

Design of Dyes of High Technical Properties for Silk by a Chemometric Approach

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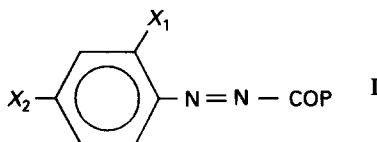
ABSTRACT

A range of amines and coupling components were explored with the aim of identifying the best structures in a series of acid azo dyes for silk. The technique of the Experimental Design in Principal Properties was used for the selection of a small number of dyes to be synthesized and tested. Fastness data have been modelled as a function of the structure by the Partial Least Squares (PLS) method. The models established allowed the prediction of the fastness of new dyes of the series. Three violet dyes, one in the training set and two in the prediction set, with outstanding fastness performance were identified.

INTRODUCTION

As a part of a wider research programme aimed at developing dyes of high technical properties for silk, we report the use of a chemometric approach to identify the best structures in a series of acid azo dyes. Many commercially available acid dyes give good results as far as dyeability of silk is concerned, but show unsatisfactory fastness characteristics.

The basic structure **I** was chosen



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where X_1 and X_2 are typical groups used in aromatic substitution and COP represents a naphtholsulphonic acid moiety.

A chemometric approach was followed in order to select a minimum number of compounds, representative of a wide series, to be synthesized and applied on silk. The technical properties (fastnesses) of the dyes were measured and modelled as a function of the structure. The models obtained were successively used to predict the properties of new dyes not yet synthesized.

The work proceeded in two steps. The first step, described in a previous report,¹ aimed at optimizing the amine component. Therefore the coupling agent (COP), 7-amino-4-hydroxy-2-naphthalenesulphonic acid was maintained fixed, while substituents of the amine component at X_1 and X_2 positions were varied.

Using the Principal Properties developed by Skagerberg *et al.*² as structure descriptors for X_1 and X_2 substituents, and the strategy of the Fractional Factorial Design,³ eight dyes were selected and successively synthesized. The fastness properties of the corresponding dyeings on silk were measured and modelled as a function of the structure by the chemometric method PLS (Partial Least Squares in Latent variables).⁴

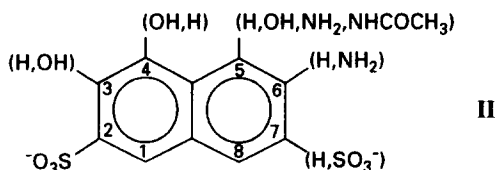
The models allowed reliable predictions for new dyes, one of which was identified as the optimum dye in the series ($X_1 = \text{NO}_2$, $X_2 = \text{COC}_6\text{H}_5$). This dye showed scores of 5 for fastness to wet treatments and a score of 4–5 for fastness to light.

In the present work we report the second step concerning the optimization of the coupling agent.

PROCEDURES

Design of the training set

The three variability points X_1 , X_2 , COP of structure I were explored by using four X_1 and X_2 combinations, i.e. four amines and five naphtholsulphonic acids of general formula II as coupling agents (COP), listed in Table 1.



Among the eight amines checked in the previous work, we chose amines 1 and 2 which gave the best dyes and amines 3 and 4 which gave dyes with

TABLE 1
Amines and Coupling Agents Explored

	Amine		Coupling agent (COP) ^b
	X ₁ ^a	X ₂ ^a	
1.	H	COC ₆ H ₅	1. H Acid (5-amino-4-hydroxy-2,7-naphthalenedisulphonic acid)
2.	NO ₂	COC ₆ H ₅	2. Acetyl-H Acid (5-acetylamino-4-hydroxy-2,7-naphthalenedisulphonic acid)
3.	H	H	3. R Acid (3-hydroxy-2,7-naphthalenedisulphonic acid)
4.	C ₆ H ₅	NO ₂	4. Gamma Acid (6-amino-4-hydroxy-2-naphthalenesulphonic acid)
			5. Chromotropic Acid (4,5-dihydroxy-2,7-naphthalenedisulphonic acid)

^a See general formula I.

