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20 Years of on-site Raman Analysis of rare works of arts: Successes, Difficulties and Prospects

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Keywords: multivariate analysis; colours; on-site; mobile instruments; authentication; optics

The study, in particular of the state of conservation, and the authentication of works of art are issues in full development and Raman microspectroscopy in conjunction with X-ray fluorescence are the reference techniques due to their perfectly non-invasive character, and the availability of mobile instruments. Although mobile instruments have been available for more than 20 years, their use has only recently exploded with the tightening of formalities allowing the movement of valuable objects and changes in practices. Our team having been among the first to develop the Raman analysis of works of art, whether in the laboratory with the development of the MOLE in 1975 at LASIR [1,2] and on site from the 2000s [3, 4] at the same time of David Smith at MNHN, Paris [5], we will focus the presentation on fire arts objects, most of which are enameled (metal, glass or ceramic). These sophisticated objects were technological achievements at their time of production, made for the elite, traded very early on at long distance, and their value which can reach now several millions of € imposes on-site and non-invasive procedures. Except for the identification of gems and some minerals [6,7], their Raman analysis requires the use of high-performance due to the simultaneous presence of vitreous phases generating a signature of broad bands and crystalline phases giving narrow peaks but mainly at low wavenumbers.[4,5,8-10] With the development of particular procedures (use of sophisticated optics (very high magnification, zoom and telescope)[11-13], micrometric stages/mapping, subtraction of the continuous background, dating from proton corrosion[14], multivariate analysis [5,15]) and an understanding/modeling of the spectra [16], the parameters of processing (temperature) are deduced [5-8] and restorations/fakes/copies are identified. The combination with on-site pXRF analysis/mapping is highlighted [17-21] as well as the interest of measuring full spectral range in order to use information present in the 'fluorescence' background.[22] Difficulties (limitation in the choice of exciting wavelength, control of the ambient temperature and lighting, preservation of the artifact, limited access time for measurement, etc.) and future developments (on-site mapping, multiscale analysis, etc.) will be discussed [23].

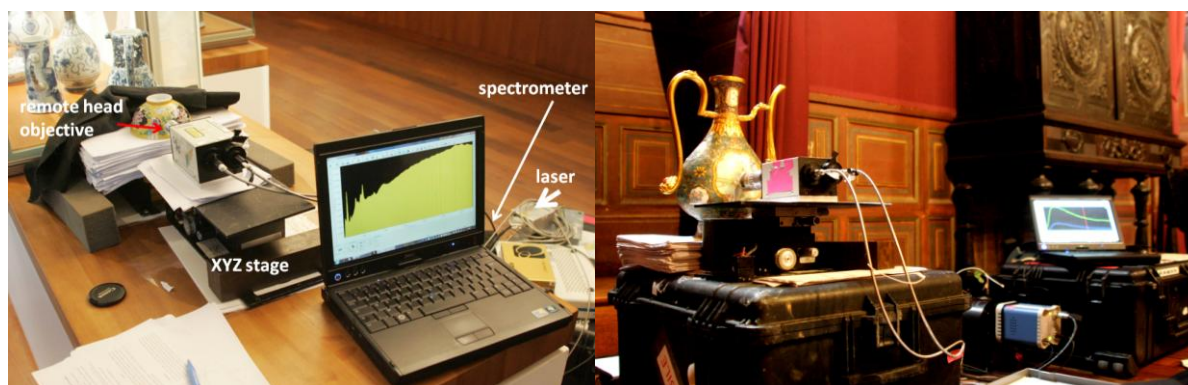


Figure 1 Examples of On-site Raman analysis using a mobile set-up.

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 AAA 2023
6-9 September 2023, Athens

**20 years
of on-site Raman analysis
of rare works of art:
successes, difficulties
and prospects**



Monaris UMR8233 Laboratory,
Sorbonne Université, Paris, France



From molecule to nano-object: Reactivity, Interactions & Spectroscopies

Outline

1. Why on-site analysis using mobile set-up
2. Instruments: Raman studies of Cultural Heritage masterpieces
an historical overview (1975 –present)
3. Required Procedures, difficulties and modeling : example: understanding the Raman signature of
glassy and crystalline silicates / pigments / opacifiers
Authentication: stained glass windows
Conservation : rock art
History of Art & Technique :Tracing the technological exchanges between Europe and Asia
blue colour
 - *Lapis lazuli or cobalt*
 - *Glass type*
4. Conclusions & perspectives

1. Why on-site analysis using mobile set-up

- **Exceptional artifacts located in secure room**

*Bibliothèque Nationale, Paris, Grandes Heures de Rohan
ca 1430-1435, Expected value : > 5 million €*



*Musée national des Arts asiatiques - Guimet
Imperial bowls, ca 1720-1750, > 3 million € each*



*Louvre, Arts déco, Cernuschi, etc.
Fondation Baur (Genève),
Galeria nazionale di Arte Moderna (Roma), etc.*

- **Unmovable Artifacts**

Rock art, Drakensberg South Africa

Stained glass windows

Sculpture, buildings, etc.

