

FT-Raman Analyses of Blue Dyes Stuff Common in Swedish Folk Art from Hälsingland during 18th and 19th Century

Nyström I^{1*}, Wilken S² and Thomas J¹

¹Department of Conservation, Faculty of Science, University of Gothenburg, Guldhedsgatan 5A, Box 130, 40530 Gothenburg, Sweden

²Department of Applied Physics, Chalmers University of Technology, 41296 Gothenburg, Sweden

Abstract

The overall aim of this study is to gain a better understanding of the historic use of woad in Sweden in the 18th and 19th centuries. A key question is, whether it is possible to distinguish between indigo from woad and exotic indigo using Raman spectroscopy? Reference samples prepared according to historic recipes using woad, exotic indigo, logwood and brazilwood - were used to dye different textile fibres - cotton, wool and linen. In addition, various reference compounds - indigotin, indirubin, kaempferol, luteolin, 3-hydroxyflavone and tryptanthrin - as well as the 'flower' of the woad dye bath were analysed to identify specific fingerprint regions for each compound. Blue threads from four historic textiles - a skirt and three rag balls - from the region of Hälsingland were then analysed in comparison to the references. A specific peak at 993 cm⁻¹ was identified in the spectra taken from the flower of the woad vat, which we suggest possibly arises from 3-hydroxyflavone. DSA-ToF-MS analysis suggests flavone-glycosides as possible candidates. However, cellulosic substrates show a broad vibration at 999 cm⁻¹ overlapping the flavone signature, thus rendering it non-diagnostic, but it might be possible to use this peak in Raman analyses supported by mass spectrometry to distinguish between indigo from woad and exotic indigo if the substrate is wool or if it is a pigment. Raman analyses of the historic samples identify the colourants as indigo and possibly woad and logwood mixed with brazilwood.

Keywords: Dyestuff; Colouring matters; Lac pigments; FT-Raman; DSA-ToF-MS

Introduction

This work is part of a larger research project "A holistic study of Decorated Farmhouses of Hälsingland", an interdisciplinary study in which methods from natural and historical sciences are applied to the decorative folk arts and crafts in the farmhouses of Hälsingland, UNESCO world heritage since 2012.

The general aim of the project is to gain new and deeper knowledge about crafts processes, painting and weaving techniques, dyeing methods and carpentry techniques. The art and crafts objects are analysed in their historical context, and the relevant research questions span over a wide range - from what materials to how the objects and manufacturing could be understood. A key question in this work is whether it is possible to distinguish between indigo from woad and exotic indigo using Raman spectroscopy? Woad, *Isatis tinctoria*, has historically been used to produce the blue dye, indigo/indigotin, which has mainly been used as a dye for textiles but also as a pigment in paintings. Indigotin prepared from woad leaves is a natural blue pigment that requires an alkaline bath, so called vat, to be used for textile dyeing [1]. Precipitated and dried indigotin can be used as a pigment for paint. The pigment can also be prepared from the blue-coloured foam of the dye vat, the so called flower. Until the 17th century woad was the most common blue dye in Europe as well as Sweden. However, in the late 17th century better quality, exotic indigo, (*Indigofera* species), imported by the various East India Companies, became increasingly common. However, according to Swedish 18th century sources woad is still a common dye [2] in Sweden.

Woad leaves contain a variety of extractable metabolites from several structural classes, but of particular interest for this study are indigoid precursors and derivatives such as isatan, isatin, indican and indoxyl as well as tryptanthrin [3-6]. Woad dyed textiles as well as woad-pigment contains indigotin, indirubin and isoindigo. In addition to indigoids woad-indigo made from the flower of the vat can contain

traces of kaempferol, luteolin and possibly other yellow flavonoids [6-10]. Hartl et al. also mentions saponins as possible components, though saponine might originate from the washing treatment [6].

