

Authenticating Turkey red textiles through material investigations by FTIR and UHPLC

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ABSTRACT

Nineteenth-century Turkey red, a cotton textile dyed by a peculiar and unique process, is found in many collections around the world. It was known for its bright colour and remarkable fastness to light exposure and washing. Light fading is a significant concern in the display of historical textiles, and understanding more about the properties of these objects may increase the accessibility of collections. This research explored the identification of historical Turkey red through non-invasive Fourier transform infrared (FTIR) spectroscopy to detect the presence of oil – a necessary step in the process – on the fibres. Around 1869, Turkey red dyers began to transition from using madder and *garancine* to synthetic alizarin, which was investigated through ultra-high-performance liquid chromatography (UHPLC). The chemical profiles of 19th-century samples and references of known dye source were used to predict whether Turkey red of unknown date was dyed with natural or synthetic dye.

INTRODUCTION

The susceptibility of historical textiles to light fading is one of the primary concerns in their care and display, complicating the accessibility of these collections. Turkey red, a cotton textile made by the eponymous and distinctive dyeing process, was produced in Western Europe from the mid-18th to the early 20th century and was lauded by consumers, dyers, and chemists for its exceptional fastness to light and wash fading. Display practices can be improved by understanding the robustness of historical Turkey red in modern, scientific terms. This requires a more reliable means than visual assessment to identify Turkey red, which this research has done through non-invasive Fourier transform infrared (FTIR) spectroscopy and micro-analysis by ultra-high-performance liquid chromatography (UHPLC).

HISTORICAL BACKGROUND

Turkey red dyeing is specific to cellulosic fibres, primarily cotton, and follows an unusual and lengthy process that was said to yield ‘the most brilliant and fastest madder red’ on cotton (Ure 1844). Success depended on familiarity with the technique, which varied between dyers and firms but followed the same general principles (Wertz 2017). The origins of Turkey red are likely Indian or Southeast Asian, where similar dyeing techniques are still practiced today (Cunningham et al. 2011). It was eventually made in Turkey and sold to European consumers, hence its name. The first European Turkey red works were established in the 1740s in France (Cardon 2003), but it was not until 1785 that Turkey red was produced in Britain when the first works was built in Glasgow, founding an industry that grew throughout the 19th century to become a significant textile manufacturer and economic power in the west of Scotland. Turkey red was dyed and printed in the Vale of Leven until 1936, when synthetic red dyes of sufficient, though not equal, quality superseded Turkey red for cost and time efficiency (Peel 1952). Technically, Turkey red is a process and a product but not a dye, because it exists only on a fibre. This complicates analysis because the full complex must be characterised in situ with the cotton, which was effectively impossible prior to the development of modern instrumental techniques. Turkey red artefacts are held in collections around the world, including the United Kingdom, France, Austria, the Netherlands, Switzerland, and the United States.

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Figure 1. Printed Turkey red, John Orr Ewing & Co, 1887. University of Glasgow Archive Services, Records of United Turkey Red Co Ltd, GB248 UGD 13/8/6

DISCUSSION OF TURKEY RED

The first step in Turkey red dyeing – preparing the cotton with sufficient oil – was the most laborious and unique to the process. The significance of the oil has been known since the 18th century (Berthollet 1791), but its chemistry in the process has never been fully understood (Cardon 2003). Oiling was initially accomplished by repeated steeping in a bath of sodium carbonate and rancid olive oil, then drying the fibres, which took two to three weeks (Chaptal 1807). After decades of research by some of the most distinguished dyers and chemists of the day, technological developments yielded Turkey red oil, the first synthetic anionic surfactant (Gunstone and Padley 1997). It was adopted by the industry in the 1870s and eliminated the need for repeated oil treatments, significantly shortening production time without altering the fundamental chemistry of the process (Wertz 2017).

