



National Institute for Criminalistics and Criminology

Laboratory Fibers and Textiles

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In situ study of cotton dyed fibers by Raman spectroscopy

Research project

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Interest in Raman spectroscopy

Raman spectroscopy

- Fast technique
- No destructive
- Suitable technique for pigments and dyes

Forensic needs

- Fast technique
- No destructive
- Sensitive regarding to the % of dye on fibers



Potential of Raman spectroscopy in forensic examination of fibers ?

Objectives of the research project

- Evaluation of the technique
- Creation of a spectral library
- Automatic attribution of unknown spectrum to a chemical class of dye
- Forensic case studies

Instrumentation

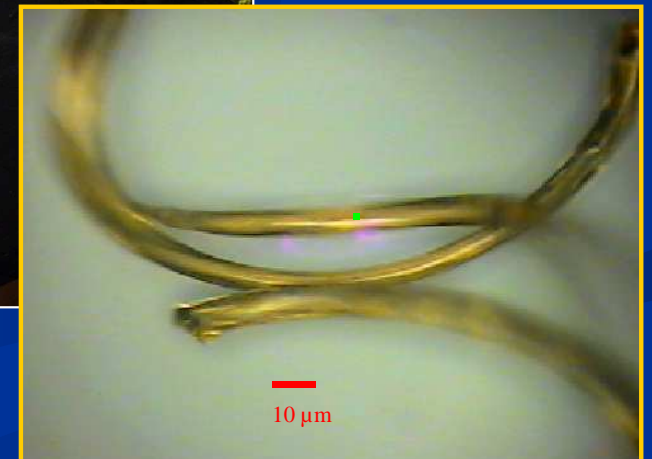
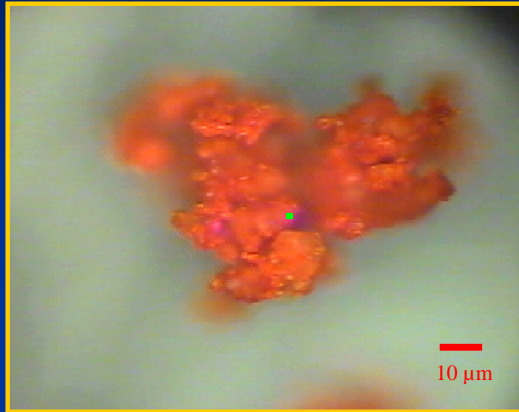
DILOR LabRam

- Confocal microscope
- 1024-256 Open Electrode CCD detector
- Lasers : 488, 514.5, 632.8 and 752.6 nm

