Application Note AN-PAN-1069

Online zinc/nickel plating bath analysis with X-ray fluorescence

Maintaining consistent bath composition in electroplating processes is vital to ensure product quality and operational efficiency. During the electroplating process, inconsistent plating bath composition can lead to defects and increased operational costs. Defects in electroplated components have far-reaching consequences including high rework costs, production losses, and customer returns due to premature wear or corrosion [1].

Zinc-nickel (Zn/Ni) coatings are renowned for their superior corrosion resistance. They offer five to six times greater protection than that of pure zinc coatings [2,3]. This makes them particularly valuable in automotive, aerospace, and marine applications. However, achieving and maintaining the optimal Zn/Ni ratio is challenging, especially with traditional monitoring methods like wet chemistry, AAS (atomic absorption spectroscopy), or ICP-OES (inductively coupled plasma optical emission spectroscopy). These methods are time-consuming and provide delayed results.

Metrohm offers the 2060 XRF Process Analyzer to address these challenges. This process analyzer uses X-ray fluorescence (XRF) to enable continuous monitoring of elemental concentrations within the plating bath, providing real-time data that guides precise chemical dosing.

INTODUCTION

Electroplating is a technique that uses electrical current to apply a thin coating of one material, such as nickel or zinc, onto the surface of another material, such as copper. Zinc and zinc-based alloys, such as zinc-nickel (Zn/Ni), are commonly used to protect steel from corrosion. Zn-Ni alloys are especially popular, as they offer a corrosion resistance that is greater than that of pure zinc [2,3].

Both alkaline and acidic Zn/Ni baths are commonly used for electroplating (Figure 1). Each bath type offers unique advantages depending on the application [4]. Alkaline Zn/Ni baths are known for producing highly uniform coatings with good throwing power, making them ideal for complex-shaped components. On the other hand, acidic Zn/Ni baths offer higher deposition rates and can deliver smooth, bright finishes that are often preferred for aesthetic applications [4].

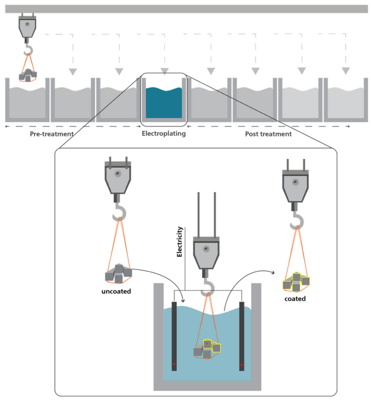


Figure 1. Illustration of a typical zinc plating process.

Electroplating baths are sensitive to various process-related fluctuations that significantly impact metal deposition and influence the final coating thickness and quality. These variations can arise due to changes in temperature, plating tank metal concentration levels, or contamination.

Analyzing the bath solution frequently is crucial to maintain stable plating conditions and minimize material waste. Continuous monitoring of the plating solutions helps ensure that the concentration of metals remains within the optimal range.

The metal content in electroplating baths is often measured manually in on-site laboratories. Classical wet chemistry techniques, AAS, and ICP-OES are commonly used for this purpose. While these methods are effective, they can be time consuming, require skilled personnel, and may not provide real-time data. This potentially leads to delayed corrections and material inefficiencies.

Modern process analytical technologies (PAT) are increasingly being adopted in electroplating operations to automate and optimize the monitoring of plating baths. These systems continuously analyze critical bath parameters such as metal concentration, pH, temperature, and conductivity in real time. All these factors directly influence the quality and uniformity of the deposited metal coating.

The 2060 XRF Process Analyzer from Metrohm Process Analytics (**Figure 2**) offers an effective solution to continuously monitor electroplating baths. By providing real-time measurements of metal concentrations such as Zn and Ni, this process analyzer helps maintain the ideal bath composition required for consistent and high-quality coatings.

Figure 2. 2060 XRF Process Analyzer for zinc/nickel baths.

APPLICATION

XRF analysis is performed using the tungsten (W) X-ray tube module equipped with a prolene window. The Vanta module operates with the pre-configured calibration method. Sample introduction is performed using PFA (perfluoroalkoxy) solenoid valves which direct the flow through a pump and into the XRF sample vessel for analysis.

