

Characterization of Synthetic Dyes by Comprehensive Two-dimensional Liquid Chromatography combining Ion-exchange Chromatography and Fast Ion-Pair Reversed-Phase Chromatography

Bob W.J. Pirok^{a,b,*}, Jitske Knip^a, Maarten R. van Bommel^{a,c}, Peter J. Schoenmakers^a

^a University of Amsterdam, van 't Hoff Institute for Molecular Sciences, Analytical-Chemistry Group, Science Park 904, 1098 XH Amsterdam, The Netherlands.

^b TI-COAST, Science Park 904, 1098 XH Amsterdam, The Netherlands.

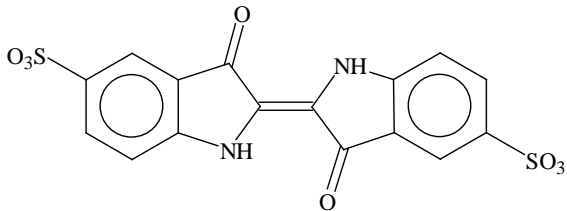
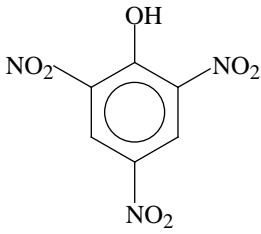
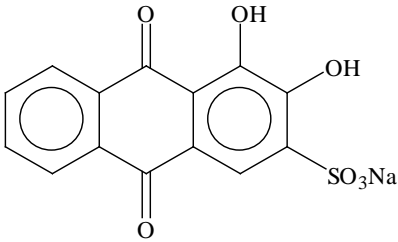
^c University of Amsterdam, Faculty of Humanities, Conservation and Restoration of Cultural Heritage, Johannes Vermeerplein 1, 1071 DV, Amsterdam.

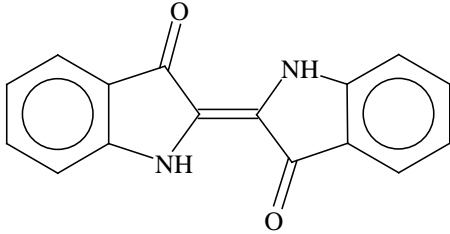
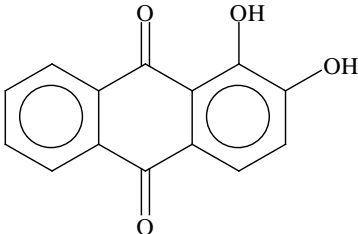
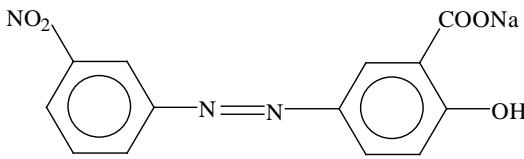
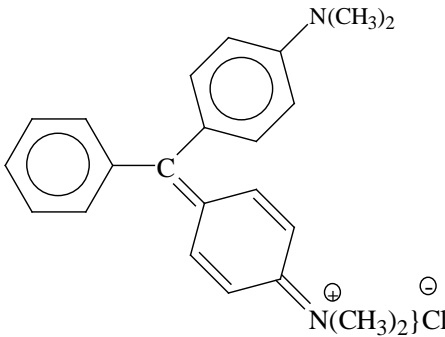
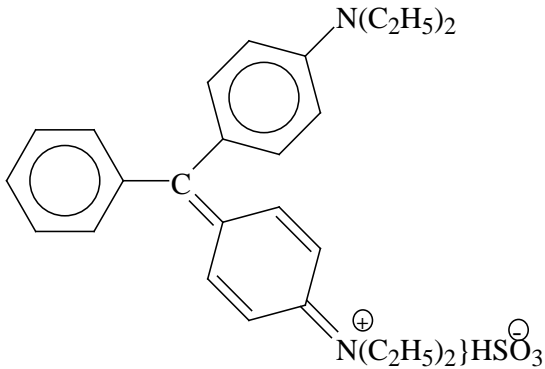
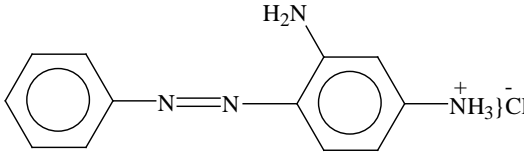
E-Mail: B.W.J.Pirok@uva.nl

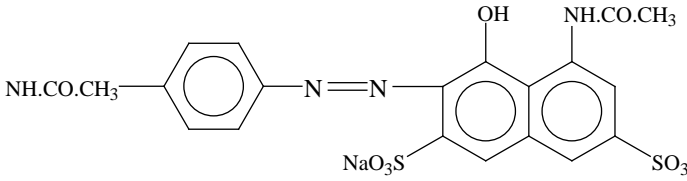
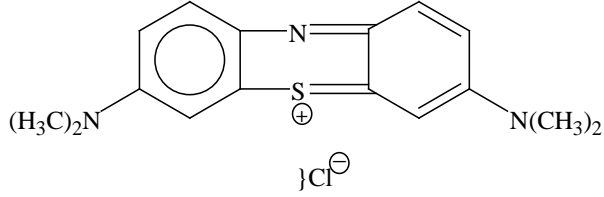
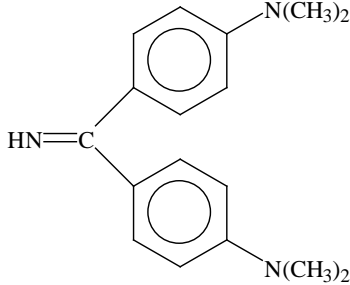
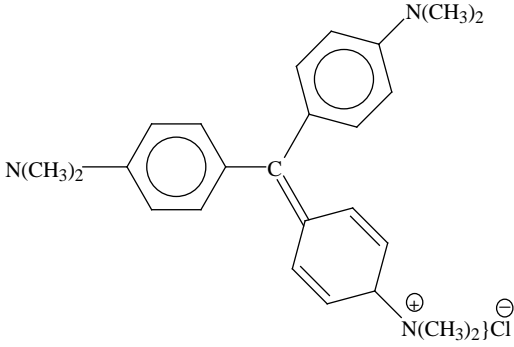
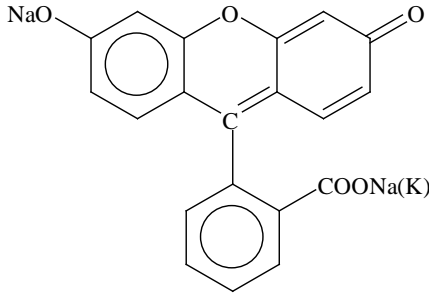
Telephone: +31629438882

