results.

Operating Parameters	
Power: 1500 watts	Plasma: 16 L/min
Nebulizer Gas Flow: 0.65 L/min	Pump: 0.5 mL/min
Aux Flow: 0.5 mL/min	Sample Volume: 0.1 mL

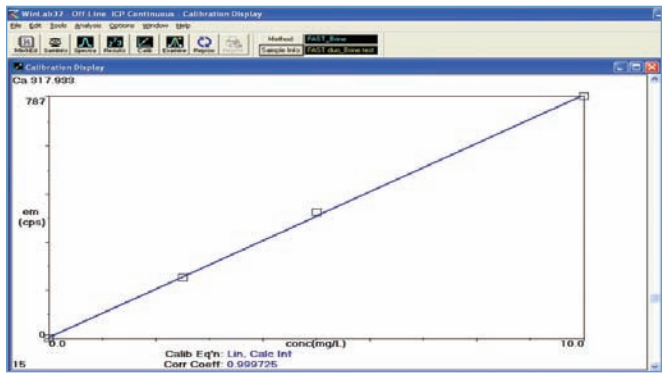
Results

Traditional methods to analyze ultra pure brines usually involve diluting the sample, thereby raising the detection limits. If the sample is not diluted, the matrix suppression caused by the high levels of NaCl will cause the detection limit to be elevated as well. With the use of pre-concentration and removal of the matrix, the detection limits remain similar to that of an undiluted aqueous solution.

Analyte	Traditional	PreConcentration	Improvement factor
Ca	8.0	0.3	20
Mg	1.7	0.2	9
Fe	6.3	0.3	21
Ba	1.4	0.4	3
S	1.1	0.1	10
Mn	1.3	0.2	6
Average MDL Improvement factor			11.5

The ICP-OES was calibrated using a multi-element standard at concentrations of 2.5 ppb, 5.0 ppb and 10.0 ppb in a matrix of 2% HNO_3. As seen in the figure below for Ca, the standards exhibited exceptional linearity.

Samples were spiked to further evaluate the system. Using traditional sample dilution introduction methods, samples needed to be spiked at 100 ppb in order to provide adequate intensity to generate acceptable recoveries. Due to the increased sensitivity of the pre-concentration system, spikes as low as 5 ppb were found to produce exceptional recoveries.



Conclusion

The Optima 7300 DV has a variety of unique features that when combined with the ESI duo FAST chelation system can easily analyze brine solutions at unprecedented detection levels. This improvement in accuracy and detection limits for impurities could lead to improved production and overall plant process control, as well as extending the life of the fluoropolymer membrane cell.

Spike Recovery Comparison (%R)		
Analyte	Traditional Introduction Spiked at 100 ppb	PreConcentration Introduction Spiked at 5 ppb
Ca	132	100.3
Mg	64	105.1
Fe	104	96.4
Ba	106	109.6
Sr	75	107.9
Mn	111	101.6

OPTIMA CONSUMABLES AND SUPPLIES

PerkinElmer offers a wide selection of consumables and supplies designed and tested to enhance the performance, productivity and reliability of every Optima 7x00 Series instrument. Precision-engineered to the most exacting standards, these products come with the peace-of-mind of a comprehensive guarantee and many offer the flexibility to be used with systems from other manufacturers.

For more information on any of our available torches, nebulizers, spray chambers, injectors or standards, please contact your sales representative or visit **www.perkinelmer.com/supplies.**

ICP Autosamplers

- Flexible rack configurations
- Fast, accurate random access
- Corrosion-resistant sampling components
- Flow-through rinse station to minimize sample-to-sample contamination
- Broad selection of productivity-enhancing systems available, including: S10 auto-samplers and a variety of CETAC and ESI autosamplers

Multiwave™ 3000

Microwave sample digestion system

- Built-in cooling system to reduce total cycle time, improving productivity
- Ideal for drying, evaporation, acid digestion and solvent extraction

FIAS

Fully automated flow-injection system

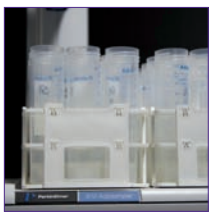
- Simplifies and speeds up analyses requiring complex sample preparation such as mercury and other hydride-forming elements

ICP Consumables

- Torches
- Nebulizers
- Standards

High-Throughput Sample-Introduction System

- Minimizes sample uptake and washout time
- Throughput increased up to 2-3 fold
- Eliminates sample contact with peristaltic pump tubing

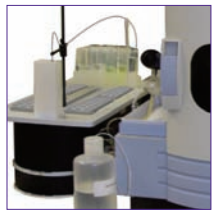


ICP Autosamplers

Multiwave 3000

FIAS

ICP Consumables



High-Throughput Sample-Introduction System

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

PerkinElmer®

For a complete listing of our global offices, visit www.perkinelmer.com/ContactUs

Copyright ©2009, PerkinElmer, Inc. All rights reserved. PerkinElmer® is a registered trademark of PerkinElmer, Inc. All other trademarks are the property of their respective owners.

The data presented in this Field Application Report are not guaranteed. Actual performance and results are dependent upon the exact methodology used and laboratory conditions. This data should only be used to demonstrate the applicability of an instrument for a particular analysis and is not intended to serve as a guarantee of performance.

008573_01