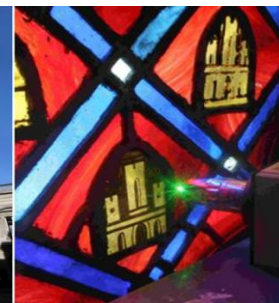


**Drakensberg
South Africa**

Objectives: authentication, documentation
conservation



**Ste-Chapelle
Paris**

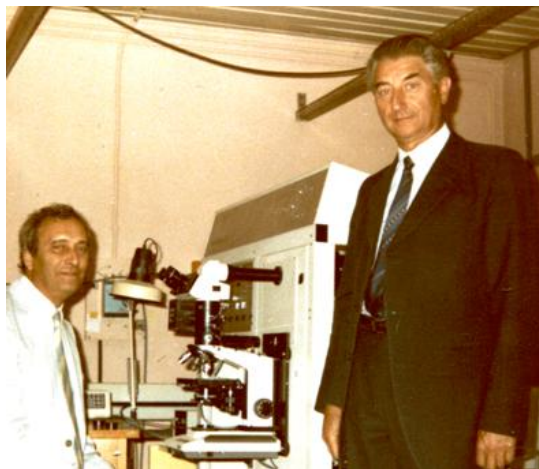


Outline

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Broad band spectra !

2 Raman studies of Cultural Heritage masterpieces : an historical overview (1974 –present)



Professor Michel Delhaye (right) presenting one of the first microprobe equipped with optical microscope (MICRODIL 28, DILOR) and a RQticon512S linear diode array detector cooled at -200°C by Peltier Effect, at LADIR CNRS, Thiais (ca 1980)

Colomban Ph. (1979). Une nouvelle technique d'analyse: la microsonde Raman, *L'Industrie Céramique*, 734, 815-820.

Dele M.L., Dhamelincoirt P., Schubnel H.J. (1980). Utilisation de la Microsonde Mole pour les inclusions dans les pierres précieuses, *L'Actualité Chimique*, 71, 39-40.

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Guichard V., Guineau B. (1986). Une nouvelle technique d'analyse des colorants. Premières applications à l'étude des tranchefiles de manuscrits médiévaux, *Gazette du livre médiéval*, 8, 1-5. https://www.persee.fr/doc/galim_0753-5015_1986_num_8_1_994

Michel Delhaye & Paul Dhamelincoirt (LASIR CNRS) were the first to build a Raman microprobe; the **MOLE (Molecular Optic Laser Examiner)** started to be commercialized in 1976 by Instrument SA Jobin-Yvon (now HORIBA Scientific)

Rapidly, replacement of the PM by a diode array detector (DILOR OMARS, MICROMARS and MICRODIL 28) and then CCD (XY DILOR, LABRAM)



Jehlicka & Culka (2022), Critical evaluation of portable Raman spectrometers: From rock outcrops and planetary analogs to cultural heritage – A review, *Anal. Chim. Acta*, 1209, 339027

LABRAM Infinity

YAG 532nm

He 633nm

End of 1990s

Transportable

High resolution

> 80 cm⁻¹

Flat background



>2010

Variety of compact, Palm-held instruments (green to nIR laser)

Poor to medium resolution > 200 cm⁻¹

The first steps

2003

3- Air-cooled laser



2 optic fibers => spectrometer
<= laser 2x3 m

1- Spectrometer : fixed parts, Peltier-cooled CCD

Musée national de Céramique, Sèvres

Ph. COLOMBAN, V. MILANDE, L. LE BIHAN
On-site Raman Analysis of Iznik pottery glazes and pigments
J. Raman Spectrosc. 35 (2004) 527-535.

