Optimizing chlor-alkali production through online chemical analysis

Alyson Lanciki, Ph.D.

Chlorine and caustic soda are used as feedstock materials in production processes for several markets including pulp and paper, petrochem, and pharma. The chlor-alkali process, accounting for 95% of production, depends on the electrolysis of brine, which first requires several purification steps. This white paper focuses on the membrane electrolysis method and describes the reasoning and benefits for choosing online and inline process analysis for the chlor-alkali industry. Reduce the risk of premature membrane fouling and save on costly energy consumption with 24/7 automated analysis.

Metrohm International Headquarters; Herisau, Switzerland

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Chlorine and Caustic Soda

Chlorine (Cl_2) ranks number 7 on the list of the most commonly produced chemical substances. It is an exceptionally reactive molecule. Chlorine is the basis for the production of numerous intermediate substances, which, in turn, are important feedstock materials in the petroleum, aluminum, paper and pulp, and pharmaceutical industries.[1,2]

Caustic soda (sodium hydroxide, NaOH) is another crucial basic chemical which enables production of organic chemical products, bleach, detergents, paper, cellulose products, and several other materials.[1–3] In many production processes, caustic soda is added in order to adjust pH or alkalinity.

What about hydrogen?

Hydrogen gas is a co-product of the chlor-alkali process. The high purity (> 99.9%) gas is generally used on site or sold to nearby facilities.

This high quality hydrogen can be used to produce chemicals (HCl, NH_3, H_2O_2, CH_3OH, and more) or even as a utility to produce steam and electricity. However, only approximately 28 kg H_2 is produced per ton of Cl_2.[4,5]

The chlor-alkali process

By far the largest part – about 95% – of the chlorine produced globally is obtained via the chlor-alkali process.[4] Caustic and chlorine are produced together in similar proportions via electrolysis of sodium (or potassium) chloride brine.

There are three main methods used to create chlorine and caustic from brine:

- membrane cell process
- mercury cell process
- diaphragm cell process

Overall reaction for all techniques:

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

Shifting production to safer technologies

The most commonly applied electrolysis technique in Europe (85%) is the membrane cell technique. All new production facilities are based on membrane cell electrolysis of brine, which does not include mercury and asbestos like the other processes.

The shift towards membrane technology is in line with Euro Chlor's voluntary agreement to phase out the installed mercury capacity by 2020. **Figure 1** illustrates the steady decrease in the use of mercury for the production of chlorine from 2001–17.[4]

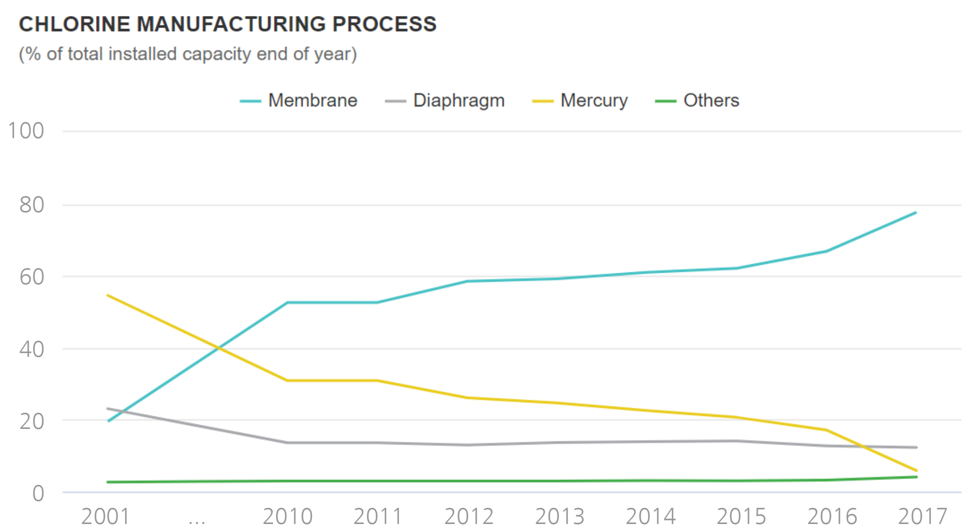


Figure 1. Industry overview (2001–17) of the different manufacturing processes which produce chlorine.[4]

Membrane Cell Electrolysis: Key Focal Points

Brine purity

The production of chlorine, caustic soda, and hydrogen begins with brine. For the process to be as efficient as possible, the brine must be free of impurities, which makes chemical analysis crucial. The presence of impurities such as calcium and magnesium (known as hardness) shorten the performance and lifetime of the membranes or can even damage the electrodes. Partial membrane blockage from precipitation reactions leads to increased electrical operational costs and the high cost associated with replacing membranes.