The oiled cotton was treated with aluminium salts, then dyed red with madder (*Rubia tinctorum* L.). The demand from the British textile industry for madder, which took years to cultivate, was huge. After Perkin invented mauveine, chemists set out to understand and replicate the structure of alizarin (1,2-di-hydroxyanthraquinone), the major component in madder. This was achieved in 1868, making alizarin the first natural molecule to be re-created in a laboratory, and commercial production began in 1869 (Travis 1993). The higher concentration, lower cost, and lack of woody material appealed to dyers. By 1873, synthetic alizarin had almost completely replaced madder in Turkey red (Knecht et al. 1893, Archibald Orr Ewing & Co. n.d.). Dyers and chemists knew that madder also contains other hydroxyanthraquinone dyes like purpurin. They recognised that the synthetic process to manufacture alizarin, heating anthraquinone (anthracene-9,10-dione) with sulfuric acid to around 270°C, produced a mixture of hydroxyanthraquinone dyes that was different than in madder. Two major components, anthrapurpurin (1,2,7-tri-hydroxyanthraquinone) and flavopurpurin (1,2,6-tri-hydroxyanthraquinone), were noteworthy because they were not known to occur in madder (Perkin 1879). They have not been identified in any modern chromatographic analysis of madder extracts (Mouri and Laursen 2012), making them useful chemical markers to determine the date provenance of historical Turkey red. Nineteenth-century Turkey red dyers also used a concentrated madder product called *garancine* that was made by heating ground madder with sulfuric acid to release more colourant (Crookes 1874).

ANALYTICAL APPROACH

The key questions for this research were whether oil could be detected on Turkey red textiles, and if the anthraquinone dyes present indicate a natural or synthetic dye source and therefore a possible date of production. To test analyses, reference samples of replica Turkey red were dyed using Turkey red oil and madder or synthetic alizarin. A late-19th-century method from esteemed British dyer J.J. Hummel (Hummel 1886) that is representative of a typical Turkey red process was followed. These samples were compared to textiles in the United Turkey Red (UTR) collection in the Scottish Business Archives (SBA) dating from the 1850s to 1900, and 19th-century

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Figure 2. DRIFTS analysis of 18th-century Turkey red (UGD 13/8/2) at the CTC with Dr Leung Tang

Turkey red in the Victoria and Albert Museum (V&A) collection from UTR and German and Swiss dyers.

FTIR SPECTROSCOPY EXPERIMENTAL

Analysis by FTIR spectroscopy was selected for its ability to detect organic compounds, its usefulness in surface analysis, and its potential non-invasive applications. The Centre for Textile Conservation (CTC) has an attenuated total reflectance (ATR) instrument that could scan the replica Turkey red. The interface posed a challenge for the historical pieces from the SBA collection because the large, fragile sample pattern books in which the textiles are pasted could not be manipulated onto the crystal. This was an opportunity to evaluate the application of a handheld FTIR instrument with a diffuse reflectance interface (DRIFTS) (Figure 2). These relatively new devices minimise object handling and have useful heritage science applications (Quye et al. 2015). DRIFTS is also more suitable for uneven textile surfaces, while ATR is better for smooth surfaces. This research compared FTIR-ATR and DRIFTS to assess their usefulness in the identification of Turkey red, expanding its potential usefulness for institutions with either instrument.

FTIR-ATR spectra were taken at the CTC on a Perkin Elmer Spectrum One FTIR spectrometer with a diamond/thallium-bromiodide C/KRS-5 crystal ATR accessory. The spectra were the average of 16 scans taken from 4000–400 cm^{-1} at 8 cm^{-1} resolution in absorbance mode. A background scan was taken of the uncovered crystal and three spectra taken from different areas on each sample, then averaged using Essential FTIR software. Spectra were taken of the replica Turkey red (3x each madder and synthetic alizarin), a replica Turkey Red dyed with madder by Debbie Bamford, two samples of cotton dyed with madder but without an oil preparation (Figure 3), a piece of 19th-century Turkey red donated to the CTC by Dr Norman Tennent, and two pieces of mid-20th-century printed cotton from UTR donated to the CTC by Judith Townson.

