Non-destructive analysis of textiles

15 November 2017

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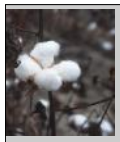
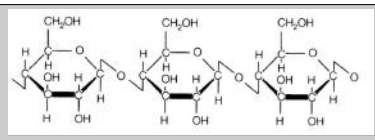
Key concepts and Goals

- Fibre identification and assessment
  - Light Microscopy
  - FTIR and NIR Spectroscopy
- Colour Measurement
  - Fibre Optic Reflectance Spectroscopy (FORS)
- Dye analysis*
  - Chromatography (UPLC)

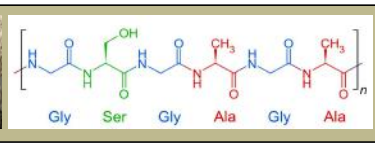
Applications & Case Studies

- Microscopy: Identification of fibres
- Infrared Spectroscopy and Micro-FTIR: Assessment of Degradation of fibres and textiles
- FORS: Dye discrimination+Fading
- UPLC: Dye analysis

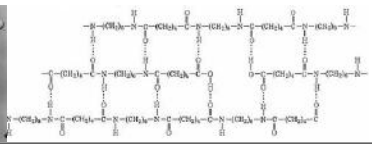




cellulose
plant
fibres

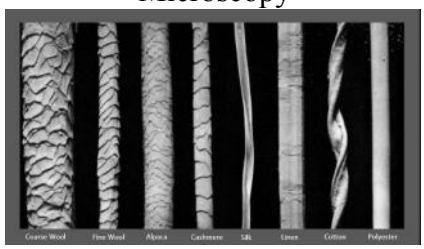


keratin
protein
animal
hair



Nylon
polymer
polyamide

Microscopy



- Recommended method for studying fibres
- Minimal sample required - far less than other techniques
- Discriminate between most natural fibres as long as the fibres are in "good" condition
- More complex for identifying synthetic polymers

Some online resources

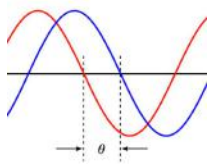
Fiber Reference Library mfa Museum of Fine Arts Boston
http://cameo.mfa.org/wiki/Fiber_Reference_Image_Library

Properties of light which are of key importance for microscopy:

- Reflection
- Refraction
- Numerical Aperture
- Polarisation

Phase Contrast

- Uses phase shifted waves of through transparent specimens cause changes in amplitude (contrast) in structures of the specimen
  - One of the most widely used in biology
  - No staining required



Polarisation of Light

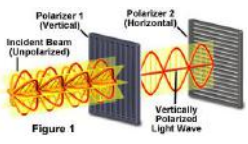


Figure 1

- The intrinsic polarisation of light can be used to improve contrast in microscopy
- Birifringence (百度百科) is a property related to different refractive indices in a material
- Pleochroism is also very characteristic

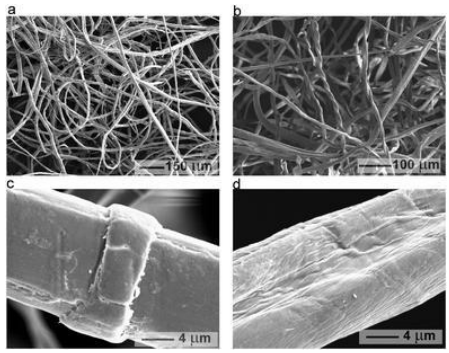
Preparation of samples

- Fibres should be isolated or separated
- Fibres can be examined either in air (n=1) (n=1.33), under a glass slide with glycerin (n=1.43)
- Mounted in meltmount or other mounting medium, with a known refractive index
- Sectioned with appropriate methods to examine core (for advanced microscopy)

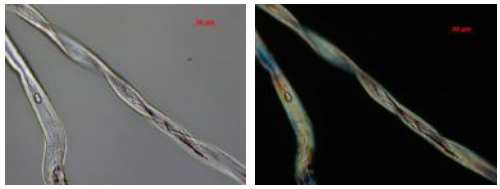
Examples of Microscopy

- Polymers
- Cotton
- Linen/Flax
- Jute
- Silk
- Many others @ Fiber Reference Library

