Application Note AN-PAN-1064

Monitoring complexing agents in galvanic baths inline with Raman spectroscopy

The main purposes of galvanic process baths include the surface refinement of workpieces and the setting of physical properties. To this end, bath additives (e.g., organic compounds or complexing agents) are regularly added in different amounts, depending on the processing load. Since the bath composition changes continuously due to the introduction of the workpieces, close monitoring of the concentration of the bath additives is necessary to ensure that the end product quality is at the highest level.

This Process Application Note presents a method to accurately analyze **complexing agents** inline in galvanic baths with a **2060 Raman Analyzer** from Metrohm Process Analytics. This enables real-time bath control and thus an increase in production efficiency and product quality.

INTRODUCTION

The electroplating process consists of using electricity to coat a material (e.g., copper (Cu)) with a thin layer of another material (e.g., nickel (Ni), zinc (Zn)), usually for protective reasons.

Zinc and its alloys (e.g., Zn/Ni) are some of the main materials used for protection against steel corrosion. However, Zn-Ni alloys are primarily used because they are five to six times stronger than pure Zn to counter corrosion [1].

Organic additives or complexing agents are added to the electrolyte solution in the bath to improve the deposition process, and hence the corrosion resistance [2].

During the electroplating process, complexing agents are used to form complexes with metal ions in the electrolyte-plating solution. These complexes help to keep the metal ions in solution, preventing their premature precipitation or unwanted side reactions. Amines, for instance, can act as complexing agents in alkaline Zn/Ni baths. They form stable complexes with metal ions (e.g., Zn^{2+} and Ni^{2+}), preventing them from reacting with other ions. This helps to control the deposition potential, improve conductivity, and suppress dendrite formation [3].

Traditionally, monitoring the concentration of complexing agents in electroplating baths is done manually. This is a cumbersome process, involving the extraction of bath samples which must be transported to a laboratory for analysis.

These actions not only fail to capture the real-time composition of the baths but also entail safety risks. The delay between sample collection and analysis can lead to prejudiced results, as changes in the electroplating process may occur before the analysis is complete.

The utilization of inline Raman spectroscopy addresses these challenges by enabling the continuous analysis of inorganic and organic components, including complexing agents, in real-time. Unlike traditional wet chemical methods, spectroscopy requires no sample preparation and can be seamlessly integrated into the electroplating process. This allows minute-by-minute insights into the bath's condition and facilitates more precise control over the deposition potential, conductivity, and dendrite formation. Not only does this enhance efficiency, but it also contributes to the safety and reliability of electroplating operations.

An inline process analyzer can be connected to the galvanic bath via fiber optics and a flow cell (Figure 1). To take advantage of the multiplexing capability (i.e., several baths in alternation), valves can be activated which ensure filling of the sample line and subsequent cleaning. The entire workflow including