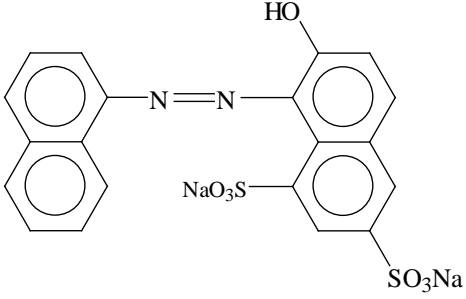
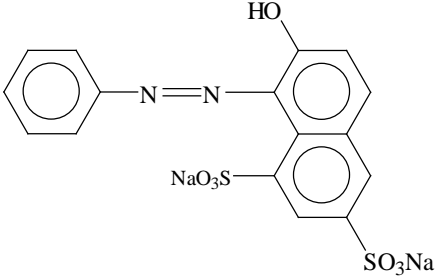
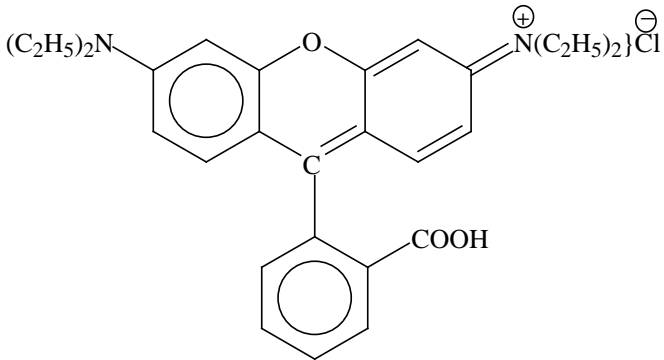
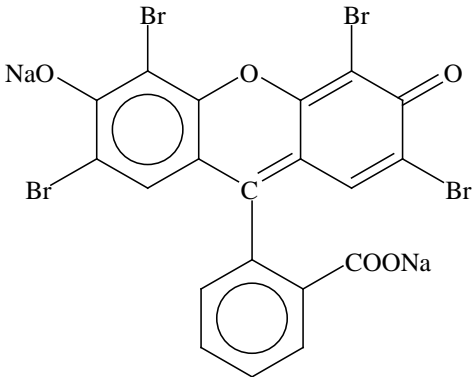
SUPPLEMENTARY MATERIAL

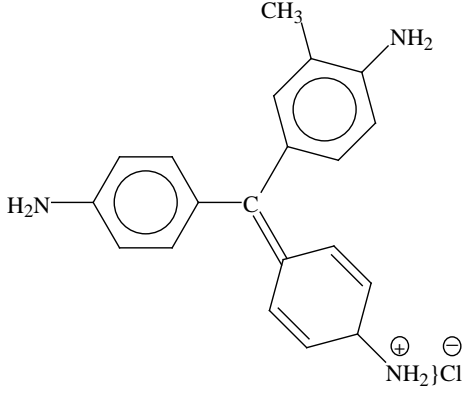
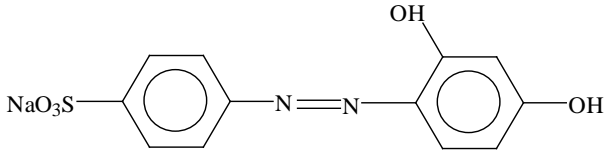
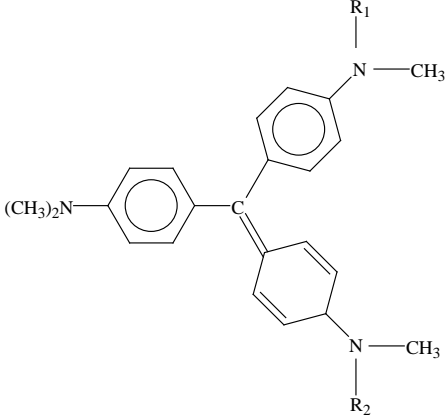
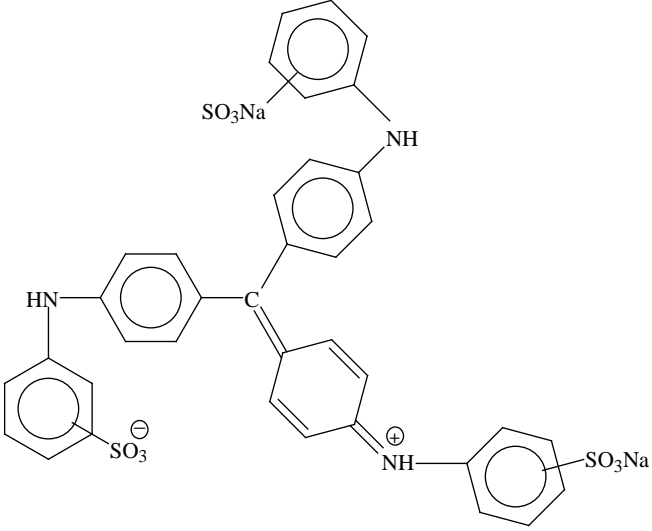
Table S1: Some representative structures of early synthetic dyes.

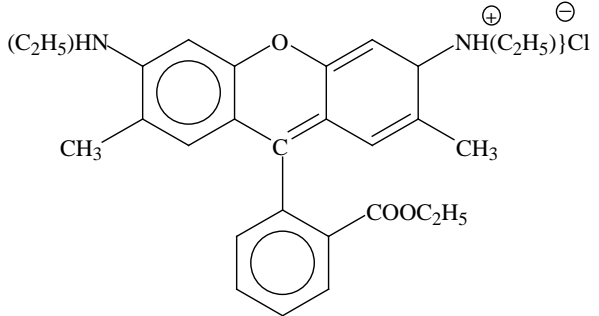
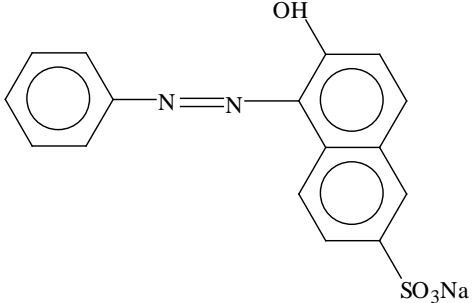
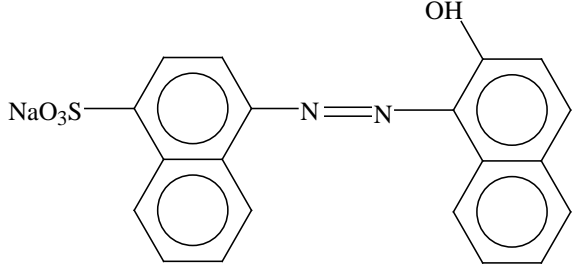
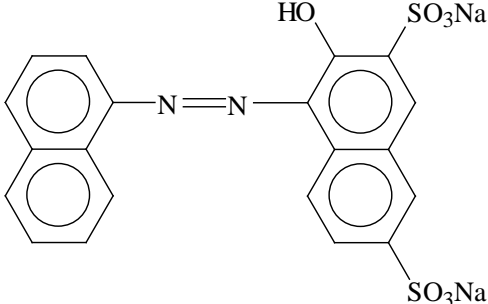
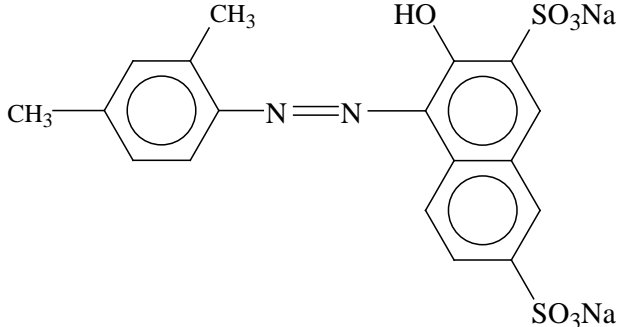
| Name | Dye class | Structure |
|-----------------|---------------|--|
| Indigo carmine | Indigoid |  |
| Picric acid | Nitro dye |  |
| Alizarine Red S | Anthraquinone |  |

