Application Note AN-PAN-1036

Online determination of alkalinity and hardness in process and make up water for beer production

Beer is a popular beverage consumed by millions of people for enjoyment, despite its humble beginnings as a water purification technique in pre-modern times. Brewing beer requires large amounts of water which must adhere to strict alkalinity, hardness, and pH parameters to ensure uniformity in flavor and appearance between each batch. Alkalinity is introduced by carbonates and hydroxides in water which raise and buffer the pH. Hardness, balanced to a large degree by the alkalinity, comes from calcium (Ca) and magnesium (Mg) ions, mainly present as hydrogen carbonates.

Depending on the concentration ranges, the 2035 Process Analyzer or the 2060 Process Analyzer from Metrohm Process Analytics are ideally suited for the fully automatic analysis of these important quality parameters in process and make-up water, as well as additional parameters like pH or conductivity. The analyzers can signal the brewery's distribution control system (DCS) to correct the water chemistry, ensuring consistent product quality.

INTRODUCTION

Beer is an alcoholic beverage consumed in most countries worldwide, made from fermented malted grains, with a wide alcohol content range from 0 to 12%. Its origins are unclear, but it has been linked to ancient civilizations, with recipes inscribed thousands of years ago upon stone tablets. Before today's hygienic practices were applied, alcoholic beverages were developed as a water purification technique, as drinking water from natural sources was likely to make one ill due to pollution and disease.

The beer brewing process is intensive and can be categorized in the following steps: malting, milling/grinding, mashing, lautering (separating and rinsing the grains from the liquid portion known as «wort»), boiling the wort, fermenting, conditioning, filtering, and finally filling bottles or barrels. Each step must be properly controlled in the process to ensure uniformity of the end product, which is important to facilitate brand loyalty. Making beer incurs a huge water footprint, requiring up to 300 L of water to create 1 L of beer, though 94–98% of that water is designated for agricultural purposes before the brewing process even begins. More and more breweries are taking steps to become more sustainable regarding their water usage, which means process optimization and more efficient practices. To this end, key quality parameters of the water used in brewing such as alkalinity, hardness, and pH value have to be determined.

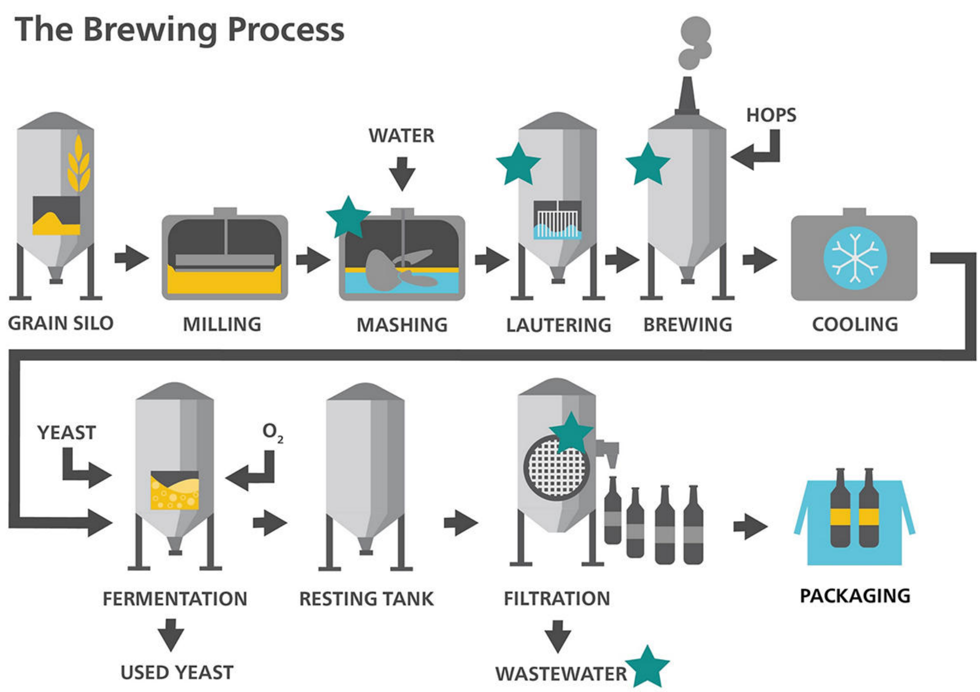

Figure 1. Online hardness monitoring during the beer brewing process (noted by green stars).

INTRODUCTION

Alkalinity in water is due to the presence of compounds such as carbonates, bicarbonates, and hydroxides which raise the pH of the water and buffer it against further pH change. Hardness constituents in water are usually calcium and magnesium ions (Ca^{2+} and Mg^{2+}). They are mainly present as hydrogen carbonates and sulfates or, in rare cases, as chlorides. Hardness is balanced to a large degree by the alkalinity.

The temperature and the composition of the water used in the initial stages of the brewing process is especially important for optimal extraction of starches from the milled grains. Temperature changes during mashing can adversely affect the fermentability of the sugars because of a narrow working temperature range (55–72 °C) for the enzymatic starch conversion processes. The pH of the water is not only important for mashing, but also in the lautering process, where some make-up water is needed for sparging (rinsing the sugar from the spent grains). If the pH of the mash or sparge water exceeds 5.7, the resulting beer will have an astringent mouthfeel due to excess tannin extraction from the grain husks. After lautering comes the boiling process where hops are added to the wort (the sugary liquid precursor to beer), and again, if the pH is above 5.7, excess tannins can be introduced. Pale ales are especially influenced by any pH changes. Pale ales do not contain roasted malts which naturally acidify the mash, so the process must be more closely monitored for the proper pH, hardness, and alkalinity.

