



Raw Material Testing to Quality Assurance



Trace contaminant workflow analysis **Brines and fine caustics**

- Ion Chromatography • Liquid Chromatography
- Inductively Coupled Plasma-Optical Emission Spectroscopy

Chlor-alkali production

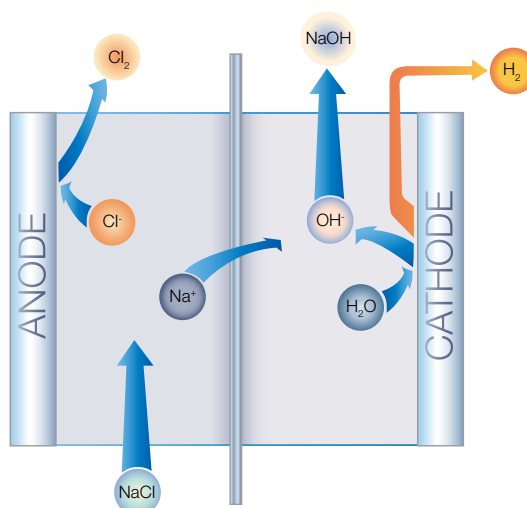
Brine (salt water), the feedstock of the chlor-alkali industry, is used in the production of chlorine, caustic soda (sodium hydroxide), soda ash (sodium carbonate), and a wide range of other products that can be used as raw material in other processes and industries. Chlorine is used to produce polymers which are then used in the manufacture of plastics, synthetic fibers, and synthetic rubber. Caustic soda is used in the production of polyester, other synthetic fibers, plastics, soaps, and detergents. Soda ash is used in the manufacture of glass, pulp and paper, and rayon.

A critical parameter in the chlor-alkali process is determining the purity of the feed brine. In the membrane cell production process of caustic soda, trace levels of alkaline earth metals (such as calcium and magnesium) and iodide can shorten the membrane life. To ensure production efficiencies, the sum of calcium and magnesium must be less than 20 ppb in 30% sodium chloride (NaCl).

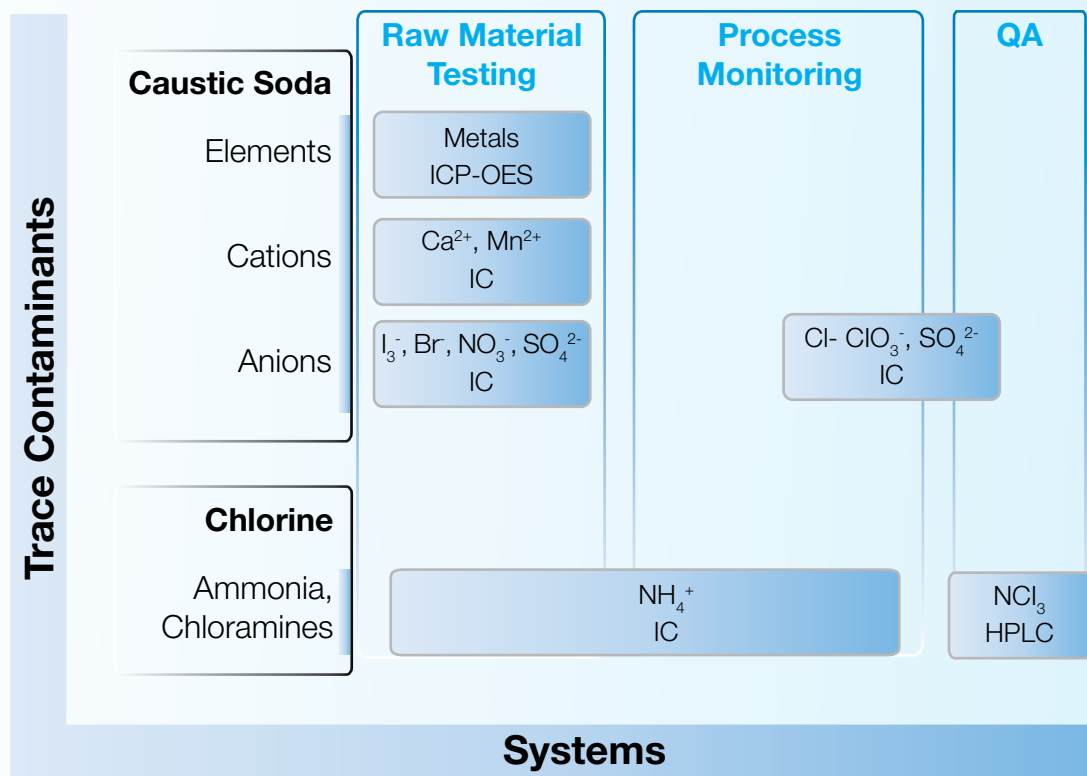
Monitoring the formation of contaminants and byproducts during salt electrolysis enables purity objectives to be achieved in an efficient and safe manner. The formation of nitrogen trichloride during the production of high-grade chlorine is a key example. When its concentrations exceed 20,000 ppm, the compound becomes explosive.