Purification treatments

Primary and secondary brine treatments are required to reduce the hardness concentration to acceptable levels. Primary treatment is a relatively inexpensive process where both sodium hydroxide and sodium carbonate are added to the raw brine, and the precipitated impurities ($CaCO_3$, $Mg(OH)_2$) are filtered out. After primary treatment, the filtered brine passes through an ion exchange unit before the electrolysis process. Impurity concentrations can reduce by a factor of 1000, such as in the case of hardness ions (Ca^{2+} and Mg^{2+}).[5]

Ion exchange efficiency

An ion exchange membrane divides the anodic and cathodic compartments, allowing passage of sodium ions (Na^+) and water molecules, but limiting chloride (Cl^-) and other anions. The membranes have an average lifetime of 3–5 years and must remain stable while being exposed to such aggressive solutions.[5] The ion exchange efficiency is vital in order to limit impurities in the concentrated caustic product.

Moisture and impurities in produced gases

The produced gases (Cl_2 and H_2) can contain moisture and other impurities (such as oxygen) after the production process. These products can be stored and transported in a liquid form after compression. Undesired moisture levels in the raw gases may lead to corrosion in storage containers with dangerous consequences over time.[5] Vaporization of the gases after storage, without proper removal of moisture beforehand, can clog the container valves and lead to further handling issues.

Concentrated caustic purity

Chemical analysis is necessary to determine the purity of the concentrated caustic soda. The resulting 33% NaOH solution is concentrated to about 50 wt-% by two- or three-step evaporation before it is stored.[4] This concentrated caustic solution contains impurities which are undesirable in certain chemical purity grades needed for manufacturing other products.

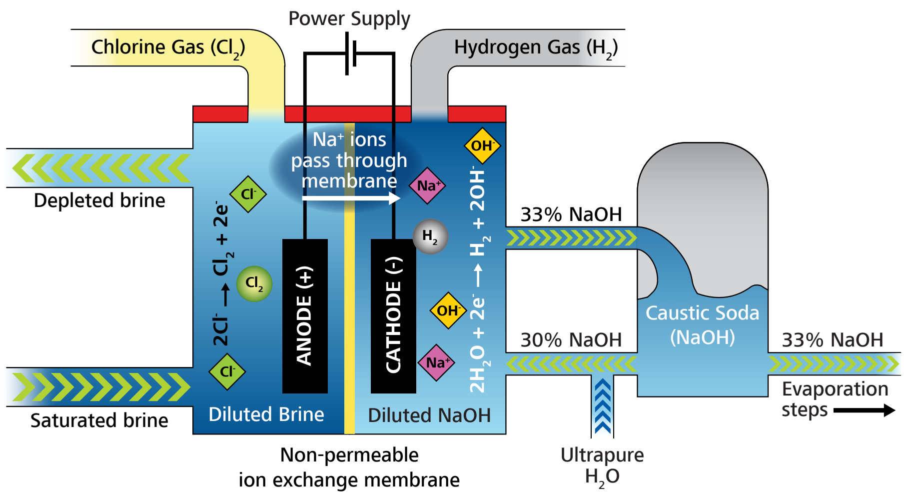
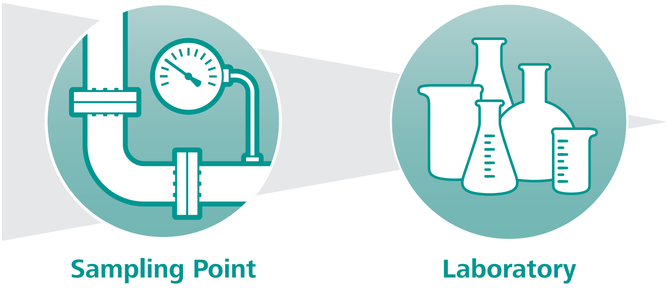


Figure 2. Diagram of the membrane cell technique for the production of chlorine (adapted from Euro Chlor).[4]

Online Process Analysis as an Advantage

Typically, laboratory analysis for several key process parameters is the norm to keep the production facility running smoothly and safely. Manual sampling from various points along the process is a necessity, which takes up valuable time. Delays in sampling, analytical measurement, and data sharing due to these offline measurement strategies can have serious detrimental effects on production efficiency and overhead costs.