Microscope objective
x500, 800 or 1000



2- Remote head

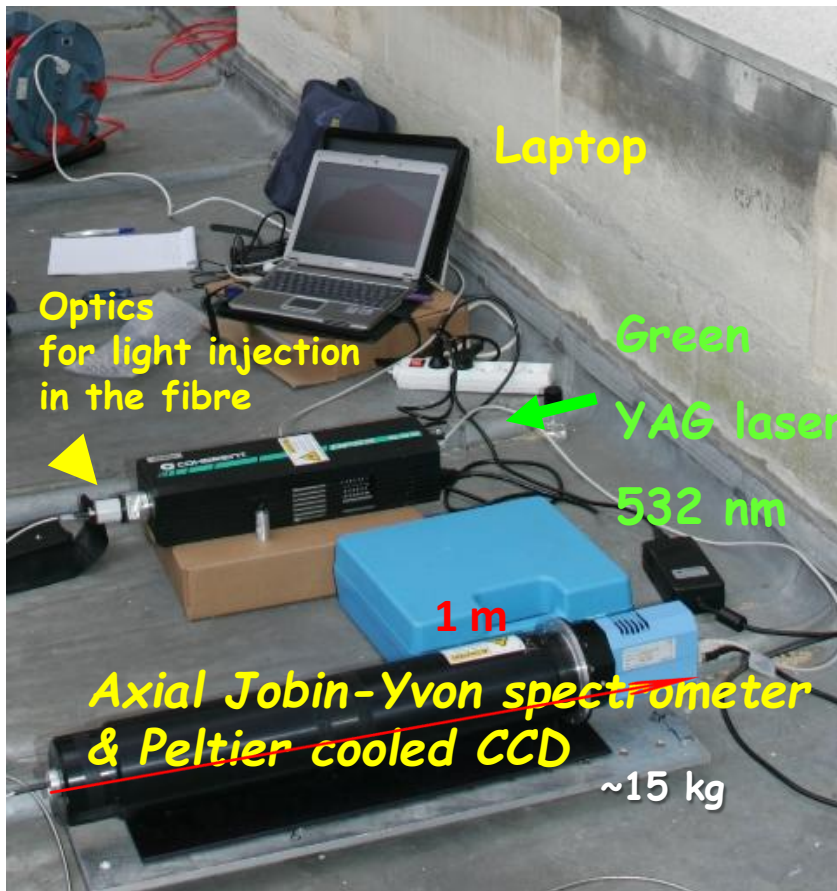
SuperHead®

X-Y-Z

Broad bands, heterogeneous materials
high magnification, thick film

Horiba Jobin Yvon

2x10m long fiber optics, 25m of electric cable



2005

High resolution
Flat background
>250 cm⁻¹



difficulty of
access by
narrow
spiral staircase

Broad bands, sunlight, access

Outside



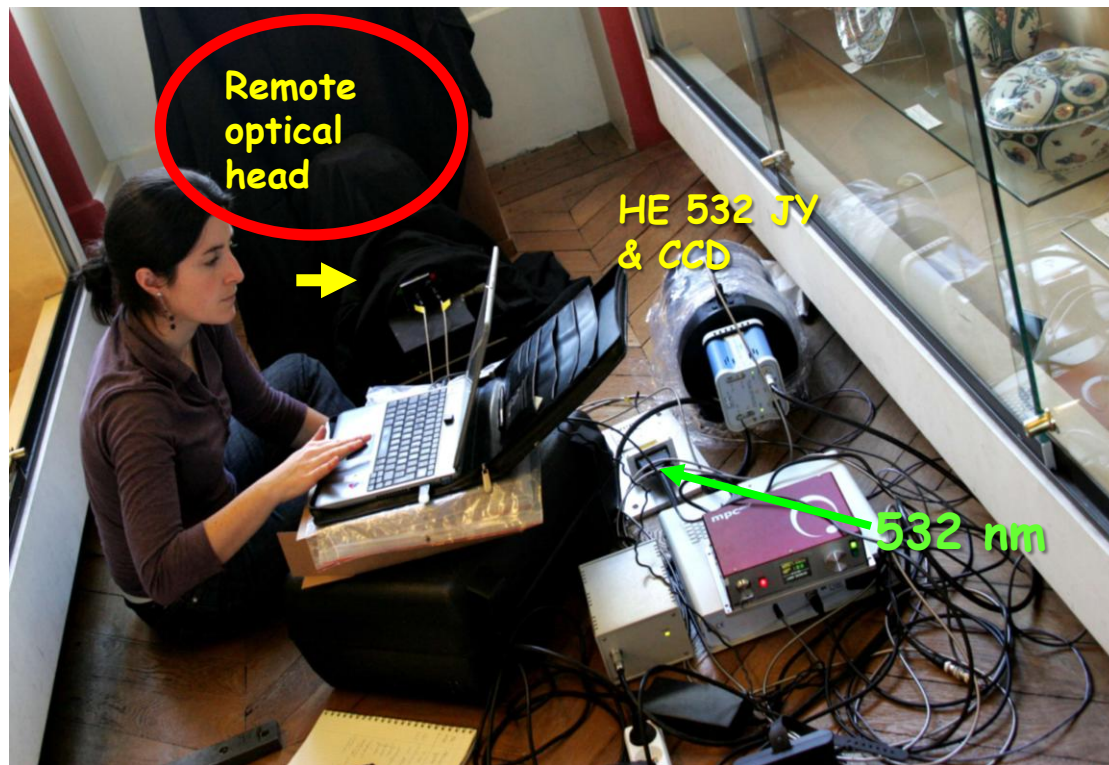
Inside



Sainte-Chapelle, île de la Cité, Paris

Ph. COLOMBAN, A. TOURNIE
On-site Raman Identification and Dating of
Ancient/Modern Stained Glasses
at the Sainte-Chapelle, Paris.
J. Cultural Heritage 8 [3] (2007) 242-256.

> 2007 : compact set up



High resolution
Flat background
>80 cm⁻¹

Laser Quantum
Ventus 100/300 mW
&
CCD and shutter boxes

Main characteristics
able to record
broad band
Raman signatures
(e.g. glass)

Musée national de Céramique, Sèvres

P. RICCIARDI, Ph. COLOMBAN, A. TOURNIE, V. MILANDE

Non-destructive on-site identification of ancient glasses: genuine artefacts, embellished pieces or forgeries ?

J. Raman Spectrosc. 40 (2009) 604-617.

