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Application note

Automatic determination of indigo and sodium dithionite in vat dyebaths

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Introduction

This article describe the results of experimental work undertaken in the last decade that let Enscada to develop a technology viable for commercial use in automatic determination of both indigo dye and sodium dithionite.

Academic research of the last decade

Indigo is a vat dye, is insoluble in an aqueous solution in its oxidised form, but is water soluble in its leuco form in an alkali solution [2]. It becomes insoluble again by oxidation after fabrics have been steeped. Sodium dithionite in an alkali solution is usually used to reduce indigo to its leuco form. Concentrations of indigo and dithionite have been monitored simultaneously by electrochemical titration using potassium hexacyanoferrate(III) as the titrant. Event though this method is widely used in at−line analyzers, there are interferences due to black sulfur dye when present as bottoming. Further, it is not possible to determine indigo at all by titration if dithionite is not present in dyebaths. Lastly, titration method has shown in the last decade to be less reliable than optical methods in continuous indigo dyebaths measurements.

In [6] a flow injection technique was introduced for continuous monitoring of reagents in dyebaths, and multivariate calibration models were developed to allow rapid determination of each dye in a mixture.
In a more recent study, flow injection analysis (FIA) was developed as a real−time analytical technique for determining leuco indigo dye concentration in a batch dyebath process. A 20−µL sample was introduced in FIA and diluted with five different reducing agents.
Absorbance measurements were made at 406 nm at the maximum of the leuco indigo absorption peak with a fiber optic coupled spectrometer. However, the method was very sensitive to atmospheric oxygen, and the concentration of leuco indigo decreased as the reduced molecules came into contact with atmospheric oxygen and oxidised [5].

Nitrogen gas was bubbled continuously into the solution to prevent this oxidation of leuco indigo.
In another study, a voltammetric sensor was developed using a rotating disc chronoamperometric technique for determining sodium dithionite and indanthrene/indigo dyes in alkaline solution by Govaert et al.[4].
Due to the absorption of the oxidised dyestuff to the electrode surface, multipulse potential steps were used to reduce the dye to soluble form and to clean the surface. In the semicontinuous determination of dyestuff at −0.6 V versus SCE, there was a small interference due to the presence of dithionite.
This method yielded a linear relation between the measured current and the dye concentration from the detection limit up to 6 g.
In [1] fiber optic sensors measured the relative absorbance and reflectance of dye solutions and dyed fabrics with respect to the standard solutions. The sampling path could be adjusted down to 0.1 mm, and absorbance was measured directly in the solution. However, the method was not suitable for measuring dye concentrations in dyebaths, so no real−time monitoring could be done in that study.
Using various dosing techniques or continuous techniques after dyeing results in a relatively long response time for determining dye concentrations.
In [7] a laser diode absorption spectrometer is coupled with a continuous dilution system for real−time monitoring of indigo dyeing of denim yarn.

The reduced form of indigo in the dyebath is continuously pumped by a peristaltic pump into a mixing cuvette, where it is diluted by a factor of 80 with aerated water and oxidised into its stable form. This solution is then pumped into the sampling cell of the laser diode spectrometer for absorption measurements. Monochromatic radiation emitted from the laser diode at 635 nm is used to measure indigo absorption at the shoulder of a broad absorption peak. A linear calibration curve is obtained in a concentration range between 10 and 150 mg/l with a linear regression coefficient of r2 = 0.9993, which corresponds to indigo concentrations in the dyebath covering the range between 0.8−12 g/l. The last implementation, event though is viable for commercial use, is limited to the automatic analysis of indigo, while sodium dithionite is not taken into consideration.

Figure 1

Enscada method for automatic analysis of indigo and sodium dithionite in vat dyebaths: Endenim automatic chemical analyzer

Endenim has been built incrementally in two phases:

Phase one, 1996: **Tintometro**

Development of Tintometro has been undertaken at a main Italian denim producer during year 1996 on indigo rope dye ranges. (figure 2)
Tintometro is an at−line analyzer. An operator has to grab the sample from dyebath and submit it to Tintometro for analysis.

Figure 2

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Phase two, 2002−2004: **Endenim**

Development of Endenim, a chemical analyzer with a full automatic sampling system.