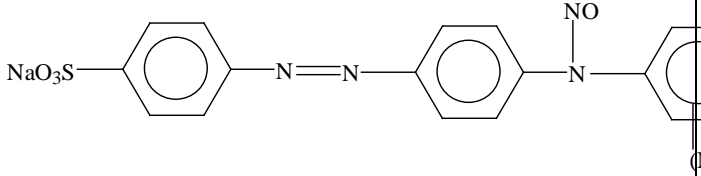
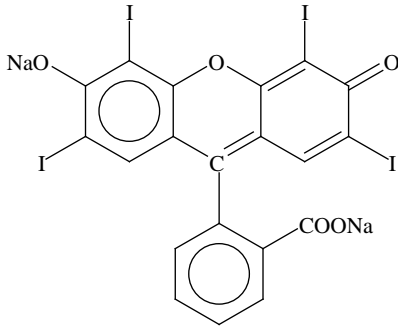
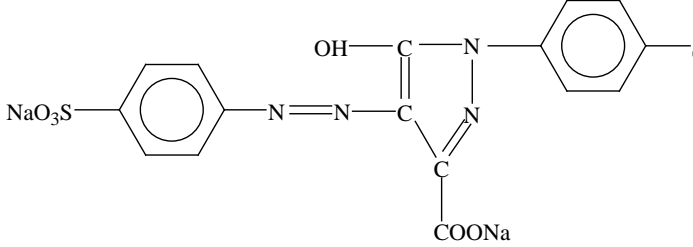
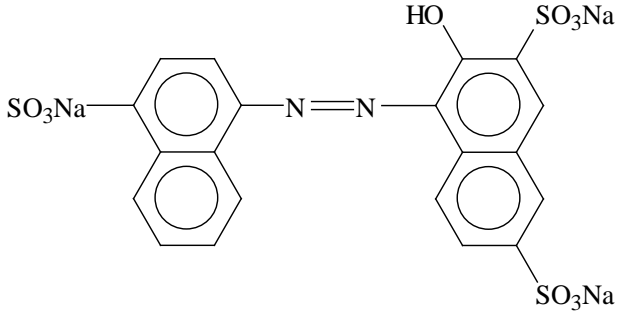
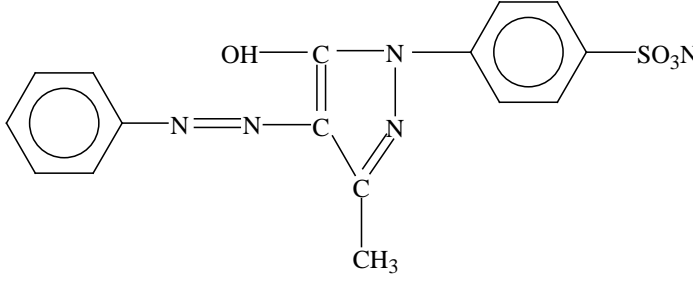
| | | |
|-----------------|----------------|--|
| Indigotin | Indigoid |  |
| Alizarine | Anthraquinone |  |
| Alizarin yellow | Monoazo |  |
| Diamond green B | Triarylmethane |  |
| Diamond green G | Triarylmethane |  |
| Chrysoidine | Monoazo |  |

| | | |
|-----------------|-----------------|--|
| Azo Fuchsine 6B | Monoazo |  |
| Methylen blue | Thiazine |  |
| Auramine | Diphenylmethane |  |
| Crystal violet | Triarylmethane |  |
| Uranine A | Xanthene |  |

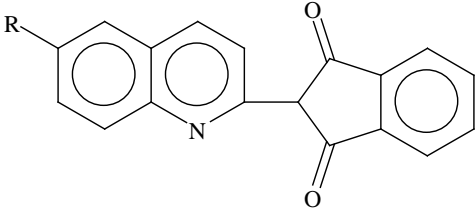
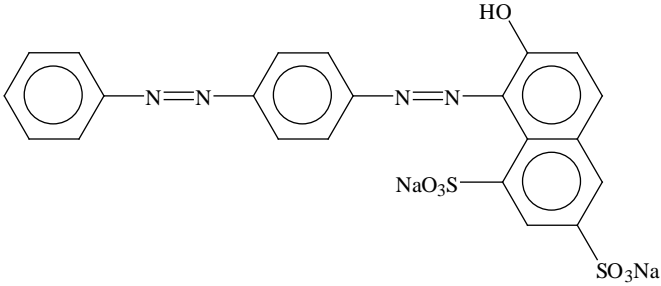
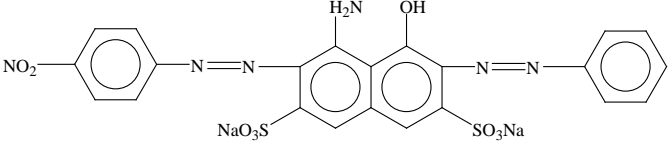
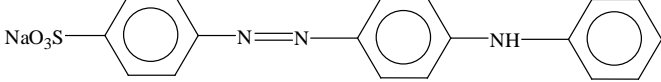
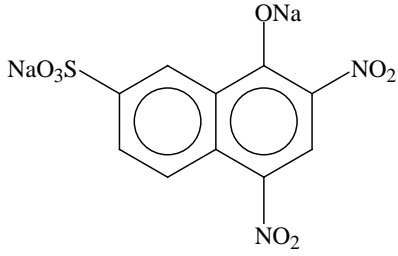
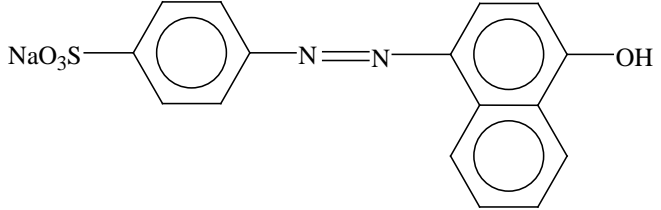
| | | |
|--------------------|----------|--|
| Crystal ponceau 6R | Monoazo |  |
| Orange GG | Monoazo |  |
| Rhodamine B | Xanthene |  |
| Eosine A | Xanthene |  |

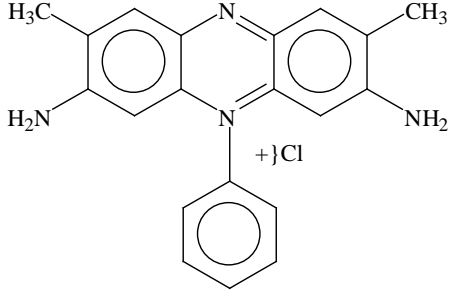
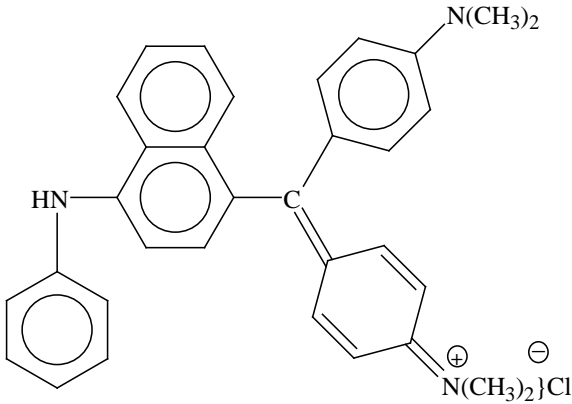
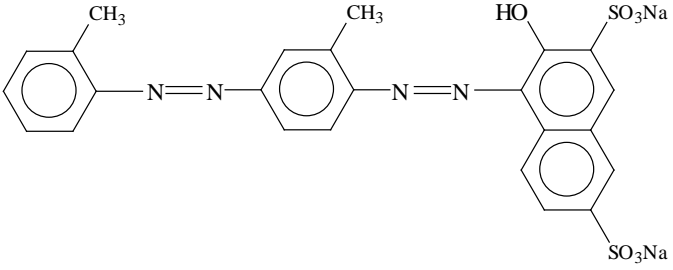
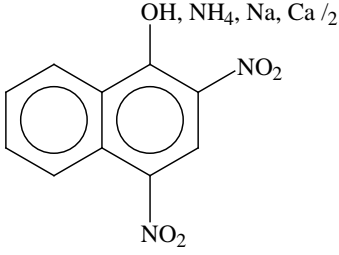
| | | |
|---------------|----------------|--|
| Fuchsin | Triarylmethane |  |
| Chrysoin | Monoazo |  |
| Methyl violet | Triarylmethane |  |
| Water blue IN | Triarylmethane |  |