High performance long working distance optics

No contact - measurements on concave surfaces - micron spot

NIKON
x50 (\Leftrightarrow magnification 500)
1000€ HT

also
x10 (100)
sd $\sim 30\mu\text{m}$
p $\sim 50\mu\text{m}$



spot diameter $\sim 4\mu\text{m}$
Along z up to $15\mu\text{m}$
easy focus

A precise
adjustment
at $1\mu\text{m}$ scale
requires a
stable
XYZ stage



Mitutoyo x50 or
x200 (\Leftrightarrow magnification 2000)
8000€ HT



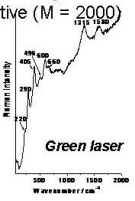
spot diameter $\sim 0.5\mu\text{m}$
(close to the limit of diffraction)
along z $\sim 2\mu\text{m}$
focus adjustment
time consuming

High magnification optics : higher quality spectra !!



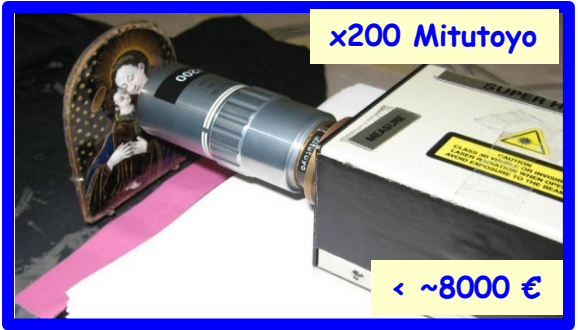
**Sanguine pigment
Paper**
 ⇒ strong fluorescence
 under green laser
 ⇒ use of a **x200 Mitutoyo**
 microscope objective (M = 2000)
 ⇒ **spot < 1 μm³**

**Haematite
carbon**



**single
grain
analysis**

M.-C. CAGGIANI, Ph. COLOMBAN
 Testing of Raman spectroscopy as a non-invasive tool
 for the investigation of glass-protected pastels
 J. Raman Spectrosc. 42 [4] (2011) 790-798.