Quality assurance testing of the final caustic or chlorine product ensures trace contaminants are within specification for key applications or as feedstock in follow-on production processes. Trace levels of chloride and chlorate in sodium hydroxide used in plating baths can cause expensive inconsistencies in the production of electronic and semiconductor devices. Similarly pure-grade chlorine, used as feedstock for production of plastic products such as urethanes, epoxy, and glycol, is essential to avoid potential corrosion issues.

Whether your chlor-alkali needs include trace contaminant analysis using inductively coupled plasma-optical emission spectroscopy (ICP-OES), high-performance liquid chromatography (HPLC), or ion chromatography (IC), Thermo Scientific™ instruments deliver reliable information for every step of your workflow. Choose from a variety of proven systems and models to suit your current and future workflow application requirements.



Analysis workflow by product



System solutions



CHROMELEON 7.2
DATA SYSTEMS

Ion Chromatography (IC)

The Thermo Scientific™ Dionex™ ICS-5000+ Reagent-Free™ HPIC™ system—now with the capability to operate continuously at 5000 psi with capillary, microbore, and standard bore columns—provides high-resolution and fast run times using the new 4 µm particle-size columns.

Matrix diversion methods using the Thermo Scientific™ Dionex™ AutoNeutralization™ or two-dimensional IC (2D-IC) systems can perform in-line neutralization of a concentrated brine solution, thereby eliminating the need for dilution and enabling trace analysis of ions at ppm and ppb concentrations (Thermo Scientific™ Dionex™ Chromeleon™ Chromatography Data System compatible).



Dionex ICS-5000+ HPIC system

High-Performance Liquid Chromatography (HPLC)

Thermo Scientific™ Dionex™ UltiMate™ 3000 UHPLC systems allow you to choose from a wide variety of modules and configurations to create the configuration that is perfect for your applications, whether they are based on conventional LC or UHPLC. Take advantage of the widest detector portfolio in the industry, including unique technologies (such as universal charged aerosol detection (Chromeleon Chromatography Data System compatible)).



UltiMate 3000 UHPLC system

Inductively Coupled Plasma–Optical Emission Spectroscopy (ICP-OES)

The Thermo Scientific™ iCAP™ 7000 Series ICP-OES provides the sensitivity to analyze high-salt matrices and overcome problems such as:

- Matrix matching issues requiring high-purity NaCl for calibration standards
- Sample transport effects caused by differences in viscosities
- Salting and clogging from continuous aspiration of heavy brine solutions



iCAP 7000 series ICP-OES



Process methodology

The chlor-alkali industrial chemical process produces sodium hydroxide (NaOH) and chlorine gas from the electrolysis of brine. The two methods in use—diaphragm and membrane—differ in how they isolate the chlorine produced at the anode from the caustic produced at the cathode, and in the final product purity.

Caustic Soda Production

Diaphragm Grade

Caustic solution prepared by the diaphragm method is approximately 14 wt% NaOH and approximately 14 wt% NaCl salt. To increase the purity of sodium hydroxide, residual salts need to be removed. This involves using an evaporative process, including precipitation and filtering the excess salt, to reach a caustic concentration of 50 wt%. This process produces a sodium hydroxide solution often referred to as Diaphragm or Commercial Grade. The following trace contaminants are present in the approximate concentrations: sodium chloride (1.0 wt%), sodium chlorate (0.3 wt%), sodium carbonate (0.2 wt%), and sodium sulfate (0.07 wt%).

