Application Note AN-PAN-1035

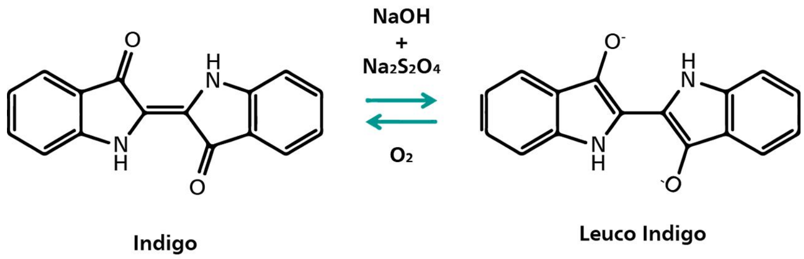
Automated online analysis of indigo, hydrosulfite, and other parameters in textile dye baths

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 - 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.