

PAPER • OPEN ACCESS

Identification of natural dyes in historical tapestries, a LC-MS/MS approach.

To cite this article: Anna Baroni *et al* 2022 *J. Phys.: Conf. Ser.* **2204** 012065

View the [article online](#) for updates and enhancements.

You may also like

- [A process algebra model of QED](#)
William Sullis
- [Current distribution mapping in insulated \(Gd,Y\)BCO based stabilizer-free coated conductor after AC over-current test for R-SFCL application](#)
Soumen Kar, Xiao-Fen Li, Venkat Selvamanickam *et al.*
- [Carbon footprint of American lifestyles: a geodemographic segmentation approach](#)
Giovanni Baiocchi, Kuishuang Feng, Klaus Hubacek *et al.*



ECS Membership = Connection

ECS membership connects you to the electrochemical community:

- Facilitate your research and discovery through ECS meetings which convene scientists from around the world;
- Access professional support through your lifetime career;
- Open up mentorship opportunities across the stages of your career;
- Build relationships that nurture partnership, teamwork—and success!

Join ECS!

Visit electrochem.org/join



Identification of natural dyes in historical tapestries, a LC-MS/MS approach.

Anna Baroni¹, Valeria Comite¹, Vittoria Guglielmi¹, Mattia Casanova², Paolo Redegalli², Paola Fermo¹

¹Dipartimento di Chimica, Università di Milano, Via Golgi 19, 20133 Milano

²Shimadzu Italia S.r.l, Via G.B. Cassinis 7, 20139 Milano

Anna Baroni: anna.baroni21@gmail.com

Abstract. The present study concerns the identification of the colouring matter in ancient tapestries of different historical periods. The investigation was performed using HPLC-DAD-ESI-MS and the results were compared with a previously created reference database. Furthermore, the characteristic fragmentation pathway provided additional information for the identification of the dyes employed.

1. Introduction

The first issue in studying historical fabrics and textile artefacts concerns the importance of knowing the materials and the techniques used in the past; secondly tapestries are frequently subject to degradation phenomena that could alter the dyes employed and finally the presence of chromophores with similar structures can make the identification of the coloring matter challenging [2].

Today the best instrumental technique in terms of selectivity and efficiency is high performance liquid chromatography coupled with mass spectrometry (HPLC-MS) that allows also to resolve complex mixtures of dyes [3].

Furthermore, the development of tandem mass spectrometers with the possibility to investigate the fragmentation pattern of a specific molecule represents a big improvement in the capability of recognizing different compounds, particularly isomers [4].

The aim of this work was to identify the dyes used in tapestries of different historical periods between 17th and 19th century.

The 17th samples were collected from the tapestries of the series “Storie di Ulisse” stored at the Quirinal palace (Rome). A Brussel manufacturing were commissioned the tapestries on the occasion of the wedding between Carlo Emanuele II Savoia and Maria Giovanna Savoia-Nemours. The artworks realized between 1665 and 1666, currently present issues connected with color fading phenomena and chromatic alterations.

The 19th century samples instead came from different tapestries of Italian manufacturing and seemed well preserved.

In the present study, specifically, the focus is set on the red yarns.



2. Experimental

2.1. Apparatus

The analyses were performed using LC-MS 8045 instrument, thanks to the collaboration with Shimadzu Italia S.r.l. The instrument was equipped with a UHPLC of NexeraTM series with photodiode array detector (PDA), electrospray ionization (ESI) and triple quadrupole, which operated both in Scan e Product Ion Scan mode. A biphenyl Restek column was used (2,1x100 mm, 2,7 μ m) and the mobile phase selected was a mixture of water (eluent A) and methanolic acid added with formic acid (eluent B); the gradient used is reported in *Table 1*.

