



Application Note AN-PAN-1018

Online analysis of acids, bases, and aluminum in anodizing baths

Anodizing is an electrochemical process that involves submerging a metal (usually aluminum) in a cool acidic bath and applying an electric current. The metal itself acts as the positive electrode (anode) in this process. This electrochemical treatment results in a tougher, more corrosion- and wear-resistant surface, while also improving the overall strength of the metal. Before the aluminum anodizing step, aluminum

surfaces are cleaned in etching baths. To maintain surface properties, online monitoring of bases (e.g., NaOH), acids (e.g., H_2SO_4 , HNO_3 , HF, H_3PO_4), and aluminum are required in the bath. This is best achieved by online titration with the 2060 TI Process Analyzer or 2026 HD Titrolyzer, depending on user requirements.

INTRODUCTION

Aluminum is the most abundant metal found on Earth and is a very reactive base metal [1]. It is suitable for industrial use because it is lightweight, conducts electricity and heat well, and resists corrosion [2].

Aluminum metal reacts with oxygen, water, or other oxidizing agents to create a protective layer of aluminum oxide (passivation) [3–5]. This natural oxide layer protects the underlying aluminum against corrosion, but with some limitations [5].

Anodizing is an electrochemical treatment that increases the thickness of the aluminum oxide layer on the metal surface. The anodizing process makes aluminum harder and more resistant against rust [6]. It involves pretreatment, core treatment, and finishing steps to complete the cycle (Figure 1) [7].

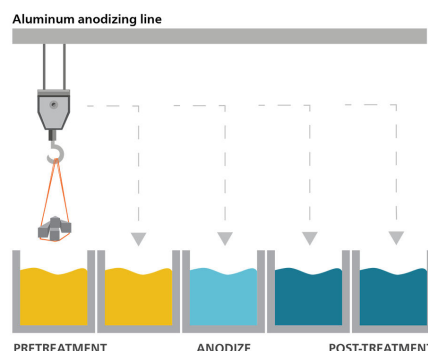


Figure 1. Illustration of a typical anodizing line.

INTRODUCTION

First, the workpiece is cleaned to remove dirt, oil, and lubricants. Then, it is treated with a special solution to remove the natural oxide layer before anodizing. This step is known as alkaline etching.

Maintaining the proper balance between dissolved aluminum and other chemicals in the etching bath is crucial in this step. This balance is often referred to as the aluminum-to-free-soda ratio.

If this ratio strays outside of the recommended range, a reaction occurs where sodium aluminate breaks down into an aluminum trihydroxide substance. This undesirable byproduct coats the workpiece and hinders the anodizing process from achieving a successful finish. In simpler terms, keeping the ideal ratio of substances in the bath ensures a smooth anodizing operation, while an inadequate mixture disrupts the process by forming a layer that blocks

anodization.

Traditionally, etching processes can suffer from inconsistencies as the etching agent (like sodium hydroxide in this case) is depleted. This depletion leads to a gradual slowdown in the etching rate, resulting in variations in the final product's appearance.

To combat these inconsistencies and ensure high-quality results, recurrent monitoring is necessary by means of an online process analyzer. These analyzers continuously track two crucial components: the concentration of the basic solution (often sodium hydroxide) and the level of dissolved aluminum within the etching bath. By maintaining these within a designated range, consistent etching is ensured throughout the process.

Additionally, anodizing baths are typically made up of a sulfuric acid electrolyte. During the anodizing process, the workpiece is made anodic so that the metal reacts with oxygen from the anion, and an oxide layer forms on the surface.

For a flawless anodized finish, meticulous control of the aluminum and sulfuric acid concentration within this bath is essential. If the aluminum concentration is too high, it can negatively impact the final surface appearance and lead to increased electrical resistance during the process. Sulfuric acid is consumed due to a degree of product drag out and must be replenished regularly to reduce running costs while still generating a high-quality finish.

While laboratory analysis has traditionally been used to monitor anodizing bath chemistry, it has limitations. This method typically involves manually collecting a sample from the bath, sending it to a lab for analysis, and then waiting for the results. This time delay can lead to inconsistencies in the anodizing

process, as the bath chemistry can fluctuate between sampling times. Additionally, laboratory analysis can be labor-intensive and costly.

