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# A simple titrimetric method for the estimation of reactive dye fixation on cellulosic fabrics

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## Abstract

A high level of fixation, of dye to fibre, is an essential feature of commercially successful reactive dyes. The commonly used methods of determining dye fixation involve either (1) collection and optical assessment of all unfixed dye within the dyebath and combined wash liquors or (2) dissolution of dyed fabric in 70% sulphuric acid and optical assessment of resulting dissolved colour. Occasionally the optical strength of dyeing has been used as a measure of dye fixation: this makes the assumption that the observed colour strength of a piece of dyed fabric is proportional to the concentration of dye.

It has been found that azo dyes fixed to cellulosic substrates are readily reduced by titanous chloride. The quantity of titanous chloride utilised in this process is readily quantified by titration, thus providing a simple and rapid method for the determination of dye fixation. The results of this method were in good agreement with those of the sulphuric acid dissolution method.

*Keywords:* Reactive dyes; Dye fixation; Titrimetric analysis; Titanium (III) chloride

## 1. Introduction

Manufacturers of reactive dyes commonly quote values for the fixation efficiency of their dyes. This represents one of the most important techno-commercial properties of a given dye since high fixation is a necessary pre-requisite for economy. Additionally, high fixation efficiency results in less colour in dyehouse effluent: this is particularly important given the difficulty associated with the destruction of reactive dye residues.

The first reactive dyes for cellulosic substrates were invariably monofunctional; that is they possessed a single electrophilic reactive group and are typified by the Procion H/P (monochlorotriazines) and Cibacron F (monofluorotriazines) ranges. These were followed by many bifunctional types such as the Procion H–E dyes: these possessed two similar (monochlorotriazinyl) reactive groups and fixed much more efficiently to cellulose than their monofunctional analogues. Subsequently heterobifunctional types were introduced, typical of these are the Sumifix Supra

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dyes which possess both monochlorotriazinyl and vinyl sulphone reactive groups within the same molecule. More recently many other ranges of heterobifunctional dyes have been introduced which usually incorporate two similar or dissimilar reactive groups. These include the Driamarene HF, Cibacron LS, Procion H-EXL and XL+ and Levafix CA ranges of dyes.

In much of the trade literature dye manufacturers claim and exemplify high dye fixation [1]. However, there appears to be a dearth of information in the academic literature concerning reliable and simple methods for the assessment of dye fixation.

At least three methods have been used for determining dye fixation. Dye manufacturers have traditionally collected, and assessed spectrophotometrically, the quantity of dye remaining in the dyebath after dyeing together with that present in each wash bath [2]. This has proved to be a useful tool for illustrating the ease of wash-off of a particular dye. Also by summing the total amount of colour within the combined used dyebath and wash liquors, the total quantity of unfixed, and thereby fixed, dye can be determined.

Another method that has been used industrially has involved the dissolution of dyed fabric or fibre in 70% sulphuric acid, followed by assessment of the quantity of dye in the resulting solution optically [2]. This method is limited only to those chromophores which are stable in 70% sulphuric acid.

Several academic workers [3–5] have used the visual strength of a piece of fabric as a measure of the amount of fixed dye. This is an extremely simple and convenient experimental technique and relies upon the concentration of dye being directly proportional to the visual depth of shade of the fabric. Although this assumption might be valid at pale depths of shade we have found this method to be unreliable at medium/heavy depths.

The determination of dye strength (effective agent content) can be achieved by many methods. These include elemental analysis [6], oxidation [7], ash determination [8] and flame photometry [9]. We have used the reduction of azo dyes with titanous chloride as a convenient method for the estimation of the strength of azo dyes after synthesis, or prior to application [10]. We now report that azo dyes covalently attached to cellulosic substrates are also readily reduced by titanous chloride, moreover the quantity of titanous chloride consumed gives a direct measure of the amount of an azo dye fixed to cellulosic fibres or fabrics.

## 2. Experimental

UV/visible spectra of dyes, in 70% sulphuric acid, were recorded using 1 cm cells and either a Phillips PU 8700 or a Camspec 350 UV/visible spectrophotometer.

Colour strength of dyed fabrics was assessed using a Datacolor International Spectraflash 600. Three reflectance readings were taken at different positions on the dyed fabric and the average of the three was taken at the wavelength of maximum reflectance, $\lambda_{max}$ and expressed as $K/S$ values.

