



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.

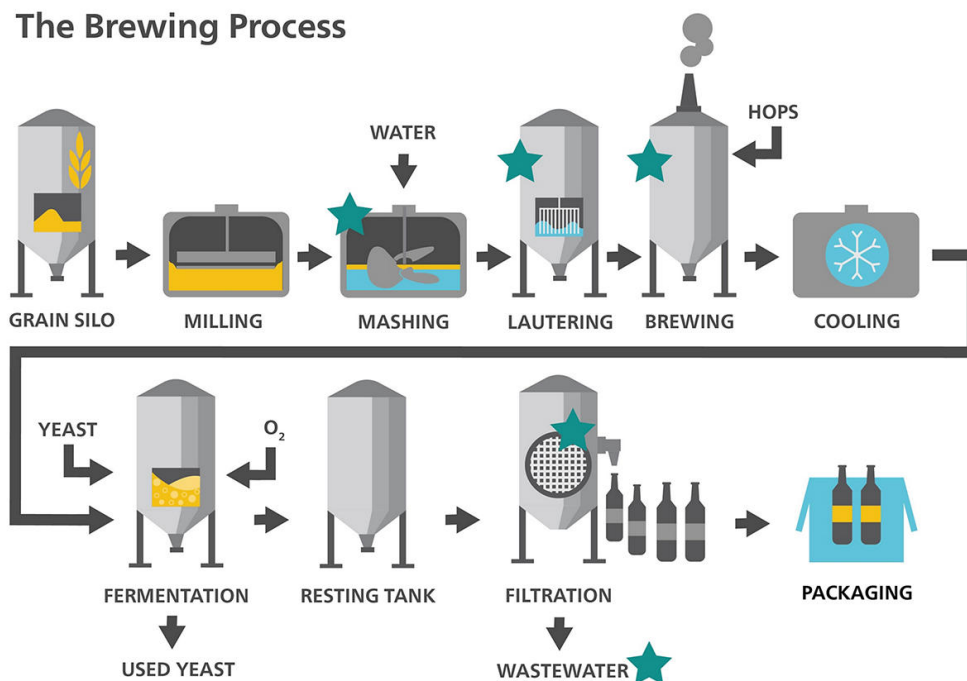


Figure 1. Online hardness monitoring during the beer brewing process (noted by green stars).

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

Le 2060 Process Analyzer est un appareil d'analyse par voie humide online adapté à un grand nombre d'applications. Cet appareil d'analyse de processus propose un nouveau concept de modularité reposant sur une plate-forme centrale, dénommée « armoire de base ».

Cette armoire de base se compose de deux parties. La partie supérieure contient un écran tactile et un PC industriel. La partie inférieure contient la partie humide flexible dans laquelle est logé le matériel nécessaire à l'analyse en elle-même. Si la capacité de base de la partie humide n'est pas suffisante pour résoudre un problème d'analyse, vous pouvez ajouter jusqu'à quatre armoires de partie humide supplémentaires à cette armoire de base afin de disposer de suffisamment d'espace pour résoudre les applications les plus difficiles. Les armoires supplémentaires sont configurables de manière à ce que chaque armoire pour partie humide puisse être combinée à une armoire à réactifs avec détection de niveau intégrée (sans contact) afin d'augmenter la disponibilité de l'appareil d'analyse.

Le 2060 Process Analyzer propose différentes techniques de chimie par voie humide : le titrage, le titrage Karl Fischer, la photométrie, la mesure directe et des méthodes d'addition standard.

Pour répondre à toutes les exigences de projet (ou à tous vos besoins), des systèmes de préconditionnement d'échantillons peuvent être fournis afin de garantir une solution analytique robuste. Nous pouvons pour ainsi dire fournir tout système de pré-conditionnement d'échantillon, tels que refroidissement ou chauffage, réduction de la pression, dégazage, filtration et bien plus encore.



2035 Process Analyzer – Potentiométrie

Le 2035 Process Analyzer pour titrage potentiométrique et mesures sélectives d'ions réalise des analyses avec des électrodes et des titrants dédiés. De plus, cette version du 2035 Process Analyzer convient également à l'analyse sélective d'ions à l'aide d'électrodes haute performance de Metrohm. Cette technique précise d'addition standard est idéale pour des matrices d'échantillons qui s'avèrent plus difficiles.

La version potentiométrique de l'appareil d'analyse délivre des résultats plus précis que toutes les techniques de mesure disponibles sur le marché. Avec largement plus de 1 000 applications déjà disponibles, le titrage est l'une des méthodes les plus utilisées dans pratiquement tous les secteurs industriels pour l'analyse de centaines de composants qui varient de l'analyse acide/base aux concentrations de métaux dans les bains galvaniques.

Le titrage est l'une des méthodes chimiques absolues les plus répandues en usage aujourd'hui. Cette technique est directe et ne requiert aucun calibrage.

Quelques options de titrage disponibles pour cette configuration :

- Titrage potentiométrique
- Titrage colorimétrique avec la technologie à fibre optique
- Détermination de l'humidité basée sur la méthode de titrage Karl Fischer