

Application Note AN-PAN-1059

Online analysis of strontium and barium in high purity brine

Chlorine and caustic soda are two of the most produced chemical substances globally. They are used to manufacture numerous intermediate chemicals, which in turn, are important feedstock materials for several industries (e.g., pulp and paper, petrochemical, and pharmaceutical). The chlor-alkali process is responsible for the majority of chlorine and caustic soda production.

The chlor-alkali process creates these two products together in similar proportions via electrolysis of sodium (or potassium) chloride brine. For the process to be as efficient as possible, the brine must be free of impurities (e.g., alkaline earth metals), otherwise the expensive membranes can become fouled which results in unexpected high maintenance costs.

Metrohm Process Analyzers can be used in several stages of this process—from monitoring impurities in raw to ultra-purified brine. This Process Application Note describes a method to determine the strontium and barium concentration in brine as early detectors of membrane fouling via online process ion chromatography. Using this multiparameter analytical technique can help reduce the risk of premature membrane fouling and avoid unexpected maintenance and high utility costs with 24/7 automated analysis.

INTRODUCTION

Different methods can be used to create chlorine and caustic soda (NaOH) from brine, but the most applied electrolysis technique in Europe is the **membrane cell technique**, since it does not include mercury and asbestos like the other options.

Figure 1 depicts an illustration of the membrane cell technique for chlorine production from saturated brine feedstock. For the chlor-alkali membrane cell technique, the anode and cathode are separated by a selective ion-exchange membrane. This allows only the positively charged Na ions to penetrate the cathode half-cell. Purified brine is pumped into the anode half-cell as an electrolyte. Then, the negatively charged Cl ions from the brine are oxidized at the anode, converting them into chlorine gas (Cl_2). At the side of the cathode half-cell, water is reduced to hydrogen gas (H_2), leaving the resulting hydroxide ions (OH^-) to react with Na^+ that has migrated through the membrane, ultimately forming NaOH.

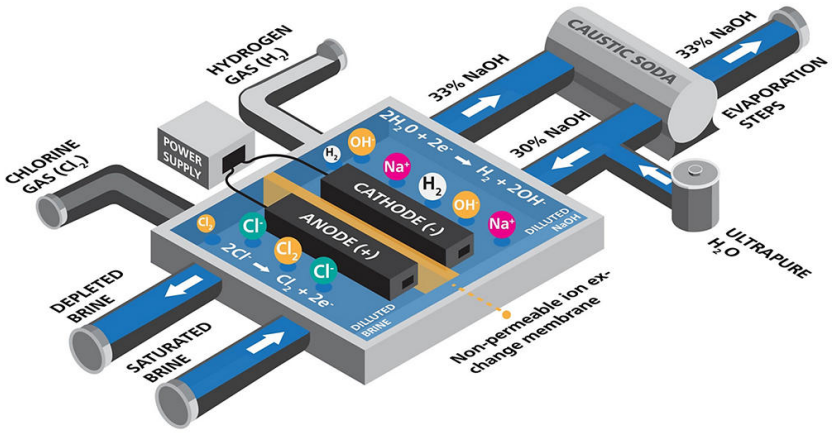


Figure 1. Diagram of the chlor-alkali membrane cell technique used to produce chlorine from saturated brine. Adapted from www.eurochlor.org.

For this process to be as efficient as possible and to avoid premature membrane fouling, the brine feedstock must be free of impurities. This makes chemical analysis of the brine indispensable.

Depending on the origin of the brine, the ionic impurities can vary. Calcium and magnesium (hardness) are the most common ionic impurities here. Monitoring these substances provides important information about the efficiency of the impurity removal prior to the electrolysis step (Figure 2). However, strontium and barium can also be present and are just as harmful to the membranes even in trace amounts. Typically, Sr^{2+} and Ba^{2+} are the first multivalent ions to break through the ion-exchange membrane, which makes them excellent parameters to monitor the life of the ion exchangers. By monitoring trace levels of strontium and barium in the purified brine, a breakthrough can be detected earlier before calcium and magnesium can foul the membrane. The desired measuring range for both of these contaminants is 10–100 µg/L.

