Application Note AN-PAN-1035

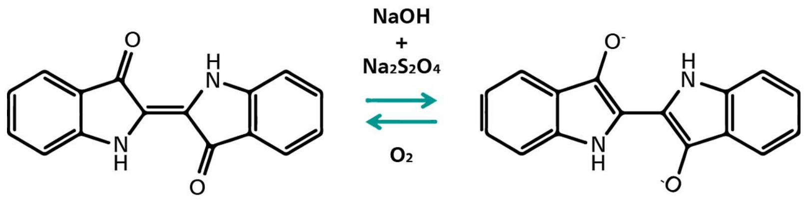
# Automated online analysis of indigo, hydrosulfite, and other parameters in textile dye baths

The size of the indigo molecule makes it difficult to dye synthetic fibers, but the large pores of cellulose (such as in cotton) accept it readily. Indigo is insoluble in water, so it must first be reduced to the water-soluble leuco-indigo form by sodium hydrosulfite in a strong alkaline bath. Good circulation within the bath is imperative for consistent dye coverage, but care must be taken not to introduce any oxygen. Fabrics must be oxidized between dips in the dye bath to set the indigo within the pores of the fibers, but multiple dips are necessary for darker, uniform coverage.

This Process Application Note is focused on monitoring indigo, hydrosulfite, and other parameters in textile dye baths using the 2035 Potentiometric and 2060 TI Process Analyzers from Metrohm Process Analytics. Many critical parameters need to be monitored and controlled to ensure high quality of the end product: the pH value for proper NaOH (alkali) dosage, the concentrations of both hydrosulfite and indigo, as well as the temperature of the bath and even the redox potential.

## INTRODUCTION

Indigo ($C_{16}H_{10}N_2O_2$, otherwise known as 2,2'-bis(2,3-dihydro-3-oxoindolyliden)) has quite a long history, originating in India as an organic, deep blue dye extracted from plants. The rarity of such a vibrant color led to its trade as a luxury commodity in many ancient civilizations. Silk, wool, and cotton were dyed with indigo, and those who wore such colored fabrics did so as a sign of wealth. By the end of the 19th century, a synthetic process to create the indigo compound industrially was discovered at BASF and is still in use today. Cotton is especially accepting of the indigo compound because of the large pore size in the cellulose fibers and does not release the molecule easily after the dye is set. This combination of color and ruggedness led to the global rise of denim/blue jeans in the past century, and no more is it seen as rare or an indicator of wealth.




**Reaction 1.** Overall reaction of indigo reduction to leuco-indigo by sodium dithionite.

Indigo itself is insoluble in water, so in order to be utilized properly as a dye, it must first be reduced with sodium hydrosulfite (sodium dithionite, $Na_2S_2O_4$) (Reaction 1) in a strong alkaline bath. It is known as a vat dye, so named because the dyeing process takes place in a contained bath called a «vat». The reduction produces a water-soluble molecule named leuco-indigo (indigo white). This is actually more of a yellow-green compound which converts back to the water-insoluble blue form in the presence of oxygen. Good circulation within the vat is necessary for consistent coverage of the compounds, though caution must be taken to limit the amount of oxygen introduced. The vat is kept at higher temperatures (up to 80 °C) which must be held constant, as this affects other parameters such as pH, consumption of the reducing agent, and the diffusion of the leuco-indigo into the textile fibers.

Multiple baths are necessary to properly dye fabrics along with circulation systems to keep concentrations stable throughout the vat because of the colloidal nature of the large dye molecule. Textiles are dipped in and gently moved around the circulating hot dye baths to ensure uniform coverage without introducing excess oxygen. Multiple dips are required for a darker blue color in the finished product, with care taken to oxidize the fabric between each dip in order to trap the leuco-indigo within the fibers. The oxidized indigo will not rinse out easily when the fabric is washed because it is now water-insoluble again. Synthetic fabrics are more difficult to dye with indigo because the large molecules have more difficulty penetrating their tightly packed fibers.

To achieve uniform color, many parameters need to be controlled for continuous dyeing processes: the pH for proper NaOH (alkali) dosage, the concentrations of both $Na_2S_2O_4$ and indigo, as well as the temperature of the vat. The redox potential of the dye bath also needs to be controlled for proper dyeing of the fabric. Manual laboratory methods can be quite cumbersome and can introduce bias depending on the analyst. Therefore, the complexity of the process necessitates inline or online analysis of the dye baths for the most precise results. A great choice for online monitoring the indigo, hydrosulfite, and other parameters such as pH and conductivity in dye baths is the 2035 Process Analyzer - Potentiometric (Figure 1) from Metrohm Process Analytics. Together with the plant circulation system, these fast-responding online process analyzers can help keep the dye bath throughput high without losing money from excess chemical consumption due to inefficient processes, ensuring the quality of the dyed fabric remains constant.