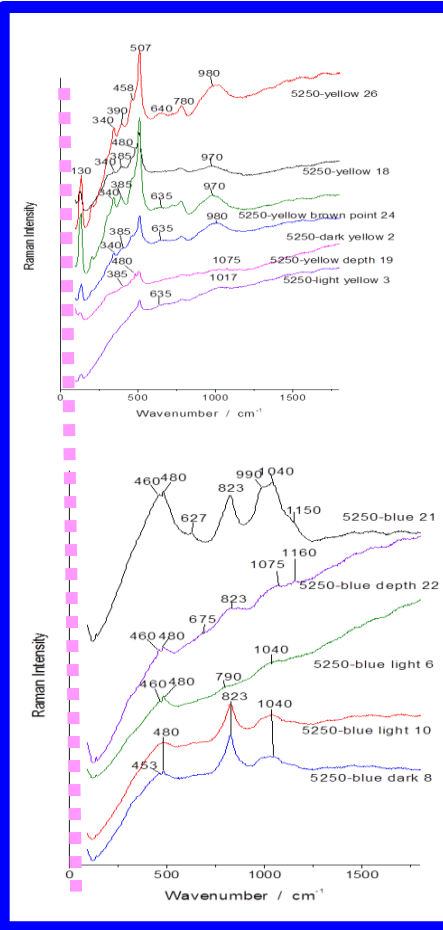
x200 Mitutoyo

< ~8000 €



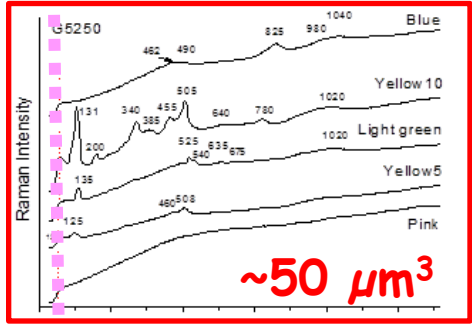
x50 Nikon

< 1000 €



ULWD x200 : ~1 μm³

standard ULWD x50



**Edge filter
> 80 cm⁻¹**

Adapted laser source(s) power (and protection from solar/bulb light) (10 to 30 mW laser beam at the sample) *easier job if the peaks are narrow*

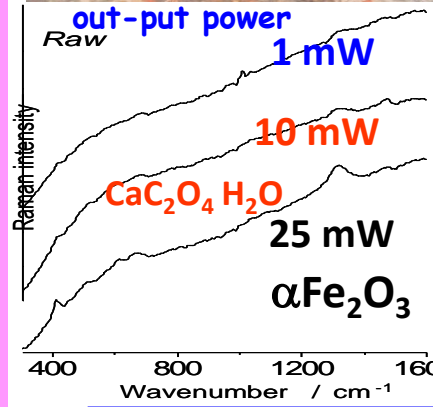
No darkness => work on evening/night
=> high laser power: x10 to 100 times
more than at the lab!



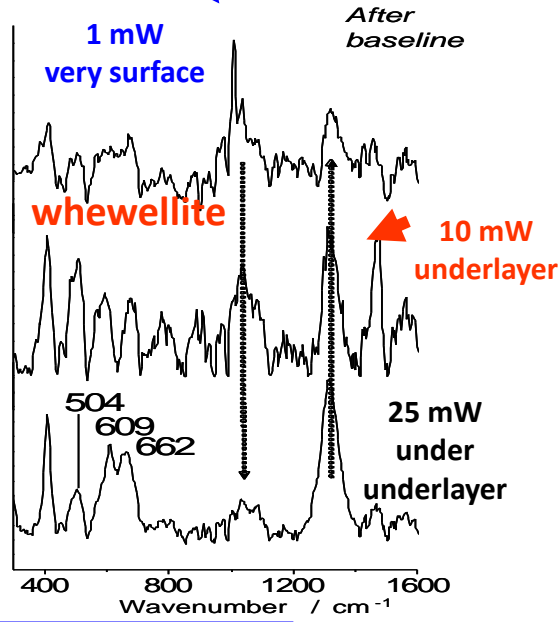
South Africa, San rock art
RSA BU1, Eastern Cap

Efflorescence:
many layers
cover the
painted
Layer

In-depth
analysis
requires
increasing
Laser
power



Gypsum surface



in depth analysis : focus & power
Pigment & surface deposits

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Conservation
History of Art & Technique: Tracing the technologies exchanges / blue colour
 - Lapis lazuli or cobalt
 - Glaze type. When Europe taught enamelling to China and Japan
4. Conclusions & perspectives

Standard colorant agent of glass: Co^{2+} ions and Co-rich spinel/olivine pigments

Cobalt not detected by EDS/XRF in some blue glass, but 0.05 wt% is sufficient to color a glass

Lapis lazuli cannot be identified by elemental analysis !

green
to
blue
Laser

Resonance
Raman
Effect

Co^{2+} & S_n^-

Only under UV laser
the Raman signature
of the host framework
is recorded

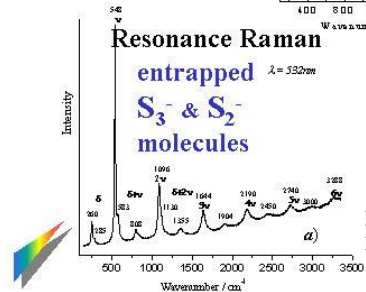
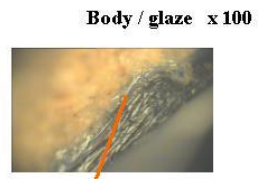
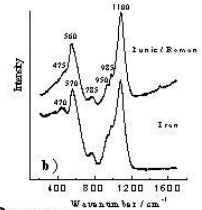
1st evidence:

Clark, R.J., Curri, M.L., Laganara, C., 1997. Raman microscopy: The identification of lapis lazuli on medieval pottery fragments from the south of Italy. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 53(4), 597-603.