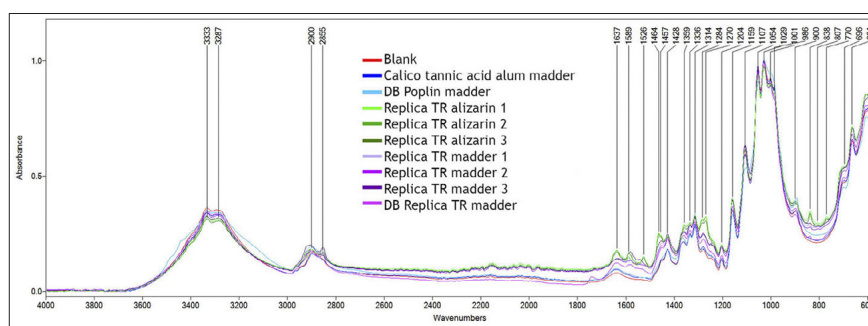


Figure 3. ATR-FTIR spectra of replica Turkey red shows bands for COO^- stretching from 1529–1428 cm^{-1} and $-\text{CH}_2-$ deformation from 1359–1270 cm^{-1}

DRIFTS spectra were taken using an Agilent 4300 Handheld FTIR. The faster instrument acquired spectra that were the average of more scans than the ATR, and its increased sensitivity toward rough surfaces makes the DRIFTS spectra more detailed. Each spectrum was the average of 128 scans taken from 5000–650 cm^{-1} at 8 cm^{-1} resolution in absorbance mode. A background of the instrument cap was taken every ten minutes and three spectra were taken from different areas on each sample for the historical pieces, six for the replicas, then averaged as before.

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IDENTIFICATION OF TURKEY RED BY FTIR SPECTROSCOPY

The FTIR analysis of Turkey red textiles was expected to reveal bands indicative of oil on the cotton when compared to calico not treated with oil. The key marker for this is the carbonyl (C=O) of the fatty acid carboxyls (COO⁻), which has a strong characteristic stretching band from 1800–1600 cm⁻¹ (Socrates 2001) and does not appear in the glucose monomer of cellulose. Figure 3 shows a band for COO⁻ stretching from 1529–1428 cm⁻¹ (Socrates 2001), but no distinct C=O peak with the exception of the piece dyed by Debbie Bamford, which appears around 1740 cm⁻¹ and may be due to her use of rancid olive oil. These bands were absent in the plain calico and no-oil dyed cotton spectra. The Turkey red samples also have higher peaks from 1359–1270 cm⁻¹ related to –CH₂– deformation vibrations (Socrates 2001) of fatty acid chains.

DRIFTS spectra of Turkey red from the UTR collection dyed from 1886–1888 (UGD 13/8/6 and 13/8/7) (Figure 4) have a much clearer band at 1712 cm⁻¹ from C=O stretching. The band for adsorbed water at 1643 cm⁻¹ (Socrates 2001) is also stronger. COO⁻ stretching is also present, though –CH₂– deformations are weaker with this interface. The method used to dye this Turkey red is not in the archive, so for comparison spectra were also taken of Turkey red in an 1846 textile dyeing and printing manual by Jean-François Persoz, *Traité théorique et pratique de l'impression des tissus*, vol. 3. These samples are accompanied by directions for Turkey red consistent with other methods reviewed for this project (Wertz 2017). The spectra (Figure 5) are consistent with those in Figure 4. There are more bands for COO⁻ stretching in the Persoz samples, likely from the oil treatment being rancid olive oil at this date.

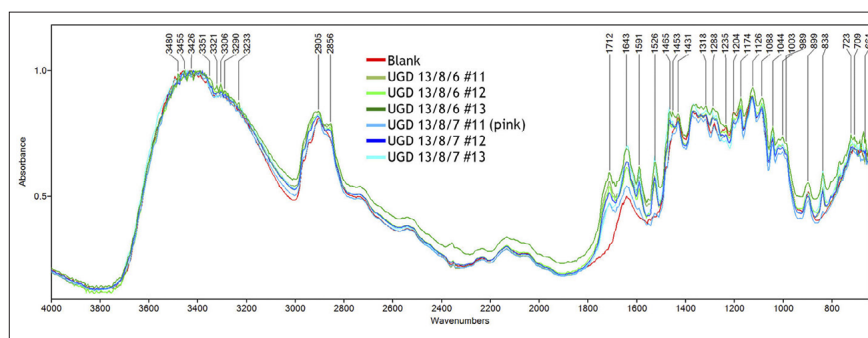


Figure 4. DRIFTS spectra of red areas on six pieces of historical Turkey red from the UTR collection, UGD 13/8/6 (1886–88) and UGD 13/8/7 (1887)