What benefits can online process analysis offer?

- higher productivity: 24/7 automated analysis directly at the sample point
- optimization though immediate process adjustment
- achievement of superior quality product, higher yields
- protection of employees' health and safety
- safeguarding of costly company assets
- minimized downtime
- increased profitability
- and more

Improvement of product quality can be achieved more easily through implementation of automated process analysis, which increases profitability for manufacturers. Rather than sampling during each working shift, analyses can be run automatically around the clock.

Time-consuming manual sampling and long distances to the laboratory are eliminated by utilizing **online**, **inline**, or **atline** process analyzers. Samples are more representative and reproducibility of results increases as the measurements are performed exactly the same, every time. Chemical analysis performed directly at the most critical process points reduces the potential for unforeseen plant shutdowns by providing data in real time to the central computing system.

Out-of-specification readings immediately trigger a warning at the control room, ensuring the fastest response to bring production back online. Analysis occurs at the sampling point, leading to more accurate and reproducible results.

Protect and Save

Online, inline, or atline process analyzers can help protect company assets and recuperate costs in several areas around the facility. **Limiting risk** while **increasing profit** is achievable through the implementation of automated online analysis techniques.

Premature membrane fouling

One of the most important components to safeguard during the electrolysis process is the membrane itself. Each chlor-alkali producer can utilize hundreds of ion exchange membranes, with average lifespans between 3–5 years.[5] The prevention of premature membrane fouling is of the utmost importance.

Inefficiency in the electrolysis process due to premature membrane fouling incurs significant costs. To maintain the same production output, an increase in electrolysis potential is required (equating to a higher utility bill). When energy consumption is kept constant after a fouling event, there will be a loss in product yield.

Current efficiency

If hardness levels in the polished brine increase over a short period (hours) due to inefficient removal processes, the current efficiency can reduce by 1–2%. This may seem insignificant, but membranes are replaced only during planned shutdowns, and over the membrane lifetime this results in a loss on the order of **€1.1–2.3 million ($1.2–2.6 million USD)**.

Additionally, the entire system must be replenished with fresh brine to stem further reductions in current efficiency from increased hardness or from other impurities blocking the membranes.

Product quality

Aside from the protection of expensive assets, online process analysis can cut costs in other areas of production. The **reduction of process variation** by constant monitoring and trend charts with integrated warning limits saves costs from product loss or reduced product quality, which requires additional processing. With 24/7 automated analysis at the sample point, out-of-specification readings instantly trigger a warning to the control room or chemical distribution system for rapid response to get the process back in order.

Manual sampling and laboratory analysis techniques may take several hours to accomplish the same results, depending on the locations of the sample points, the laboratory, and the analyst.

Time is of the essence when it comes to process optimization—samples taken manually are no longer representative of the process conditions as time passes during transport. Temperature, pressure, and other parameters also change, which can affect the accuracy of the obtained data.

Online and Inline Process Application Solutions for the Chlor-Alkali Industry

There are numerous applications for this industry which can be elevated from time-consuming manual techniques to automated online or inline process analysis solutions. A selection of these applications is given below.

Measurement of carbonate and caustic levels in brine

The initial stage of brine purification utilizes caustic soda (NaOH) and sodium carbonate (Na_2CO_3) to remove excess hardness via precipitation reactions. The purified raw brine is polished further with ion exchange resins before it travels to the membrane cell for electrolysis.

Measurement of the concentration of carbonate and caustic soda in brine can provide important information about the impurity removal process. If these levels are too low, the ion exchange resin overloads with impurities more quickly, negatively affecting downstream processes.

Online titration of these parameters allows accurate dosage of NaOH and Na_2CO_3 to the settling tanks.

