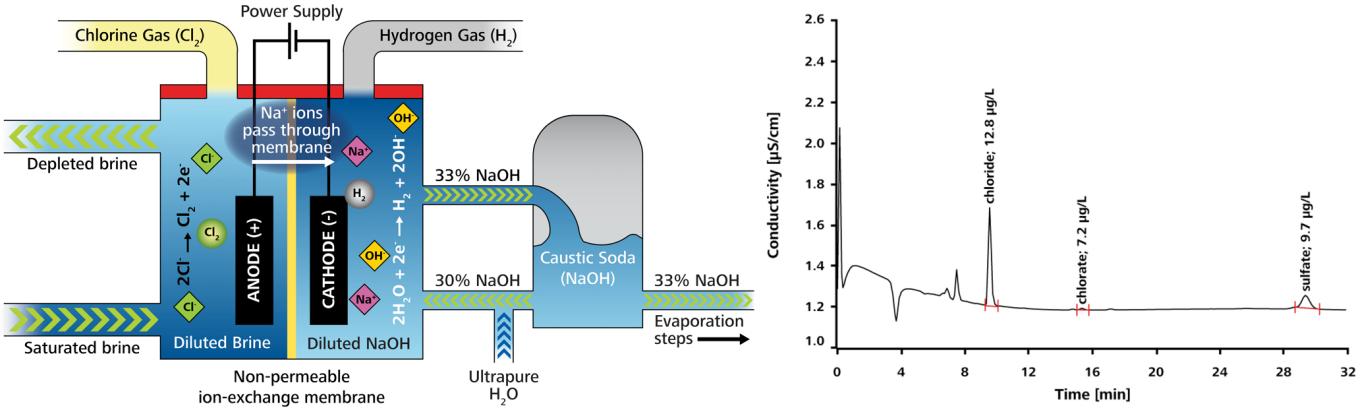
Online Determination of Anions in 50% NaOH and 50% KOH by Ion Chromatography According to ASTM E1787-16

The production of caustic soda (sodium hydroxide, lye, NaOH) and caustic potash (potassium hydroxide, KOH) is extremely significant, as these are mainly used as precursors for many other chemicals used in all industries. For example, the pulp and paper industry is especially reliant on concentrated caustic soda for chemical pulping of wood in the Kraft Process, and the agro-chemical industry is heavily reliant on KOH. Caustic soda and caustic potash are produced alongside chlorine in the chlor-alkali process, which is explained in more detail in **AN-PAN-1005**. In this process, chlorine and caustic soda (or potash) are produced via electrolysis of sodium chloride (or potassium chloride) brine, mainly with the membrane-cell technique. Some production plants make both NaOH and KOH in the same cell room, though generally the brine circuits are kept separate to avoid time-consuming cleaning and purging processes between the different brines. In both situations, the caustic product is concentrated to about 50 wt-% by two or three step evaporation before it is stored. This concentrated product contains impurities from the salts used which are undesirable in certain chemical purity grades needed for the subsequent production processes.

Typically, anionic impurities in 50 wt-% caustic soda or potash are determined by gravimetric or titration methods which require a variety of reagents with diverse shelf lives and hazards. In 2016, the **ASTM method E1787-16** was released, specifying ion chromatography to measure bromide (Br^-), chlorate (ClO_3^-), chloride (Cl^-), fluoride (F^-), nitrate (NO_3^-), phosphate (PO_4^{3-}), and sulfate (SO_4^{2-}) in concentrated NaOH or KOH solutions. Anions of primary interest are **Cl^-**, **ClO_3^-**, and **SO_4^{2-}**, as shown in the chromatogram below.



Left: Diagram of the membrane-cell technique used to produce concentrated NaOH and KOH alongside Cl_2 (source material: www.eurochlor.org).
Right: 100 µL injection of 50% KOH sample (diluted 1:10), using Metrohm Inline Sample Preparation (MISP) techniques for extra application flexibility.

The Process Ion Chromatograph from Metrohm Process Analytics is ideal for ASTM E1787-16, able to continuously measure and monitor anionic impurities in caustic soda and caustic potash in a robust housing suitable for such a process environment. Metrohm offers many fully automatic inline sample preparation techniques for ion chromatography, making analysis even more hands-off and flexible. Automated calibration guarantees excellent detection limits, a high reproducibility, and excellent recovery rates.

The caustic stream is sampled frequently, giving up-to-date information about the status of the membrane cells. The Process IC can provide an alarm if pre-set warning or intervention concentration limits are reached, helping to save costs by preventing irreparable damage due to membrane fouling and other problems. One Process Ion Chromatograph has the possibility to

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connect to up to 20 sample streams, meaning multiple cells with different end products could be monitored for impurities by a single instrument.

The Process Ion Chromatograph can run for extended periods in less-frequented areas as there is adequate space reserved for reagents, canisters of ultrapure water and/or prepared eluent, and level sensors to ensure that you are always alerted when liquid levels are low. By choosing a built-in eluent module and optional PURELAB® flex 5/6 from ELGA® for continuous pressureless ultrapure water supply, the Process IC can be configured to run even trace analyses autonomously.

The Process IC is available with either one or two measurement channels, along with integrated liquid handling modules and several automated sample preparation options.

Application: Concentrated KOH and NaOH samples can be analyzed according to ASTM E1787-16, with Metrohm Inline Sample Preparation techniques for extra application flexibility. Analyte detection is by conductivity.

Remarks: For sulfate quantification, it is essential to use perchloric acid ($HClO_4$) for the inline neutralization. An anion trap (A Trap 1) should be used in line with any ultrapure transfer water to ensure the highest quality results. For high concentrations of chloride, potentiometric titration can be used. Metrohm Process Analytics offers potentiometric titration for samples above 2 mg/L Cl^-.

References: **IC Application Note S–243**, **IC Application Note S–303**, AW IC CH6-1108-082012

Other helpful links: **Selection of important standards relating to the chemical industry**

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