^b See general formula II.

poor properties. The possible combinations of four amines and five coupling agents correspond to 20 dyes, among which 10 dyes, listed in Table 2, were selected using the technique of D-optimal designs.⁵

D-optimal designs are more appropriate than factorial designs for handling constrained problems like the selection of molecular structures.⁶

The selected dyes were synthesized and the fastness of their dyeings on silk measured.

TABLE 2
Structure of the Selected Dyes

Dye	Amine		Coupling agent (COP)
	X ₁	X ₂	
1	C ₆ H ₅	NO ₂	H acid
2	H	COC ₆ H ₅	Acetyl-H acid
3	H	COC ₆ H ₅	Chromotropic acid
4	H	H	R acid
5	NO ₂	COC ₆ H ₅	Gamma acid
6	C ₆ H ₅	NO ₂	R acid
7	C ₆ H ₅	NO ₂	Chromotropic acid
8	H	COC ₆ H ₅	Gamma acid
9	H	H	Acetyl-H acid
10	NO ₂	COC ₆ H ₅	H acid

TABLE 3
Substituent Descriptor Values

<i>Substituent</i>	<i>PP1</i>	<i>PP2</i>	<i>PP3</i>	σ_m	<i>MR</i>
C ₆ H ₅	0.364	0.008	0.170		
NO ₂	-0.678	-0.746	-0.177		
COC ₆ H ₅	0.044	-0.500	0.842		
H	-1.000	0.612	-0.048	0.00	1.03
Cl ^a	-0.592	-0.115	-0.040		
OH	-0.828	0.547	-0.518		
NH ₂	-0.718	0.798	-0.505		
NHCOCH ₃	-0.186	0.057	-0.683		
N=NC ₆ H ₅	0.800	-0.504	-0.591		
SO ₃ H				0.55	10.38

^a Substituent present in the prediction set of dyes.

Data analysis and structure description

Fastness data were modelled as a function of the structure by PLS. PLS is a regression method based on Principal Component Analysis (PCA) aimed at detecting cause-and-effect relationships between a *y* variable or a *Y* block (fastness data) and an *X* block (structure descriptors). The PLS method has already been described.^{4,7}

The structure was described using the Principal Properties from the literature² for X₁ and X₂ substituents of the amine component and for substituents at the 3, 4, 5, 6-positions of the coupling component (COP, general formula II) and σ_m and MR⁸ for substituent at the 7-position. The corresponding values are listed in Table 3.

EXPERIMENTAL

Intermediates

4-Aminobenzophenone, aniline, 3-nitro-4-aminobenzophenone, 4-aminobiphenyl, 2-chloro-4-nitroaniline, R acid, Chromotropic acid, Gamma acid and H acid were commercial samples.

2-Amino-5-nitrobiphenyl was prepared¹ by nitration of 2-(*p*-toluenesulphonamido)biphenyl with nitric acid and subsequent hydrolysis with concentrated sulphuric acid.

Acetyl-H acid was obtained by acetylation of the amino group of H acid according to the method reported in the literature.⁹

TABLE 4
Spectroscopic Data of the Dyes

<i>Dye</i>	λ_{max} (nm)	$\log \epsilon$
1	550	3.80
2	532	4.23
3	514	4.39
4	491	4.21
5	542	4.26
6	503	4.17
7	529	4.24
8	508	4.20
9	531	4.15
10	560	3.80
11^a	534	4.24
12^a	506	4.14
13^a	535	4.08

^a Dyes of the prediction set.

Dye synthesis

The dyes were synthesized by diazotization of the corresponding amine with a solution of sodium nitrite (dyes **4**, **9**, **11**) or with nitrosylsulphuric acid (dyes **1**, **2**, **3**, **5**, **6**, **7**, **8**, **10**, **12**, **13**) and subsequent coupling with the sodium salt of the naphtholsulphonic acid at pH 8.^{1,10} Coupling takes place *ortho* to the hydroxy group, i.e. at the 3-position for COP 1, 2, 4, 5 and at the 4-position for COP 3. The dyes were purified by the method previously reported.¹ Purity was checked by thin layer chromatography. The visible absorption maxima and absorptivities, reported in Table 4, were determined spectrophotometrically from aqueous solutions.