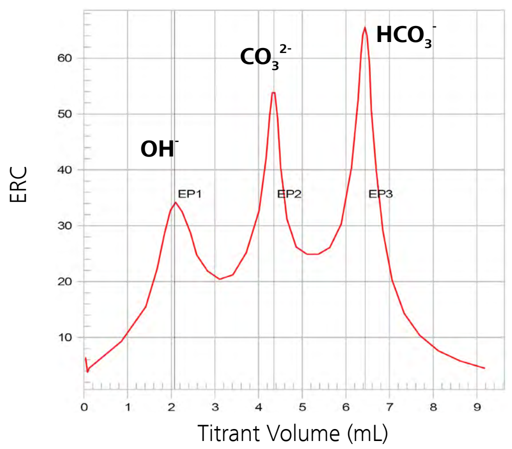


Figure 3. Three inflection points are present when OH^- and CO_3^{2-} in brine are titrated with acid. The first point is hydroxide, the second is carbonate, and third is bicarbonate. Data provided by a Metrohm Process Analytics brand wet chemical industrial process analyzer.

Determination of hardness in brine (Inlet Resin Treatment)

After primary treatment, the purified brine passes through an ion exchange unit prior to the electrolysis process.

The efficiency of the settling and resin treatments can be calculated based on accurate determination of hardness before (and after) the secondary treatment commences. Upstream control of brine quality helps to overcome costly problems, such as the blockage of electrolysis membranes or shutdown due to premature exhaustion of the ion exchange resin.

This measurement can be accomplished quickly online in a matter of minutes with titration.

Related application note:
Hardness in Brine: AN-PAN-1005
https://www.metrohm.com/en/applications/AN-PAN-1005

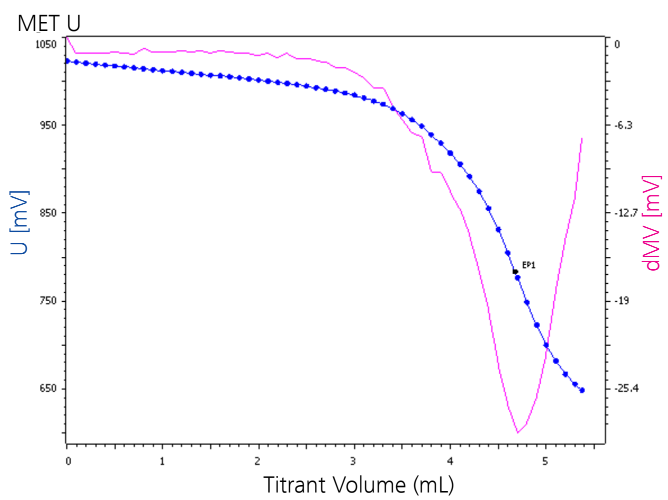


Figure 4. Online titration for total hardness in brine (mg/L range) at the inlet of the resin treatment. Data provided by a Metrohm Process Analytics brand wet chemical industrial process analyzer.

Determination of hardness in brine (Outlet Resin Treatment)

Hardness determination in ultrapure brine is necessary to prevent damage downstream in the electrolysis process. Very costly remediation procedures are necessary if the membranes are fouled.

The trace amounts present after the secondary purification process are commonly determined photometrically with a color indicator. Online analysis is a dependable solution, offering both extremely low detection limits and highly accurate results, giving extra assurance that expensive company assets are being safeguarded.

Related application note:
Hardness in Brine: AN-PAN-1005
https://www.metrohm.com/en/applications/AN-PAN-1005

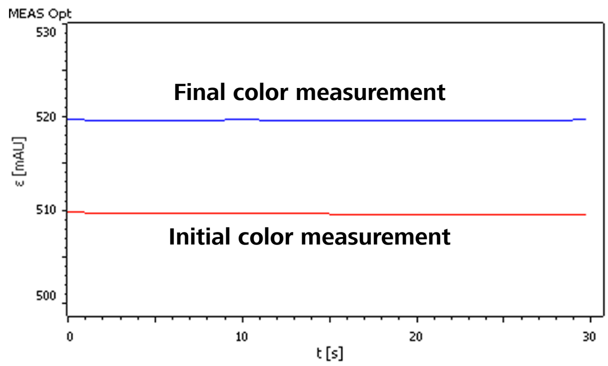


Figure 5. Initial and final online colorimetric measurements of hardness in brine at the µg/L range. Data provided by a Metrohm Process Analytics brand wet chemical industrial process analyzer.

Determination of chlorine (Cl_2) in depleted brine

Depleted brine can be recycled and resaturated for continued use in membrane cell electrolysis, reducing costs incurred during the multiple purification steps of the raw brine. Total dechlorination of the depleted brine can be achieved when using the membrane cell technique.