Ewer, 13th Lapis lazuli as unexpected blue pigment in Iranian Lâjvardina ceramics



Abû'l Qâsim Kâshani alchemist's treatise 14th



Calcium-rich glaze
Si 70.5 at%
Ca 14.7 at%
Co 0.9 at%
(Ni, Cr, Zn)

Lapis lazuli = lazurite + diopside
Ph. Colomban, *J. Raman Spectrosc.* 34 (2003), 420
Improve the blue shade

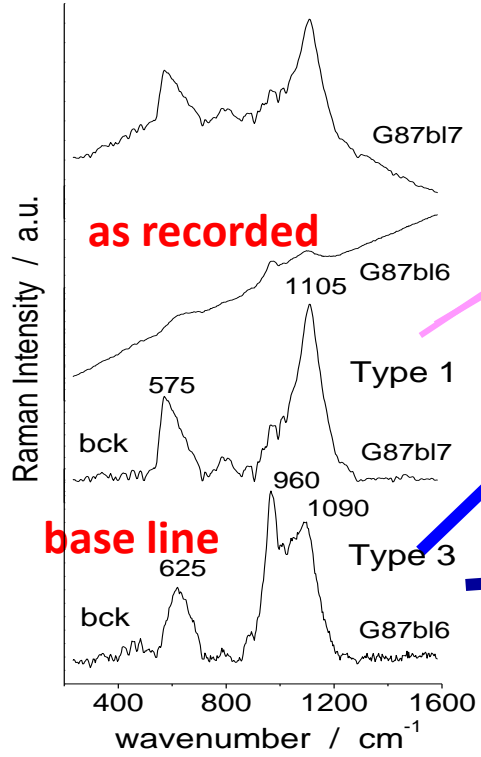
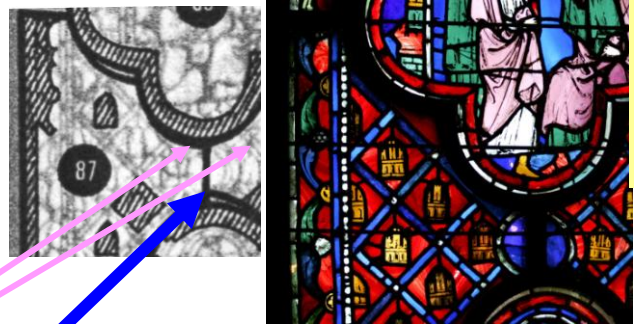
- Lapis lazuli evidenced in
- Ptolemaic glass/glaze
- 1st c BCE (Egypt)
- Roman glass
- 1st c. BCE (Pompei)
- 13th c. Normand Court (Sicilia, Apulia)
- 14th c. Iran
- 14th-15th c. Mamluks
- 18th Meissen Saxony

both Co & lapis lazuli

CVMA (historians)
Corpus vitraerum Medii Aevi
Attribution (googles)
Dashed = 19th c. restoration

L. Grodecki et al.: white: medieval; dashed: 19th c.
Stylistic visual examination, 1950

Built 13th century
Destruction of the basement
of stained glass windows
during French Revolution (~1790)
Restoration ~1870 by taking
pieces everywhere +
addition of new pieces



Na-glass 19th c.

K-glass 13th c.

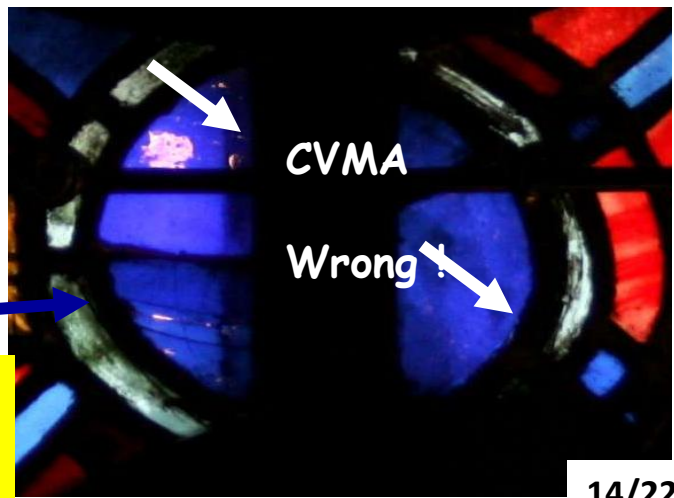
50% wrong !