Each analyzer is connected to two dye ranges.
At the end of 2004 Endenim has undertaken all operation tests and passed them in three installation sites. (figure 3)

Phase three, 2006: **IHPA**
(Indigo Hydrosulfite Process Analyzer)

IHPA has been designed for the international market with modularity and serviceability in mind.
It consists of the following two modules:

a Sensor Actuator Manager Unit (SAMU) and a Sample Conditioning Unit (SCU). (figure 4)

Figure 3

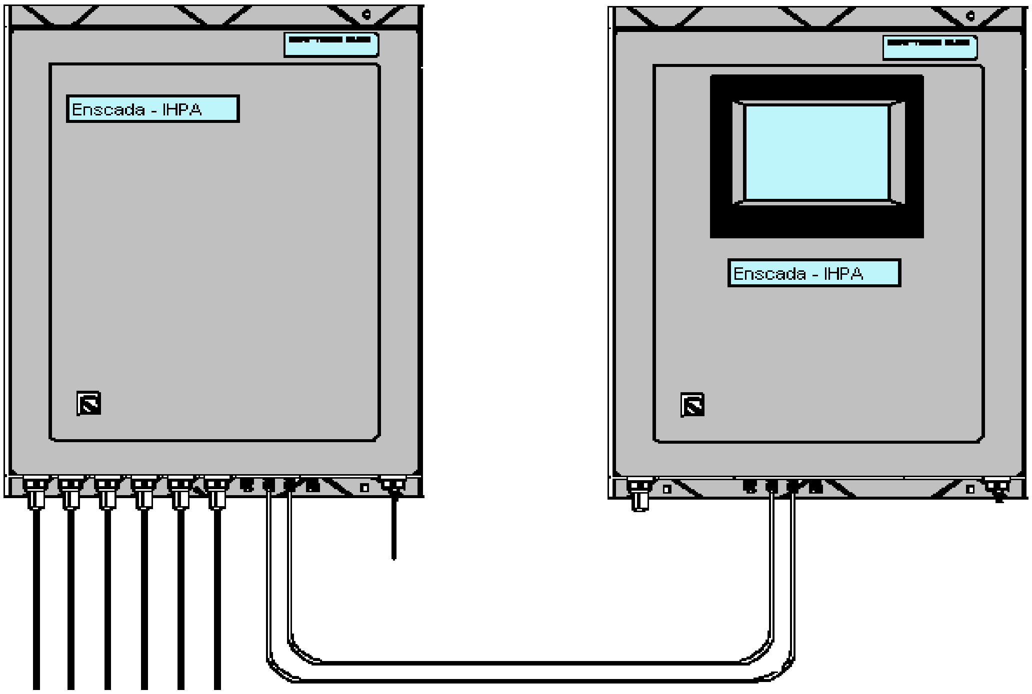

Figure 4

Sample Conditioning Unit (SCU)

Sensor Actuator Manager Unit (SAMU)

SAMU is a sampling system controller and a communications gateway/bridge to exchange measurements and configuration data between the sensor/actuators, contained inside the SCU.

SAMU is an embedded computing device furnished with an industry common operating system and chemometric software that manage the calibration.

Both Endenim and IHPA require that the dyer or the chemical analyst performs the calibration on an as need or regular basis by manual sampling the indigo circulation.

IHPA SCU is connected to the indigo dye range by means of a sampling loop connected to the recirculation of the dye liquor as shown in figure 5. The SCU performs all the necessary operations for the conditioning of the bath. After conditioning, the SAMU can read the concentrations of indigo dye and sodium dithionite in g/l units.

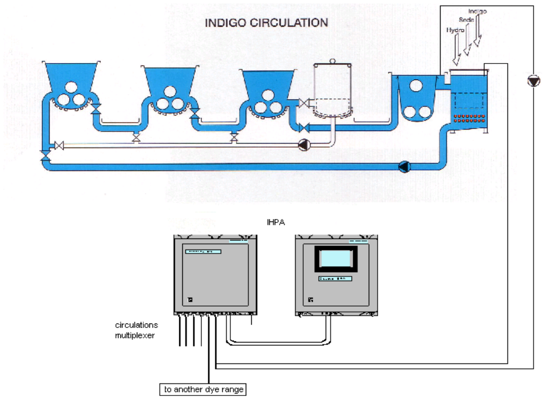

Figure 5

Endenim results

In this article we want to show five main experimental results of Endenim technology:

Range of indigo analysis is very high: 0.0 − 30.0 g/l.

Endenim SCU covers the indigo concentration range between 0.0 − 30.0 g/l and the sodium dithionite concentration range between 0.0 − 3.0 g/l. Some customers produce dark indigo shades using 15.0 − 20.0 g/l indigo dyebaths.