Cotton vs. Flax under SEM



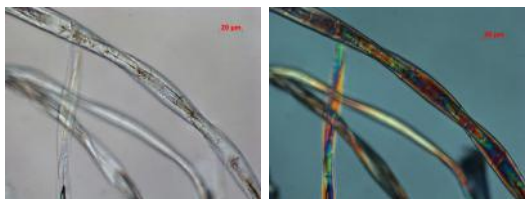
Examples of fibres: Cotton



From Cameo: Fiber Reference Library

Cotton: Historical Dress

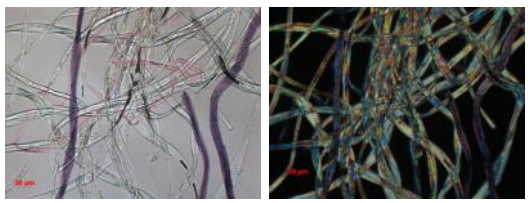
Meltmount **Phase Contrast- Pleochroism**



From Cameo: Fiber Reference Library

Cotton: Historical Dress

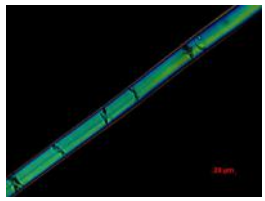
Normal Light **Polarised light**



From Cameo: Fiber Reference Library

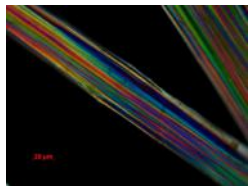
Flax

Permount (n=1.513) **Phase Contrast**

From Cameo: Fiber Reference Library

Jute

From Cameo: Fiber Reference Library

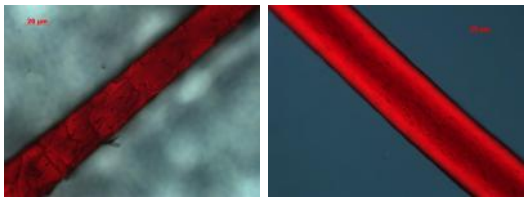
Animal fibers: hairs or silk

Sheep's Wool **Silk (note triangular shape)**


From Cameo: Fiber Reference Library

Wool: Historic Textile

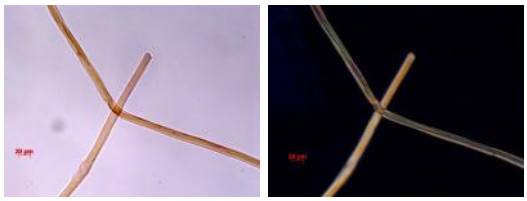
Observable (unmounted) **Meltmount n=1.539**



From Cameo: Fiber Reference Library

Silk

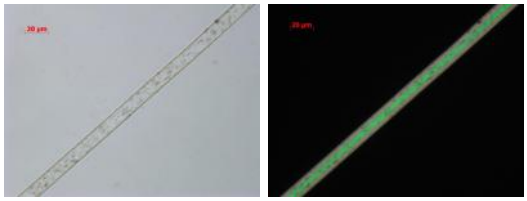
Bright field **Crossed Polars**



From Cameo: Fiber Reference Library

Synthetic fibres

Polyester bright field **crossed polars**



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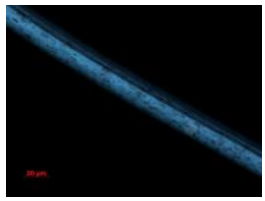
Synthetic fibres

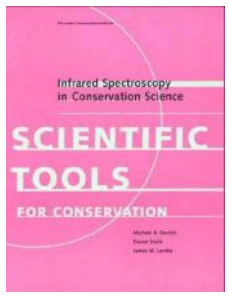
Acrylic **Acrylic crossed polars**

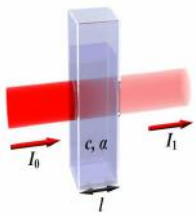
From Cameo: Fiber Reference Library

Introduction to IR Spetroscopy

- Common technique used for the analysis or organic (and inorganic materials)
- Semiquantitative analysis of a range of cultural heritage materials
- A very powerful tools for the assessment of degradation
- In IR absorption, frequencies which match the natural vibrational frequencies of molecules will be absorbed



Absorbtion: Beer Lambert Law

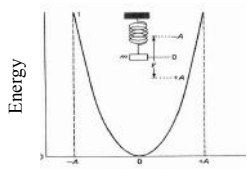


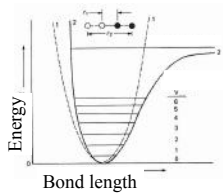
$$T = \frac{I}{I_0} = 10^{-\alpha \ell} = 10^{-\varepsilon \ell c}$$

FTIR sensitivity: approximately 1 %*

Simple model of infrared absorption

- In molecules, the chemical bond exerts an elastic force between atoms
- Absorption takes place only for discrete frequencies that correspond to the energy separation of vibrational levels





Molecular vibrations - Mathematics

- Molecular vibrations can be divided in two basic types
  - Stretching
  - Bending
- For a molecule made of two atoms having masses m_1 e m_2