The determination of chlorine in (depleted) brine is necessary due to the high concentrations which can be found in the recycled bulk solution.

Online monitoring in this part of production leads to more efficient chlorine removal processes, creating an even safer working environment. Measurement of chlorine in (depleted) brine is possible in an online manner via titration.

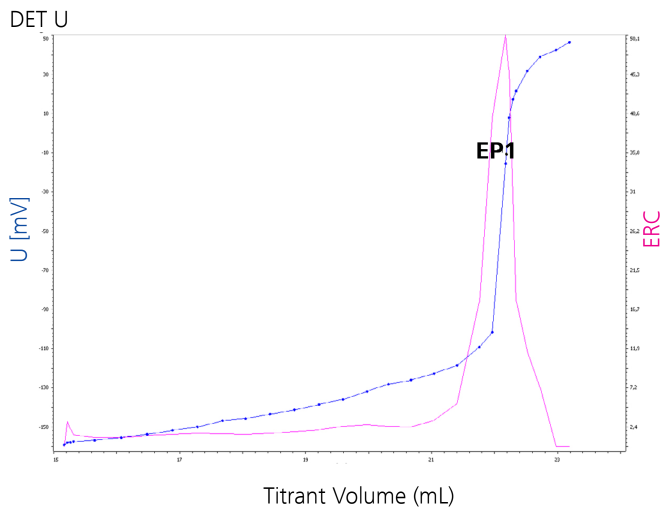


Figure 6. Online monitoring of Cl_2 (mg/L range) is simple with the use of an electrode while titrating the sample. Data provided by a Metrohm Process Analytics brand wet chemical industrial process analyzer.

Accurate monitoring of hypochlorite (ClO^-) in brine

Hypochlorite (ClO^-) is formed by side reactions during electrolysis of the brine. A certain amount of the produced hydroxide can migrate back across the ion-exchange membrane into the anode compartment, leading to formation of hypochlorite and chlorate. These impurities can result in a loss of current efficiency of up to 7% in the production of caustic soda.[5]

This application can be performed online with a process analyzer utilizing a standard electrode for quick, simple, and accurate analysis.

Monitoring low-level chlorine (Cl_2) in brine and waste streams

The chlorine concentration in depleted brine (and waste) should be reduced to low levels after acid treatment with HCl to decrease the pH. In the membrane cell technique, the depleted brine is treated further with chemical reducing agents, activated carbon, or catalytic reduction, which can result in chlorine levels below 0.5 mg/L.[5]

Online determination of these lower concentrations in waste streams gives confidence that emitted chlorine levels are within the strict environmental limits. Online process analysis utilizing the photometric measurement technique handles this application challenge with ease, providing sufficient data to catch spikes in Cl_2 emissions which manual sampling can easily miss.

Monitoring chloride (Cl^-) levels in caustic soda

A common contaminant in the produced caustic solution is chloride. However, low-chloride NaOH is required for many applications.

Monitoring the concentration of Cl^- in the NaOH solution online can assist the purification process and trigger other procedures by alerting the operator if levels are out of specification. The measurement can be carried out online photometrically with a process analyzer, saving time and increasing the efficiency of the process.

Online measurement of trace anion impurities in 50% caustic soda

The purity grade of the resulting caustic soda is important for several reasons, for example, requirement of high purity for the production of pharmaceuticals or the ability for the manufacturer to command a higher sale price for high quality NaOH. Typically, anionic impurities in 50 wt-% caustic soda or potash are determined by gravimetric or titration methods.

ASTM method E1787-16 specifies 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.[6] Anions of higher interest are chloride, chlorate, and sulfate as shown in **Figure 7**.

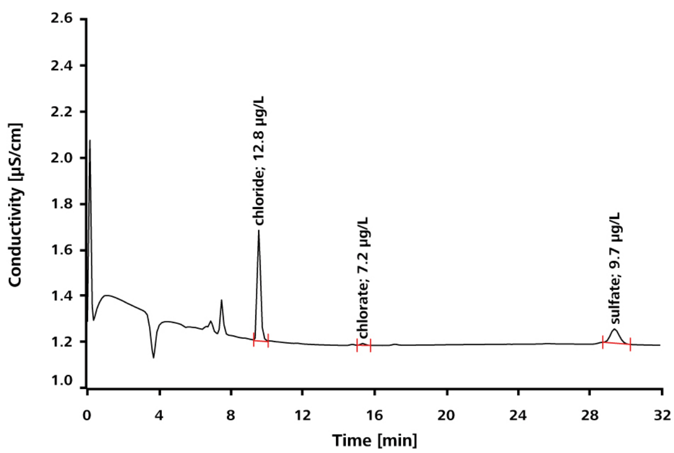


Figure 7. Sample chromatogram for measurement of chloride (Cl^-), chlorate (ClO_3^-), and sulfate (SO_4^{2-}) via Metrohm ion chromatography (IC).

