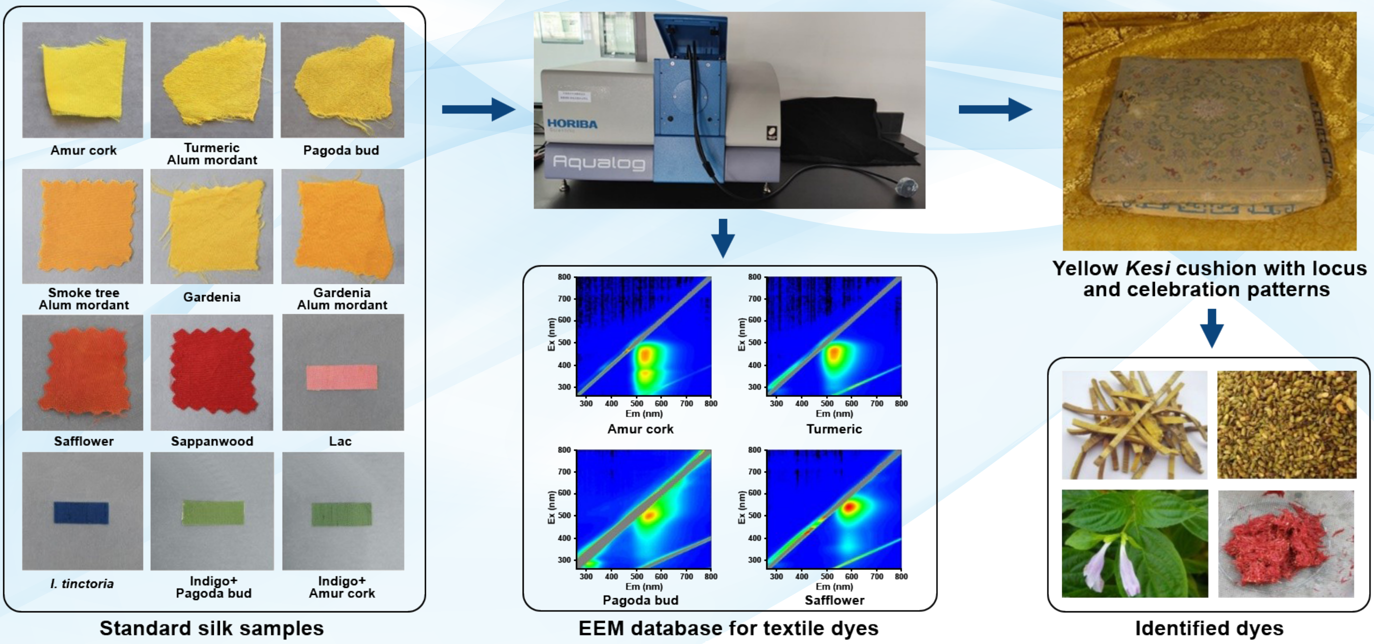
HORIBA

Fluorescence

Non-Invasive Analysis of Historical Chinese Textile Dyes using EEM Fluorescence Spectroscopy

Application Note
Art Conservation
FL252001

Graphic Abstract



Introduction

The preservation and study of historical textiles presents unique analytical challenges. Traditional destructive sampling methods, while providing detailed chemical information, are often impractical or ethically problematic when dealing with irreplaceable cultural artifacts. This application note describes a breakthrough non-invasive analytical approach using Excitation-Emission Matrix (EEM) fluorescence spectroscopy for identifying natural dyes in Chinese royal textiles from the Qing dynasty (1616-1912 CE).

The Challenge

Historical Chinese textiles, particularly those from the Qing dynasty, employed sophisticated dyeing techniques using natural materials derived from plants and animals. These textiles often exhibit:

- Complex multi-component dye systems
- Similar visual appearances despite different source materials
- Sophisticated processing techniques (fermentation, mordanting, over-dying)
- High cultural value precluding destructive analysis