Membrane Grade

The membrane cell method is preferred over the diaphragm and mercury methods as it uses the least amount of electricity while producing a higher purity caustic—one that is approximately 35 wt% NaOH. As in the diaphragm method, evaporation is utilized to raise the concentration up to the nominal 50 wt% solution. The process produces a caustic known as Membrane Grade. Trace contaminants are present at relatively lower concentrations: NaCl (100 ppm), sodium chlorate (10–50 ppm), sodium carbonate (0.05 wt%) and sodium sulfate (25–50 ppm).

Semiconductor Grade

The highest purity caustic, known as electronic or semiconductor grade, can be achieved by further evaporation of the 50% solution to reduce the salt concentration, which is then diluted to the 50% concentration. Trace contaminants are present in the following approximate concentrations: NaCl (10 ppm) and sodium sulfate (5 ppm).

Chlorine Gas Production

Chlorine is produced simultaneously with caustic in a near one-to-one mass ratio by the electrolysis of salt. An important consideration for chlorine producers is the quality of the chlorine gas produced from membrane plants, as it can contain higher oxygen content than other methods. For certain applications, such as those found in the semiconductor and polymer industries, a purer-grade chlorine gas is required. For these applications, chlorine liquefaction and vaporization is used to reduce the oxygen content in chlorine. While this process effectively improves the purity of the chlorine, it can result in the accumulation of chlorinated tars or "taffy" byproducts and the formation of nitrogen trichloride, a volatile and hazardous oil.



Raw material testing — caustics

The presence of trace metals—such as magnesium, calcium, and manganese—in the brine feedstock can poison the ion-exchange membrane cell and halt the chlor-alkali process. Iodide, present at ppb concentrations, is another critical analyte to measure as it can interact with trace levels of alkaline earth metals at the membrane surface and compromise the membrane's useful life.

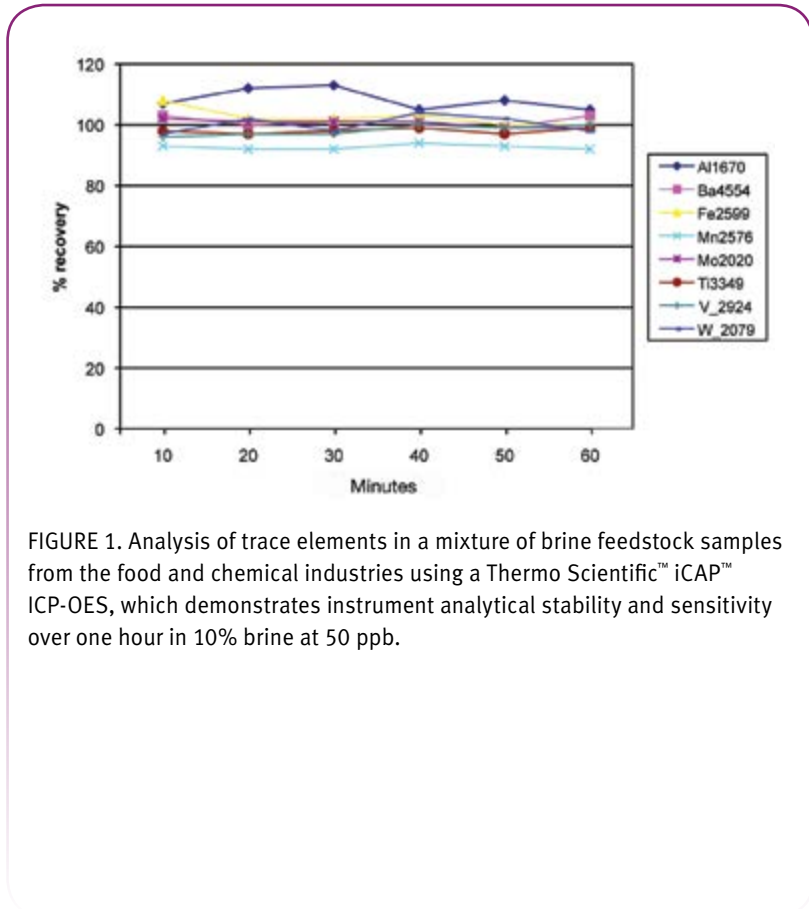


FIGURE 1. Analysis of trace elements in a mixture of brine feedstock samples from the food and chemical industries using a Thermo Scientific™ iCAP™ ICP-OES, which demonstrates instrument analytical stability and sensitivity over one hour in 10% brine at 50 ppb.