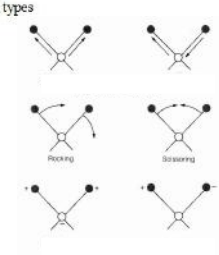
$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \qquad \mu = \frac{m_1 m_2}{m_1 + m_2}$$

- The energetic separation between 2 vibrational levels is:

$$\Delta E = h\nu = \hbar\sqrt{k/\mu} \Rightarrow \frac{hc}{\lambda} = \frac{h}{2\pi}\sqrt{\frac{k}{\mu}}$$

- In terms of wave numbers

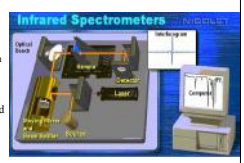
$$\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}} \qquad \bar{\nu} = \frac{1}{\lambda} = \frac{\nu}{c}$$

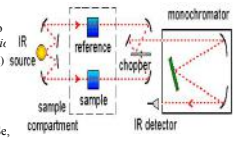


- The strength constant k depends on the bond type (simple, double,..)
- Equations above allows us to estimate the spectral band for IR absorption
- **Beyond the "fundamental band", other absorption bands corresponding to higher harmonics ($2^{\nu 6}$, $3^{\nu 6}$) are present, even if they show lower intensity**

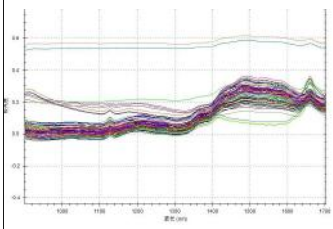
FTIR Absorption: Inside an instrument

- A spectrometer (or spectrophotometer) is made of:
  - radiation source, a dispersive element (e.g. diffraction grating), detection subsystem
- Source
  - Usually a blackbody emitter with temperature between 1500 and 2200 K
    - tungsten lamp for normal measurements (**NIR** and **MID-IR**)
    - special lamps for **far infrared** measurements
- Dispersive element
  - based on a diffraction grating as in UV/VIS spectrometers
    - Usually the double beam configuration is used to *compensate for water vapour and e CO_2 absorptic*
  - based on interferometric methods in Fourier transform (FTIR) spectrometers
- Detectors
  - Photoconductive detectors
    - Thin slabs of semiconductor materials: PbS, PbSe, HgCdTe (77 K)
    - HgCdTe (MCT) detectors for imaging
  - Thermal detectors



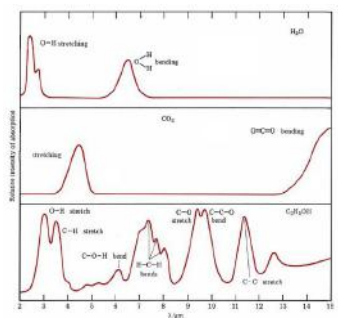


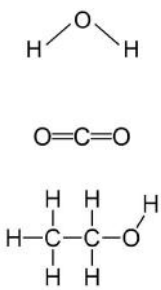
Near IR instrument:



NIR: wavelength: 750- 2500 nm (12,8000 - 4,000 cm^{-1}) (sensor: InGaS)

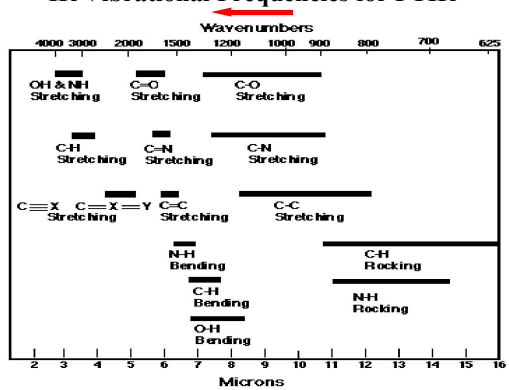
FTIR spectroscopy of simple molecules





Functional Groups are key to spectral **interpretation**

IR Vibrational Frequencies for FTIR



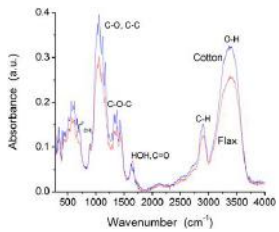
Applications of FTIR

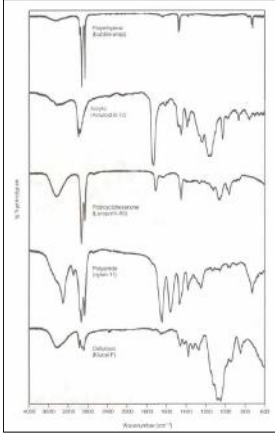
- How do we prepare samples?
  - Usually FTIR is used in Transmittance
    - KBr, Nujol, thin films on NaCl
  - Requires sample preparation and careful isolation of material
- Non-destructive alternatives
  1. Reflectance FTIR (for IR Reflective materials)
  2. Attenuated Total Reflectance
  3. Near Infrared Reflectance