| | | |
|-------------------|----------|--|
| Rhodamine 6G | Xanthene |  <chem>CC1=C(C(=O)OCC)C(=C2C=C(C)C(NC)N2)C3=CC=C(C)C3N</chem> |
| Croceine Orange G | Monoazo |  <chem>CC1=CC=C(C=C1)/N=N/C2=CC(=C3C=CC(=C3S(=O)(=O)[Na])O2)O</chem> |
| Fast red AV | Monoazo |  <chem>CC1=CC2=C(C=C1)C=CC=C2S(=O)(=O)[Na]/N=N/C3=CC(=C4C=CC=C4O)C=C3</chem> |
| Fast Red B | Monoazo |  <chem>CC1=CC=C(C=C1)/N=N/C2=CC(=C3C=CC=C3S(=O)(=O)[Na])C(=C2O)S(=O)(=O)[Na]</chem> |
| Ponceau RR | Monoazo |  <chem>CC1=CC(C)=CC=C1/N=N/C2=CC(=C3C=CC=C3S(=O)(=O)[Na])C(=C2O)S(=O)(=O)[Na]</chem> |

| | | |
|-----------------|----------------|--|
| Azo Flavine 3 R | Monoazo |  |
| Patent blue V | Triarylmethane | |
| Erythrosine | Xanthene |  |
| Tartrazine | Monoazo |  |
| Amaranth | Monoazo |  |
| Flavazine L | Monoazo |  |

| | | |
|--------------------------|----------------|--|
| Metanil yellow | Monoazo | |
| Amido Naphthol red G | Monoazo | |
| Congo red | Diazo | |
| Yellowish light green SF | Triarylmethane | |
| Brilliant yellow | Diazo | |
| Ponceau 3RO | Monoazo | |

| | | |
|-------------------|-----------|--|
| Quinoline yellow | Quinoline | <p>R=H or CH₃ mixture of mono, di and tri sulfonated dye</p>  |
| Cotton scarlet | Diazo |  |
| Amido black 10B | Diazo |  |
| Orange IV | Monoazo |  |
| Naphthol yellow S | Nitro |  |
| Orange I | Monoazo |  |

| | | |
|-----------------|----------------|--|
| Safranin T | Azine |  |
| Victoria blue B | Triarylmethane |  |
| Wol red B | Diazo |  |
| Martius yellow | Nitro |  |

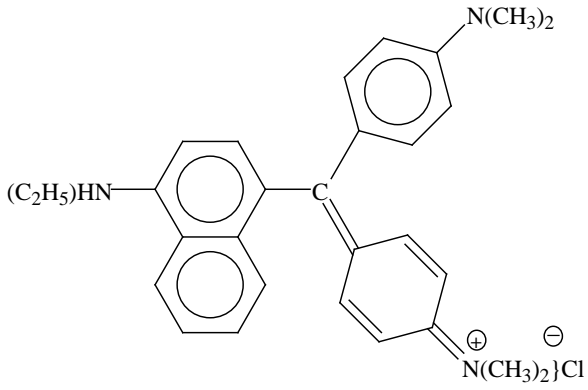
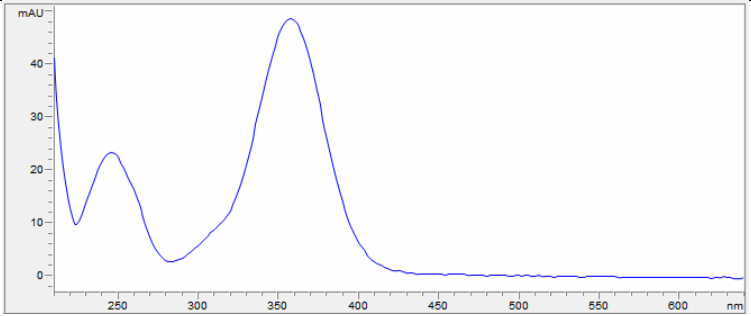
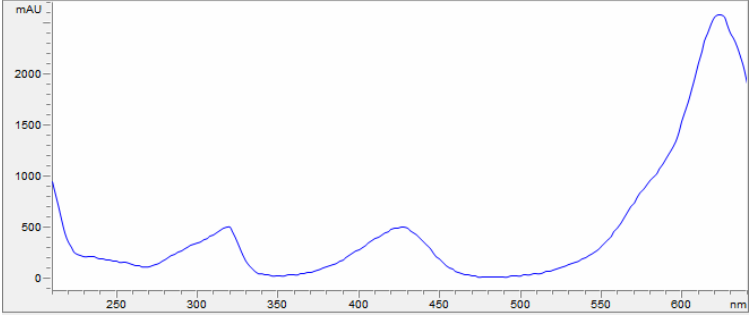
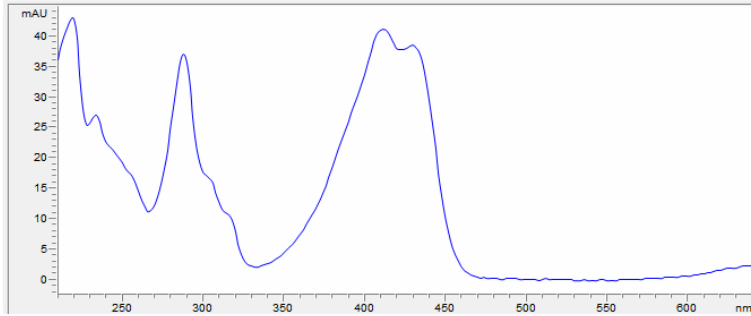
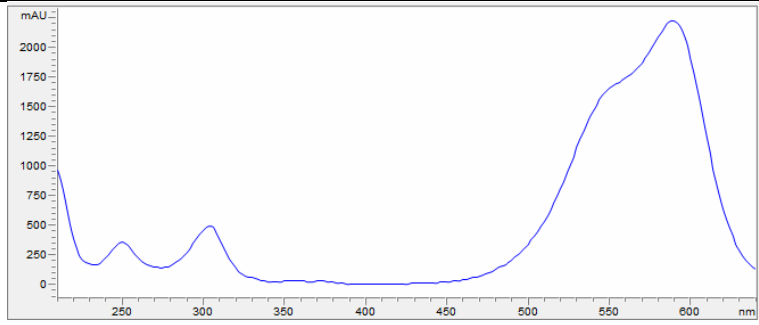
| | | |
|-----------------|----------------|--|
| Victoria blue R | Triarylmethane |  |
|-----------------|----------------|--|

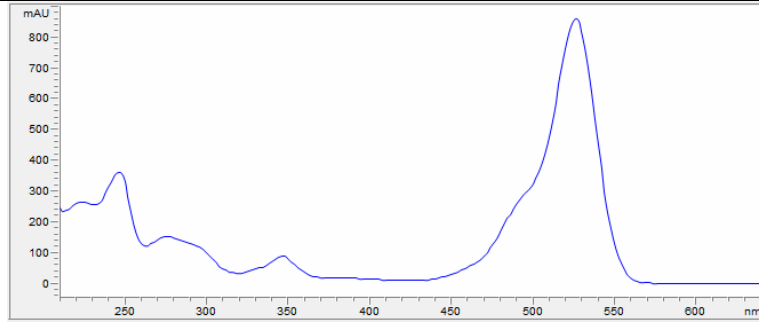
Table S2: Tentatively identified extracted UV-vis spectra

| Tentative identification | UV-vis spectrum |
|-------------------------------------|--|
| Auramine (1) |  |
| Diamond Green G (2) |  |
| Quinoline Yellow (3a) – Component 1 |  |