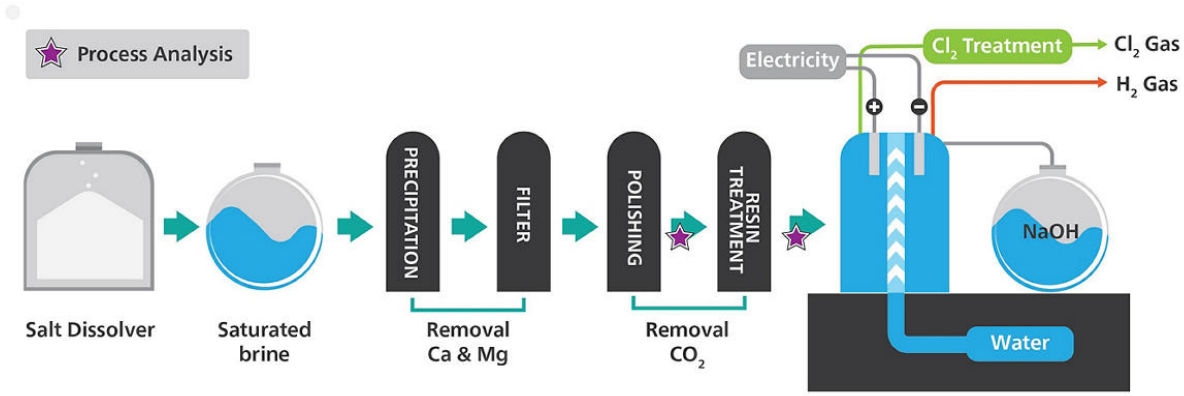


Figure 2. Schematic diagram of the overall chlor-alkali process with stars noting the ideal areas for online process analysis.

The most frequently applied analytical techniques for the determination of strontium and barium in brine are ion chromatography (IC), inductively coupled plasma mass spectrometry (ICP-MS), and ICP optical emission spectrometry (ICP-OES). Although ICP is a multiparameter technique covering large analytical ranges, it is also expensive, cannot easily be implemented online, and requires knowledgeable staff. Furthermore, the detection limit of strontium and barium is not low enough with ICP compared to IC analysis, and the operational costs for ICP are higher because of the use of large amounts of high purity argon.

Metrohm Process Analytics offers a solution for monitoring strontium and barium in brine: the 2060 Ion Chromatograph (IC) Process Analyzer featuring combined Inline Preconcentration and Inline Matrix Elimination. With one injection, the 2060 IC Process Analyzer is able to quantify strontium and barium. The analysis system is fed directly and continuously with samples via a bypass in the process stream.

Automatic calibration guarantees excellent detection

limits as well as high reproducibility and recovery. Additionally, the 2060 IC Process Analyzer provides alarms if pre-set warning or intervention concentration limits are reached, helping to save costs by preventing premature membrane fouling.

APPLICATION

The analysis is carried out fully automatically using Inline Preconcentration (Metrosep Chel PCC 1 VHC/4.0.) combined with Inline Matrix Elimination. The detection of trace levels of strontium and barium is done through a conductivity detector. This combination of techniques enables the possibility to measure very low amounts of strontium and barium in highly concentrated brine (Figure 3), achieving a measuring range of 12–120 µg/L for both analytes.