FIGURE 2. Analysis of manganese in brine feedstock by IC. Shown is an overlay of three injections of an undiluted brine using a concentrator column in combination with a Thermo Scientific™ Dionex™ IonPac™ CS12A and suppressed conductivity detection. The nominal concentration of manganese (Peak 3) is 91 ppb.

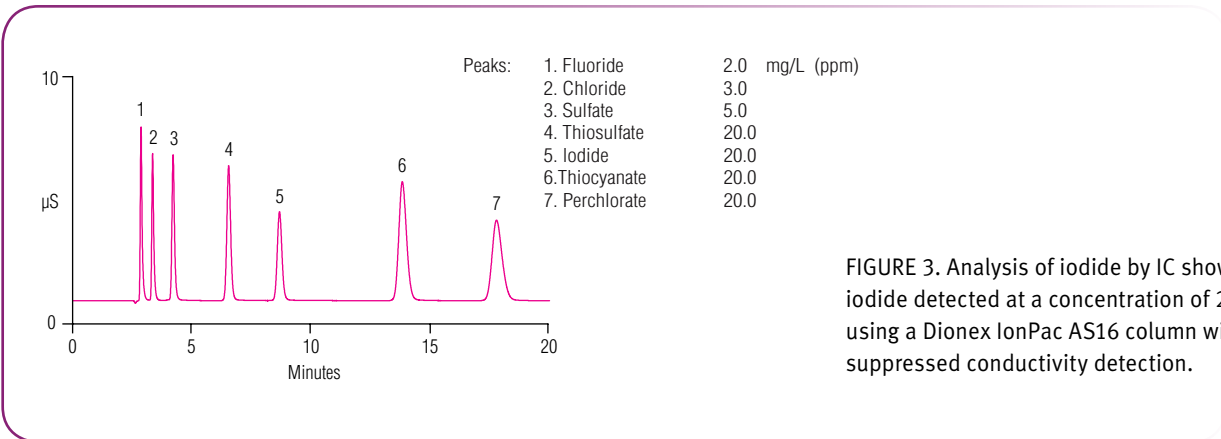
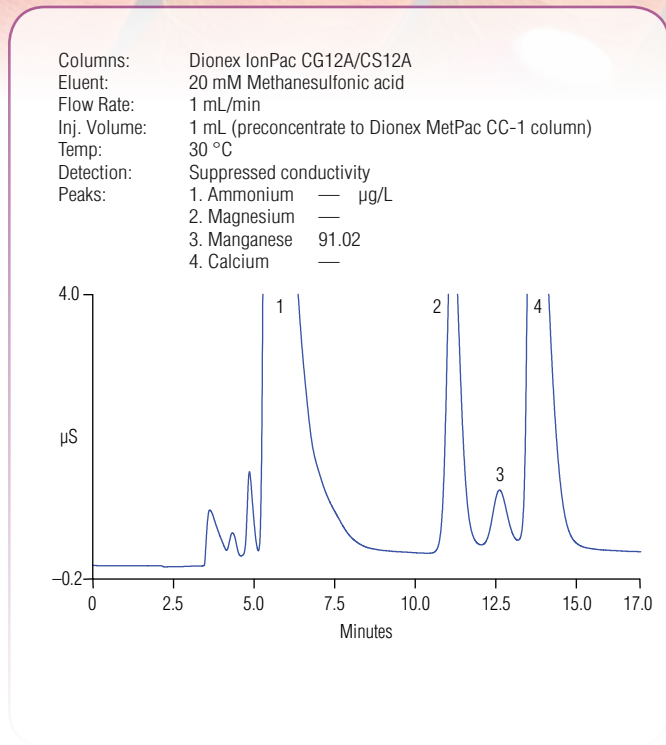


FIGURE 3. Analysis of iodide by IC showing iodide detected at a concentration of 2 ppm using a Dionex IonPac AS16 column with suppressed conductivity detection.

Process monitoring and QA—caustics

Caustic manufacturers need an accurate method to monitor the concentration and assure the quality of sulfate, chloride, chlorate (resulting from sodium hydroxide coming in contact with chlorine gas), and other anions in the chlor-alkali process. This requires methods that remove interfering matrix ions and organic contaminants. Typical dilution can be ineffective as it can compromise detection limits by reducing both the concentration of the matrix ions and the ions of interest. Two commonly used approaches include: 1) an off-line sample pretreatment process, and 2) an IC or in-line AutoNeutralization IC process.