Small scale exhaust dyeings, 5–20 g of fabric, were conducted using Rotadyer machines with stainless steel dyeing tubes of 100 or 500 ml capacity. Dyeings were carried out at a liquor ratio of 20:1 and at five depths of shade, namely 1%, 2%, 4%, 6% and 9% dye omf. Salt and alkali concentrations were according to the manufacturers' recommendations.

### 2.1. Determination of the strength (effective agent content) of dyes

Titanous chloride reductively cleaves aryl azo derivatives quantitatively, producing two equivalents of aminoaryl derivative (aniline in the case of azobenzene) with the consumption of four equivalents of titanium (III) chloride. This reduction is utilised in the determination of the strength of azo dyes [10]. In this method titanous chloride, of accurately known strength, is titrated against a solution of an azo dye. This results in rapid discharge of colour and the end point, when colour is completely discharged, allows calculation of the strength of the dye.

Because titanous chloride is readily oxidised in air it was necessary to determine the exact strength of each solution immediately before use. This was done by titrating against a dye of accurately known strength in order to determine the exact strength (titanous factor, Tf) of the titanous chloride solution immediately before use.

A sample of dye of unknown strength (ca. 0.2 g) was dissolved in distilled water (100 ml) in a conical flask together with potassium sodium tartrate buffer (20%, 20 ml). The contents of the flask were heated to boiling under an argon atmosphere and titrated against freshly standardised titanous chloride solution (ca. 0.1 N). The results were taken as the mean of three readings. The Mole In, that is, the number of grams containing 1 mole of dye, was calculated as described below (see Section 3).

### *2.2. Determination of dye fixation*

#### *2.2.1. Dissolution in 70% sulphuric acid (Method A)*

In the first stage of this method a sample of commercial dye was dissolved in 70% sulphuric acid in order to determine the optical absorbance per unit weight of dye. Secondly, a sample of dyed fabric was digested in the same solvent and the optical strength determined; this allowed calculation of the concentration of covalently bound dye, and hence the percentage fixation of dye.

Thus a sample of commercial dye (ca. 0.1–0.2 g) of known effective agent content was dissolved in 70% sulphuric acid (1 l) and the optical density measured. This solution was diluted successively by factors of 2, 4 and 8: in each case a graph of absorbance versus concentration was a straight line indicating adherence to Beer's Law. Additionally, from the slope of the straight line the molar extinction coefficient of the dye could be determined.

Similarly, dyed fabric or fibre, typically 0.1–1.0 g, depending on the depth of the shade, was added to cold 70% sulphuric acid (ca. 20 ml) with stirring in a 25 ml graduated flask. After dissolution was complete, generally 0.5–2.0 h, further solvent was added up to 25 ml. The amount of colour in this solution was then determined colorimetrically.

#### *2.2.2. Reduction of fixed dye with titanous chloride (Method B)*

Dyed cotton fabric (ca. 3 g) was cut into small pieces (ca. 2 × 2 cm) and placed in a 3-necked flask under argon. Potassium sodium tartrate buffer solution (20% w/v: 40 ml) and water (60 ml) were added. After heating the mixture to boiling, titanium (III) chloride solution (nominally 0.2 m in 6 N HCl ex Fisher; 8 ml) was added and the hot mixture agitated under argon at 80–85 °C for 20 min, after which time colour had been completely discharged. Fabric was then removed, excess liquor squeezed out by hand and the damp fabric washed with hot distilled water, the washings being returned to the flask. The excess titanium chloride remaining in the clear solution was then back titrated, at 80–85 °C, against a solution of standard dye, in this case Procion Orange MX-2R (6 g/l), until the added dye is no longer discharged by the excess titanium chloride and an orange colour persists.

## 3. Results and discussion

### *3.1. Measurement of dye fixation by sulphuric acid dissolution (Method A)*

The absorbance of each commercial dye was measured in 70% sulphuric acid. All appeared to adhere to Beer's Law in this solvent: in each case a graph of absorbance ($A$) versus concentration of dye in mg $l^{-1}$ [Dye], was a straight line, of the type $A = m[\text{Dye}]$. Table 1 lists the value of $m$ for each dye. Additionally, the value of the absorbance remained essentially unchanged over 24 h indicating that the dyes were stable over the timescale of the experiments.