In contrast, online process analyzers offer a more efficient and reliable solution for maintaining optimal bath chemistry. These instruments continuously monitor the concentration of critical parameters within the bath, such as dissolved aluminum, sodium hydroxide, and sulfuric acid (free acid). This near real-time data allows for immediate adjustments to be made, ensuring the bath chemistry remains within the designated range 24/7.

The elimination of manual sampling combined with the continuous monitoring offered by online analyzers significantly reduces the risk of bath chemistry fluctuations, ultimately leading to fewer defects and the need for rework. By providing a constant flow of accurate data, online process analyzers empower manufacturers to achieve consistent, high-quality anodizing results.

APPLICATION

Online monitoring of the alkaline and acidic components as well as aluminum by titration is possible with the 2060 TI Process Analyzer (**Figure 3**) or the 2026 HD Titrolyzer (**Figure 4**) from Metrohm Process Analytics. The selection of the optimal process analyzer depends on the specific monitoring requirements (multiparameter or single parameter, respectively).



Figure 3. The 2060 TI Process Analyzer from Metrohm Process Analytics can monitor several critical parameters online in the anodizing process.

Table 1. Parameters to monitor in an anodizing line and their expected concentration ranges.

Part of process	Parameter	Range [g/L]
Etching bath	Alkalinity	50–120
	Aluminum	70–150
Anodizing bath	Free acid	0.1–300
	Aluminum	1–10

REMARKS

Aluminum is also an ideal material for other surface treatment applications. It can be cleaned using acid pickling processes to ensure complete passivation. A pickling process is also used to prepare the aluminum for applying a conversion coating as a protective surface layer.



Figure 4. The 2026 HD Titrolyzer from Metrohm Process Analytics can monitor up to two critical parameters online in the anodizing process.

CONCLUSION

To ensure optimal surface properties are obtained during aluminum anodizing, continuous monitoring of both the cleaning chemicals (basic and acidic solutions) and the aluminum itself is crucial. This can

be effectively accomplished through online process analysis using either the 2060 TI Process Analyzer for multiparameter analysis or the 2026 HD Titrolyzer for single-parameter monitoring.

REFERENCES

1. Atwood, D. A.; Yearwood, B. C. The Future of Aluminum Chemistry. *Journal of Organometallic Chemistry* **2000**, *600* (1–2), 186–197. DOI:10.1016/S0022-328X(00)00147-9
2. Paz Martínez-Viademonte, M.; Abrahams, S. T.; Hack, T.; et al. A Review on Anodizing of Aerospace Aluminum Alloys for Corrosion Protection. *Coatings* **2020**, *10* (11), 1106. DOI:10.3390/coatings10111106
3. Zumdahl, S. S. *Introductory Chemistry*, 5th edition.
4. Spira, N. *Aluminum Oxidation: Does Aluminum Rust?*. Kloeckner Metals Corporation. <https://www.kloecknermetals.com/blog/aluminum-oxidation-is-aluminum-corrosion-resistant/> (accessed 2024-06-03).
5. Keijzer, M. *PICKLING, AN EXCELLENT SURFACE TREATMENT FOR ALUMINIUM*; Technical bulletin TB 2004/17; Vecom, 2004.
6. *How does Anodizing Increase Corrosion Resistance?*. <https://www.anoplate.com/news-and-events/how-does-anodizing-increase-corrosion-resistance/> (accessed 2024-06-03).
7. Dorigotti, D. Anodising Aluminium: Everything You Need to Know. *Dragon Metal Manufacturing*, 2023.

AN-PAN-1012 Online analysis of nickel ion and hypophosphite content in electroless nickel plating baths

AN-PAN-1019 Online analysis of acids and iron in

pickling baths

AN-PAN-1064 Monitoring complexing agents in galvanic baths inline with Raman spectroscopy

BENEFITS FOR ONLINE PROCESS ANALYSIS

- **Higher quality final product** and increased metal turnover (MTO) due to online determination of bath parameters.
- **Enhanced** reproducibility, production rates, and profitability (less waste).
- **Fully automated diagnostics** – automatic alarms for when samples are out of specification parameters.



CONTACT

Metrohm Middle East
FZC
E2-05 SAIF Zone
120747 Sharjah, UAE

info@metrohm.ae

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.