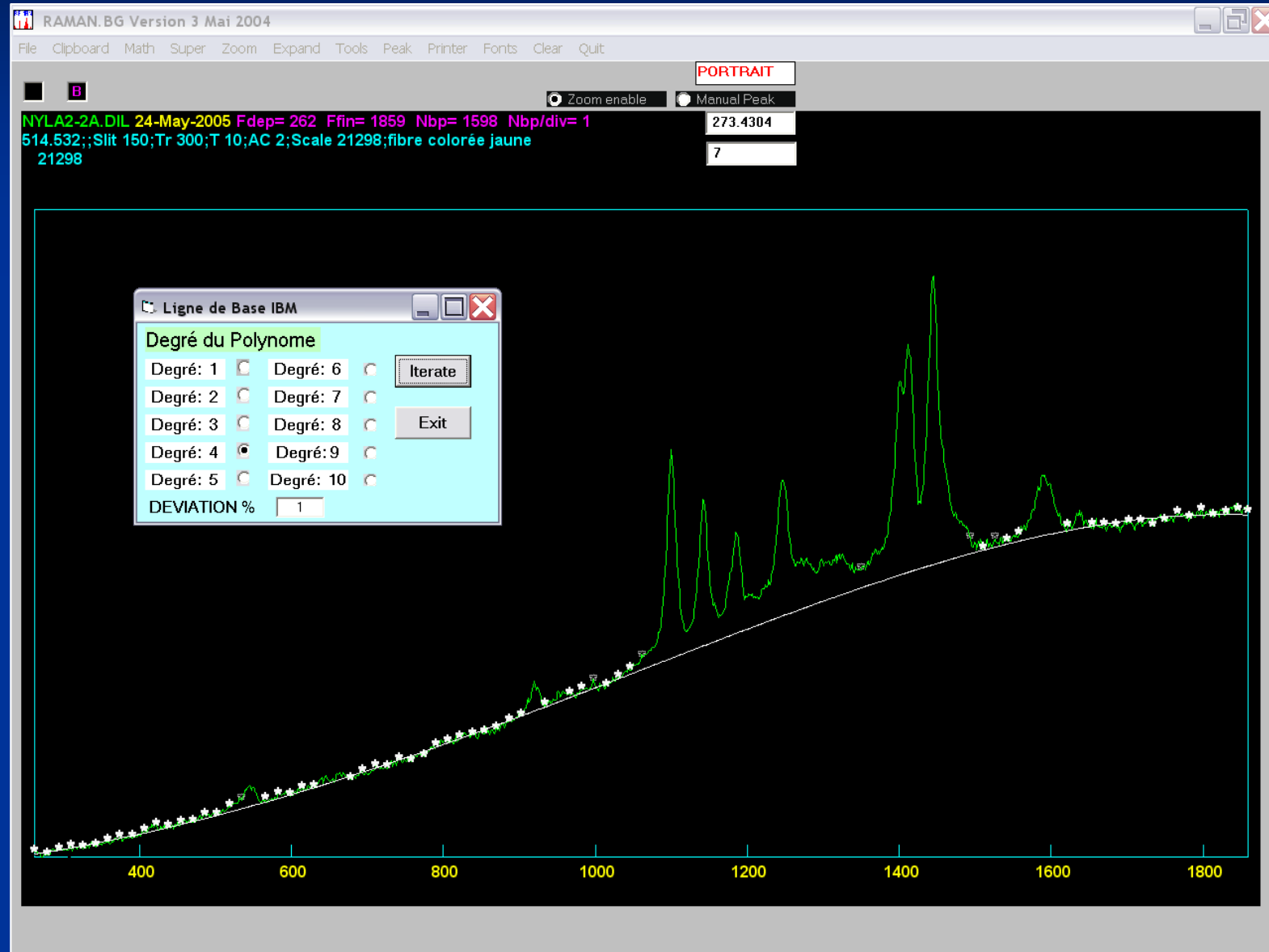
BRUCKER FT-Raman

- Laser : 1064 nm

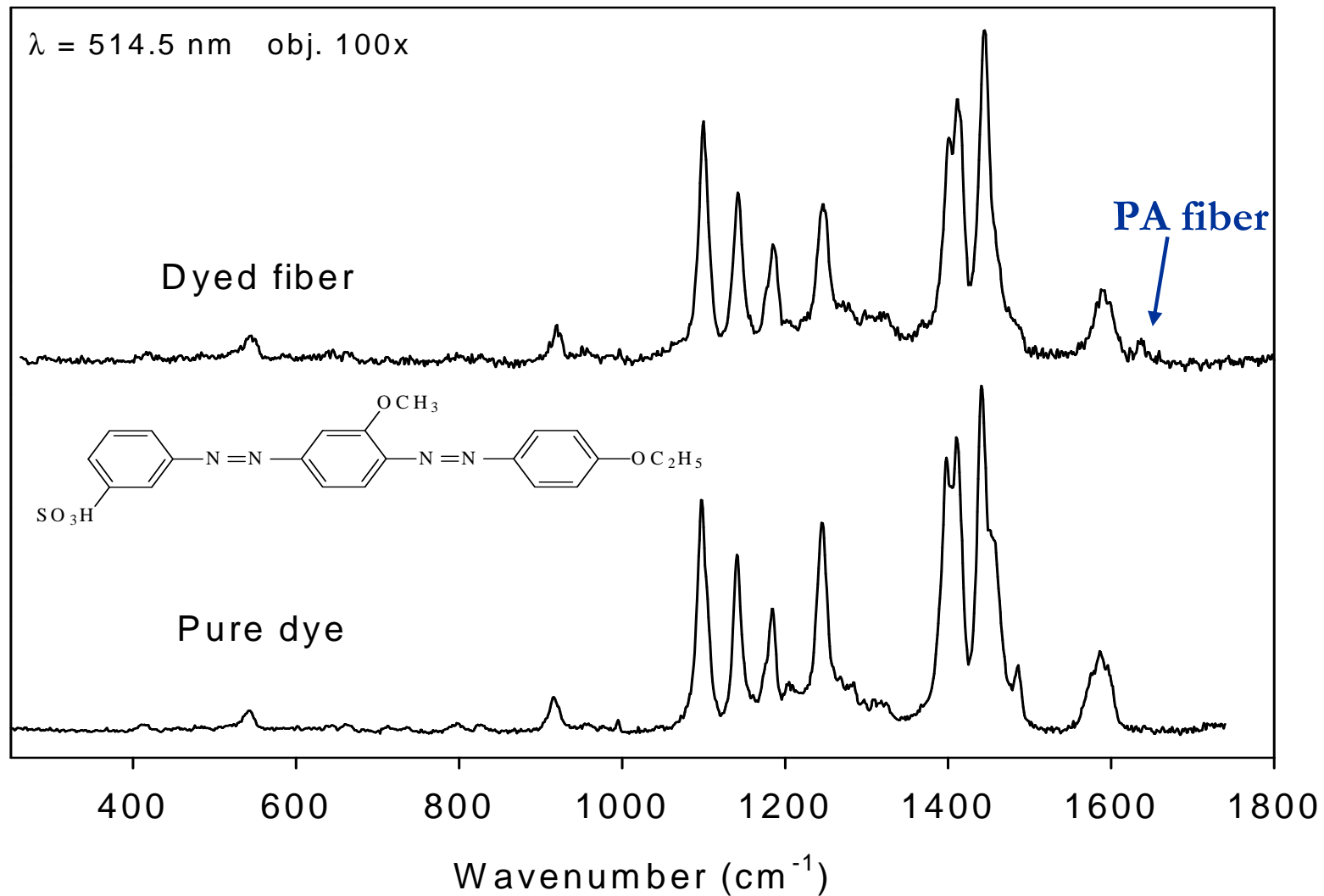
Measurement



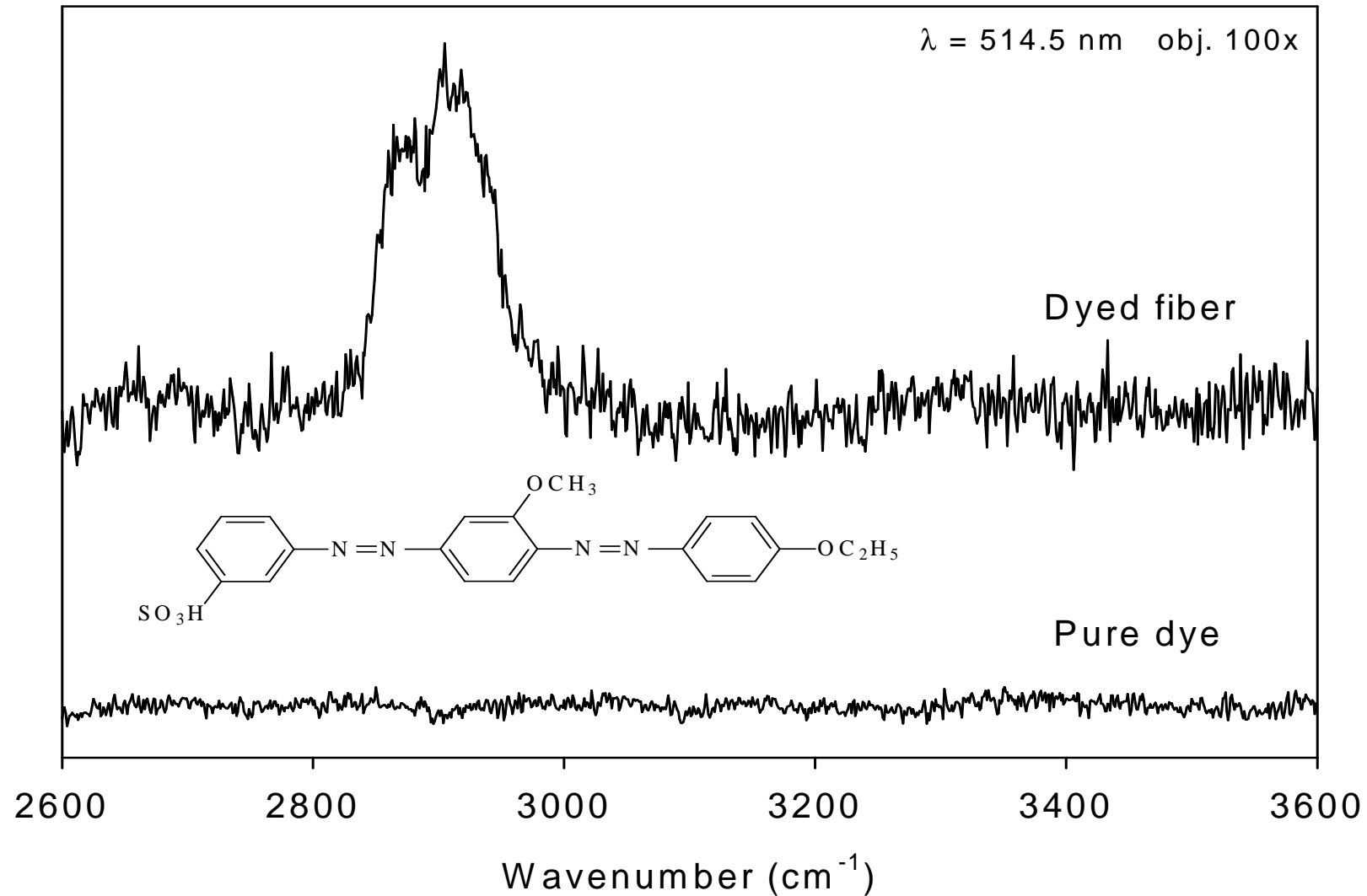
Data processing



Dye and dyed fiber



Dye and dyed fiber



Study of cotton dyed fibers

- Selection of mono-dyed cotton fibers from our fibers reference collection on the basis of the *Colour Index* book
 - chemical class
 - chemical constitution
- 172 samples
- Analysis by Raman spectroscopy (514,5 nm)
- Creation of a spectral library in OMNIC software