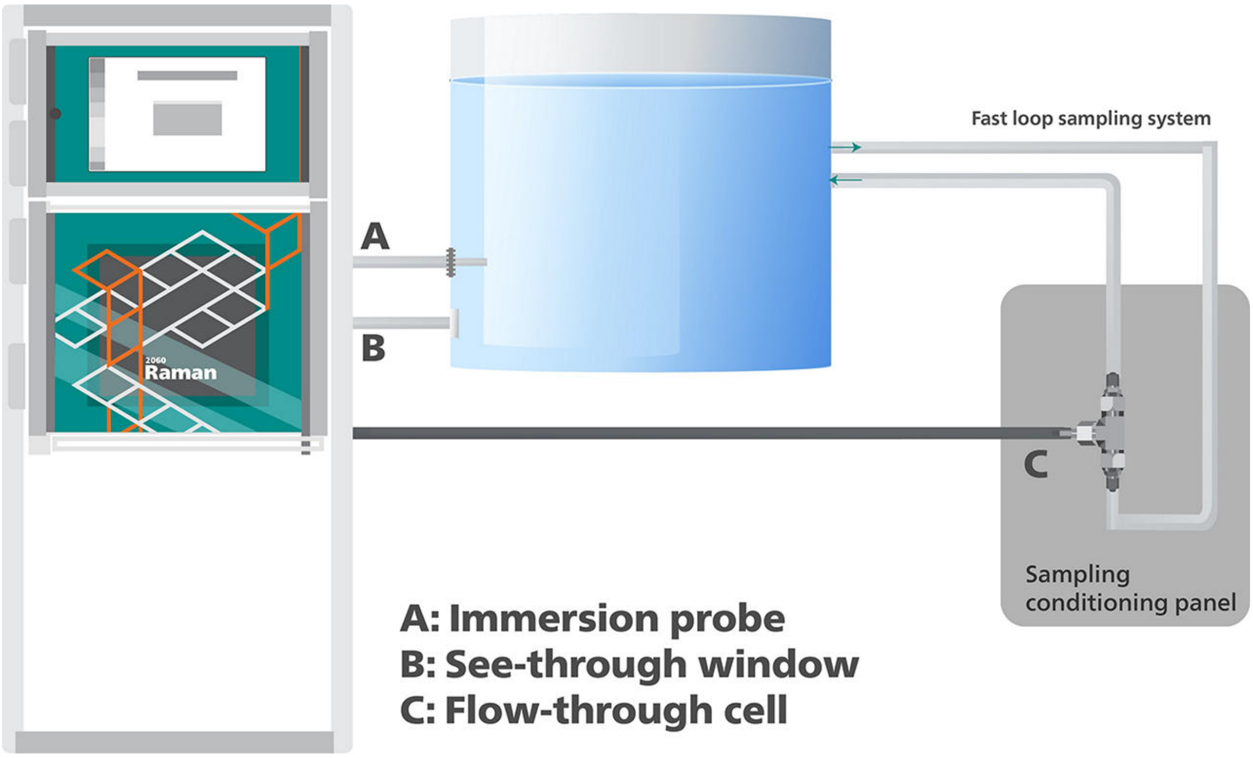

Figure 1. Illustration of a typical wet bench setup showing three different ways (A–C) to connect to the galvanic process bath for continuous inline monitoring of its composition with process Raman spectroscopy.

Figure 2. The 2060 Raman Analyzer is ideal for quantitative inline analysis of complexing agents in galvanic baths.

APPLICATION

For automated analysis during routine operation, the application is developed in advance by Metrohm Process Analytics. For this purpose, spectra are recorded with the 2060 Raman Analyzer (Figure 2). The spectra are correlated with data from a reference analysis method and a robust calibration model is created.

The calibration model is used automatically in the process. The user receives the results of the concentration measurement both in tabular form and as a process trend chart (Figure 3). The values can be transferred to a process control system via a process communication interface.

Table 1. Process parameters measured by the 2060 Raman Analyzer in electroplating baths.

	Concentration [g/L]
Organic additives (electrolytes)	0–100 ± 0.5

RESULTS

The trend chart in Figure 3 shows the results of inline Raman analysis of organic additives in a galvanic plating bath compared to the reference analysis which is performed manually. Inline analysis captures the process changes much better, allowing manufacturers to adjust bath composition quicker, saving costs.

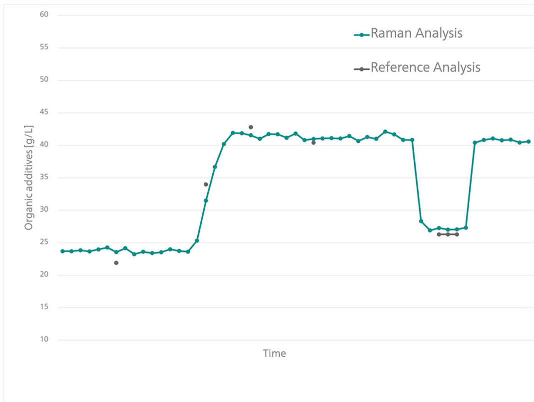

Figure 3. Trend chart of the inline Raman measurements made by the 2060 Raman Analyzer for the determination of the organic additives.

REMARKS

A reference method must still be in use. An appropriate range of samples covering the process variability should be analyzed by both methods (i.e., primary reference and Raman) to build an accurate Raman model.
Correlations are made to process specifications. The correct Raman probe must be placed in-situ in a manner that provides sufficient sample contact with the probe tip window. Correct probe design and proper placement in process equipment is highly important.

CONCLUSION

Raman spectroscopy is an easy-to-use analytical technique that identifies liquids and solids within seconds. The 2060 Raman Analyzer from Metrohm Process Analytics is a high-performance Raman system designed for monitoring different processes like electroplating.

Together with Metrohm's Vision and IMPACT software, the 2060 Raman Analyzer can be used to acquire real-time results, increase productivity, and lower production costs.

RELATED APPLICATION NOTES

- AN-PAN-1012 Online analysis of nickel ion and hypophosphite content in electroless nickel plating baths
- AN-PAN-1018 Determination of acids, bases and aluminum: galvanic industry – metal surface treatment
- AN-T-223 Analysis of electroplating baths

BENEFITS FOR RAMAN IN PROCESS

- **«Real-time» feedback** to the process to guarantee a high level of control for coatings.
- **Early detection** of bath failures.
- **Multiple parameters** from a single measurement.
- Unique Raman spectra that serve as specific fingerprints for **material identification**.

REFERENCES

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CONFIGURATION

2060 Raman Analyzer

The 2060 Raman Analyzer is a non-destructive inline process analyzer that implements Raman spectroscopy to deliver accurate and real-time process monitoring. Thanks to its self-monitoring capabilities, high-throughput spectrometer, and long-lasting laser stability, it provides immediate insights into chemical composition and enables timely adjustments for optimal process control, ensuring consistent product quality, and enhancing overall operational efficiency.

Up to 5 probes and/or flow cells can be connected to the analyzer. All 5 channels can be configured independently from each other in the embedded proprietary software.