Attenuated total reflectance (ATR)

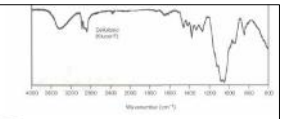
- ATR is a sampling method which requires direct contact between a material and an IR transparent crystal (eg. Diamond, Germanium, ZnSe)
- IR radiation travels through the crystal and probes only the top few micrometers of the sample
  - based on refractive index mismatch between sample and ATR crystal

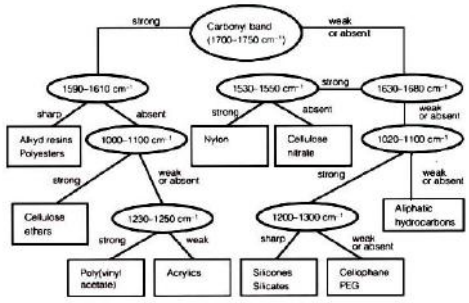
Flax vs. Cotton FTIR

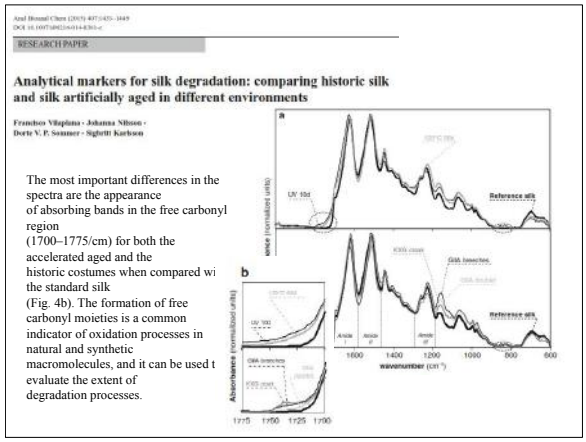




Example **of FTIR to distinguish between organic materials**







RESEARCH PAPER

Analytical markers for silk degradation: comparing historic silk and silk artificially aged in different environments

Francisco Vilaplana · Johanna Nilsson · Dorte V. P. Sommer · Sigrid Karlsson

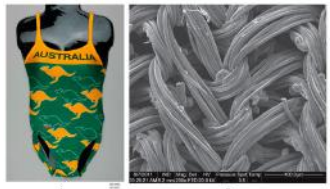
The most important differences in the spectra are the appearance of absorbing bands in the free carbonyl region (1700–1775/cm) for both the accelerated aged and the historic costumes when compared wi the standard silk (Fig. 4b). The formation of free carbonyl moieties is a common indicator of oxidation processes in natural and synthetic macromolecules, and it can be used t evaluate the extent of degradation processes.

Studies in Conservation

ISSN: 0039-3630 (Print) 2047-0584 (Online) Journal homepage: http://www.tandfonline.com/loi/ysic20

ATR-FTIR as a tool for assessing potential for chemical ageing in Spandex/Lycra®/elastane-based fabric collections

Christopher E. Marjo, Sue Gatenby, Anne M. Rich, Bin Geng & Suzanne Chee



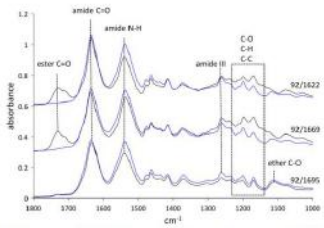
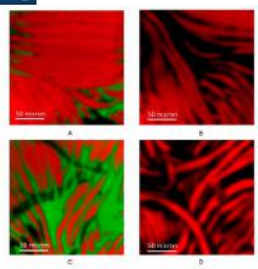
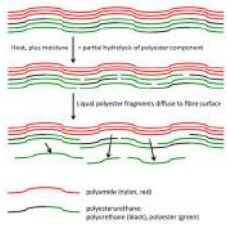


Figure 5 ATR-FTIR spectra of 92/1622, 92/1669, and 92/1695 (black) showing the effects of aqueous NaOH at 50°C for five hours (blue). Vertical axis is absorbance units and horizontal axis is in wavenumbers (cm⁻¹).