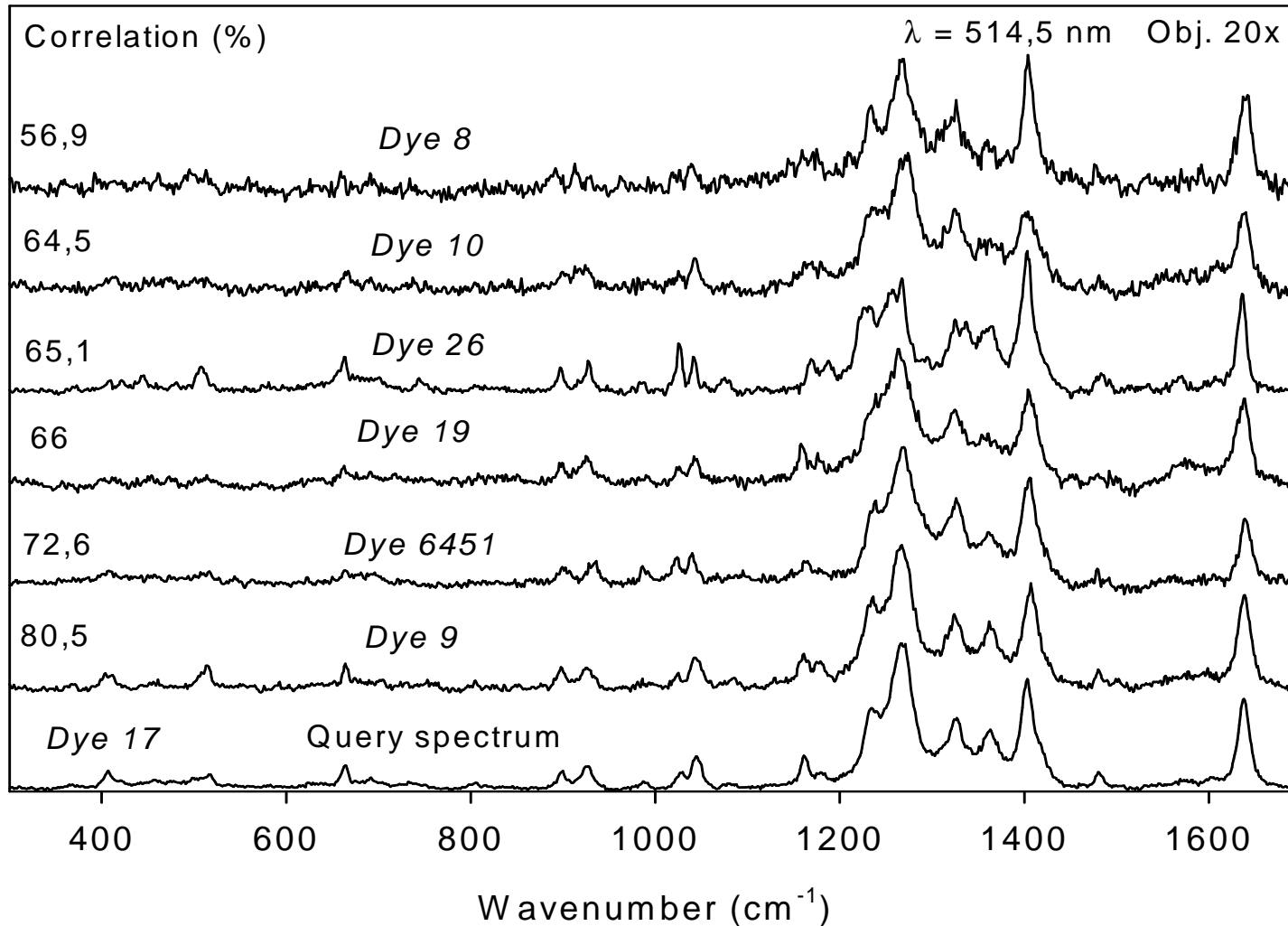
Selected chemical classes

- Azo (56 samples)
- Anthraquinone, -noid (62 samples)
- Indigoïd (11 samples)
- Oxazine
- Phtalocyanine
- Di-, triphenymethane
- Stilbene
- Thiazole
- Sulphur
- ...