**Figure 1.** 2035 Potentiometric Analyzer from Metrohm Process Analytics.

## APPLICATION

The simultaneous monotonic titrations of hydrosulfite and indigo in indigo dye baths are performed in a closed vessel under nitrogen gas with potassium ferricyanide ($K_4Fe[CN]_6$) as a titrant and a reagent mix (NaOH + dispersing agent). The Metrohm Process Analytics 2035 Potentiometric and 2060 TI Process Analyzers (Figures 1 and 2) are ideally suited for the fully automatic execution of these analyses, as well as additional parameters like pH or conductivity.

**Table 1.** Textile dye bath measurement parameters

| Parameters | Range |
|---|---|
| Hydrosulfite | 0.25–4 g/L |
| Indigo | 0.25–7 g/L (can be expanded to measure higher ranges) |

## REMARKS

The analysis of sodium hydrosulfite and indigo must be carried under $N_2$ gas in order to prevent the evaporation and oxidation of dye with ambient air. If the sample line contains fabric particles, it needs to be filtered before the sample inlet of the analyzer to prevent blockages. This method can also be used for loop dying applications for threads and yarns.

## CONCLUSION

The Metrohm Process Analytics 2060 TI Process Analyzer and 2035 Potentiometric Process Analyzer can not only measure the concentration of indigo and hydrosulfite, but also pH and conductivity measurements to give an overall health status of the dye baths without delay.

**Figure 2.** 2060 TI Process Analyzer from Metrohm Process Analytics.

## BENEFITS FOR TITRATION IN PROCESS

- **Detect process upsets** via automated analysis.
- **Increased product throughput**, reproducibility, production rates, and profitability.
- **Better color uniformity** is achieved by constantly monitoring the chemical composition of the baths.
- **Fully automated diagnostics** – automatic alarms for when bath samples are out of the specified parameters.


## CONTACT

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## CONFIGURATION

### 2035 Process Analyzer – Potentiometrie

Der 2035 Process Analyzer verwendet für die potentiometrische Titration und ionenselektive Messungen spezielle Titriermittel und Elektroden. Diese Gerätevariante des 2035 Process Analyzers ist zudem geeignet für ionenselektive Analysen mit Hochleistungselektroden von Metrohm. Dieses genaue Standardadditionsverfahren ist ideal für kompliziertere Probenmatrices.

Die potentiometrische Gerätevariante des Analysengeräts bietet unter allen auf dem Markt angebotenen Messverfahren die genauesten Resultate. Mit weit mehr als 1000 bereits verfügbaren Applikationen ist auch die Titration in nahezu allen Industriezweigen eines der meist eingesetzten Verfahren zur Analyse Hunderter von Komponenten und reicht von der Säure-Base-Analyse bis zur Bestimmung der Metallkonzentrationen in Galvanikbädern.

Die Titration ist eine der gängigsten chemischen Absolutmethoden, die heute verwendet wird. Das Verfahren ist unkompliziert und benötigt keine Kalibrierung.

In dieser Konfiguration erhältliche Titrationsvarianten:

- Potentiometrische Titration
- Kolorimetrische Titration mit Lichtleitertechnologie
- Wassergehaltsbestimmung nach der Karl-Fischer-Titrationsmethode

## 2060 Process Analyzer

Der 2060 Process Analyzer ist ein Online-Analysengerät für die Nass-Chemie, das sich für zahlreiche Anwendungen eignet. Dieser Prozessanalysator bietet ein neues Baukastensystem, das eine zentrale Plattform hat, den sogenannten „Basisschrank.

Der Basisschrank besteht aus zwei Teilen. Der obere Teil enthält einen Touchscreen sowie einen Industrie-PC. Im unteren Teil befindet sich der flexible Nassteil, in dem die Hardware für die eigentliche Analyse untergebracht ist. Wenn die Kapazität des Nassteils aus der Grundausstattung nicht ausreicht, um eine analytische Herausforderung zu bewältigen, kann der Basisschrank auf bis zu vier weitere Nassteilschränke erweitert werden. So lässt sich sicherstellen, dass selbst für die anspruchsvollsten Anwendungen genügend Platz vorhanden ist. Die zusätzlichen Schränke lassen sich so konfigurieren, dass jeder Nassteilschrank zwecks Erhöhung der Betriebszeit des Analysengeräts mit einem Reagenzienschrank, der über eine integrierte (kontaktlose) Füllstandserfassung verfügt, kombiniert werden kann.

Der 2060 Process Analyzer bietet verschiedene nasschemische Methoden: Titration, Karl-Fischer-Titration, Photometrie, Direktmessung und Standardadditionsverfahren.

Zur Erfüllung aller Projektanforderungen (oder all Ihrer Bedürfnisse) sind auch Probenaufbereitungssysteme erhältlich, die eine stabile Analyselösung garantieren. Wir können jedes Probenaufbereitungssystem liefern, unter anderem zum Kühlen oder Heizen, Druckmindern oder Entgasen, Filtrieren und für vieles mehr.