The study demonstrates the value of ATR-FTIR for identification of elastane fabrics that may require specialized storage in a humidity-controlled environment

Design objects made of PVAc 1960s -1970s

Taraxacum
Dandelion

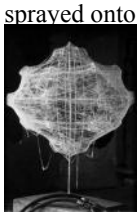
Fantasma
Ghost

Nuvola
Cloud

Lenticchia
Lentil

Zucca
Pumpkin

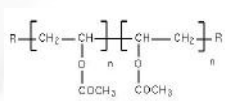
Taraxacum – 1960s "Cocoon" blend sprayed onto a wire frame

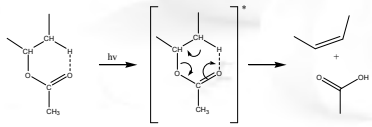


http://www.achillecastiglioni.it/it/studio.html

Polyvinyl Acetate - PVAc

- Known degradation which is highly dependent on ageing conditions → combination of chain scission/cross-linking reactions
  - Norrish Type-II Photodegradation → Formation of acetic acid "vinegar syndrome"
- Loss of additives and plasticers

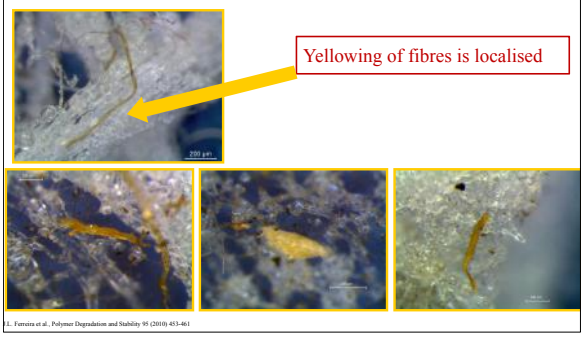




L. Ferreira et al., Polymer Degradation and Stability 95 (2010) 453-461

Microscopy

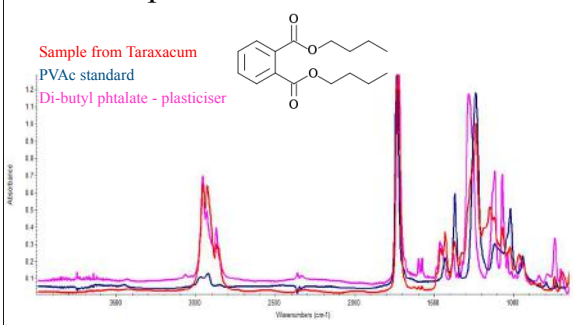
Internal fibers



L. Ferreira et al., Polymer Degradation and Stability 95 (2010) 453-461

Components of Cocoon:FTIR

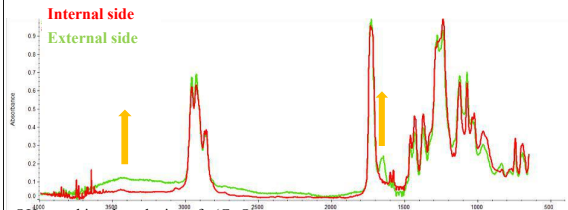
Sample from Taraxacum
PVAc standard
Di-butyl phtalate - plasticiser



Toja et al., Anal Bioanal Chem 2011 Mar; 399(9):2977-86

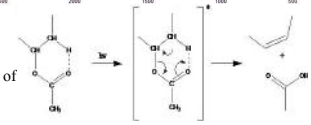
Micro-FTIR spectroscopy – ATR (Diamond)

Zucca
Internal side
External side



OH stretching, broadening of ν(C=O)

→ Unsaturation of the polymer back-bone
→ Ester fragmentation and formation of Acetic Acid

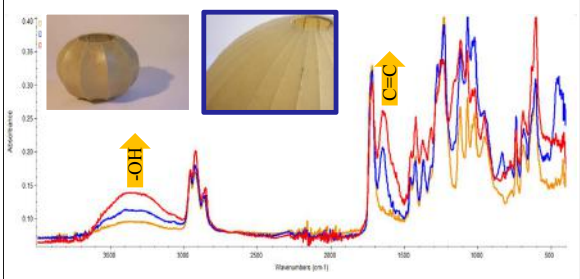


FTIR:comparison between different lamps

Zucca

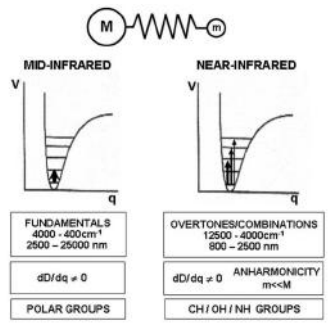
Lenticchia lamp - external

Lenticchia lamp - internal

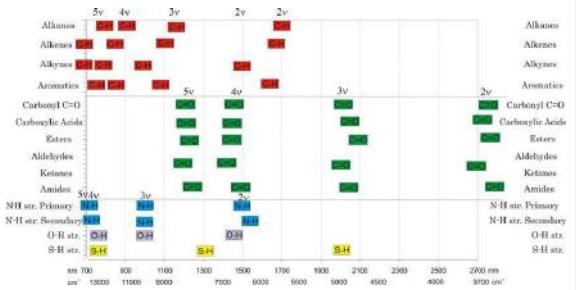


L. Ferreira et al., Polymer Degradation and Stability 95 (2010) 453-461

NIR and Mid IR Spectroscopy



Where are overtones?



