Application Note AN-PAN-1038

Power generation: analysis of the m-number (alkalinity) in cooling water

One way to maximize heat transfer efficiency and reduce costs in a power plant is by controlling the water chemistry in the cooling circuit. This cooling water is kept alkaline to maintain the protective oxide layer on the metal piping throughout the water circuit. However, alkalinity above the recommended range increases the probability of scale formation (deposition), so it is buffered with carbonate (CO_3^{2-}) and bicarbonate ions (HCO_3^-). Titration of the cooling water to pH 4.5 gives the so-called «m-alkalinity» (methyl orange alkalinity), a measure of total alkalinity. Below this pH, there is no more alkalinity present, only free acid (H^+), carbonic acid (H_2CO_3), and CO_2.

This Process Application Note details the online analysis of alkalinity in cooling water. This method offers results in less than 30 minutes, meaning faster response times for out of specification readings. In combination with the power plant's Distributed Control System (DCS), online monitoring of this parameter using a process analyzer ensures that corrosion can be controlled before it affects the power plant efficiency, ultimately decreasing downtime and lowering maintenance costs.

INTRODUCTION

One way to maximize heat transfer efficiency and reduce costs in a power plant is by controlling the water chemistry in the cooling circuit (Figure 1). Cooling water is used to condense the exhaust steam from the turbine to water, which is then sent back to the water-steam circuit as feed water. The heat of condensation (energy) from the steam is transferred to this cooling water as it flows through kilometers of (titanium) piping in the condenser. The water chemistry depends on the type of power plant, cooling circuit design, and construction materials. Every cooling circuit has a unique design and its own analytical requirements.

The cooling water temperature is reduced either by once-through cooling, in which the water is taken from the environment and returned at a slightly higher temperature, or in a circuit in a cooling tower. Water requirements for once-through cooling circuits are much more demanding because of the large volumes needed for continuous cooling. Oxygen (among other impurities) is also prevalent in the water taken from rivers and lakes, leading to corrosion in the pipelines if not removed adequately. Continuous circulation of the cooling water increases the concentration of contaminants in the circuit but uses much less water.

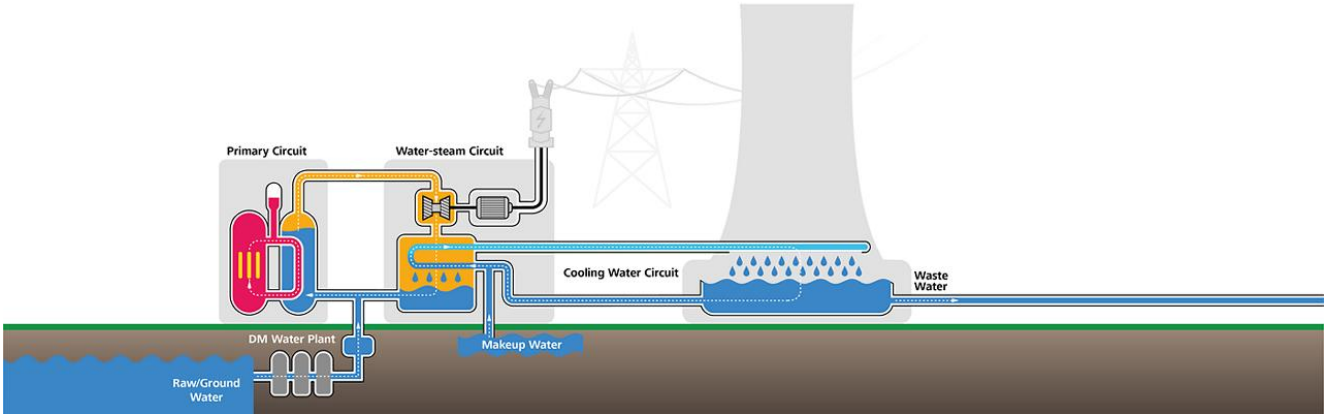

Figure 1. Schematic diagram of a thermal power plant. The cooling circuit (right) is an important attribute in two- and three-cycle power plants.