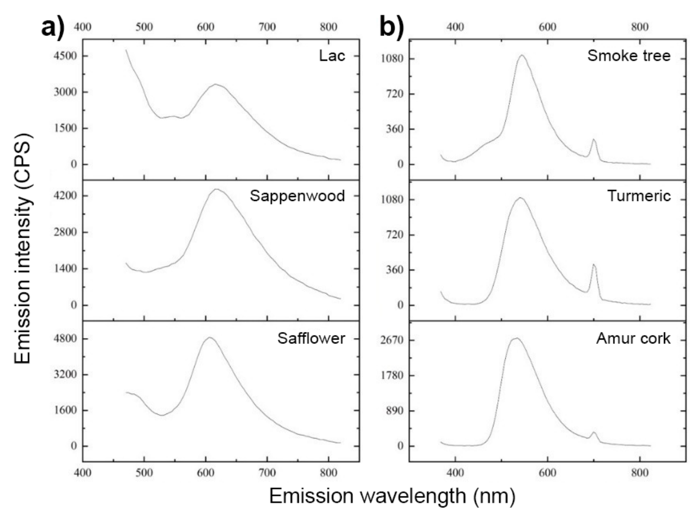


Figure 1. Fluorescence emission spectra of traditional Chinese red and yellow natural dyes: (a) excited by a light wavelength of 450 nm; and (b) excited by a light wavelength of 350 nm.

Traditional analytical methods, such as liquid chromatography-mass spectrometry (LC-MS), require sampling and complex sample preparation, making them unsuitable for well-preserved museum artifacts.

The EEM Fluorescence Solution

EEM fluorescence spectroscopy offers a non-invasive alternative that creates a "fluorescent fingerprint" for each dye system. The technique captures three-dimensional data:

- Excitation wavelength (y-axis)
- Emission wavelength (x-axis)
- Fluorescence intensity (z-axis)

This comprehensive spectral information enables discrimination between dyes that appear visually similar, and provides insights into historical dyeing processes.

Key Analytical Capabilities

Dye Identification

The method successfully identifies major dye categories used in Qing dynasty textiles:

Yellow Dyes:

- Amur cork tree (Phellodendron species): Dual fluorescence centers at Ex/Em = 360/535 nm and 450/535 nm
- Turmeric (Curcuma longa): Single center at Ex/Em = 460/530 nm
- Pagoda bud (Styphnolobium japonicum): Weak fluorescence at Ex/Em = 450/550 nm
- Smoke tree (Cotinus coggygria): Variable patterns depending on mordanting
- Gardenia (Gardenia jasminoides): Shifts from Ex/Em = 350/540 nm (raw) to 370/600 nm (baked)

Red Dyes:

- Safflower (Carthamus tinctorius): Dual centers at Ex/Em = 370-400/590-610 nm and 540/590-610 nm
- Chinese sappanwood (Caesalpinia sappan): Characteristic at Ex/Em = 550/640 nm
- Lac dye (Kerria species): Dual centers at Ex/Em = 400/460 nm and 455/620 nm

Blue Dyes:

- Indigo (various Persicaria and Indigofera species): Fluorescence at Ex/Em = 350-400/400-450 nm