Table 1. Gradient used

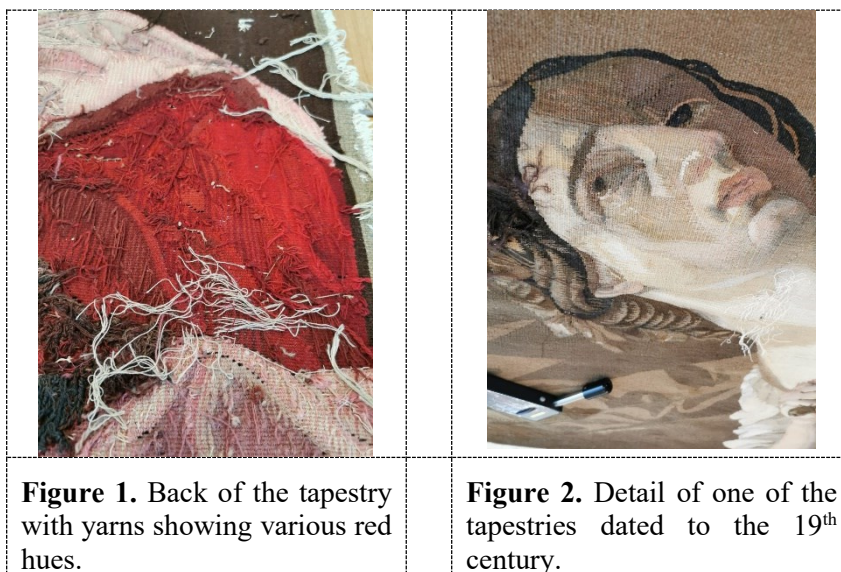
Time (min)	A(%conc.)	B(%conc.)
0	95,0	5,0
1,00	90,0	10,0
3,00	45,0	55,0
10,50	0,0	100,0
12,00	0,0	100,0
12,01	95,0	5,0
0	95,0	5,0

2.2. Extraction of fibres

The red dyes were extracted from the textile fibers, prepared accordingly to a methodology previously set-up [1,5] with an acid-methanolic mixture. Samples were treated with 3 mL of CH₃OH and 100 μ L of HCl. The solution was kept in a water bath at 70°C for 1h. Then, the solution was dried under N₂ gentle stream. The residual matter was finally dissolved in 120 μ L of CH₃OH before injection[5, 6].

3. Analytical results

The red yarns belonging to tapestries of different historical periods showing many hues, from pink to violet (*Figure 1*). Samples were collected and investigated in order to understand the type of dyes involved and their chemical nature.



At the beginning the focus was put on fibres coming from a tapestry dated to 17th century; the use of madder as main dye was shown in all the samples. Specifically, the presence of the anthraquinone compounds alizarin 239 m/z [M-H]⁻ and purpurin 255 m/z [M-H]⁻ together with other compounds was studied, as reported in *Table 2*. All the identified anthraquinones were compared both with the database previously created and the literature data [7,8,9].

Table 2. List of compounds identified in sample 1R

	t_R , min	[M-H] ⁻ , m/z	Fragment ions, m/z (CE, V) ¹
Munjistin	6,5	283	265(20), 239(20), 211(20), 195 (20)
Pseudopurpurin	6,7	299	255 (20), 227(40)
Lucidin	7,4	269	251 (20), 222(20), 195 (40)
Alizarin	7,7	239	211(20), 210(40), 167(20), 127(40), 101 (40)
Xanthopurpurin	8,0	239	211(20), 210 (40), 195(20), 167(40)
Purpurin	8,7	255	227 (20), 183 (40), 171(40), 129(40), 101(40),
Rubiadin	8,9	253	225(20), 209(40), 195(40)
Nordamnacanthal	10,8	267	239 (20), 211(20), 195(40)

¹ Collision energies expressed in Volt are indicated in the brackets near the fragment ions.

The analysis performed on yarns collected from tapestries of the 19th century (*Figure 2*) highlighted the use of a mixture of madder and cochineal in all the samples; the second one was identified thanks to the presence of carminic acid 491 m/z [M-H]⁻, kermesic 329 m/z [M-H]⁻ and flavokermesic acids 313 m/z [M-H]⁻, as reported in *Table 3*. All the identified compounds were compared both with the database previously created and with the literature data [1,10, 11].