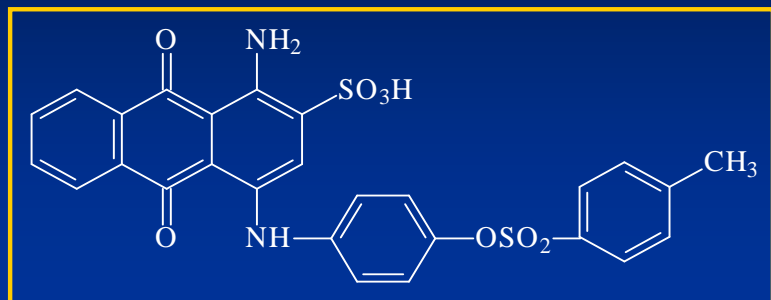
Preliminary results

- Fluorescence masks Raman signal (20 % samples)
- Raman spectra quality depends on fluorescence
- Discrimination is effective
 - Raman spectrum = fingerprint of the molecule
- Assignment to a class within the spectral library is
 - optimal for very similar dye molecules
 - difficult without similar reference molecules

Example



Example



Query sample

80,5 %



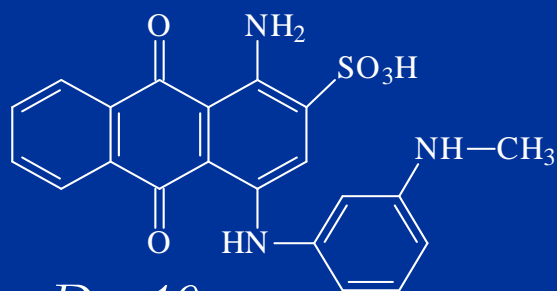
Dye 9

72,6 %