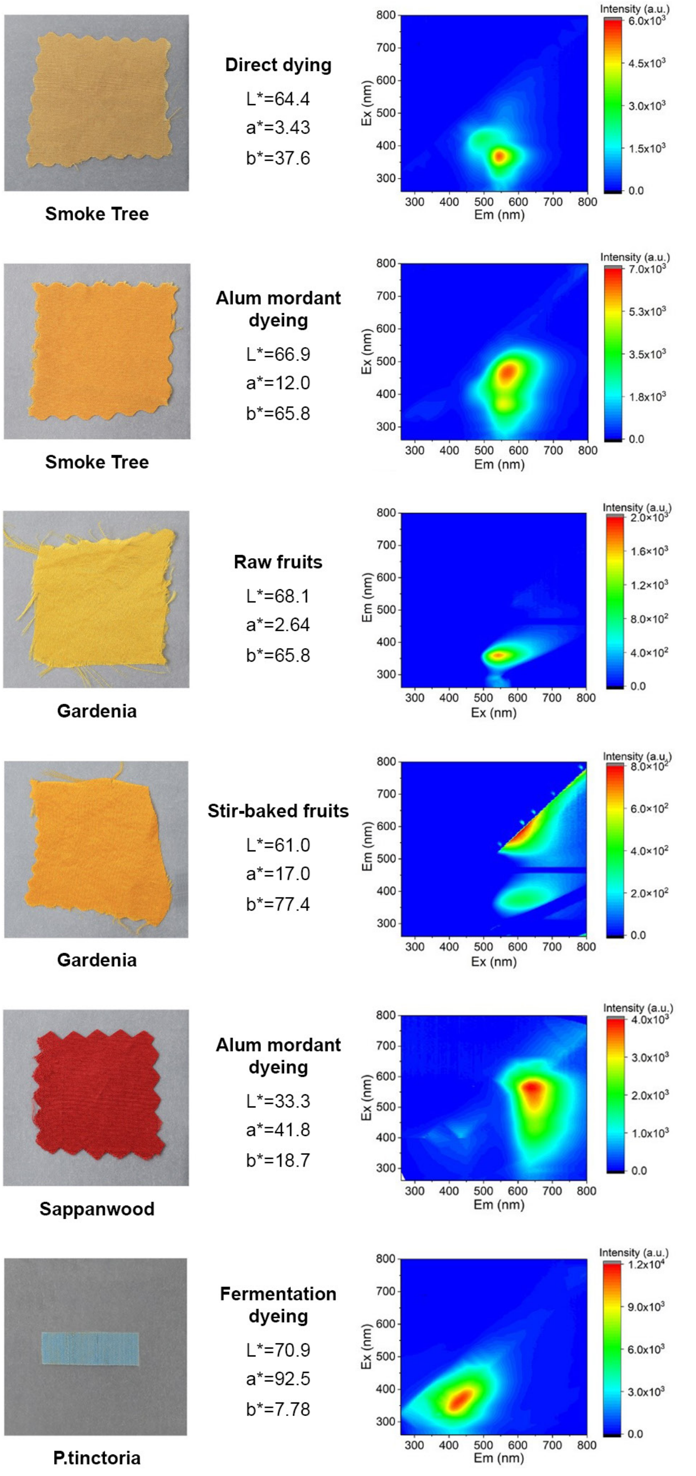


Figure 2. Representative EEM spectra of Chinese traditional dyes

Process Differentiation

The technique reveals important processing information:

Fermentation Detection:

Microbial fermentation of pagoda bud produces a distinctive red fluorescence peak at 660 nm, serving as a marker for this traditional Chinese technique.

Mordanting Effects:

Different mordanting treatments produce distinguishable spectral patterns, particularly evident in smoke tree preparations.

Over-dyeing Analysis:

Complex green colors achieved through indigo-yellow combinations can be decoded, with spectral dominance determined by relative fluorescence intensities.

Practical Applications

Museum Conservation

- Non-destructive screening of textile collections
- Authentication of historical dyeing practices
- Monitoring degradation processes
- Informing conservation treatment decisions

Historical Research

- Documenting regional dyeing preferences (Northern vs. Southern weaving bureaus)
- Understanding technological evolution in textile production
- Reconstructing historical color palettes

Case Study Results

Analysis of yellow lotus-patterned kesi cushions from the Hall of Mental Cultivation (Emperor Daoguang period, 1821-1851 CE) revealed:

- Front surfaces: Over-dyed with amur cork tree and pagoda bud
- Back surfaces: Single amur cork tree dyeing
- Green areas: Indigo combined with amur cork tree
- Red areas: Safflower dyeing
- Attribution: Inner Court Weaving and Dyeing Bureau (based on safflower preference)