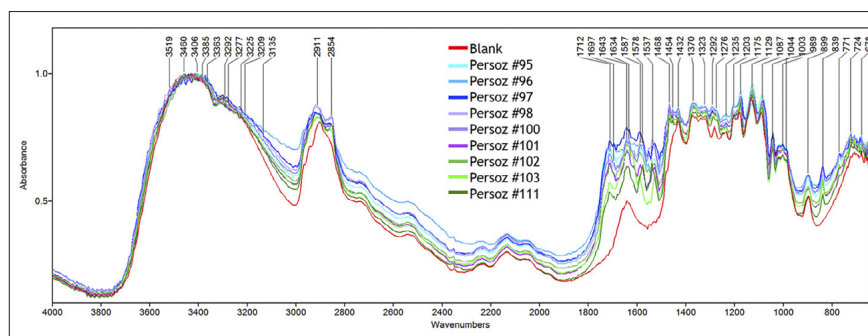


Figure 5. DRIFTS spectra of Turkey red samples in dyeing manual *Traité théorique et pratique de l'impression des tissus* by Jean-François Persoz, vol. 3, 1846

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Figure 6. Printed Turkey red, Order 313, January 1858. University of Glasgow Archive Services, Records of United Turkey Red Co Ltd, GB248 UGD 13/8/3. The inset image is of a fibre sample taken from the frayed edge (blue box)

This analysis found that the presence of the oil on the fibres, which is imperative in the Turkey red process, is a useful chemical marker for non-invasive identification of Turkey red textiles by FTIR-ATR and DRIFTS. The fatty acid C=O and COO⁻ groups, which do not appear in the cellulose of calico, produce strong stretching bands that were detected by either technique, though better results were obtained with the DRIFTS instrument, which was also more appropriate for the historical objects.

UHPLC EXPERIMENTAL

High-performance liquid chromatography (HPLC) has been a valuable tool for the identification of dyes on historical textiles. Although it requires taking a sample, it is justified by the value of the information gained for improving object history and care. UHPLC, a relatively new improvement on the technique, is a more efficient system that provides better results from even less sample. Segments of red thread about 0.5–1 cm long were taken for dyes analysis from the unfinished edges of Turkey red in the UTR collection at the SBA (Figure 6) and the items at the V&A. A two-step ‘soft’ extraction method was used to remove the dyes from the fibres (Han 2016). The fibre sample was placed in a 1-mL flat-bottomed glass vial and 50 µL dimethyl sulfoxide (DMSO) added. Open vials were placed in a Talboys dry block heater at 80°C for 10 minutes, then removed and the DMSO extracted with a micropipette and retained in a second vial. The fibre was extracted again with 75 µL solution made of 0.5 M oxalic acid/acetone/water/methanol (1:30:40:30 v/v/v/v) and the vials returned to the block heater for 15 minutes at 80°C. The remaining extract was vacuum evaporated to dryness by placing the vials in a Büchi R-215 Rotavapor at 40°C and 16 mbar for 30 minutes. The extracts were combined by reconstituting the fibre residue with the DMSO portion. It was then filtered through a 0.2 µm PTFE (Teflon) syringe filter to remove particulates, and collected in a vial insert.

Reference compounds include a sample of 19th-century *garancine* provided by the Catalyst Science Discovery Centre (Widnes, England, UK) and samples of 19th-century madder and synthetic alizarin kindly donated by the TU Dresden Historical Dyes Collection (Dresden, Germany). The madder and *garancine* references were extracted following a method from Mouri and Laursen (Mouri and Laursen 2012) and the alizarin was dissolved in methanol and diluted with DMSO.