Examples of NIR

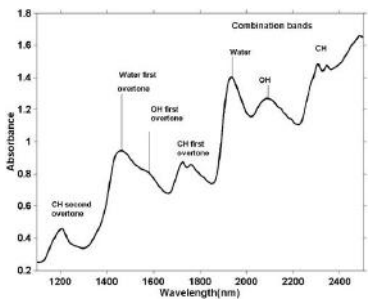
Metrohm NIRSystems

Application Bulletin 413_1_EN

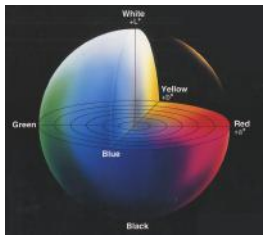
Analysis of textile using near-infrared spectroscopy

NIR spectroscopy has been long used in the textile industry to differentiate fiber types for carpet recycling. Blend analysis of different polymer fibers can be analyzed with NIR spectroscopy as well. Real-time analysis of the application of polyvinyl alcohol (PVA or PVOH) sizing to warp yarn has been done with NIR online process analyzers. Common fiber identified with NIR include: cotton/linen, merchandized cotton, acrylic, modified acrylic, acetate, triacetate, Nomex®, Kevlar® (K-29, K49, and K129), nylon-6, nylon-6,6, silk, polyester, cationic and disperse dyeable polyester, polypropylene, PVA and PVC.

NIR Combinations: many relate to bonds with Hydrogen so it is ideal for studying textiles



How can we describe differences between colours?



Fibre Optic Reflectance Spectroscopy

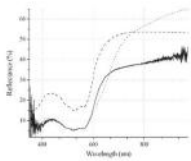
- Measure the light reflected from a surface using a spectrometer to record the spectrum of the light
- The spectrum of the reflected light indicates more than simply the colour of light, and covers a wide range (depending on the detector) from between 400-1200 nm
- Calibrated white light with a broad emission in the visibile can be used as a source

The instrument @ Getty

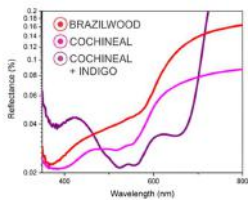
FORS up close

FORS Applications: spectral similarity with database

Luciana Gabriella Angelini, Sabrina Tozzi, Susanna Bracci, Franco Quercioli, Bruno Radicati & Marcello Picollo (2010) CHARACTERIZATION OF TRADITIONAL DYES OF THE MEDITERRANEAN AREA BY NON-INVASIVE UV-VIS-NIR REFLECTANCE SPECTROSCOPY, Studies in Conservation, 55:sup2, 184-189, DOI: 10.1179/sic.2010.55.Supplement-2.184

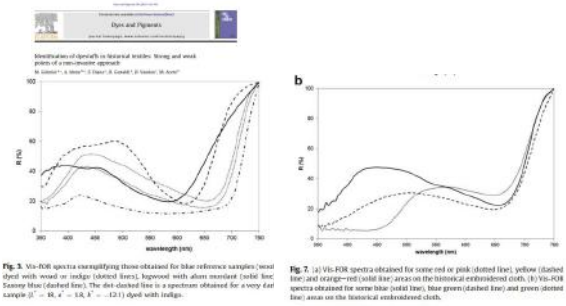


FORS Applications



Identification of natural red and purple dyes on textiles by Fiberoptics Reflectance Spectroscopy M.A. Maynez-Rojas, E. Casanova-González, J.L. Ruvalcaba-Sil PII: S1386-1425(17)30107-5 DOI: doi: 10.1016/j.saa.2017.02.019

FORS Applications -Dye analysis?



Results show that the technique is able to give preliminary information. In particular, absorption bands would at least the suggestion, of the use of a specific blue or red dyestuff.