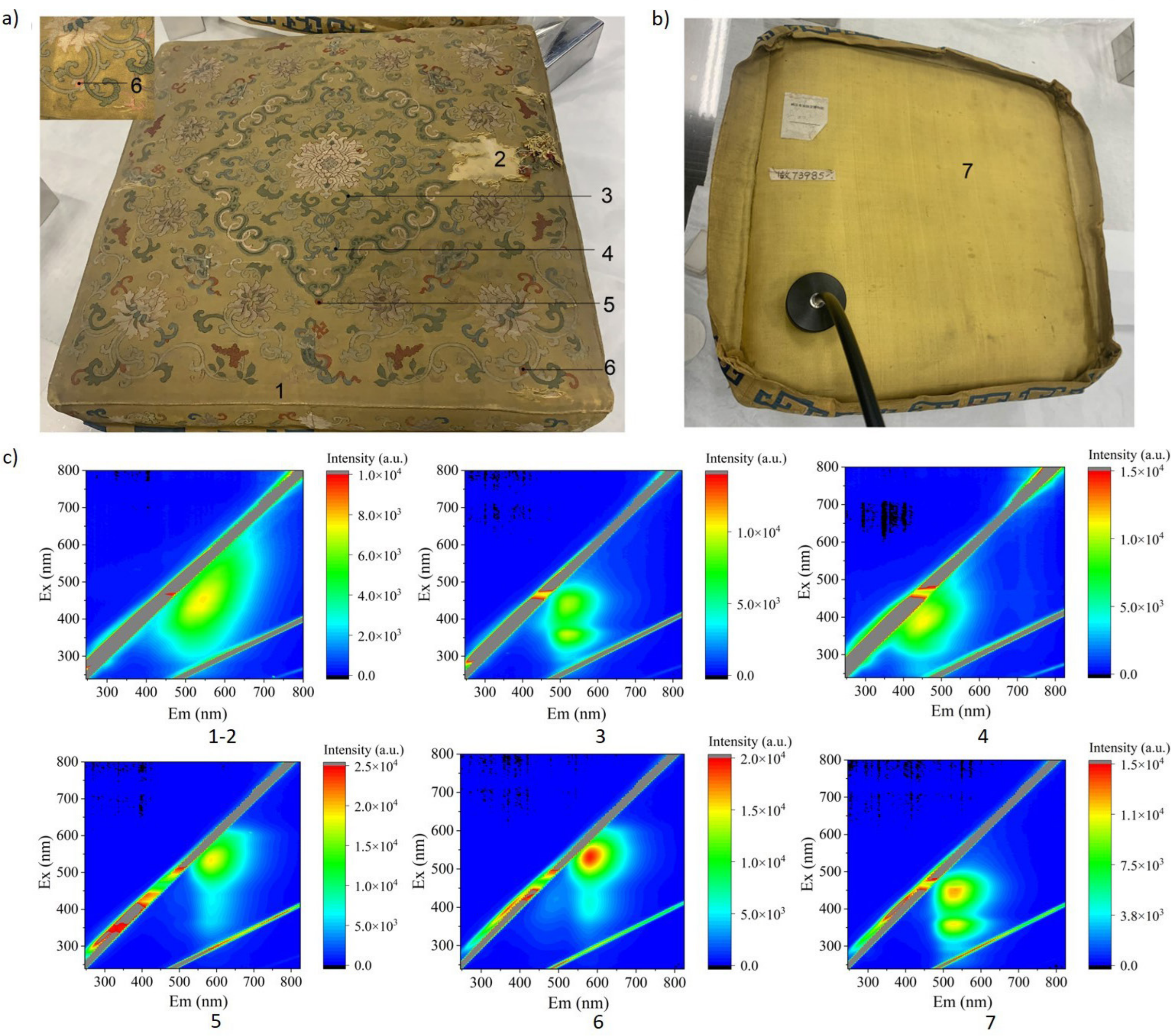


Figure 3. Yellow *kesi* cushion studied and characteristic EEM spectra. a) frontal view of the cushion; b) back view of the cushion; c) the EEM spectra at the indicated locations.

Analytical Considerations

Sample Requirements

- Uniform colored area (0.8 cm diameter minimum)
- Direct contact with fiber optic probe
- No sample preparation required

Spectral Interpretation

- Fluorescence intensity varies significantly between dye types
- Strong fluorophores may mask weaker signals in over-dyed samples
- Background subtraction from undyed substrate essential
- Integration time normalization required for quantitative comparisons

Limitations

- Cannot distinguish between indigo species with identical chemistry
- Limited effectiveness for very weak fluorophores
- Requires comprehensive reference database for identification

Future Direction

The EEM fluorescence database developed for Qing dynasty textiles establishes a foundation for broader applications in cultural heritage analysis. The methodology shows promise for ancient paintings and calligraphy analysis, where similar natural dyes were frequently employed as pigments. Leather and ivory screen examination represents another potential application, as these materials often incorporated the same organic colorants used in textile production. Cross-cultural textile studies could benefit significantly from this approach, enabling comparative analysis of dyeing traditions across different civilizations and time periods. Additionally, the success of laboratory-based EEM fluorescence analysis points toward the development of portable instrumentation specifically designed for field analysis, which would enable on-site examination of artifacts in museums, archaeological sites, and private collections without the need for specialized laboratory facilities.

Conclusion

EEM fluorescence spectroscopy represents a significant advancement in non-invasive cultural heritage analysis. The technique successfully addresses the critical need for dye identification in precious historical textiles while preserving their integrity for future generations. The comprehensive spectral database established for Qing dynasty materials provides a foundation for broader applications in art conservation and historical textile research.

Acknowledgement:

This application note is based on the research published by Zhao, L., Wang, Y., Zhang, Y., Wang, X., Lei, Y., & Gu, A. (2024). "Non-invasive analysis of Chinese traditional dyes in royal textiles of the Qing dynasty by excitation–emission matrix fluorescence." Archaeometry, 1-25. https://doi.org/10.1111/arcm.13027. The original study was conducted at the Conservation Department, The Palace Museum, Beijing, China, and the Key Laboratory of Calligraphies and Paintings Conservation (The Palace Museum), Ministry of Culture and Tourism, Beijing, China.

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