St Louis
(Louis IX)
Christ Passion
Relics
reliquary

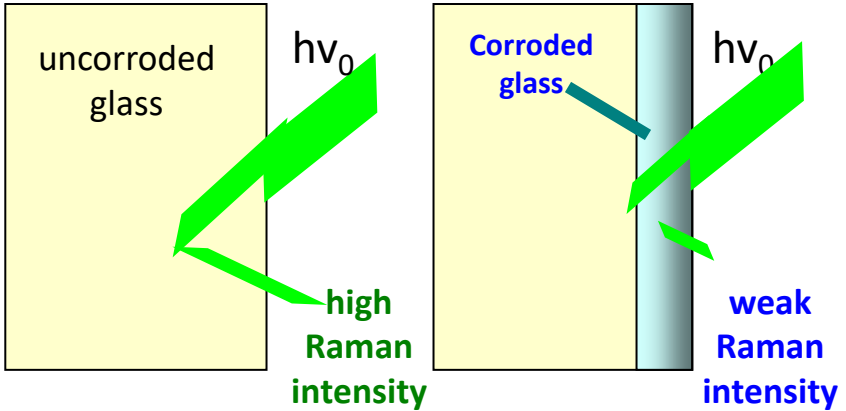
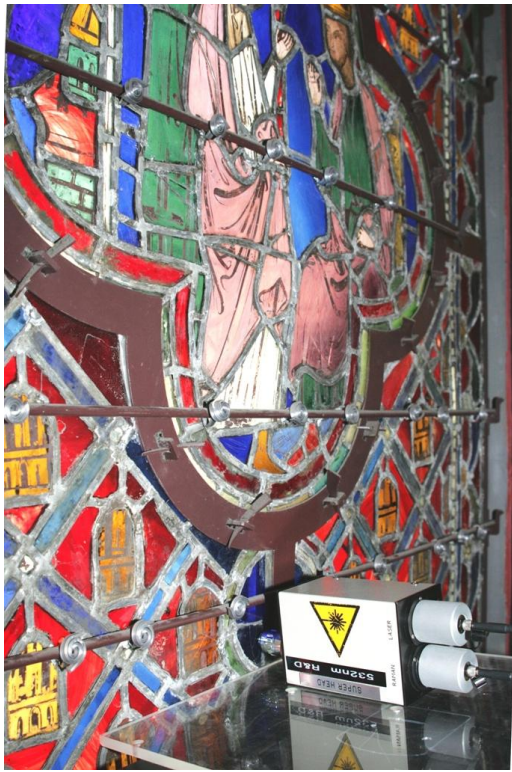