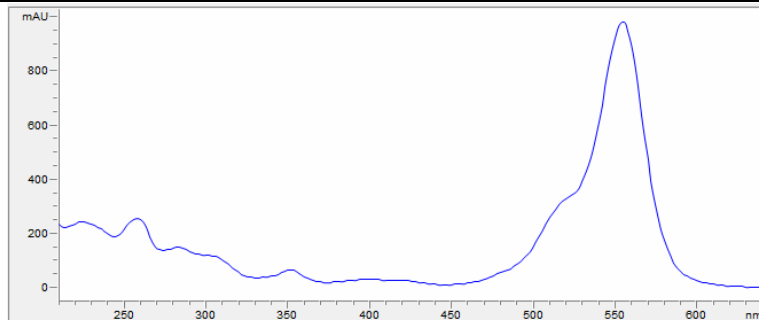
Crystal Violet (4)



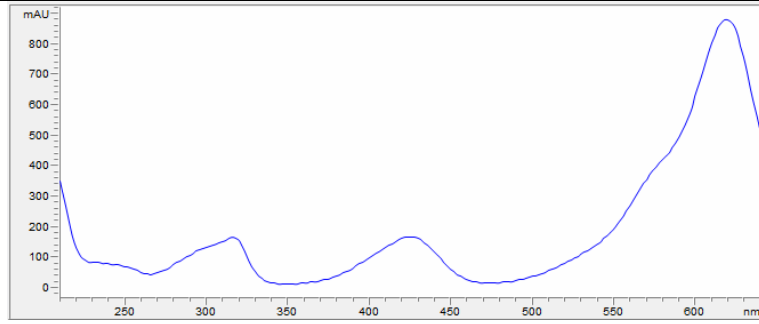
Rhodamine G (5)



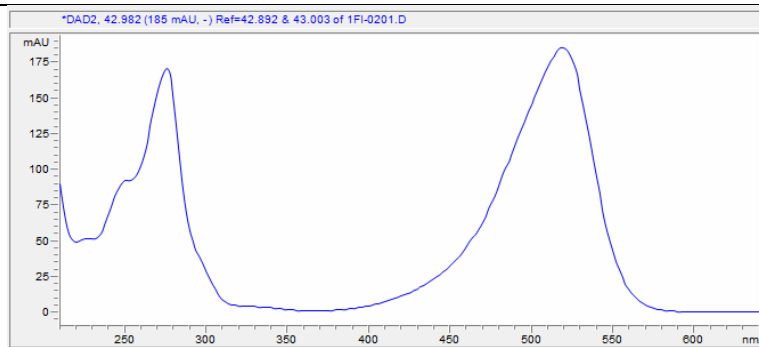
Rhodamine B (6)



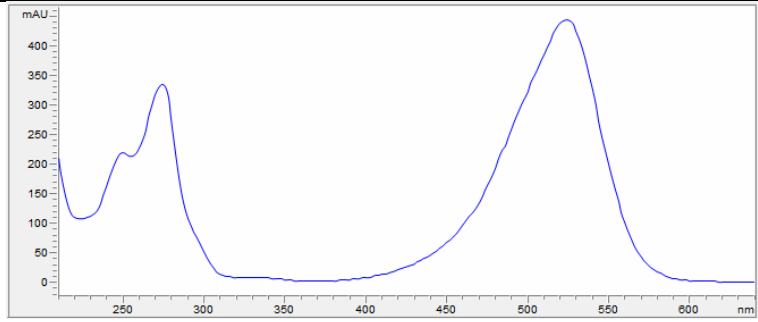
Diamond Green B (7)



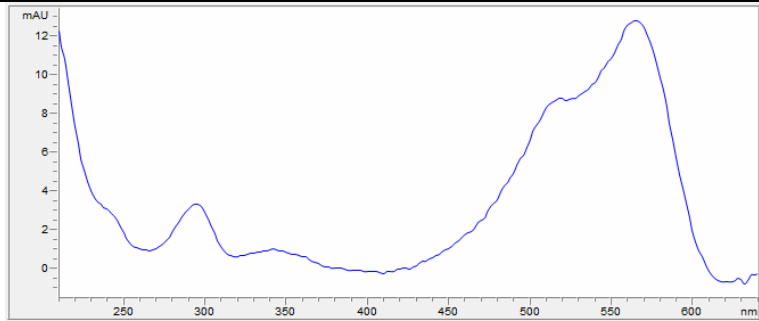
Safranin T (8a) – Component 1



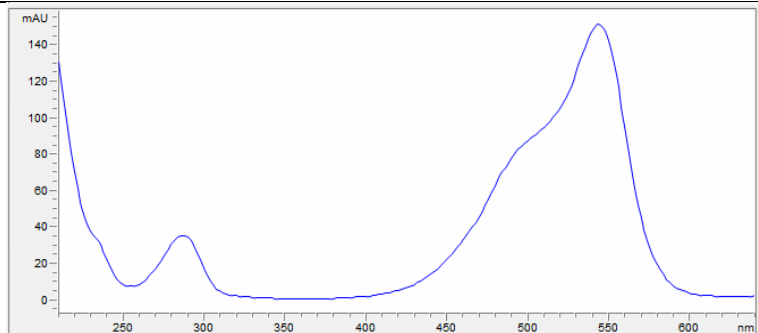
Safranine T (8b) – Component 2



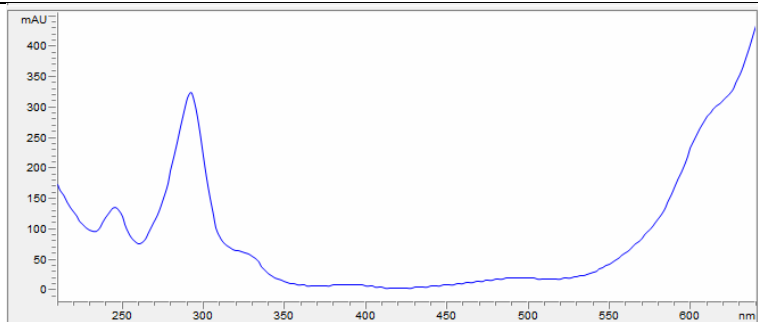
Methyl Violet (9)



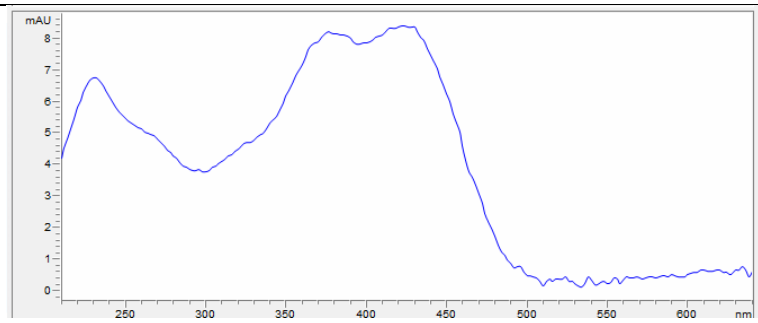
Fuchsine (10)



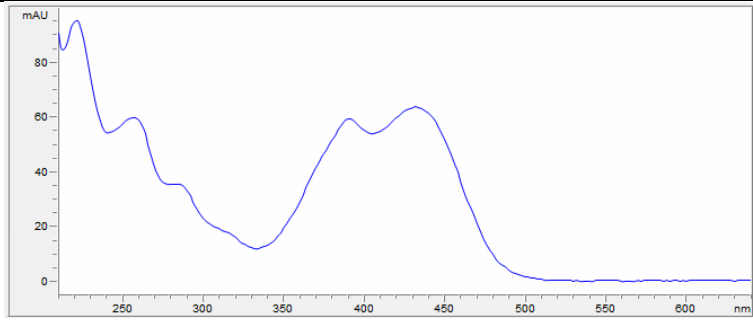
Methylene Blue (11)