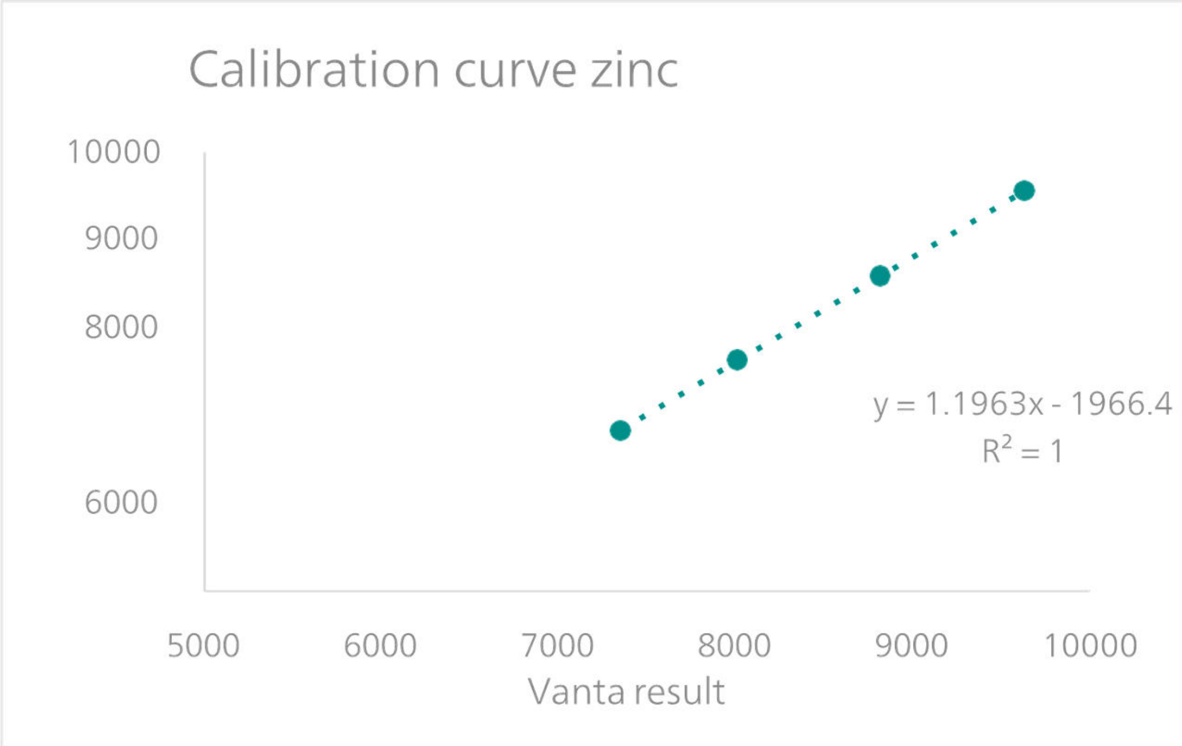
Table 1. Measuring range of different bath constituents in zinc/nickel plating baths as determined with the 2060 XRF Process Analyzer.

Parameter	Measuring range (g/L)
Zinc	6.5–9.5
Nickel	0.5–2.5

CALIBRATION

Linear calibration is established for both zinc and nickel concentrations by measuring the corresponding XRF response across a specified concentration range. For zinc, a calibration curve is created for concentrations ranging from 6.5 to 9.5 g/L, while for nickel, a similar curve is constructed within the 0.5 to 2.5 g/L range (**Figure 3**). The calibration process involves spiking the bath sample with known amounts of zinc and nickel, and each measurement is repeated in triplicate for accuracy. The results are used to determine the concentration of zinc and nickel in plating baths. This ensures precise and reliable analysis with an excellent correlation (R2 values of around 0.998 for both elements).