In the off-line neutralization process the sample is diluted and manually neutralized with a Thermo Scientific™ Dionex™ OnGuard™ II Cartridge prior to injection onto a Dionex IonPac AS9-SC column with suppressed conductivity.



FIGURE 4. IC analysis in caustics with matrix elimination, which shows the detection of anions in 0.38N NaOH after sample pretreatment with a Dionex OnGuard II Cartridge.

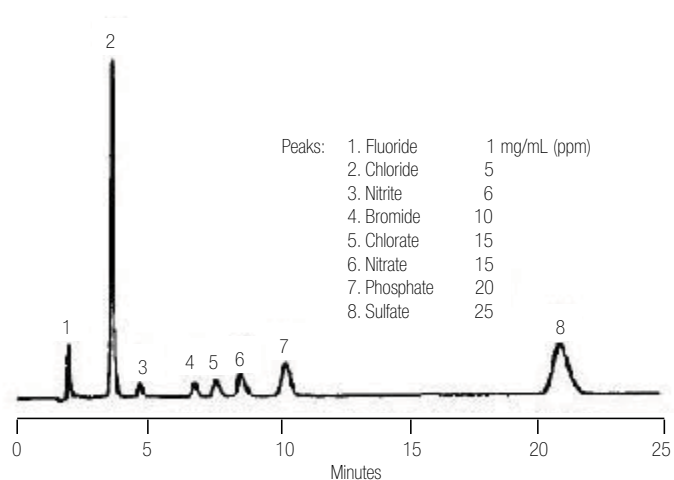
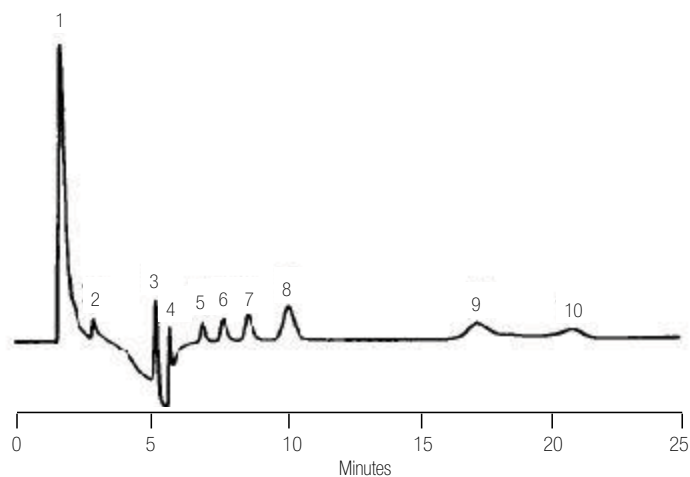


FIGURE 5. IC analysis in caustics without matrix elimination, which shows the detection of anions in 0.38N NaOH without Dionex OnGuard II sample pretreatment. Without proper sample pretreatment, it is not possible to obtain accurate results and the chromatography is compromised.





The Dionex single pass neutralization pretreatment enables an automated matrix elimination method that uses an in-line membrane-based neutralizer device coupled with IC to determine analytes of interest in a concentrated base or acid sample.

For the chlor-alkali process:

- Here the caustic sample is first loaded into a 25 μ L sample loop. The sample is then switched in line and the concentrated base from the sample loop is directed to the Thermo Scientific™ Dionex™ ASRN™ Anion Self-Regenerating Neutralizer. There the sample is partially neutralized, then transferred to the 5000 μ L loop.
- The recycle valve is then actuated to direct the sample through the Dionex ASRN neutralizer a second time to complete the neutralization. Following the doublepass neutralization process, the sample anions can be focused onto a concentrator column before eluting them onto an analytical column.