Having determined that each dye obeys Beer's Law in 70% sulphuric acid, samples of dyed fabric, of accurately known weight, were dissolved in the same solvent. After dissolution the optical

Table 1
Dissolution of dyes in 70% sulphuric acid

| Procion dye | Yellow H-4R | Yellow MX-GR | Navy H-ER |
|---|---|---|---|
| Slope of graph | 0.0162 | 0.0372 | 0.0133 |

density of the resulting solution was recorded. From this, and the data listed in Table 1, it was possible to calculate the concentration of dye, and thus the fixation of dye to the fibre or fabric.

### *3.2. Measurement of dye fixation by titration against titanium (III) chloride (Method B)*

Titanium (III) chloride, when used as a reducing agent, itself undergoes oxidation

$$Ti^{3+} \rightarrow Ti^{4+} + e^-$$

Nitro-, nitroso-, azo-compounds, quinones; indophenols and many dyes such as indigo, triarylmethane and azo dyes can be reduced with titanium (III) chloride.

Examples are depicted below:

$$R{-}NO + 4H^+ + 4Ti^{3+} \rightarrow 4Ti^{4+} + R{-}NH_2 + H_2O$$

$$R{-}NO_2 + 6H^+ + 6Ti^{3+} \rightarrow 6Ti^{4+} + R{-}NH_2 + 2H_2O$$

$$R_1{-}N{=}N{-}R_2 + 4H^+ + 4Ti^{3+} \rightarrow 4Ti^{4+} + R_1{-}NH_2 + R_2{-}NH_2$$

$$\text{Quinones} + 2H^+ + 2Ti^{3+} \rightarrow 2Ti^{4+} + \text{Hydroquinones}$$

$$\text{Dyes} + xH^+ + Ti^{3+} \rightarrow xTi^{4+} + \text{Leuco-compounds}$$

Reduction of a monoazo dye with titanium chloride can be depicted as follows ($R_1/R_2$ = [hetero] aromatic group)

$$\begin{array}{r} 4Ti^{3+} \rightarrow Ti^{4+} + 4e^- \\ R_1{-}N{=}N{-}R_2 + 4H^+ + 4e^- \rightarrow R_1{-}NH_2 + R_2{-}NH_2 \\ \hline R_1{-}N{=}N{-}R_2 + 4Ti^{3+} + 4H^+ \rightarrow 4Ti^{4+} + R_1{-}NH_2 + R_2{-}NH_2 \end{array}$$

The reduction of one mole of a monoazo dye thus formally requires 4 g atoms of hydrogen; that is, the azo group has a hydrogen factor of 4. Thus it is possible to estimate the strength of azo dyes, or any other readily reduced choromophore of the type listed above, by titration against a titanium (III) solution of known strength.

In the first stage the strength of the titanium (III) chloride solution was accurately determined by titration against a dye of known strength: this was necessary because titanous salts are readily oxidised in air and therefore need to be standardised immediately before use.

The titanous factor, Tf, of the titanium (III) chloride solution was determined (using Eq. (1)) by titration against a reference sample of Procion Red MX-GR

$$\text{Titanous factor (Tf)} = \frac{\text{Weight taken (g)} \times \text{Hf} \times 10{,}000}{\text{Volume of titre (ml)} \times \text{M.I.}} \quad (1)$$

M.I. = Mole In, i.e. the number of grams of dye containing one mole of dye.
Hf = Hydrogen factor, i.e. the number of gram atoms of hydrogen formally required to reduce one mole of dye. For one azo bond the Hf is four, for two azo bonds the Hf is eight and so on.
Tf = Titanous factor.

The M.I. strength of each unknown dye was then calculated by applying Eq. (2) and the percentage strength from Eq. (3)

$$\text{M.I.} = \frac{\text{Weight taken (g)} \times \text{Hf} \times 10{,}000}{\text{Volume of titre (ml)} \times \text{Tf}} \quad (2)$$

$$\text{Strength (\%)} = \frac{\text{Molecular weight of dye}}{\text{M.I.}} \times 100 \quad (3)$$

The strength of each sample of commercial dye was then determined by this method. Having done this, samples of cotton fabric were dyed according to the manufacturers' recommendations, at various depths of shade, typically 1% to 10% dye on mass of fabric.