Analysis was performed on a Waters ACQUITY UPLC H-Class system with Empower 3 software at the CTC. The system consists of a sample manager with a flow through needle, a quaternary solvent manager, a column with thermal control, and a photodiode array (PDA) detector. The column was a Waters C18 Ethylene Bridged Hybrid (BEH) Shield column (150 mm × 2.1 mm i.d., particle size 1.7 µm) with a Waters C18 BEH Shield VanGuard pre-column (5 mm × 2.1 mm i.d., particle size 1.7 µm) to protect the column from particulates. Samples were left at room temperature and the column heater set to 40°C. A volume of 4 µL was injected and with PDA acquisition from 210–800 nm at a resolution of 1.2 nm. A general dyes gradient elution was used with the solvents: (A) 10% (v/v) aqueous methanol; (B) 100% methanol; (C) 1% (v/v) aq. formic

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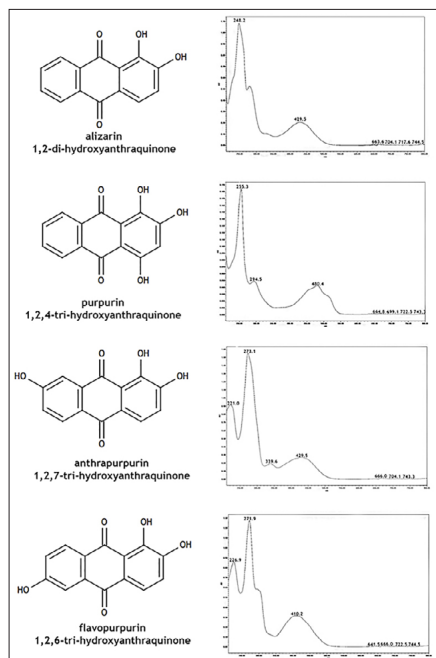


Figure 7. Structures, systematic names, and UV-Vis spectra for the four major dyes found on Turkey red – alizarin, purpurin, anthrapurpurin, and flavopurpurin

acid. All gradients are linear and the flow rate was set at 0.2 mL/min; gradient parameters are provided in Table 1.

Table 1. Gradient elution parameters for UPLC analysis

Time (min)	% Solvent A	% Solvent B	% Solvent C
0	80	10	10
1.33	80	10	10
2.33	74	16	10
5.33	55	35	10
9	55	35	10
14	30	60	10
25	5	85	10
26	0	100	0
30	0	100	0
32	80	10	10
40	80	10	10

UHPLC ANALYSIS OF TURKEY RED

Dyes from 100 fibre samples of 19th-century Turkey red of known and unknown date and the replica samples were analysed. The results were extracted at 430 nm, a useful wavelength for orange and red compounds. The peaks in the textile and alizarin chromatograms are exclusively hydroxyanthraquinones appearing around 18–26 minutes, while madder and *garancine* also contain more non-dye compounds. This analysis focused on the four major compounds present in historical Turkey red and identified them through retention time (RT) and UV-Vis spectrum (Figure 7). Some RT shifts were observed and later traced to an internal seal failure on the instrument, but the data was determined to still be useful.

The chromatogram of 19th-century synthetic alizarin (Figure 8a) has peaks for anthrapurpurin and co-eluting alizarin and flavopurpurin. The peak for flavopurpurin consistently co-eluted with alizarin, even with adjustments to the gradient. In general, the hydroxyanthraquinones eluted close together, often with low peak resolution. The chromatograms for Turkey red dyed before 1869 had alizarin and purpurin and no flavopurpurin. Occasional trace anthrapurpurin appears that is also in the *garancine* reference, and may be a by-product of its manufacture. Figure 8b is the chromatogram for the sample in Figure 6, dyed in 1858. In Figure 8c, Turkey red dyed in 1878 has peaks for anthrapurpurin and flavopurpurin indicative of synthetic alizarin. About ten unidentified minor components were also seen, some of which may be indicative of a dye source. Further identification of unknowns was not possible without MS/MS facilities. Chromatograms of Turkey red samples with unknown date of manufacture were consistent with data from the known pieces and it was fairly easy to predict a natural or synthetic dye sources. This information was used to determine that two books in the SBA collection (dates unknown) were made after 1869 based on the presence of synthetic alizarin.