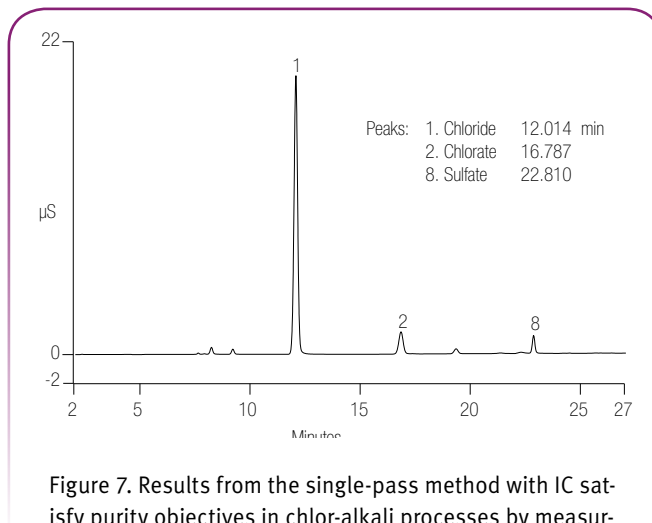


Figure 7. Results from the single-pass method with IC satisfy purity objectives in chlor-alkali processes by measuring trace levels of chlorate, chloride, and sulfate in a faster, more effective manner

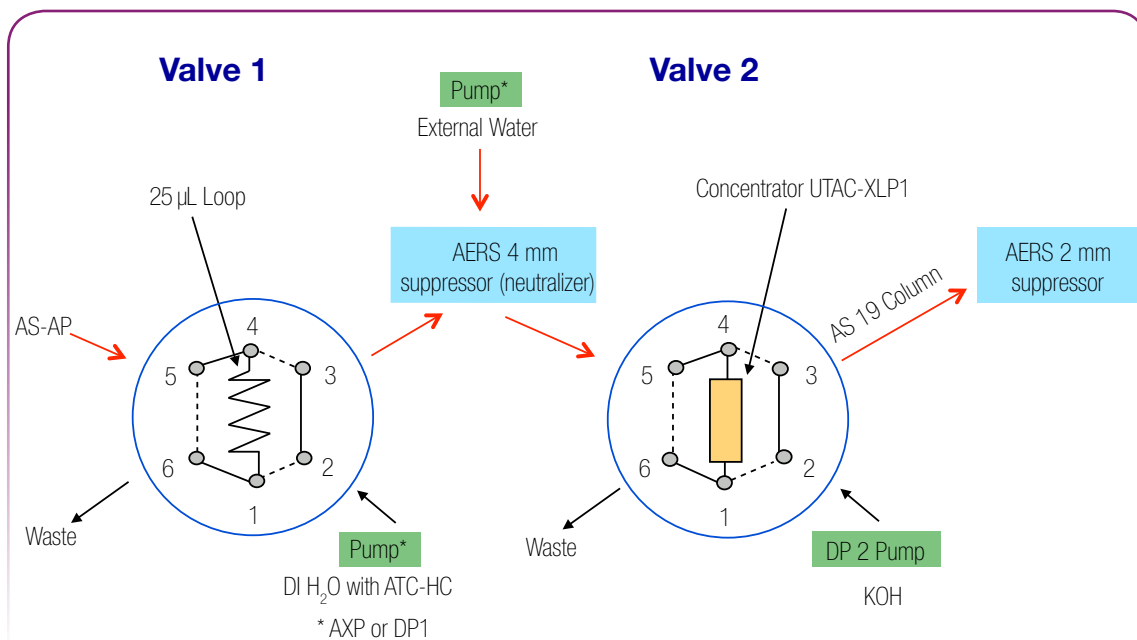
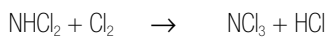
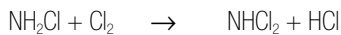
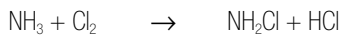


FIGURE 6. Single-pass pretreatment and IC analysis configuration.

Raw material testing and process monitoring—Cl₂

A key contaminant in the production of chlorine gas is nitrogen trichloride. Considered an explosive above a concentration of 20,000 ppm, it is formed by the following series of chemical reactions:



To prevent the formation and build-up of nitrogen trichloride, it is essential to monitor ammonium and chloramines. If present in brine feedstock, chloramines can lead to the formation of NCl₃ in electrolytic cells which accompany the chlorine gas and condense with the liquid chlorine. If used as feedstock for other processes, the concentration of NCl₃ will increase as the compressed liquid chlorine is depleted resulting in a potential hazard. If additional

purification is required during the production of chlorine gas, the repeated concentration and evaporation of the liquid chlorine used to enrich the chlorine gas to a higher-grade purity will also increase the concentration of NCl₃.