CALIBRATION



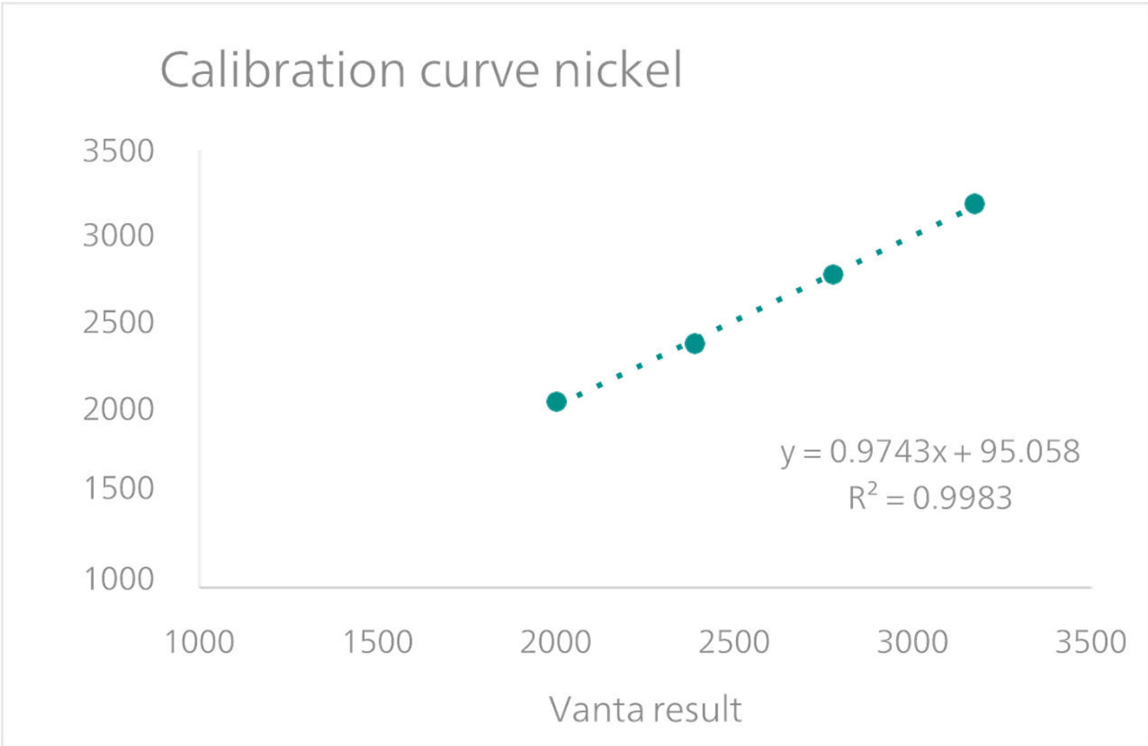


Figure 3. Calibration curve for plating bath samples in the range of 6.5–9.5 g/L zinc (top) and 0.5–2.5 g/L nickel (bottom).

REMARKS

The 2060 XRF Process Analyzer offers real-time continuous monitoring of zinc and nickel concentrations in electroplating baths. Other complementary techniques like titration can be integrated to track additional parameters such as pH and conductivity.

CONCLUSION

The 2060 XRF Process Analyzer is a reliable solution for the metal finishing industry, offering real-time monitoring of zinc and nickel concentrations in electroplating baths. Its ability to continuously measure these key bath parameters ensures consistent coating quality, reduces material waste, and improves process efficiency.

RELATED APPLICATION NOTES

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

AN-PAN-1068 Online analysis of copper, tin, and zinc in white bronze baths by XRF

BENEFITS OF ONLINE PROCESS ANALYSIS

- **Safer working environment for employees** – no exposure to dangerous chemicals.
- **Guaranteed consistent** coating thickness.
- **Early detection of deviations** – avoid reprocessing.
- **Enhances quality control** – more accurate understanding of real process conditions.
- **Ensures production of high-quality final products** via the quick response to variations in bath conditions.

REFERENCES

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CONTACT

Metrohm Brasil
Rua Minerva, 161
05007-030 São Paulo

metrohm@metrohm.com.br

CONFIGURATION

2060 XRF Process Analyzer

The **2060 XRF Process Analyzer** is a non-destructive online process analyzer employing Energy-Dispersive X-ray Fluorescence (EDXRF) technology. This analyzer ensures precise and nearly real-time monitoring of liquid sample streams within industrial processes.
With the capacity to connect up to 20 sampling points, the **2060 XRF Process Analyzer** facilitates seamless online XRF analysis. As part of the 2060 Platform, it seamlessly integrates multiple analysis techniques into one unified platform. Experience the power of combining XRF with titration or photometry for comprehensive process insights like never before.