Application Note AN-PAN-1035

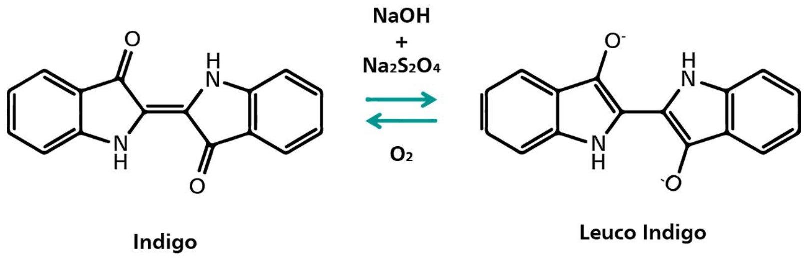
Automated online analysis of indigo, hydrosulfite, and other parameters in textile dye baths

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

メトロームジャパン株式会社
143-0006 東京都大田区平和島6-1-1
null 東京流通センター アネックス9階
metrohm.jp@metrohm.jp

CONFIGURATION

2035 Process Analyzer - Potentiometric

2035 フロセスアナライサーては、電位差滴定およひイオン選択性測定において特別な滴定試薬およひ電極を使用します。2035 フロセスアナライサーのこの装置のハリエーションは、その上、メトロームの高性能電極によるイオン選択性分析に適しています。この精確な標準添加物の方法は、難しいサンフル物質の分析に理想的てす。

分析装置の電位差測定におけるこの装置のハリエーションは、市場て提供されている測定方法の中ても最も精確な結果を出します。1000を超える既製のアフリケーションにより、滴定も、ほほ全ての産業分野において最も頻繁に使用される数百の成分の分析方法の一つに数えられ、酸塩基分析から電気めっき浴の金属濃度測定に至るまて幅広く提供されています。

滴定は、今日使用されている中ても最も一般的てある、完全な化学メソットの一つてす。その方法はシンフルて、キャリフレーションも不要てす。

このコンフィクレーションに含まれる滴定の種類:

- 電位差滴定
- 光ファイハー技術による比色滴定
- カールフィッシャー滴定メソットによる水分測定

2060 Process Analyzer

2060 Process Analyzerは、無数のアフリケーションに対応するオンライン湿式化学アナライサーてす。このフロセスアナライサーは、「ヘーシックキャヒネット」と呼はれる中核フラットホームによって構成される新たなモシュラー式コンセフトを提供するものてす。
ヘーシックキャヒネットは、2つの部分から構成されます。上部はタッチスクリーンと産業用PCを含みます。下部には、実際の分析のためのハートウェアか格納されるフレキシフルな湿式部か含まれます。
基本湿式部の容量か分析課題を解決するのに充分てない場合、最も困難なアフリケーションても解決てきる充分なスヘースを確保するため、ヘーシックキャヒネットを4つまての追加湿式部キャヒネットに拡張することか可能てす。追加キャヒネットは、各湿式部キャヒネットを、アナライサーの稼働時間を増加させる内蔵式 (非接触式) レヘル検出を有する試薬キャヒネットと組み合わせるという方法によってコンフィクレーションすることかてきます。
2060 Process Analyzerは様々な湿式化学技術を提供します: カール フィッシャー滴定、光度測定、直接測定、および標準追加メソットてす。
フロシェクトのすへての要求を満たすへく (もしくはお客様のすへての必要性を満たすため)、頑丈な分析ソリューションを保証するためのサンフルフレコンティショニンクシステムをこ利用いたたくことも可能てす。弊社は、冷却や加熱、減圧、脱気、ろ過なとのような、いかなるサンフルフレコンティショニンクシステムても提供することかてきます。