In this study we have produced different blue dyes - woad, exotic indigo, logwood and brazilwood - and then used the prepared dye baths to colour textile fibres - cotton, wool and linen. These materials were prepared according to historic recipes and methods [11-14]. In addition woad reference materials, e.g., woad leaves from a woad ball, factory made woad pigment and woad pigments taken from the flower of the woad vat as well as commercially supplied compounds and colouring matters - indigotin, indirubin, kaempferol, luteolin, myricetin, quercetin, rhamnetin, emodin, 3-hydroxyflavone and tryptanthrin - were analysed and used as references to identify specific fingerprint regions for each dye. These references were then compared with historic samples--four blue textile threads: one from a skirt from Delsbo Parish and three threads from rag balls found in the Bortom Åa farmhouse were analysed. The skirt is woven in half wool, with woollen weft and linen warp, in a dark blue colour. The sample was taken from the linen weft, in a damaged area just below the waistband, and it is designated as sample 1. The other three blue threads come from three cotton rag balls are designated samples 2, 3 and 4; all sample sources are shown in Figure 1. The sample threads were taken from torn edges of the textile ribbons.

***Corresponding author:** Ingallil Nystrom, Department of Conservation, Faculty of Science, University of Gothenburg, Guldhedsgatan 5A, Box 130, 40530 Gothenburg, Sweden, Tel: +46(0)317865701; Fax: +46317864703; E-mail: Ingallil.nystrom@conservation.gu.se

Received March 29, 2016; Accepted April 14, 2016; Published April 19, 2016

Citation: Nystrom I, Wilken S, Thomas J (2016) FT-Raman Analyses of Blue Dyes Stuff Common in Swedish Folk Art from Hälsingland during 18th and 19th Century. Chem Sci J 7: 123. doi:[10.4172/2150-3494.1000123](https://doi.org/10.4172/2150-3494.1000123)

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Figure 1: Pictures of the historic objects, a skirt and rag balls. Samples were taken from the blue threads in each.

Experimental Methods

A Bruker MultiRAM FT-Raman spectrometer equipped with an infrared laser source at 1064 nm (Nd:YAG) was used on both references as well as historic samples. The resolution was 2 cm^{-1} . The laser power and number of scans varied depending on the type of sample, the dyestuff references were exposed for 1000 scans at 200 mW whereas the historic samples as well as textiles references were exposed for 20000 scans at a laser power of 20-50 mW.

A Perkin Elmer AxION 2 Time of Flight Mass Spectrometer (ToF-MS) equipped with a field-free, APCI-like direct sample analysis (DSA) source was used to collect both positive and negative mode high resolution mass spectra of the dyed fibres and reference materials, see **Supplementary File S1**. Samples were analysed without extraction or chromatographic separation with ca. 15 seconds or less needed to collect spectra to identify the primary constituents of the analyte.

Results and Discussion

The Raman spectra of the indigotin standard, the woad pigment and the woad from the flower of the vat are shown in Figure 2. The spectra of indigo of the various origins are very similar, as noted in several references [15,16]. The main peaks can be assigned according to literature, with the strongest signals observed at 1572 cm^{-1} originating from the ring stretching mode as well as a shoulder at 1582 cm^{-1} due to the stretching vibrations of the conjugated system of C=C, C=O and N-H groups [13,14]. Other signatures can be assigned to vibrations of this conjugated system (at 1365, 1624 and 1701 cm^{-1}), C-H rocking vibrations at 1248, 1461 and 1482 cm^{-1} as well as rocking vibrations of N-H groups at 1224 cm^{-1} , all assigned according to Ref. [13]. Vibrations of the five- and six-membered rings can be identified at 545, 675, 757, 1015, and 1310 cm^{-1} [15,17]. Woad from the flower of the vat has an additional feature, a medium signal at 993 cm^{-1} . Otherwise the spectrum is nearly identical with the one of the woad pigment and the standard indigotin. One notable difference is a somewhat stronger background possibly due to a combination of more contributing colouring matters.