The fixation efficiency of each dye was then assessed both by sulphuric acid dissolution and by reduction with titanous chloride, at each depth of shade. Table 2 lists the data for Procion Navy H-ER, a bis(monochlorotriazinyl-)disazo derivative. It can be seen that the results of the two methods are in good agreement. Similarly excellent agreement was obtained between the two methods in assessing the fixation efficiency of a cold dyeing type, Procion Yellow MX-GR (Table 3).

Table 2
Procion Navy H-ER fixation to cotton

| % Dye applied (omf) | *K*/*S* | Weight, mg, of dye fixed per gram of fabric by sulphuric acid dissolution (Method A) | Percent fixation by acid dissolution | Weight, mg, of dye fixed per gram of fabric by titanous titration (Method B) | Percent fixation by titanous titration |
|---|---|---|---|---|---|
| 2 | 18.3 | 18.2 | 91 | 18.5 | 93 |
| 4 | 27.7 | 34.5 | 86 | 32.2 | 81 |
| 6 | 30.8 | 47.5 | 79 | 51.6 | 85 |
| 9 | 33.1 | 70 | 78 | 67.3 | 75 |

Also, cotton was dyed with Procion Yellow H-E4R and the fixation determined by the two methods. Results are listed in Table 4.

Additionally cotton was dyed with a novel disazo reactive dye. The fixation by the sulphuric acid dissolution (Method A) was in excellent agreement with the value found by titration using titanous chloride (Method B). Results are listed in Table 5.

From inspection of the results it can be seen that even at heavier depths of shade the agreement between the two methods is excellent: 78% vs. 75% for Procion Navy H-ER, 34% vs. 35% for Procion Yellow MX-GR, 80% vs. 85% for Procion Yellow H-E4R and 43% vs. 42% for a novel disazo dye. A particularly valuable feature of this method is that it thus provides a relatively simple

Table 3
Procion Yellow MX-GR fixation to cotton

| Dye applied (%) | *K*/*S* | Dye fixed (mg/g) (Method A) | Dye fixed (mg/g) (Method B) | % Fixation (Method A) | % Fixation (Method B) |
|---|---|---|---|---|---|
| 2.5 | 19.7 | 12.9 | 12.1 | 76 | 72 |
| 5 | 26 | 20.6 | 18.4 | 61 | 54 |
| 10 | 25.8 | 23.2 | 23.5 | 34 | 35 |

Table 4
Procion Yellow H-E4R fixation to cotton

| Dye applied (%) | *K*/*S* | Dye fixed (mg/g) (Method A) | Dye fixed (mg/g) (Method B) | % Fixation (Method A) | % Fixation (Method B) |
|---|---|---|---|---|---|
| 2 | 14.3 | 18.8 | 17.2 | 94 | 86 |
| 4 | 23.9 | 34 | 32.0 | 85 | 80 |

Table 5
UMIST novel disazo yellow dye applied to cotton

| Dye applied (%) (under different conditions) | *K*/*S* | Dye fixed (mg/g) (Method A) | Dye fixed (mg/g) (Method B) | % Fixation (Method A) | % Fixation (Method B) |
|---|---|---|---|---|---|
| 7 | 22.4 | 11.7 | 10.0 | 20 | 17 |
| 5 | 24.6 | 15.0 | 14.8 | 35 | 35 |
| 5 | 25.8 | 17.7 | 17.4 | 41 | 41 |
| 5 | 26.4 | 15.7 | 17.0 | 37 | 40 |
| 10.5 | 30.3 | 36.8 | 36.0 | 43 | 42 |
| 10 | 26.6 | 16.5 | 18.4 | 19 | 22 |

and accurate determination of reactive dye fixation at heavier depths of shade, where we have found $K/S$ values to be unreliable indicators of dye fixation.

## 4. Conclusions

A novel and simple method for the determination of the percent fixation of reactive azo dyes to cellulosic substrates has been developed. This avoids the use of highly corrosive concentrated sulphuric acid and prolonged timescales.

The results achieved using this method are in good agreement with those obtained using dissolution of dyed fabric or fibre in concentrated sulphuric acid.

The novel method should be applicable to any other class of dyes, such as nitro dyes, which are readily reduced by titanium (III) salts and to other types of hydrophilic fibres and fabrics, as well as to some dyes that are unstable in 70% sulphuric acid.

The method appears to give very good agreement with that of sulphuric acid dissolution at heavier depths where $K/S$ values are not always reliable indicators of fixation.

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