Although anthraquinone dyes are of good fastness, knowing exactly which compounds are present on historical Turkey red improves the ability to predict the effects of light exposure during display. There is very little

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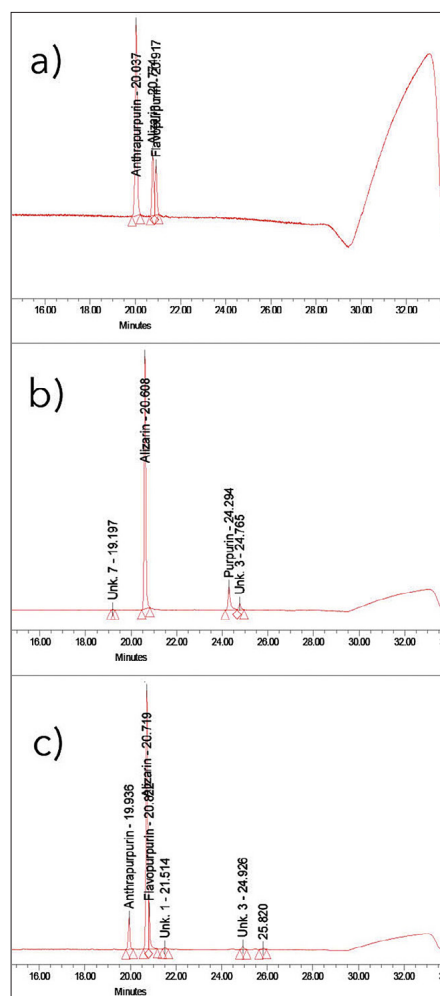


Figure 8. Chromatograms of a) 19th-century synthetic alizarin from BASF; b) UGD 13/8/2 #1, 1858; c) UGD 13/8/8 #5, 1878

research thus far on early synthetic alizarin, which contains a different mixture of dyes than madder and merits further investigation.

CONCLUSION

This research found that Turkey red can be identified by the oil treatment on the cotton, which was a fundamental step in the process, through FTIR-ATR and DRIFTS. This was determined by the oil bands visible above the bulk cotton signal because fatty acids from the oil treatment contain COO^- and C=O groups. These are not present in cellulose and have strong stretching vibrations. Overall, both techniques were successful, but the DRIFTS interface was superior in terms of detection and suitability for the historical textiles. FTIR offers a quick, non-invasive means to identify Turkey red based on the presence of an oil treatment.

The dye analysis of 19th-century Turkey red and reference dyes by UHPLC indicate it is possible to identify the type of dye used in the process and an approximate date of production. Textiles dyed with synthetic alizarin have peaks for anthrapurpurin and flavopurpurin, as seen in Figure 8a, which form during synthesis and do not occur in madder. Turkey red dyed with madder has peaks for alizarin and purpurin. Samples with trace anthrapurpurin and no flavopurpurin may have been dyed with *garancine*, but a larger sampling of *garancine* references is needed to draw stronger conclusions. Further research beginning at the CTC in February 2017 will continue to study the fastness and stability of Turkey red textiles.

ACKNOWLEDGEMENTS

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MATERIALS LIST

Acetone (ACS grade, $\geq 99\%$), purpurin ($\geq 90\%$ dye)
Sigma Aldrich
www.sigmaaldrich.com

Oxalic acid dihydrate (99+%), alizarin (97%)
Acros Organics
www.acros.com

DMSO (HPLC grade), formic acid (analytical grade 98-100%), methanol (HPLC grade)
Fisher Scientific
www.fishersci.com

Anthrapurpurin
Pfaltz & Bauer
www.pfaltzandbauer.com

Ultrapure water was supplied by a Millipore Direct-Q 3 UV water purifier (18.2 M Ω resistivity).

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