Application Note AN-PAN-1035

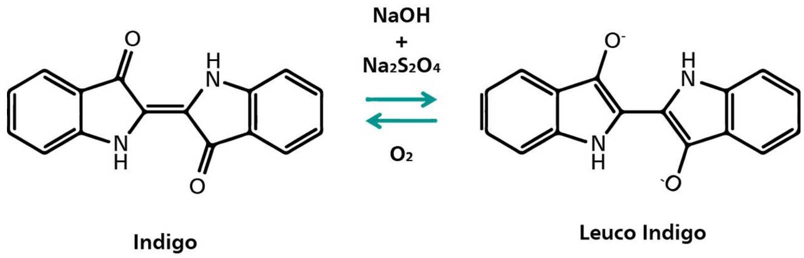
Automated online analysis of indigo, hydrosulfite, and other parameters in textile dye baths

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

用于位滴定和子性量的 2035 Process Analyzer 程分析,可使用用和滴定行分析。此外,版本的 2035 Process Analyzer 程分析用于使用万通高性能行子性分析。一精的准溶液技是理品基的理想方法。

此位分析款型的分析可提供当前市上所有量技的最精果。滴定法作最常用的分析方法之一,具有超 1000 用可供使用,能分析数百成,从酸/元素直到解池中金属度,可用于几乎任何行。

滴定法是目前使用最广泛的化学方法之一。技易行,无需校准。

可用于此配置的部分滴定:

- 位分析滴定
- 使用光技的比色滴定
- 基于·休滴定法定水

2060 Process Analyzer

2060 Process Analyzer 是一在湿化学分析,用于无数用。此程分析提供了一个新的模化概念,由一个称«主机»的中心平台成。

主机由部分成。上部包含触摸屏和工算机。下部含有柔性取部,其中放有用于分析的硬件。如果主取部容量不足以分析挑,那主机可以展多四个外的取部机,以保有足的空来最具挑性的用。附加机的配置方式使每个取部机可以与具有集成(非接触式)液位的合使用,以增加分析的正常行。

2060 Process Analyzer 提供不同的湿化学技:滴定法、舍滴定法、光度定、直接量和准添加入法。

足所有目要求(或足的所有需求),可提供品理系,以保分析解决方案可靠。我可以提供任何品理系,如冷却或加、和脱气、等。