Table 3. List of compounds identified in sample SA3

	t_R , min	$[M-H]^-$, m/z	Fragment ions, m/z (CE, V) ¹
dcII	4,4	475	431 (15), 353(35), 341(15), 311(15), 282(35)
Carminic acid	4,5	491	447 (15), 357 (15), 339 (35), 327(15), 299 (35), 298 (55), 285 (35), 283(35)
Flavokermesic acid	5,9	313	269 (15), 254(35)
Kermesic acid	6,0	329	285(15), 257(35)
Munjistin	6,3	283	265(20), 239(20), 211(20), 195 (20)
Pseudopurpurin	6,8	299	255(20), 227(20), 157(40)
Alizarin	7,7	239	211(20), 210(40), 165(40), 127(40), 101(40)
Purpurin	8,7	255	227(20), 182(40), 171(40), 157(40), 143(40), 129(40), 101(40)
Nordamnacanthal	10,7	267	239 (20), 211(20), 195(20)

¹ Collision energies expressed in Volt are indicated in the brackets near the fragment ions.

4. Conclusions

The HPLC-DAD-ESI-MS technique was suitable for the identification of various species of anthraquinones in different type of dyes, even in ancient artifacts where concentration of the colouring matter could have been lowered during time or where degradation processes could have been occurred.

Furthermore, as observed for the samples of 19th century, it was possible to highlight the use of mixture of dyes. Particularly the possibility to collect the fragment ions spectra was fundamental to confirm the attributions.

Finally hypothesis were done on the type of madder used. The anthraquinones found in the sample 1R, compared with literature [12], allowed the attribution to the *Rubia tinctorum*. However quantitative analysis will be performed in order to confirm the attribution.

References

- [1] Fermo, P., Comite, V., Guglielmi, V., Schiavoni, M., Boanini, E., Bonomi, R., Monfasani, E. Red organic colorant used to dye textile artifacts: From mock-up samples preparation to analytical characterization (2020) International Journal of Conservation Science, 11 (SpecialIssue1), pp. 371-378.
- [2] Raffaëly L. et al, *Optimisation of ESI-MS detection for the HPLC of anthraquinone dyes*, in Dyes and Pigments, 77, 2008, 191-203.
- [3] Surowiec I. et al., *HPLC-MS of anthraquinoids, flavonoids, and their degradation products in analysis of natural dyes in archaeological objects*, in J. Sep. Sci., 30, 2007, 2070-2079.
- [4] Balakina G. G. et al., *HPLC and molecular spectroscopic investigations of the red dye obtained from an ancient Pazyryk textile*, in Dyes and Pigments, 71, 2006, 54-60.
- [5] De Luca E. et al., *Multi-technique investigation of historical Chinese dyestuffs used in Ningxia*

carpets, in *Archaeol. Anthropol. Sci.*, 9, 2017, 1789-1798.

[6] Colombini M.P., *Colour fading in textiles: A model study on the decomposition of natural dyes*, in *Microchemical Journal*, 85, 2007, 174-182.

[7] Derksen G. C. H. et al., *Analysis of anthraquinones in Rubia tinctorum L. by liquid chromatography coupled with diode-array UV and mass spectrometric detection*, in *Journal of Chromatography A*, 978, 2002, 119-127.

[8] Rosenberg E., *Characterisation of historical organic dyestuffs by liquid chromatography–mass spectrometry*, in *Anal. Bioanal. Chem.*, 391, 2008, 33-57.

[9] Szostek B. et al., *Investigation of natural dyes occurring in historical Coptic textiles by high-performance liquid chromatography with UV-Vis and mass spectrometric detection*, in *Journal of Chromatography A*, 1012, 2003, 179-192.

[10] Lech K., Jarosz M., *Identification of Polish cochineal (Porphyrophora polonica L.) in historical textiles by high-performance liquid chromatography coupled with spectrophotometric and tandem mass spectrometric detection*, in *Anal. Bioanal. Chem.*, 408, 2016, 3349-3358.

[11] Lech K. et al., *Identification of unknown colorants in pre-Columbian textile dyed with American cochineal (Dactylopius coccus Costa) using high-performance liquid chromatography and tandem mass spectrometry*, in *Anal. Bioanal. Chem.*, 407, 2015, 855-867.

[12] Blackburn R. S., *Natural dyes in madder (Rubia spp.) and their extraction and analysis in historical textiles*, in *Coloration Technology*, 133, 2017, 449–462