Dyeing of silk

A degummed silk twill fabric made with 23 dtex three-ply raw yarn was used for the dyeing tests. Degumming of the fabric was carried out by the method previously reported.¹¹

The dyes were applied to degummed silk in a refluxing thermostatted bath at 85° (± 0.1)C°, with a liquor ratio of about 200:1 at pH 4 (5% Na₂SO₄ and 5% dye on the weight of fibre).

Fastness assessment

Fastness to light and to mild washing, to dry cleaning and perspiration were measured according to standard procedures.¹² The fastness data are listed in Table 5.

TABLE 5
Fastness Values of the Selected Dyes

<i>Dye</i>	<i>Fastness</i>				<i>Light</i>
	<i>Washing (mild)</i>	<i>Dry cleaning</i>	<i>Perspiration</i>		
			<i>Acid</i>	<i>Alkaline</i>	
1	4	5	5	5	4-5
2	4	5	4-5	5	4
3	3	5	5	5	4-5
4	2-3	5	4	4	3-4
5	5	5	5	5	7
6	3-4	5	5	5	3
7	4	5	5	5	6
8	5	5	5	5	6
9	2	4	4	3	3-4
10	3-4	5	5	4	4

The values evidence the excellent performance of dye **5**, which gives violet dyeings with scores near the top of the scale both for wet and light fastness.

Calculations

For the construction of D-optimal design RSI/Discover Package of BBN Software Products Corp., Cambridge, MA, USA, was used on a COMPAQ 4/66 computer. PLS analysis was carried out using the SIMCA-3B package developed by Wold and co-workers at the University of Umeå.

RESULTS AND DISCUSSION

Separate PLS models were established for wash fastness and light fastness. Fastnesses to dry cleaning and to perspiration were not modelled because they showed a low variability along the series with scores generally near the top of the scale. Wash fastness was modelled by a three-component model explaining about 87% of the y variance. The results of the PLS analysis are detailed in Table 6.

A three-component model was calculated for light fastness, explaining about 86% of the y variance. The results are reported in Table 7. Both the PLS models evidenced the relevance of the coupling component (COP), with the presence of the NH_2 -group at the 6-position as the most important

TABLE 6
Wash Fastness: Variable Loadings b and Corresponding Modelling Power ψ for Each Component of the PLS Model

	$b1$	$\psi1$	$b2$	$\psi2$	$b3$	$\psi3$
y variable	1.00	0.51	1.00	0.55	1.00	0.63
x variables						
X1-PP1	0.00	0.00	0.45	0.66	0.00	0.64
PP2	-0.19	0.07	-0.18	0.10	0.28	0.18
PP3	0.04	0.00	0.44	0.61	-0.06	0.60
X2-PP1	0.27	0.26	-0.12	0.26	0.12	0.23
PP2	-0.22	0.13	-0.31	0.43	-0.18	0.47
PP3	0.27	0.24	-0.15	0.27	0.11	0.23
COP position						
3-PP1	0.00	0.00	-0.23	0.01	-0.08	0.00
PP2	0.19	0.07	0.09	0.03	0.31	0.12
PP3	-0.05	0.00	0.31	0.15	0.01	0.08
4-PP1	0.18	0.07	-0.15	0.07	0.24	0.09
PP2	-0.18	0.07	0.15	0.07	-0.24	0.09
PP3	-0.18	0.07	0.15	0.07	-0.24	0.09
5-PP1	-0.17	0.05	-0.17	0.06	0.42	0.32
PP2	0.15	0.03	0.24	0.13	-0.45	0.53
PP3	0.17	0.05	0.20	0.11	-0.45	0.48
6-PP1	0.33	0.46	-0.13	0.51	-0.01	0.47
PP2	0.33	0.46	-0.13	0.51	-0.01	0.47
PP3	-0.33	0.46	0.13	0.51	0.01	0.47
7- σ_m	-0.33	0.46	0.13	0.51	0.01	0.47
MR	-0.33	0.46	0.13	0.51	0.01	0.47
Variance explained (%)	76.4		79.8		86.3	

feature improving the properties. A minor effect was shown by the substitution at X₁ and X₂-positions of the amine component.