After examining a number of candidates suggested in the literature that could contribute to the vat spectrum, we present 3-hydroxyflavone (3-HF) in the same Figure 2 with signatures at 991 cm^{-1} as well as at 1309, 1566, 1595 and 1619 cm^{-1} . The strong feature at 991 cm^{-1} could very well be due to vibrations from 3-HF. A match in the high wavenumber region is not as straightforward to identify, however as there is a strong vibrational overlap it could be possible that 3-HF

contributes to the slightly smaller valley around 1613 cm^{-1} in the vat spectrum compared to the standard indigo and woad pigment spectra, respectively. As various hydroxyflavones have been characterized in the literature a vibrational assignment is straightforward. The strong features at 1566, 1595 and 1619 cm^{-1} are due to stretching vibrations of the conjugated system of C=C, C=O in addition to an O-H bend [18]. The strong signal at 992 cm^{-1} is due to various ring contributions in addition to a C-C bond deformation [18].

Now we will try to apply this new insight, that a Raman peak at 993 cm^{-1} could be used as an indicator for woad, to historic samples found at Bortom Åa.

Historic samples

In the following we present the results of the spectral analysis of four historic samples. First, **sample 1**, a blue thread from a skirt from Delsbo parish was selected. The Raman spectrum of the blue thread is shown in Figure 3 together with the spectrum of standard indigotin as well as linen to serve as references. All features of sample 1 can be assigned to the references and we therefore conclude that standard indigotin can be identified as the only dyestuff and thus probably exotic indigo has been used as the dye. DSA-ToF-MS analysis complements this analysis with the presence of indigoids and tryptanthrin with diagnostic features at m/z 263 and m/z 249, respectively, are suggested [3]. A very small feature at m/z 134 has been assigned to indoxyl, the

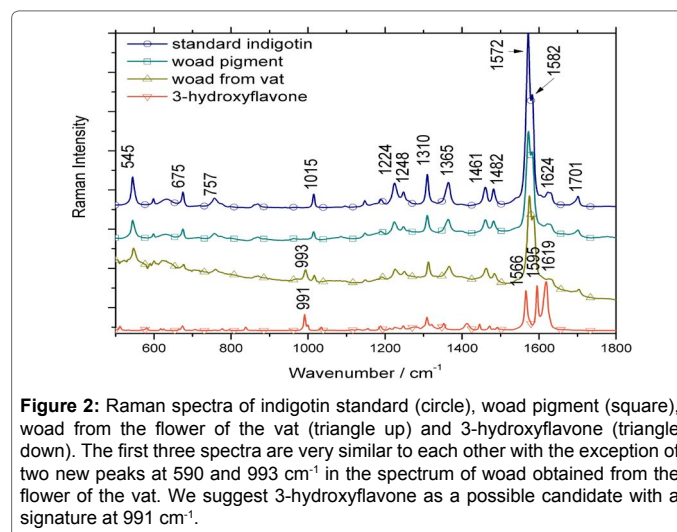


Figure 2: Raman spectra of indigotin standard (circle), woad pigment (square), woad from the flower of the vat (triangle up) and 3-hydroxyflavone (triangle down). The first three spectra are very similar to each other with the exception of two new peaks at 590 and 993 cm^{-1} in the spectrum of woad obtained from the flower of the vat. We suggest 3-hydroxyflavone as a possible candidate with a signature at 991 cm^{-1} .