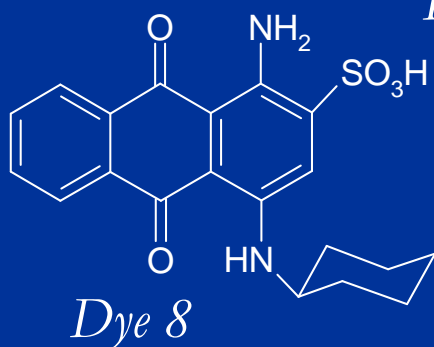
Dye 6451

64,5 %



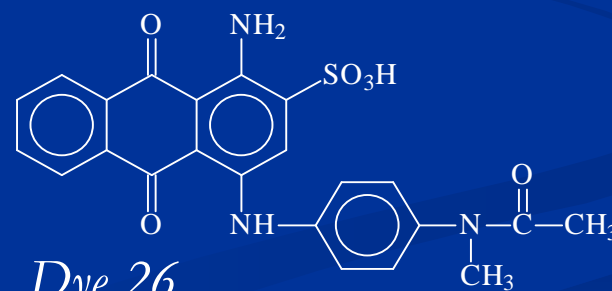
Dye 10

56,9 %



Dye 8

65,1 %



Dye 26

66 %



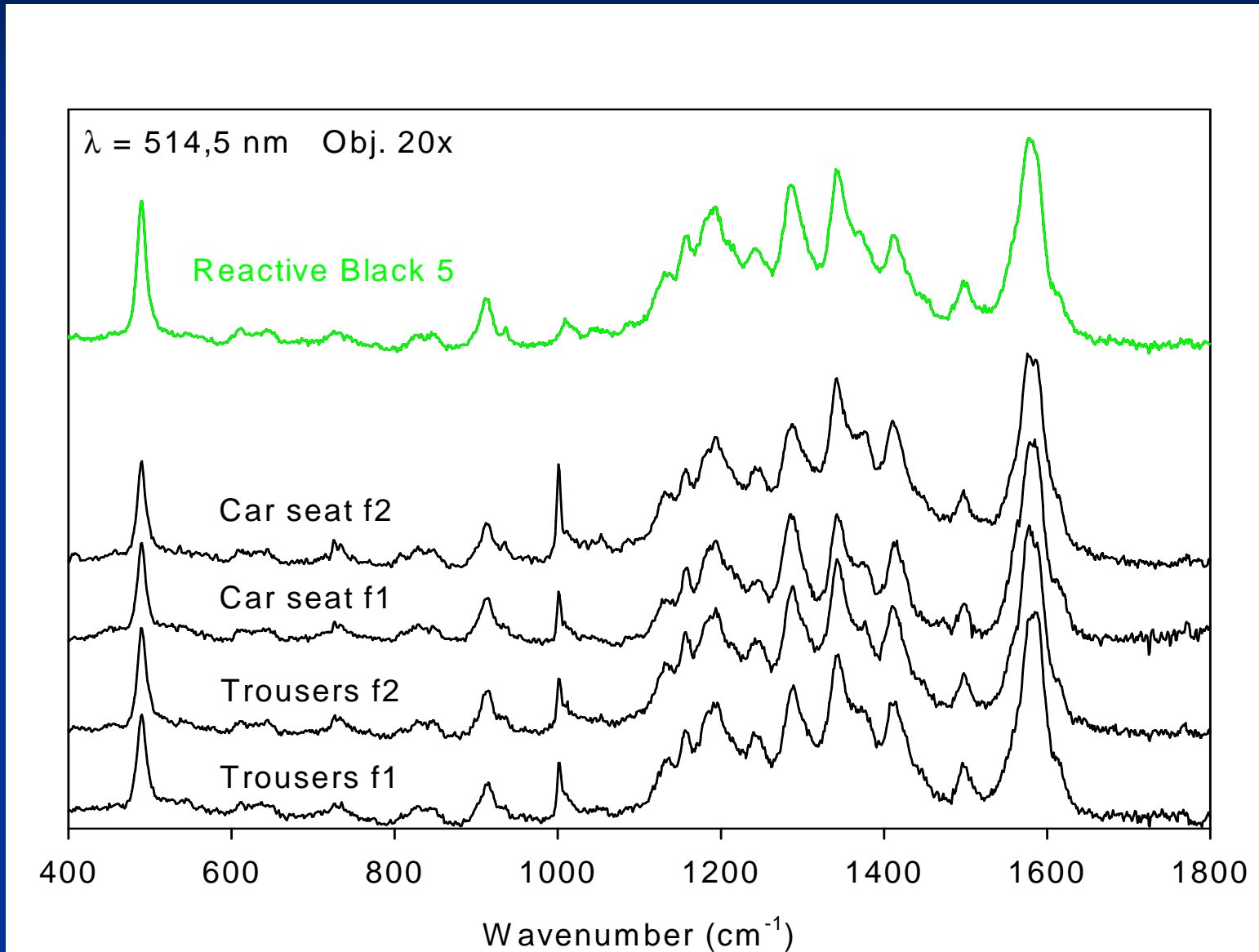
Dye 19

Case study 1

Comparative study for evidence of contact

- Cotton dyed fibers from a black trousers
- Cotton black fibers collected on a car seat

Case study 1

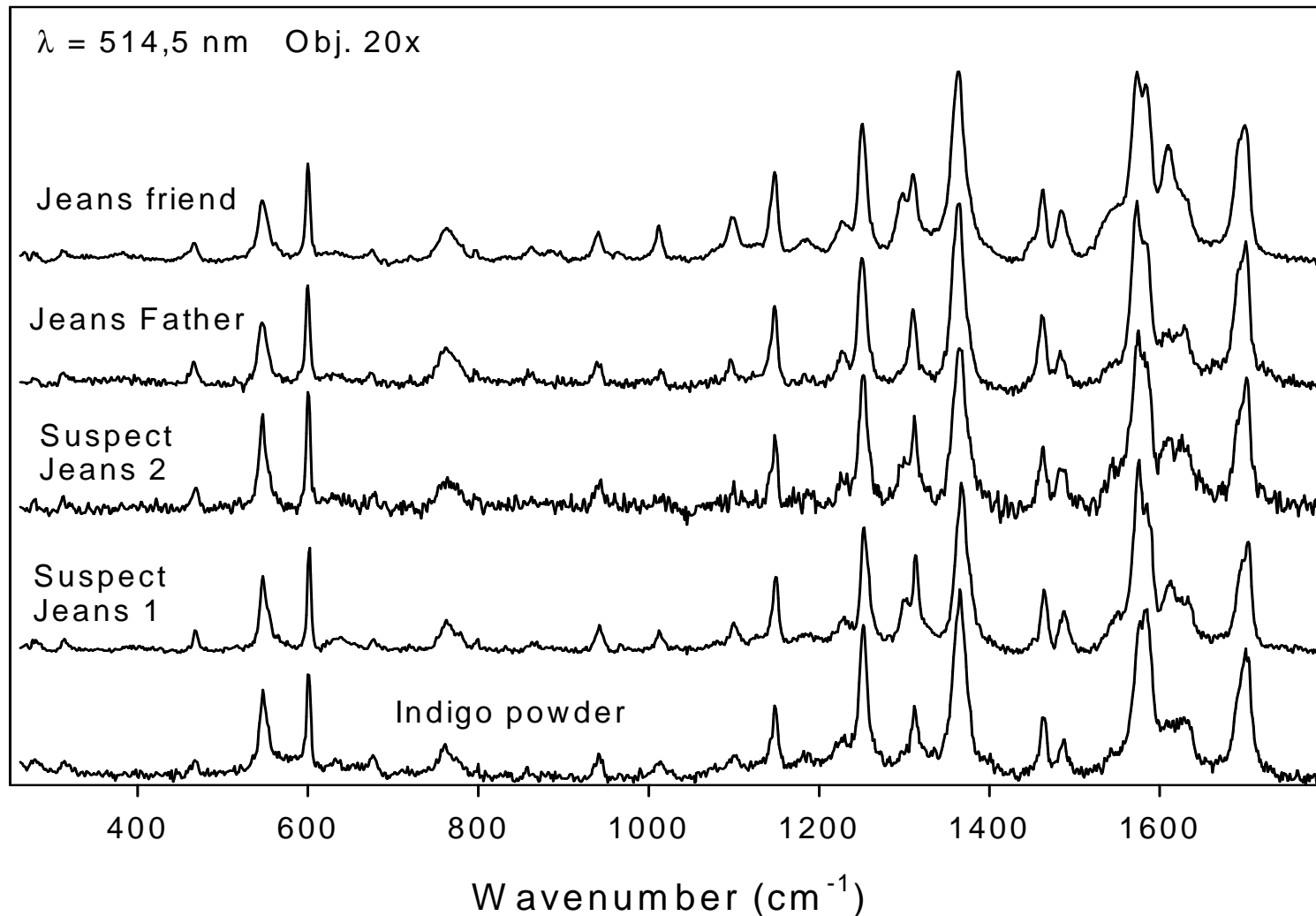


Case study 2

Investigative study for evidence of contact

- Cotton blue dyed fibers collected on victim
- Blue jeans ?