The indigo measurement precision at low concentration levels is high: 0.01 g/l.

Indigo detection require high precision at low concentrations. Endenim features very precise measurement at low concentrations. High stability of the measurement is required at low concentrations, because the small variations of indigo concentrations, below 3.0 g/l, are highly visible on the final dyed fabrics. In our tests Endenim precision in this range overtaken the precision of electrochemical titration using potassium hexacyanoferrate(III) as the titrant.

The analyzer require low maintenance.

The main result of Endenim operation is reliability. The required maintenance is low, even with high concentration dyebaths. The maintenance can be easily programmed, based on metric counters present on the analyzer.

Modularity.
Endenim sample conditioning unit performs indigo and sodium dithionite analysis in a modular, independent and integral way.

Low cost of operation.
The main cost of operation is the refilling of not analytical grade reagents.

Conclusions:
with these five main goals achieved, it is possible to satisfy every customer who has a visible and consistent upper management support of process analytical chemistry.

Enscada expertise

- Enscada is able to design process spectrometers for UV/VIS applications.
- Enscada is able to design sample conditioning units.
- Enscada is able to develop embedded SAMs (Sensor Actuator Managers), with chemometrics software for calibration purposes. SAM is a sampling system controller and a communications gateway/bridge to exchange measurements and configuration data between the bus−sensor/actuators.

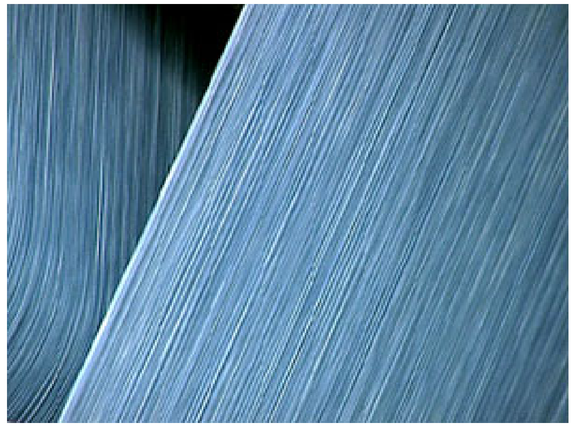

Figure 6

Organisation issues:

Although this article has focused upon the technologies involved in the automatic determination of indigo and sodium dithionite in vat dyebaths, it may not be obvious to many readers that successful implementation is more dependent upon corporate organisational issues than upon the instrumentation itself. This is a bold statement. Process analytical chemistry is highly multi−disciplinary[8]. It involves process engineers and chemists who know what they want to measure and where it can be measured, instrumentation technicians who will maintain the instrument, technology gatekeepers who look for new instrumentation, analytical chemists who perform the laboratory chemical analyses upon which the calibration is based, and researchers who likely perform the initial feasibility studies.
There are also specialists in data communication, safety and others. Therefore, the person who identifies the instrument may not be the same person who calibrate it, or who is the eventual "owner" of the equipment. The person who develops the calibration may not be responsible for its maintenance over time.
Companies that establish the means for this "internal technology transfer" among their various groups will have the greatest likelihood of achieving the benefits of on−line analytical technology described above. A fundamental requirement for such success *is visible and consistent upper management support of process analytical chemistry*.
Without this, workers will be less inclined to "stick their neck out" and try a new technology that may help their organisation to improve product quality more efficiently. This is difficult in an era of corporate downsizing where concern for job security does not inspire workers to take such risks. This is also made difficult in most instances because these instruments are often installed in existing, profitable processes. Their benefit is not "all or nothing", but rather incremental, which is harder to justify. Sometimes, catching a major process upset early pays for the entire cost of the instrument. In other words, if everything worked perfectly there would be no need for automatic analytical instrumentation in the first place. Lastly, for companies just beginning to consider such on−line technology, it is important to build advocacy with early success by judicious selection of the first application.

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Figure 8

Customer references

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Figures

The front page figure shows the first Endenim installation beside a sheet dye range in Italy in 2002.

Figure 1 shows the first indigo dyebath box on a dye range.

Figure 6 shows a yarn sheet at the exit of the first dyebath box.

Figure 8 is an enlarged view of figure 3. Endenim is shown between two sheet indigo dye ranges in Italy in 2004. Endenim's built−in automated stream switching allows the user to analyze the indigo circulations of two dye ranges.

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