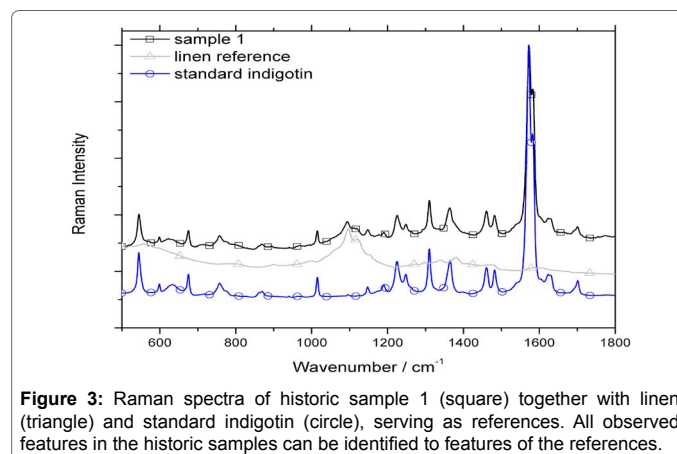


Figure 3: Raman spectra of historic sample 1 (square) together with linen (triangle) and standard indigotin (circle), serving as references. All observed features in the historic samples can be identified to features of the references.

major indigoid precursor in *Indigofera* species and minor precursor in *Isatis* species [3,5].

Returning to the Raman analysis and comparing with a tryptanthrin standard we cannot identify signatures of tryptanthrin clearly (Figure 1), which can be due to the low concentration (18% of that of indigoids according to MS intensity analysis) in combination with many signatures in similar regions and high chance for overlap. The next historic sample, **sample 2**, was collected at Bortom Åa taken from a rag ball. In Figure 4, we present the Raman spectrum of sample 2 together with spectra of references from bleached cotton as well as standard indigotin and indirubin. In general the spectrum of sample 2 had a stronger background, with features mainly from the textile and several more smaller features compared to sample 1, therefore the analysis is more complex. The strongest signatures can be easily assigned to the cotton textile, at for example 1097, 1222 as well as at 1381 cm^{-1} . Standard indigotin can be identified due to the presence of signals at 1017, 1310, 1572 and 1582 cm^{-1} . A notable difference to the spectra of both historic sample 1 and standard indigotin can be seen at the signals around 1572–1582 cm^{-1} . Here, the vibrations are of almost equal intensity whereas in standard indigotin the vibration at 1572 cm^{-1} is much stronger. This could be an indication of either molecular changes of indigotin or the presence of another component, e.g., indirubin with a strong vibration at 1587 cm^{-1} . Several weaker additional features can be observed at 970, 998, 1181, 1282 and 1321 as well as at 1406 cm^{-1} . Indirubin could be a possible candidate for some of the additional features with peaks at 963, 1291 and 1402 cm^{-1} .

Complementary DSA-ToF-MS analysis confirmed the presence of indigo dyes with a strong feature at m/z 263. Moreover, a feature at m/z 249 corresponding to tryptanthrin as well as the feature tentatively assigned as being due to an indazole carbaldehyde at m/z 147 could be identified. A cross reference check with the Raman spectra with the purpose to look specifically for signatures of tryptanthrin could not identify a significant match in the respective regions within the limit of our detection. Generally, the positive mode mass spectrum is much more complex than the one of historic sample 1 and there are several, as yet unidentified, peaks with significant relative intensities. Features at m/z 239 and m/z 287, corresponding to a hydroxy flavone and a tetra-hydroxy flavone (e.g., kaempferol) respectively are absent, as is a feature at m/z 134 which has been assigned to indoxyl in historic sample 1. Therefore, the feature at 998 cm^{-1} in the Raman spectrum is most likely not due to 3-HF as suggested in the dyed textile reference analysis. Close inspection of the bleached cotton textile reference showed that a broad feature at 999 cm^{-1} could overlap any signature of woad in that region.