Online ion chromatography fulfills all specifications of **ASTM method E1787-16**.[6] Sample preconditioning techniques such as matrix elimination make the analysis of anion impurities in concentrated caustic solutions simple and easy to perform in an online capacity. Safety of employees is increased when reducing the need for manual sampling and handling of such corrosive chemicals. Additionally, integration of a built-in eluent production module and ultrapure water supply allows even easier autonomous online operation.

Related application note:
Online Determination of Anions in 50% NaOH and 50% KOH by IC (ASTM E1787-16): AN-PAN-1046
https://www.metrohm.com/en/applications/AN-PAN-1046

Inline determination of low-level moisture in chlorine gas

Moisture determination in the produced gases (Cl_2, H_2) is necessary to overcome corrosion in storage containers and transport pipelines.[5] Vaporization of the gases after storage can also clog the container valves and lead to further handling issues.

The inline determination of moisture content in the gas at different points in the drying process gives information regarding the efficiency of the dryers and the endpoint of the drying process. This application is possible to perform inline without chemical reagents using near-infrared spectroscopy (NIRS).

NIRS requires a reference (primary) method, such as Karl Fischer titration, to ensure the developed model is accurate and robust. However, manual analysis of samples is sharply reduced, along with the exposure to hazardous reagents and dangerous samples.

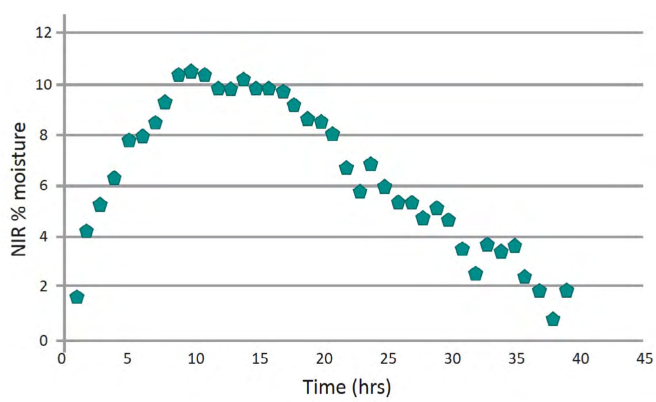


Figure 8. Example of a process trend chart monitoring the moisture content in gas over several days. Measurements performed with a Metrohm Process Analytics spectroscopic process analyzer (NIRS) using fiber optics and inline flow cells.

Summary

Chlorine, caustic soda (and potash), as well as hydrogen are important products for the basic chemical industry, as they are used in several downstream processes to create multiple consumer goods. The chlor-alkali process, utilizing the membrane cell technique, is the predominant method in which to produce these chemicals. High-purity brine is required to overcome extremely costly damage to the membranes during electrolysis of the bulk solution. The resulting products must be chemically analyzed to determine the efficiency of the processes involved as well as to ensure high quality standards. Additionally, some parameters such as moisture content can have a detrimental effect on the storage and transport of these products.

Generally, time-consuming manual sampling and laboratory analysis methods are the norm, which can put employees at risk (health and safety). Additionally, the liberated samples are no longer completely representative of the process from which they were removed, as temperature, pressure, or many other factors differ from the process after manual sampling.

Online and inline analysis techniques performed with robust and rugged industrial process analyzers can overcome many challenges which face every industry. There are several automated solutions available to provide these services 24/7. Utilizing online titration, photometry, ion chromatography or even inline spectroscopic techniques such as NIR analysis, companies can increase the efficiency of their operations and reduce downtime due to unforeseen events. Results are more reliable and accurate when automated as human error is removed from the equation. Improvement in the safety of the employees is an added bonus through the elimination of manual sampling and analysis.

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Contact: 041-info@metrohm.com