Validation and predictions

The established models were used to calculate the fastness values of the ten dyes of the training set and to predict the fastness of new dyes not yet synthesized. In Table 8 the calculated values and residuals are listed. The residual values show that the model can be used for predictive purposes.

Among the dyes for which high fastness values were predicted, three were synthesized and their fastness properties on silk were measured. The results reported in Table 9 show a good agreement between predicted and experimental values.

TABLE 7
Light Fastness: Variable Loadings b and Corresponding Modelling Powers ψ for Each Component of the PLS Model

	$b1$	$\psi1$	$b2$	$\psi2$	$b3$	$\psi3$
y variable	1.00	0.47	1.00	0.56	1.00	0.62
x variables						
X1-PP1	-0.06	0.00	0.45	0.28	-0.27	0.48
PP2	-0.15	0.03	-0.21	0.03	0.25	0.10
PP3	-0.02	0.00	0.45	0.25	-0.29	0.50
X2-PP1	0.27	0.26	-0.31	0.46	-0.12	0.47
PP2	-0.16	0.04	-0.12	0.00	0.33	0.19
PP3	0.27	0.25	-0.33	0.50	-0.09	0.50
COP position						
3-PP1	0.01	0.00	-0.35	0.07	0.11	0.03
PP2	0.17	0.05	-0.02	0.00	-0.07	0.00
PP3	-0.11	0.00	-0.03	0.00	-0.41	0.26
4-PP1	0.22	0.13	0.00	0.07	0.24	0.14
PP2	-0.22	0.13	0.00	0.07	-0.24	0.14
PP3	-0.22	0.13	0.00	0.07	-0.24	0.14
5-PP1	-0.12	0.00	-0.21	0.00	0.28	0.12
PP2	0.11	0.00	0.31	0.07	-0.34	0.33
PP3	0.12	0.00	0.26	0.04	-0.32	0.24
6-PP1	0.34	0.52	0.00	0.49	0.02	0.45
PP2	0.34	0.52	0.00	0.49	0.02	0.45
PP3	-0.34	0.52	0.00	0.49	-0.02	0.45
7- σ_m	-0.34	0.52	0.00	0.49	-0.02	0.45
MR	-0.34	0.52	0.00	0.49	-0.02	0.45
Variance explained (%)	72.1		80.7		85.4	

TABLE 8
Calculated Values of Fastness and Residuals

Dye	Fastness to washing		Fastness to light	
	Calcd	Δ^{oa}	Calcd	Δ^{oa}
1	4.1	-0.1	5.0	-0.5
2	3.7	0.3	3.7	0.3
3	3.4	-0.4	4.2	0.3
4	2.0	0.5	3.4	0.1
5	5.0	0.0	6.7	0.3
6	3.7	-0.2	2.9	0.1
7	3.8	0.2	5.4	0.6
8	4.9	0.1	6.3	-0.3
9	2.4	-0.4	4.0	-0.5
10	3.5	0.0	4.4	-0.4

^a Δ^o = difference between experimental and calculated values.

TABLE 9
Structures and Fastness Predicted and Experimental Values of the Designed Dyes

Dye	Amine		COP	Fastness			
	X_1	X_2		Washing		Light	
				Calcd	Exp.	Calcd	Exp.
11	Cl	NO ₂	Gamma Acid	4.9	4.5	7.1	7
12	H	C ₆ H ₅	Gamma Acid	4.5	4.5	6.3	6
13	C ₆ H ₅	NO ₂	Gamma Acid	5.1	5	7.6	8

CONCLUSIONS

From the results of the present and the previous work Gamma Acid was identified as the best coupling component. Dye 5 of the training set and dyes 11 and 13 of the prediction set proved to be the optimum dyes of the series. Particularly, dye 13 showed fastness values not reached by commercially available violet dyes for silk.¹³

In conclusion, application of Experimental Design techniques and of PLS modelling allowed us, with limited synthesis and testing work, to explore a wide range of amines and coupling components and to establish new dyes for silk in the red-violet-blue range with fastness performance rarely achieved.

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