Another blue thread, **sample 3**, from a different rag ball was examined and the respective Raman spectrum is shown in Figure 5. Besides features from the cotton textile, 3 show several strong signatures at 1141, 1179, 1260, 1264, 1299, 1404, 1434, 1450 cm^{-1} . Additional signatures at 1225 as well as at 1572 and 1582 cm^{-1} can be assigned to the standard indigotin reference. Note that the vibrations around 1582 cm^{-1} are again of almost equal intensity indicating a change of some sort compared to the original standard reference. The Raman spectrum of 3 also displays the feature at 997 cm^{-1} which most likely originates from the bleached cotton textile and therefore overlaps any possible woad signature. The feature at 1264 cm^{-1} could possibly originate from tryptanthrin which has a matching vibration at 1263 cm^{-1} . Furthermore, the standard indirubin reference could be identified with matching vibrations at 1292, 1406 and 1462 cm^{-1} , leaving several features unassigned. When doing complementary DSA-

ToF-MS analyses the presence of something with a similar mass than tryptanthrin is suggested as well as of two glycosides (different from the woad vat reference), and neither kaempferol, luteolin nor 3-HF. Microscopic analysis confirms the bare-eye observation that this type of historic sample seems to be very washed/used/possibly degraded as the cotton fibres are more like wool in its appearance (Figure 6).

The fourth textile, **sample 4**, was also characterized with Raman spectroscopy and the spectrum can be seen in Figure 7. The spectrum looked very different compared to the other samples, especially as no signatures of indigotin could be found. Vibrations could instead be found at 1312, 1368, 1447, 1520, 1574 and 1597 as well as at 1652 cm^{-1} . After checking several other possible blue colouring matters we were able to assign these spectral features to brazilwood with features at 1319, 1364, 1569 and 1607 cm^{-1} (broad peak), containing brazilin and brazilin. The broad feature at 1607 cm^{-1} is probably due to aromatic ring stretching vibrations from the dye chromophore and lignin in brazilwood (redwood) (Figure 7). The reference textile consisting of brazilwood coloured wool shows similar features although not as profound as the pure brazilwood reference. A few features seem to have been influenced by the colouring process as both strong features around 1600 cm^{-1} are no longer visible. Instead additional Raman vibrations may be assigned, namely at 1449 and 1652 cm^{-1} which can be assigned to signatures of wool which are also visible in the microscope image (Figure 6). As there are no indigoids present, the potential signature of woad at 998 cm^{-1} is also absent. Additional features at 1096 and 1125 cm^{-1} can easily be identified with the cotton reference.

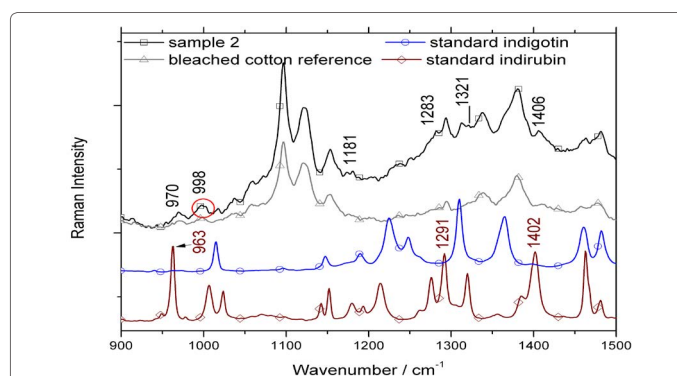


Figure 4: Raman spectra of historic sample 2 (square), a bleached cotton reference (triangle) and the colouring matters indigotin (circle) and indirubin (diamond).

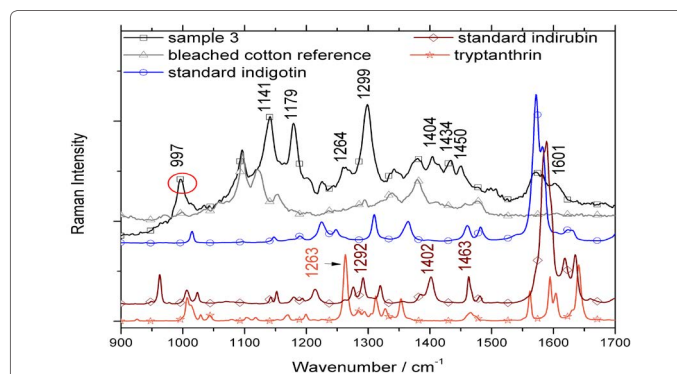


Figure 5: Raman spectra of sample 3 (square) together with a bleached cotton reference (triangle) and indigotin (circle), indirubin (diamond) and tryptanthrin (star) references.