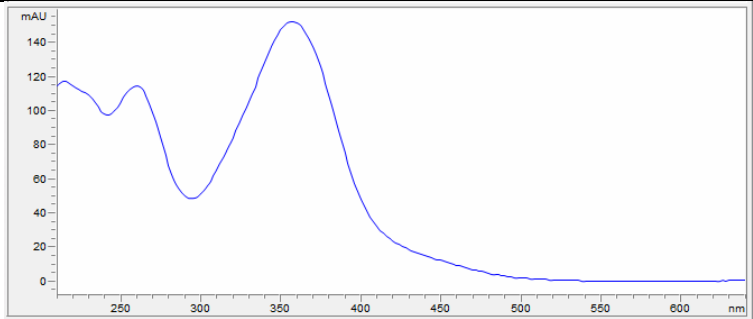
Martius Yellow (12a) – Component 1



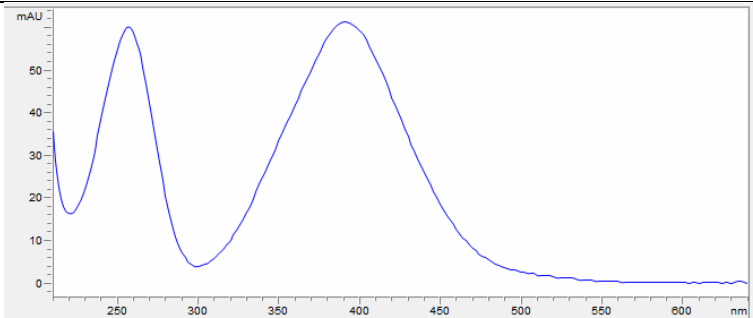
Martius Yellow (12b) –
Component 2



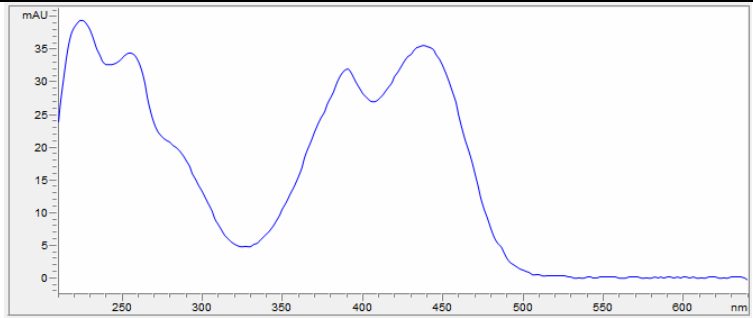
Pitric Acid (13)



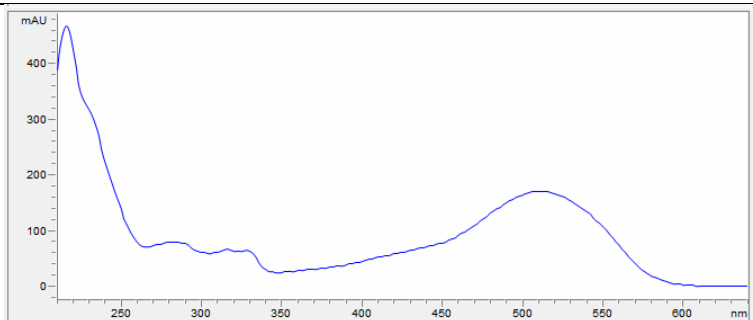
Flavazine L (14)



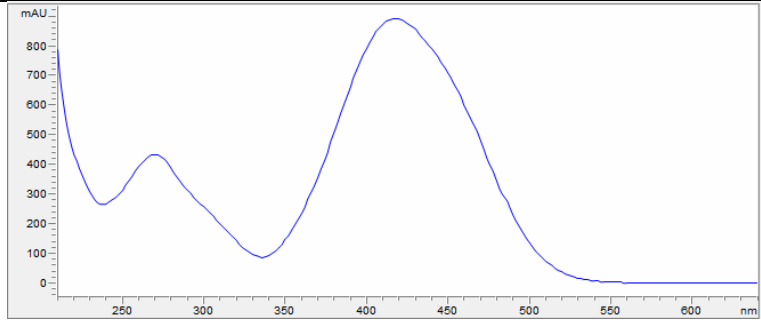
Naphthol Yellow S (15)



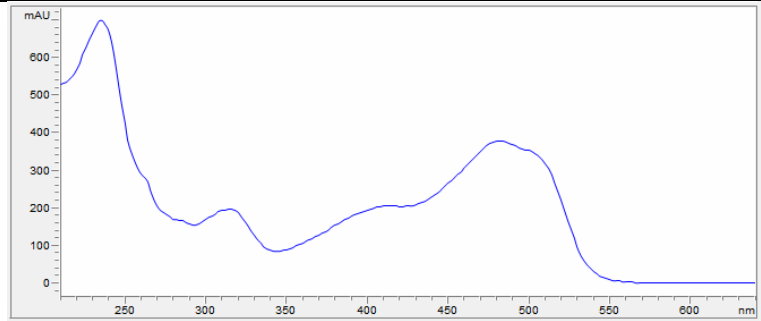
Fast Red AV (16)



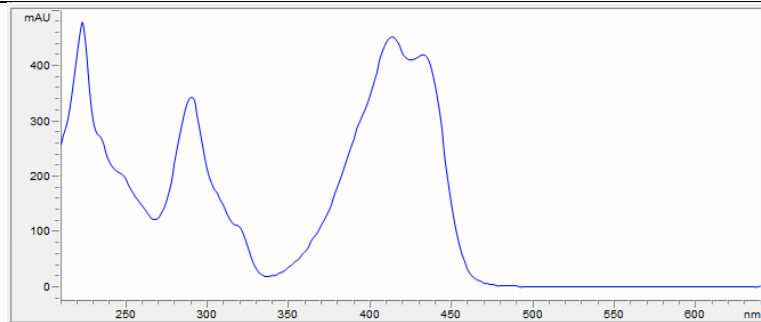
Metanil Yellow (17)



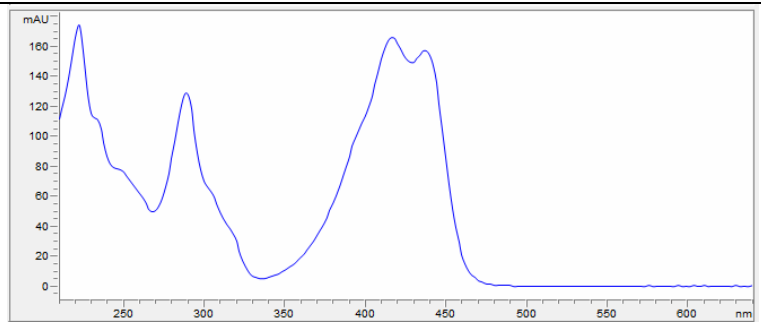
Crocein Orange GG (18)