In order to extract the proper compounds, keep the pH within specifications, and brew the same flavors over multiple batches, both alkalinity and hardness of the process and make-up water must be monitored and kept at proper levels. The Metrohm Process Analytics 2060 and 2035 Process Analyzers (Figures 2 and 3) are ideally suited for the fully automatic execution of these important analyses, as well as additional parameters like pH or conductivity. The process analyzer can send an alarm to the plant control system if alkalinity or hardness levels are not optimal, signaling the distribution control to correct the water chemistry, ensuring consistent product quality.

Figure 2. 2060 Process Analyzer.

APPLICATION

These are titrimetric methods for the online analysis of alkalinity and hardness in process and make-up water for breweries.

Alkalinity is determined in an acid/base titration with hydrochloric acid (HCl) and a standard solution using a combined pH-glass electrode. Results are calculated based on the first inflection point. The alkalinity is expressed as mg/L calcium carbonate ($CaCO_3$). When measuring both free and total alkalinity, the values are obtained from the first and second inflection points.

For hardness determinations, Ca^{2+} and Mg^{2+} form stable complexes with EDTA at pH 10. In this application, Ca^{2+} and Mg^{2+} can be determined by potentiometric titration using an ion-selective electrode (Cu-ISE). Results are expressed in mg/L Ca^{2+}. Other methods are also available for determining total and Mg^{2+} hardness.

Additionally, inline pH sensors can be connected to the 2060 Process Analyzer to guarantee a fully integrated system, leading to better process control.

Figure 3. 2035 Process Analyzer.

Table 1. Brewery measurement parameters for water

Parameters	Range [mg/L]
Alkalinity ($CaCO_3$)	0–110
Hardness (as Ca^{2+})*	8–200

CONCLUSION

Alkalinity, pH value, and hardness play crucial roles during the brewing process. Out-of-specification values impair the extraction of starches and can negatively affect the taste of the beer. Close monitoring of the process and make-up water is therefore required, which is made possible by implementing a 2060 or 2035 Process Analyzer from Metrohm Process Analytics in the brewery for optimal water chemistry around the clock.

RELATED APPLICATION NOTES

AN-PAN-1029: Peracetic acid (PES) as disinfectant for PET bottles

AN-PAN-1031: Hydrogen peroxide as delousing agent in salmon farms

AN-PAN-1049: Online determination of bromate and other disinfection byproducts in drinking & bottled water with IC

BENEFITS FOR TITRATION IN PROCESS

- **Improved product quality** and manufacturing efficiency
- **Ensure regulatory compliances** for process and make-up water
- **Detect process upsets** via automated analysis

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CONFIGURATION

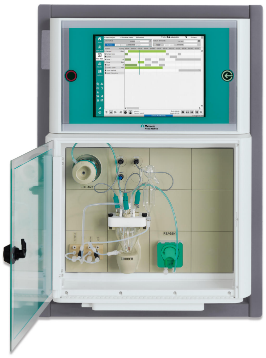
2060 Process Analyzer

The 2060 Process Analyzer is an online wet chemistry analyzer that is suitable for countless applications. This process analyzer offers a new modularity concept consisting of a central platform, which is called a «basic cabinet».

The basic cabinet consists of two parts. The upper part contains a touch screen and an industrial PC. The lower part contains the flexible wet part where the hardware for the actual analysis is housed. If the basic wet part capacity is not sufficient enough to solve an analytical challenge, then the basic cabinet can be expanded to up to four additional wet part cabinets to ensure enough space to solve even the most challenging applications. The additional cabinets can be configured in such a way that each wet part cabinet can be combined with a reagent cabinet with integrated (non-contact) level detection to increase analyzer uptime.

The 2060 process analyzer offers different wet chem techniques: titration, Karl Fischer titration, photometry, direct measurement and standard additions methods.

To meet all project requirements (or to meet all your needs) sample preconditioning systems can be provided to guarantee a robust analytical solution. We can provide any sample preconditioning system, such as cooling or heating, pressure reduction and degassing, filtration, and many more.



2035 Process Analyzer - Potentiometric

The 2035 Process Analyzer for Potentiometric Titration and Ion-Selective Measurements performs analyses with dedicated electrodes and titrants. Additionally, this version of the 2035 Process Analyzer is also suitable for Ion-Selective Analysis using Metrohm high performance electrodes. This accurate standard addition technique is ideal for more difficult sample matrices.

The potentiometric version of the analyzer offers the most accurate results of all measuring techniques available on the market. With far more than 1000 applications already available, titration is also one of the most used methods for analysis in almost any industry for hundreds of components varying from acid/base analysis to metal concentrations in plating baths.

Titration is one of the most widespread absolute chemical methods in use today. The technique is straightforward with no need for calibration.

Some titration options available for this configuration:

- Potentiometric titration
- Colorimetric titration with Fiber Optic Technology
- Moisture determination based on the Karl Fischer titration method