Figure 6: Microscope analysis of the fibers using a USB Dino Lite microscope with a magnification of 243X. Sample 1 is the linen thread from the skirt. Sample 2 is a cotton thread from rag ball nr 1. Sample 3 is also cotton from rag ball nr 2 and sample 4 is a thread consisting of cotton mixed with some wool from rag ball nr 3.

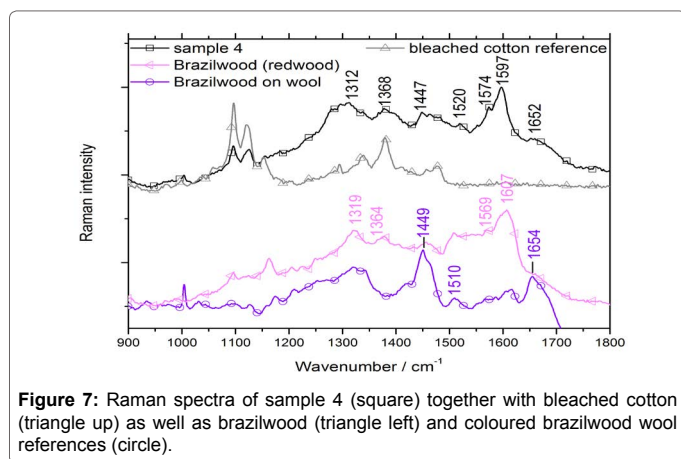


Figure 7: Raman spectra of sample 4 (square) together with bleached cotton (triangle up) as well as brazilwood (triangle left) and coloured brazilwood wool references (circle).

DSA-ToF-MS confirmed both the absence of indigoids as well as flavonols and the presence of brazilein which could be from either Brazil wood or Log Wood at m/z 283 in the negative mode spectra.

Conclusion

We show in this study that it is possible to distinguish between woad and exotic indigo on references made according to historic recipes as well as on the pigment taken from the flower of the vat. The major distinction is due to additional yellow dyes found in the woad dyed textiles, for example kaempferol, luteolin and other hydroxyflavones. Applied to the specific historic samples from Bortom Åa studied in this case, we were not able to identify the yellow colouring matters. This can be due to that they have been washed out. In general however, we cannot exclude the possibility that these could be found in for example paint made of woad vat or other textiles that are unwashed. The results of the historic textiles investigated here show the presence of exotic indigo and brazilwood as the colouring matters as well as tryptanthrin that might indicate woad, in one of the cases. Further investigation on paints from Bortom Åa and other textiles is needed in order to look at more samples to be able to verify our theory.

Acknowledgements

The project is funded by the Swedish Research Council (VR). The references used in the study have been produced by Katarina Olars, Textile Conservator, Mia Olsson Textile Artist and Andreas Roxvall Painting Conservator. Besides

the authors, the main project participants are: Anneli Palmaskold, Ethnologist at the Department of Conservation, University of Gothenburg, Johan Knutsson, Art Historian at Carl Malmsten furniture studies, Linköping University, Yvonne Fors and Kaj Thuresson, both are chemists at The Swedish National Heritage Board (RAA), Thomas Zack, Geologist at Earth Science, University of Gothenburg, Aleksandar Matic and Florian Nitze both are Physicists at Applied Physics, Chalmers University of Technology.

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Citation: Nystrom I, Wilken S, Thomas J (2016) FT-Raman Analyses of Blue Dyes Stuff Common in Swedish Folk Art from Halsingland during 18th and 19th Century. Chem Sci J 7: 123. doi:10.4172/2150-3494.1000123