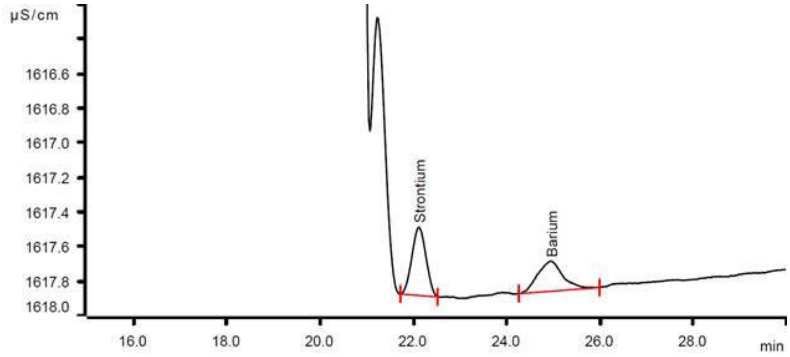


Figure 3. Chromatogram of a brine sample (>300 g/L NaCl) spiked with strontium and barium. A 4 mL sample aliquot was preconcentrated on the Metrosep Chel PCC 1 VHC/4.0 and then eluted on a Metrosep C6 separation column. The strontium and barium peaks are well separated from the large sodium matrix peak. Very low detection limits of multivalent cations in highly concentrated brines can be reached with this method.

The many intelligent sample preconditioning techniques offered by Metrohm ion chromatography (e.g., preconcentration and matrix elimination) make the analysis of cationic impurities in brine solutions simple and easy to perform in an online capacity. Integration of a built-in eluent production module and optional PURELAB® flex 5/6 from ELGA® for continuous pressureless ultrapure water supply allows easy autonomous online operation around the clock.

Table 1. Specifications for the determination of strontium and barium with online IC in ultra-purified saturated NaCl brine.

	Range	LOD
Strontium	12–120 µg/L	12 µg/L
Barium	30–120 µg/L	30 µg/L

TYPICAL RANGES



Figure 4. 2060 IC Process Analyzer

CONCLUSION

The Metrohm Process Analytics 2060 IC Process Analyzer can reliably measure trace amounts of strontium and barium in industrial brines commonly used in the chlor-alkali industry. This analysis method used in the analyzer allows chlor-alkali producers to prevent the premature fouling of expensive ion exchange membranes used in the process as well as the significant costs for replacement and maintenance.

RELATED DOCUMENTS

White Paper: Optimizing chlor-alkali production through online chemical analysis
AN-PAN-1058 Online determination of lithium in brine streams with ion chromatography
AN-PAN-1005 Analysis of calcium, magnesium in brine
Flyer: Trace monitoring of strontium in brines
Brochure: Chlor-Alkali Industry – Dependable online, inline, and atline solutions for your process needs

BENEFITS FOR ONLINE ANALYSIS

- **Low utility and maintenance costs** by preventing premature membrane fouling
- **Stable baseline and 24/7 operation** due to Inline eluent preparation
- **Safe working environment** due to automated sampling
- **Excellent detection limits**, **high reproducibility**, and **superior recovery rates** owing to automated sampling and calibration
- **High precision analyses** for a wide spectrum of analytes with multiple detector options



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CONFIGURATION



2060 IC Process Analyzer

The **2060 Ion Chromatograph (IC) Process Analyzer** from Metrohm Process Analytics is based on the modular 2060 platform concept. This modular architecture enables the separation of the cabinets in different locations around a plant and the connection to up to 20 sample streams for time-saving sequential analysis at multiple areas inside of a plant.

This analyzer has no limits in terms of hardware, software, and applications customization. From continuous eluent production module, wet part modules for sample conditioning, and multiple IC detector blocks, the 2060 IC Process Analyzer has all the options for any industrial application.

The 2060 software is an «all-in-one» software solution that controls the analyzer to perform routine analysis, with different operation methods, time sheets, and trend charts. Furthermore, thanks to the variety of process communication protocols (e.g. Modbus or Discrete I/O), the 2060 software is programmable to send automatic feedback and alarms to the process and take action if necessary (e.g., re-measure a sample, or start a cleaning cycle). All of these features ensure fully automatic diagnostics of the industrial process – around the clock, seven days a week.



Metrosep Chel PCC 1 VHC/4.0

Preconcentration column for polyvalent cations. Monovalent cations are removed by matrix elimination prior to injection.