Microfading to assess light sensitivity as a function of light dosage:

- http://blogs.getty.edu/iris/conservation-tools-the-microfading-tester/

Chromatographic analysis of dyes

- **Chromatography**: a physical method of separation that distributes the components of a substance or mixture between two phases, one stationary, the other mobile.
- The sample to be analysed is dissolved (or dispersed) in a fluid, the mobile phase, which carries it through another material, the stationary phase. The constituents of the sample travel at different speeds and so are separated.
- Mobile phase:
  - gas – gas chromatography, GC;
  - liquid (liquid chromatography, LC: high-performance liquid chromatography, HPLC; UHPLC, etc.)
- Stationary phase:
  - filter paper (paper chromatography);
  - thin layers of adsorbent material – silica gel, acetylated cellulose, etc. (thin layer chromatography, TLC);
  - columns packed with adsorbent material (silica, etc.) of very fine particle size (HPLC, UHPLC).

Chromatographic analysis of dyes

How does this work?

- The constituents interact with the stationary phase to different extents, some strongly, others weakly; they also have different solubilities in the mobile phase (where this is a liquid). The separation is based on this different partitioning of the constituents between the mobile and stationary phases: the solvent mixture and the paper, or adsorbent coating on the plate, or the column packing.
- Separation can be influenced by
  - Choosing a mixture of solvents, aqueous (water) and non-aqueous (organic) as the constituents probably have different solubilities: some are polar – more soluble in water, others are non-polar – more soluble in organic solvents such as acetonitrile or methanol. The solvents are known as eluents.
  - The choice of coating on the TLC plate or the column packing; e.g. some coating materials have been modified by chemical treatments so that, for example, polar molecules come off the column or plate and into the solvent stream more readily, so early in the analysis.
  - Varying the solvent mixture (LC) or changing the temperature (GC) over the course of the experiment.

Chromatographic analysis of dyes

How are the constituents detected?

- The time taken for a constituent to travel between the point of injection into the solvent or gas stream and its detection is its retention time.
- At its simplest, identification of an unknown dye constituent may be made by comparison of its retention time with those of known standards.
- Other properties are also used, such as the colour of the spots on the TLC plate; behaviour under UV illumination; etc.
- Detection
  - TLC, paper chromatography – essentially visual;
  - HPLC - instrumental, based on properties of the sample constituents (e.g. UV-visible absorption, fluorescence); molecular fragmentation (mass spectrometry); etc.

Chromatographic analysis of dyes

How is the dye extracted from the textile fibre?

- Many methods have been tried for the extraction of both natural and synthetic dyes from textiles, including
  - Solvent extraction
  - The use of complexing agents (EDTA – ethylenediaminetetraacetic acid, for example)
  - Acid hydrolysis
  - A combination of any of these
- Commonly used solvents are dimethyl sulfoxide (DMSO) and dimethyl formamide (DMF).
- Acid hydrolysis is very widely used, especially for mordant dyes. The most widely used method is to heat with a solution of hydrochloric acid, water and methanol, 37% HCl: H_2O: MeOH, 2:1:1; evaporate to dryness; dissolve the sample in the solvent of choice (methanol, DMSO, DMF …) for analysis.
- Hydrochloric acid may react with the constituents of the dye, changing or even destroying them. Much work has been carried out recently on the use of milder acids, such as oxalic and trifluoroacetic acids, to avoid these changes as far as possible.
- Other reagents have also been used.
- Some dyes (safflower red, for example) may require special treatment.

Chromatographic analysis – methods of extraction

Natural dyes

Type of dye	Examples	Method of extraction	Comments
Direct	saffron, turmeric, Amur cork tree	DMSO or DMF	In practice the methods may be combined: DMSO, followed by acid hydrolysis. Some dyes need special treatment.
Vat	indigo, shellfish purple	DMSO or DMF	
Mordant	madder, cochineal, sappanwood, Chinese pagoda tree, young fustic	Acid hydrolysis	

Synthetic dyes

Type of dye	Examples	Method of extraction	Comments
Direct	Brilliant yellow (Direct yellow 4)	Acid hydrolysis can be used for all	Commonly 37%HCl: H_2O: MeOH, 2:1:1; milder acids can also be used. Some dyes need special treatment.
Acid	Picric acid (Acid dye), Indigo carmine (Acid blue 74), Ponceau RR (Acid red 26)		
Basic	Fuchsin (Basic violet 14), Methyl violet(Basic violet 1, etc) Malachite green (Basic green 4)		
Mordant	Alizarin (Mordant red 11)		