Case study 2



Case study 2

At this stage of Raman investigations

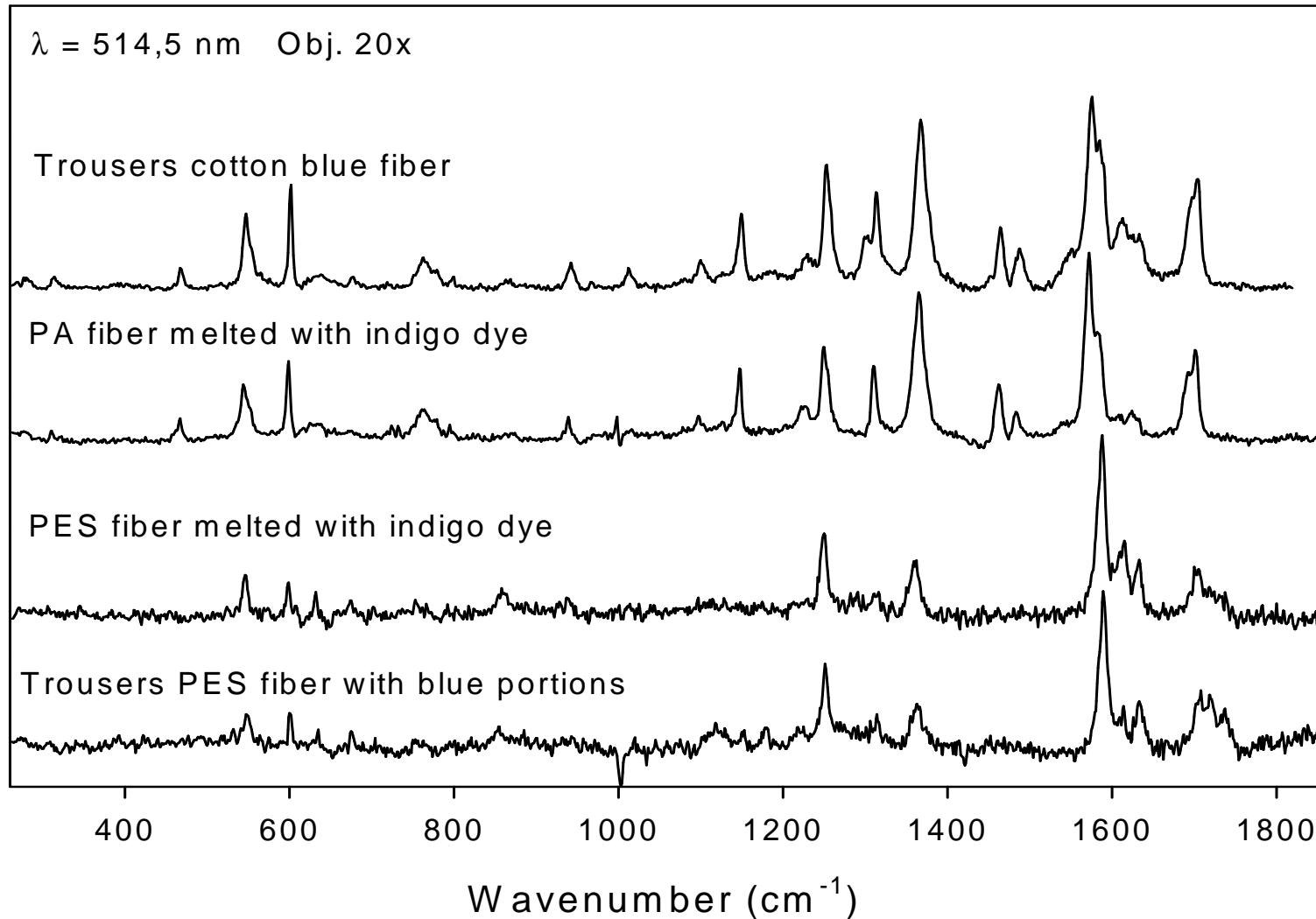
→ Every jeans dyed with indigo is a possible source