Cooling water is kept alkaline to maintain the protective oxide layer on the metal piping throughout the water circuit. Acidic water will dissolve the protective oxide layer and the metal surface. However, alkalinity above the recommended range increases the probability of scale formation (deposition). The water is therefore buffered against further pH changes with carbonate (CO_3^{2-}) and bicarbonate ions (HCO_3^-) (Reaction 1).

Traditionally, the water can be analyzed by laboratory titration. However, this methodology does not provide timely results and requires human intervention to implement the laboratory analysis results to the process. Online process analysis allows constant monitoring of water quality without long waiting times in the laboratory, giving more accurate and representative results directly to the control room.

Optimal water chemistry begins with an online analyzer such as the 2026 Titrolyzer from Metrohm Process Analytics. Save time and increase efficiency without manually sampling process points. Online analysis helps protect against corrosion and fouling in the cooling water circuit, allowing more uptime and reducing maintenance costs. Titration to pH 4.5 indicated by a pH electrode gives the so-called «m-alkalinity» (methyl orange alkalinity), also a measure of total alkalinity. Below a pH of approximately 4.3 there is no more alkalinity present, only free acid (H^+), carbonic acid (H_2CO_3), and CO_2. Therefore:

$$m - alkalinity = [HCO_3^-] + [CO_3^{2-}] + [OH^-]$$

Reaction 1. Overall reaction of m-alkalinity.

APPLICATION

Titration is performed with 0.1 mol/L hydrochloric acid (HCl) to pH 4.5. The endpoint is detected automatically by recording the change of pH/mV signal in relation with the dosed amount of titrant. A suitable pH electrode is used for accurate indication of this pH/mV change. In addition to the 2026 Titrolyzer, the 2035 Potentiometric, and 2060 TI Process Analyzers (Figures 2 and 3) can also monitor alkalinity online, guaranteeing high process efficiency and low operating and energy costs.

Figure 2. 2035 Process Analyzer – Potentiometric.

Figure 3. 2060 TI Process Analyzer from Metrohm Process Analytics.

Table 1. Thermal power plant measurement parameters * Other concentrations below the stated range can be measured by changing the concentration of the reagents.

Parameters	Range
m-alkalinity	0–110 mmol/L *
$CaCO_3$	0–1000 mg/L *

CONCLUSION

Metrohm Process Analytics offers a wide range of online process analyzers to monitor power plants around the clock. From single parameter analyzers (e.g., 2026 Titrolyzer) to multiparameter analyzers (e.g., 2035 Process Analyzer – Potentiometric and the 2060 TI Process Analyzer)—all of these solutions can measure alkalinity, helping to safeguard plant operation and optimize process cooling efficiency.

RELATED APPLICATION NOTES

AN-PAN-1003 Amine ("rich" and "lean") and free & total CO_2

BENEFITS FOR TITRATION IN PROCESS

- **Increased longevity** of valuable company assets
- Monitor **multiple sample streams** (up to 10) for more savings per measurement point and results
- **Safer working environment** and automated sampling
- **Fully automated diagnostics** – automatic alarms for when samples are out of specified parameters

CONTACT

Metrohm Brasil
Rua Minerva, 161
05007-030 São Paulo
metrohm@metrohm.com.br

CONFIGURATION

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

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.

2026 Titrolyzer

The 2026 Titrolyzer performs potentiometric titrations by means of a high precision burette system and high performance electrodes. Different titration types include acid/base, redox and precipitation titrations. A self-finding inflection point technique can be applied for most applications. It is also possible to use the analyzer to measure pH in situations where inline sensors would otherwise fail.

Additionally, the 2026 Titrolyzer can perform the dynamic standard addition method by means of the high precision burette and high performance Ion Selective Electrodes (ISE). This method adapts the standard addition volume to the actual sample concentration by means of a dynamic differential approach. Moreover it takes into account ISE slope values over several ranges. This means that ISEs can be used to their ultimate low or high measuring ranges. An accompanying temperature measurement eliminates possible temperature effects on the analysis results.

Several markets are a perfect fit for the 2026 Titrolyzer such as chemical, petrochemical, semiconductor, environmental, mining, steel/metal, and potable water.

Selected applications include:

- Acidic or alkaline solutions
- Chloride
- Hydrogen peroxide
- Hardness
- Cyanide
- Copper
- Hydrogen fluoride
- pH
- and more