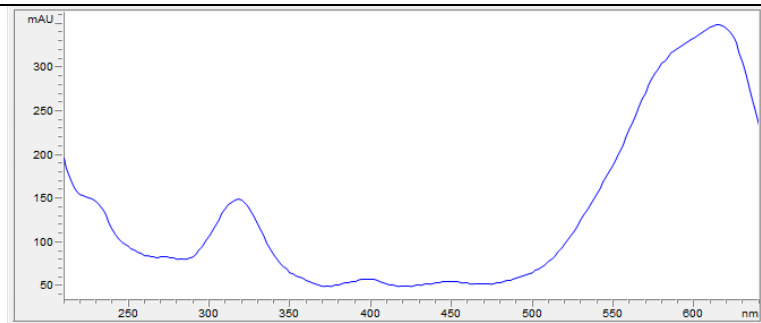
Quinoline Yellow (3b) –
Component 2



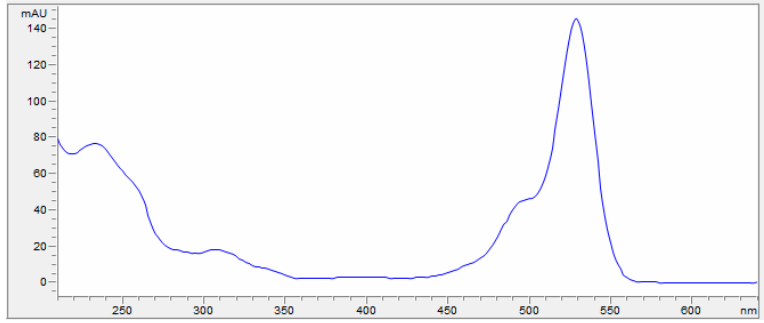
Quinoline Yellow (3c) –
Component 3



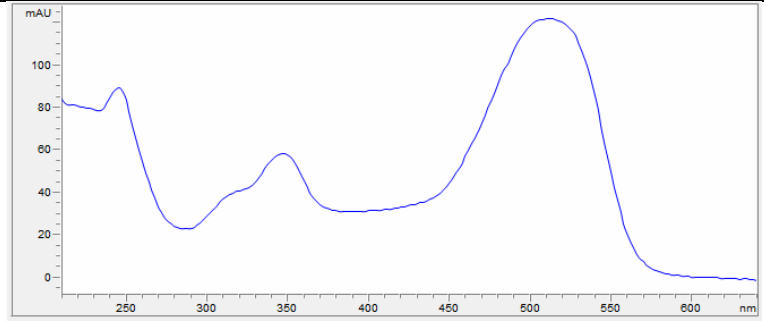
Victoria Blue B (19)



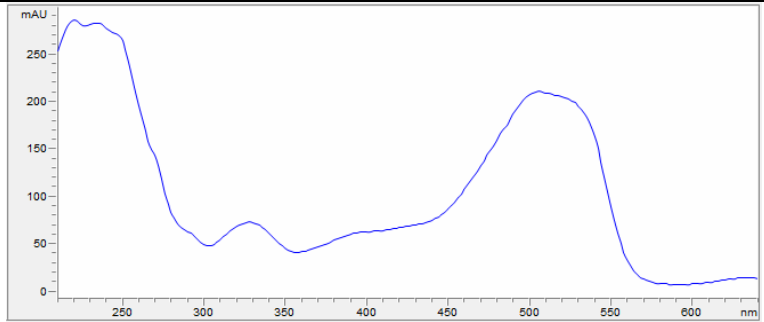
Eosine (20)



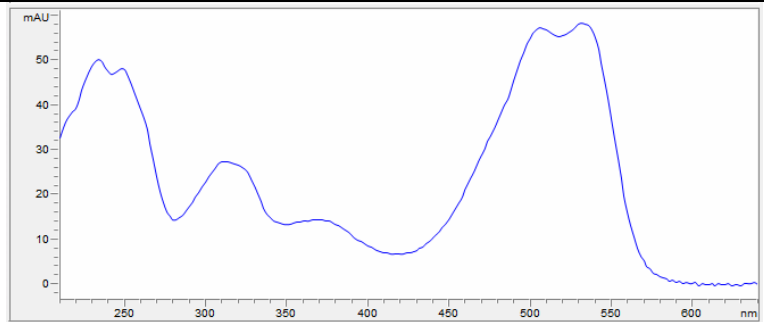
Wool Red B (21)



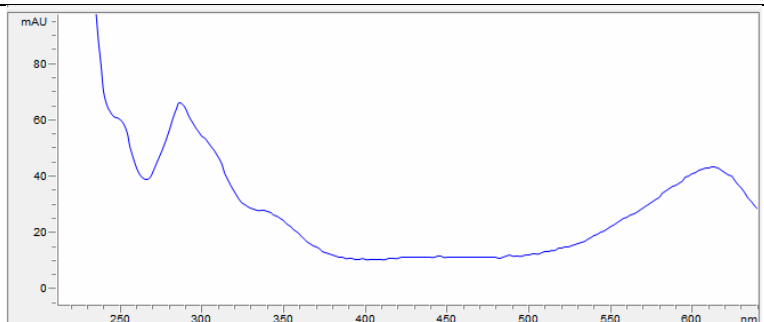
Ponceau RR (22)



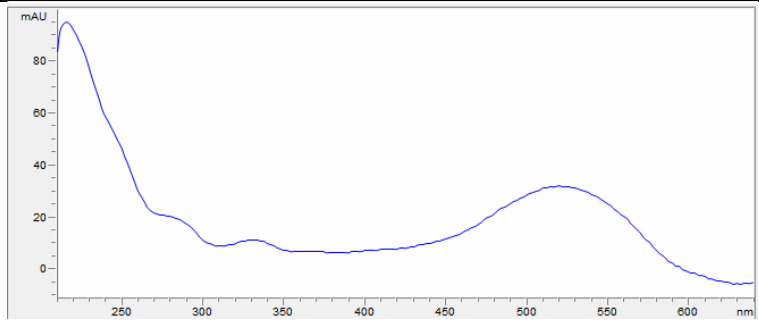
Fast Acid Magenta B (23)



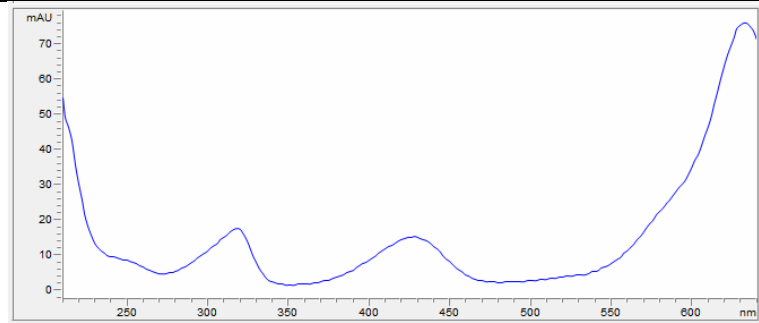
Indigo Carmine (24)



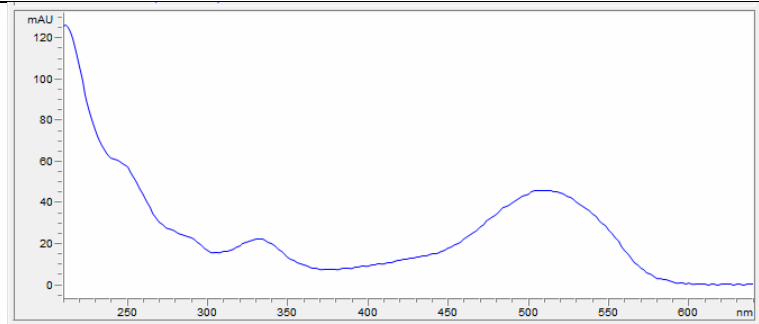
Crystal Ponceau (25)