BUT

A particular aspect of the suspect's jeans

→ Undyed PES fibers are used for the weft yarn

Case study 2

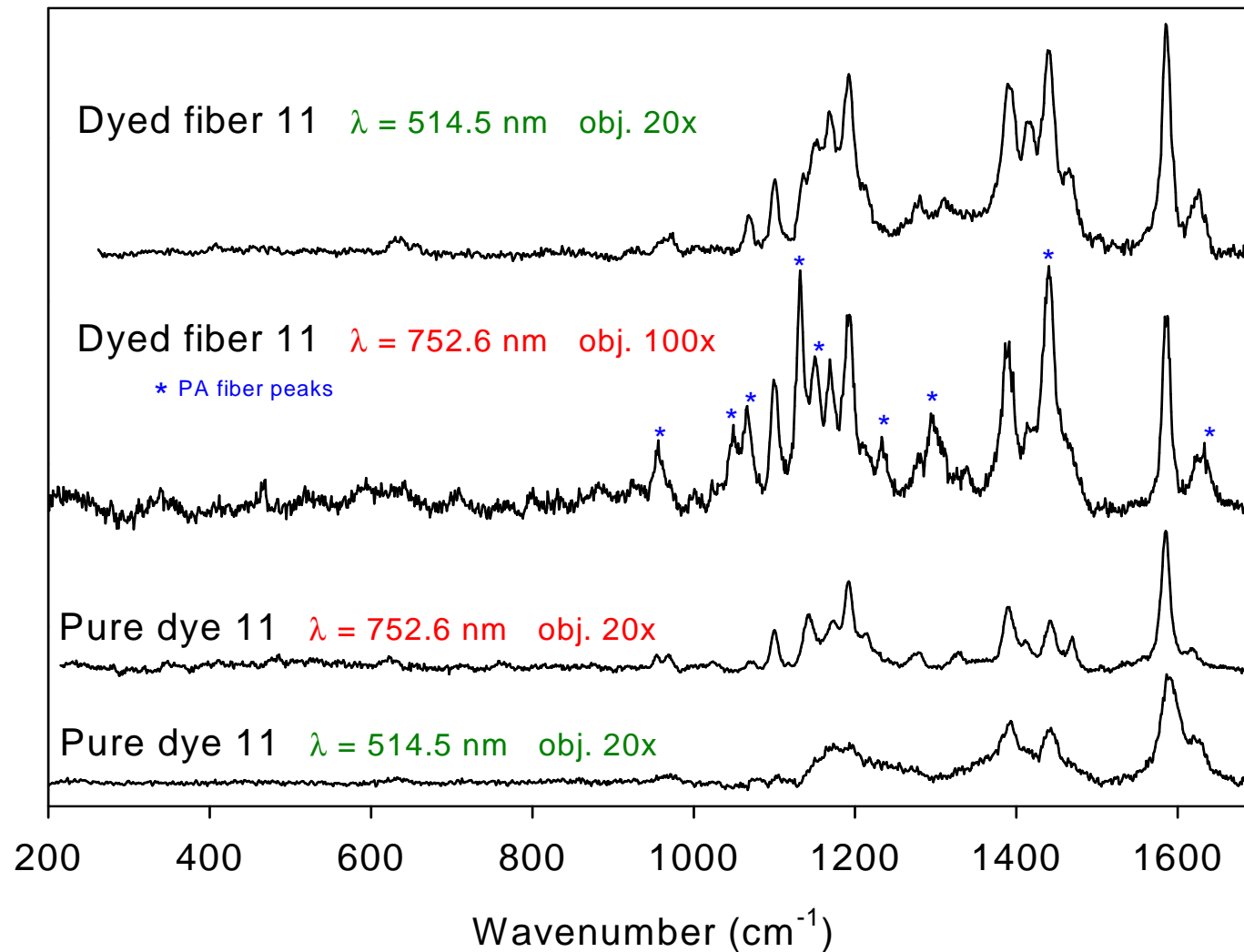


Further work

- Development of statistical tools based on discriminant analysis
- Interest for poly-dyed cotton fibers
- Extension of study to wool
- Daily application to forensic case studies

Thank you for your attention

Laser wavelength



Evaluation is positive

- Raman resonance spectra of dyed fibers
 - higher signal from the dye (minor component)
- Laser choice
 - Green excitation
 - a little bit more fluorescence
 - but a stronger Raman signal
 - Red excitation
 - several peaks of the fibre in the dye signal

Colorants Sirius lumière

*Bleu Sirius lumière FFRL	0.5%		3%		25
—					
*Bleu Sirius lumière FFGL	0.5%		3%		26
—					
*Bleu Sirius lumière 6G	0.5%		3%		27
—					
*Vert Sirius lumière BB	0.5%		3%		28
—					
*Vert Sirius lumière BL	0.5%		3%		29
—					
*Brun Sirius lumière G	0.5%		3%		30
—					
*Brun Sirius lumière R	0.5%		3%		31
—					
*Brun Sirius lumière 3R	0.5%		3%		32
—					
*Brun Sirius lumière GR	0.5%		3%		33
—					
*Brun Sirius lumière BR	0.5%		3%		34
—					
*Brun Sirius lumière BRL	0.5%		3%		35
—					
*Brun Sirius lumière T	0.5%		3%		36

* voir page 6.

Commercial catalogue

Case study 1