Chromatographic analysis – example

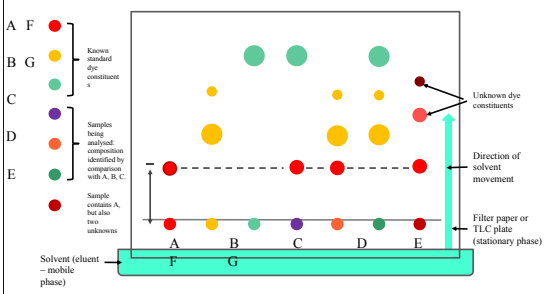
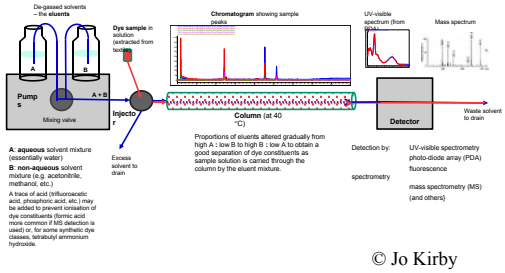


Diagram of typical UPLC set up



Analysis in practice

Velvet fabric, dated late 15th to 16th century, Ottoman. Victoria & Albert Museum, London, -1882.

Detail of motif

Detail of reverse

Lisa Monnas, *Renaissance Velvets*, London, V & A Publishing, 2012; David Peggie, Rachel Morrison and Jo Kirby, 'Appendix: Dye analysis', pp. 157 – 8, also details in text.

Analysis in practice

Samples: 1) Yellowish-green warp thread; 2) Dark orange-red warp thread; 3) Pale blue-green warp thread

Extraction of dye: Sample of thread placed in a 2 ml glass test tube, 2:1:1 (v/v/v) mixture of 37% HCl/MeOH/H_2O (400 µl) added. Test tube heated in a water bath at 100 °C for precisely 10 min; cooled rapidly under cold water; extract evaporated at 60 °C under a steady stream of nitrogen. Methanol/water (1:1) solution added to the dry residue, typically between 4 and 50 µl, depending on colour of the resulting solution.

Analytical conditions: Agilent Technologies 1200 Series capillary pump, operating in capillary mode, and vacuum degasser; flow rate through the column 10 µl min^{-1}; 2 µl sample loop; manual injection. Targa ODS C18 reversed phase column, 5 µm packing, 150 x 0.5 mm i.d. maintained at a temperature of 40 °C.

Eluents: (A) 99.9% water/ 0.1% trifluoroacetic acid ; (B) 94.9% acetonitrile/ 5% methanol/ 0.1% trifluoroacetic acid.

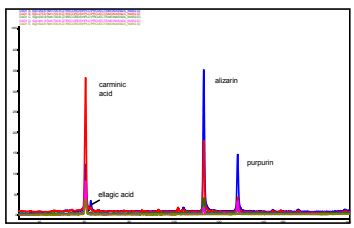
Detector: HP 1100 diode array detector, monitoring signals at 254, 275,330, 491 and 540 nm, set to record in 2 nm steps, reference 700 nm; band width 8 nm; flow cell path length 10 mm, 0.5 µl volume, 4 nm slit width.

Gradient

Time (minutes)	% Solvent B
0.00	5.0
5.00	5.0
85.00	25.0
160.00	50.0
190.00	95.0
220.00	95.0
225.00	5.0

+ 15 minutes post-run time

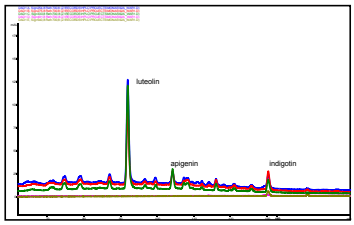
Analysis in practice



Detail of chromatogram given by Sample 2, orange-red warp thread.

Alizarin and purpurin suggest the presence of madder dye; note that the use of a milder acid or another reagent might provide additional information on madder constituents present. Carminic acid is the principal constituent of cochineal dye, but is also present in certain Old World insects unrelated to cochineal. From the date of the textile that the insect source is *Porphyrophora hameli*, so-called Armenian 'cochineal'. Ellagic acid is derived from oak galls or similar, used to weight the silk after processing.

Analysis in practice



Detail of chromatogram given by Sample 1, yellowish-green warp thread.

Luteolin and apigenin (together with the absence of certain other possible components) suggest the presence of weld dye; note that the use of a milder acid or another reagent would provide additional information on constituents present. Several plants give indigotin and so far it has not been possible to distinguish the sources analytically. Possible sources are woad and *Indigofera* species (imported into Europe, Turkey and countries further east from India at that time). Sample 3, blue-green warp thread, also contained indigotin; no yellow dye could be detected.

Conclusions

- Optical microscopy is very powerful for observation of fibres but it is usually necessary to try different mounting media
- IR spectroscopy is ideal for identifying fibres and their degradation but is limited by detection limits (1%)
- Fibre optic reflectance are key for assessing colour and colour changes which can also be mathematically converted to CIELAB or other colour space
- For dye analysis UPLC is the most useful technique but requires extraction of dye molecules