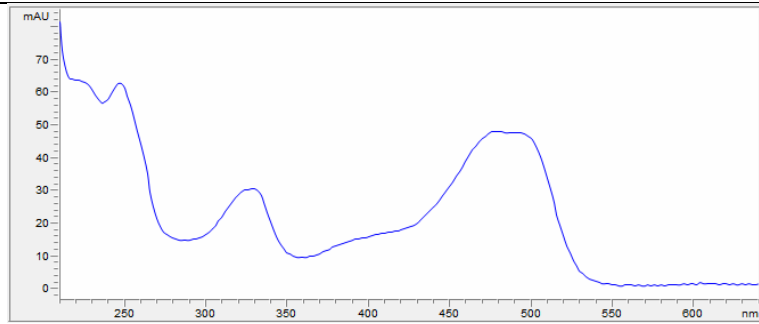
Patent Blue V (26)



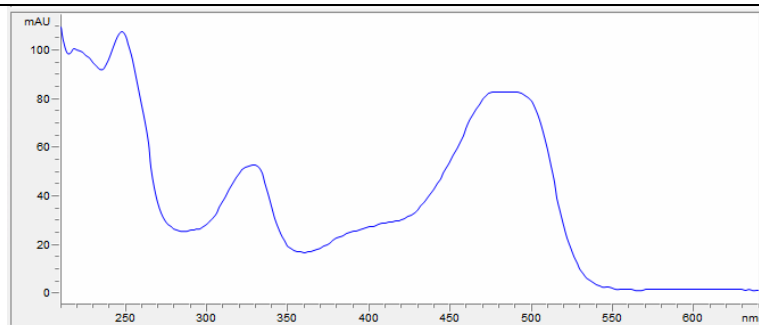
Amaranth (27)



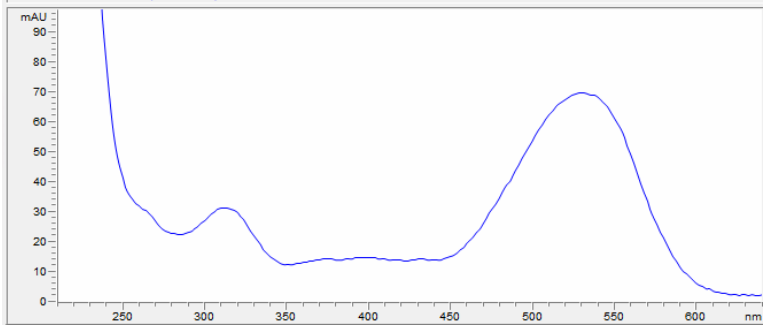
Orange GG (28a) – Component 1



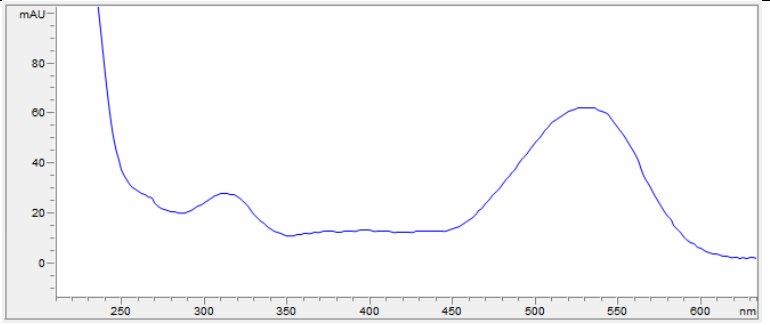
Orange GG (28b) – Component 2



Amido Naphtol Red G (29a) –
Component 1



Amido Naphtol Red G (29b) –
Component 2



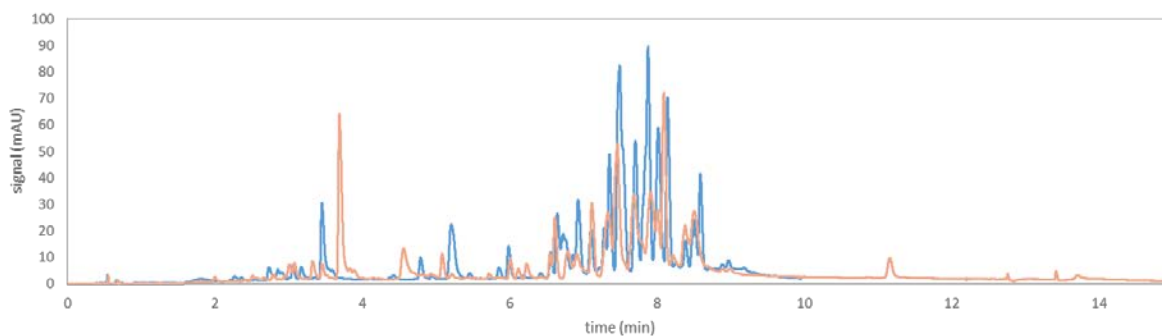


Figure S1: Overlay of UV chromatograms of the separation of a mixture of 54 synthetic dyes by (ion-pair) RPLC with 5 (red) and 10 mM (blue) TMA in the mobile phase. Gradient analysis, mobile phase A: ion-pair in water/acetonitrile 95:5 [v/v], pH=3, B: acetonitrile/water 95:5 [v/v]. UV detection at 450 nm. Flow: 1.0 mL/min, Column: Agilent ZORBAX Eclipse Plus RRHT 50 × 4.6 mm i.d. 1.8- μ m particles. Injection volume: 1.0 μ L.

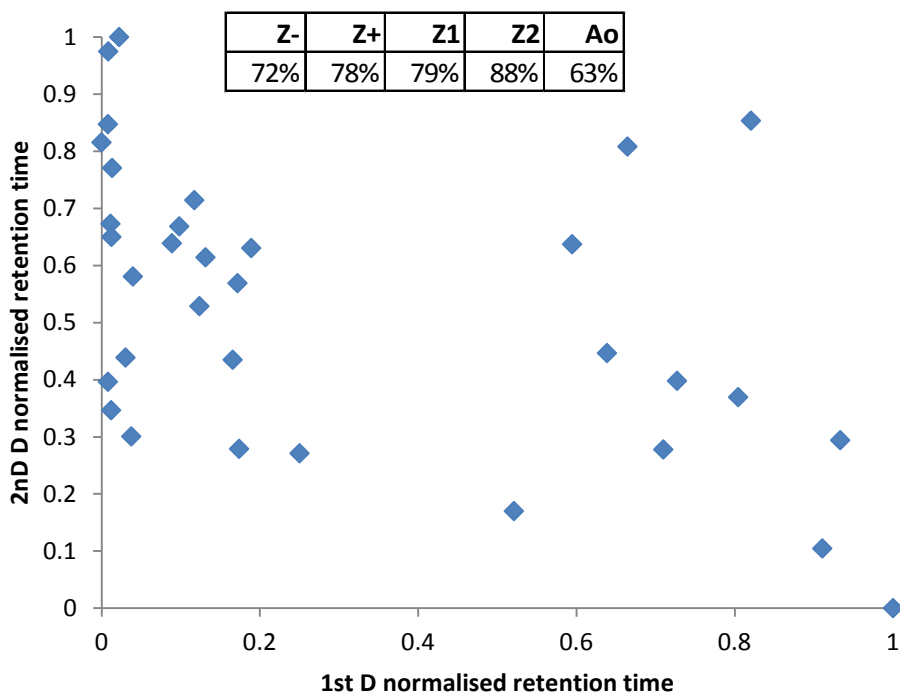


Figure S2: Orthogonality calculated using the asterisk conceptⁱ.

ⁱ M. Camenzuli, P.J. Schoenmakers, A new measure of orthogonality for multi-dimensional chromatography, *Anal. Chim. Acta.* 838 (2014) 93–101. doi:10.1016/j.aca.2014.05.048.