Two approaches are used to measure for potential buildup of nitrogen trichloride in the brine during production of chlorine gas. The first is to directly measure the accumulation of nitrogen trichloride. The second approach is to measure the ammonia compound precursors that result in the formation of nitrogen trichloride. The following are examples of both approaches.

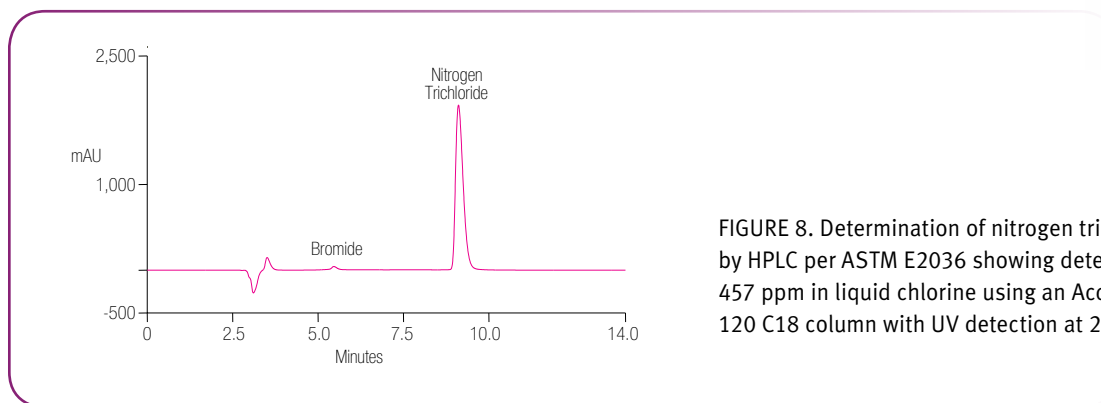
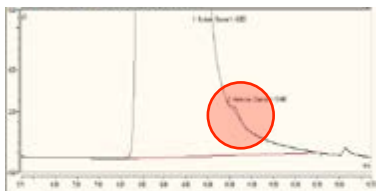


FIGURE 8. Determination of nitrogen trichloride by HPLC per ASTM E2036 showing detection of 457 ppm in liquid chlorine using an Acclaim 120 C18 column with UV detection at 221 nm.



Column: Dionex IonPac CS16
 (4 × 250 mm)
 Eluent: 30 mM MSA
 Flow Rate: 1.00 mL/min
 Inj. Loop: 2000 µL
 Temp: 30 °C
 Detection: Suppressed conductivity

A

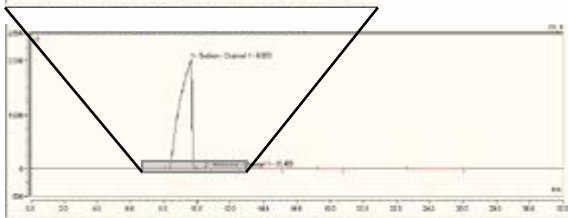
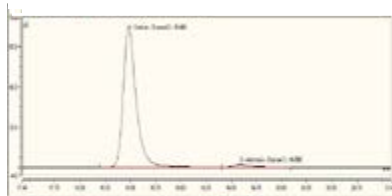


FIGURE 9A. Analysis of ammonium by 2D-IC, First dimension.



Column: Dionex IonPac CS16
 (2 × 250 mm)
 Eluent: 30 mM MSA
 Flow Rate: 0.50 mL/min
 Inj. Loop: 2000 µL
 Temp: 30 °C
 Detection: Suppressed conductivity

B

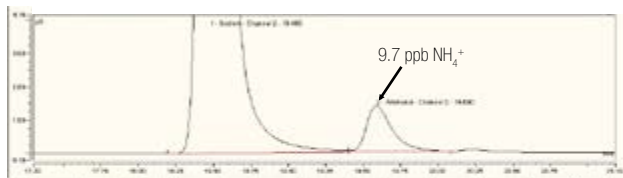


FIGURE 9B. 2D-IC matrix diversion; NH_4^+ is clearly detected at 9.7 ppb in a high-sodium matrix following a 2D-IC approach.



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Korea +82 2 3420 8600
Netherlands +31 76 579 55 55
Singapore +65 6289 1190
Sweden +46 8 473 3380

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