signature &
intensity

K-glass
original
Middle-age

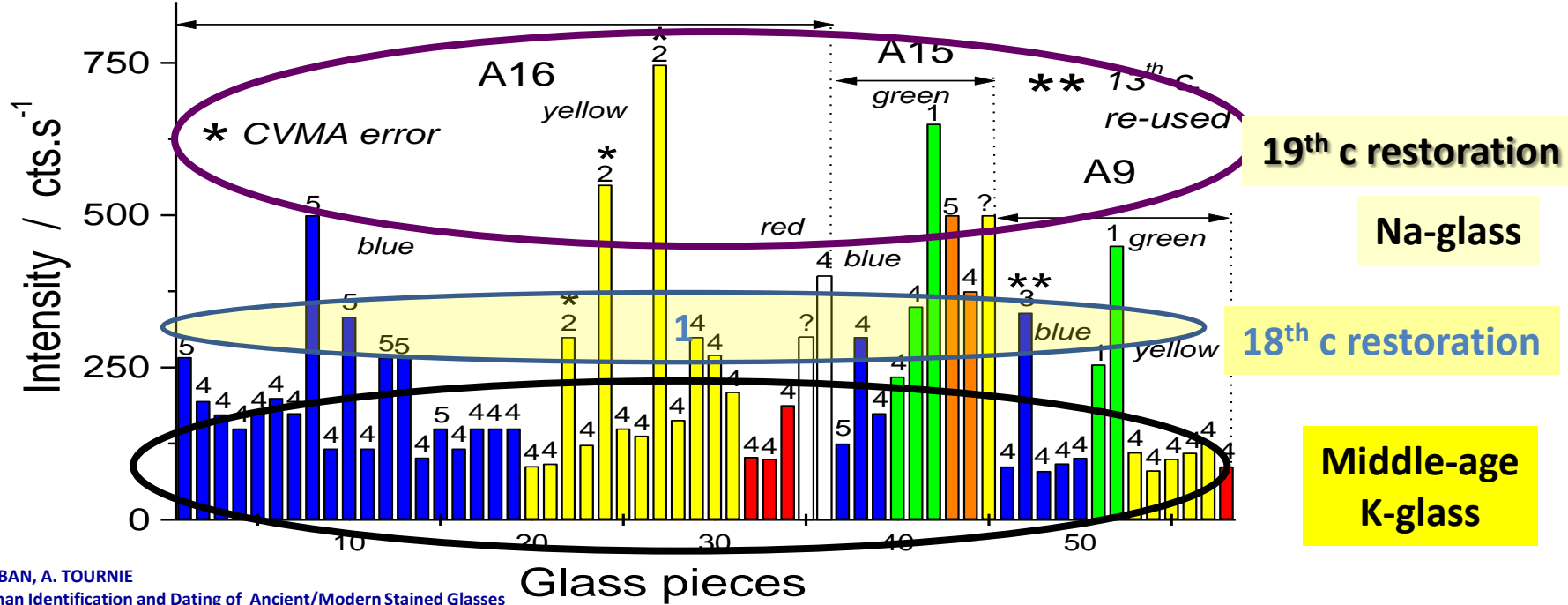


Absolute intensity changes ⇔ dating



Surface corrosion by meteoritic water

Weathering: loss of optical quality of the glass => differentiation between old corroded & restored glasses



Ph. COLOMBAN, A. TOURNIE
 On-site Raman Identification and Dating of Ancient/Modern Stained Glasses
 at the Sainte-Chapelle, Paris. J. Cultural Heritage 8 [3] (2007) 242-256.

- 4: potash-glass (mediaeval)
- 1,2: soda-glass (19th c.)
- 5: soda-glass (18th c.?)

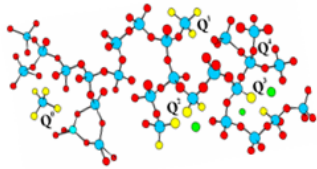
Dating

Weathering = loss of optical quality of the glass surface
 on-site out-side measurements => differentiation
 between old corroded & restored glass pieces

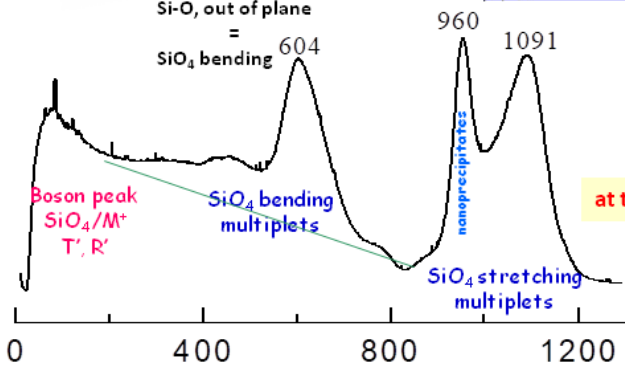
Middle ages

Raman modelling of the Si-O network

Glassy polymeric Si-O network

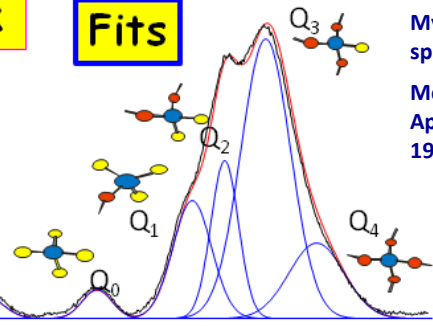


Si-O, out of plane
= SiO₄ bending



SiO₄ bending
Multiplets
10 E δ₃ bands

Fits



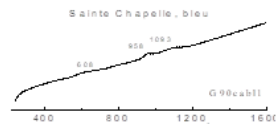
SiO₄ stretching
Multiplets
5 A₁ v₃ bands

Baseline
subtraction

at the laboratory!

- Q₀ isolated tetrahedron
- Q₁ Si-O-Si bridge
- Q₂ 2 Si-O-Si bridges
- Q₃ 3 Si-O-Si bridges
- Q₄ full polymerised = SiO₂

on site !
Need to define a baseline
subtraction procedure



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Spectrum



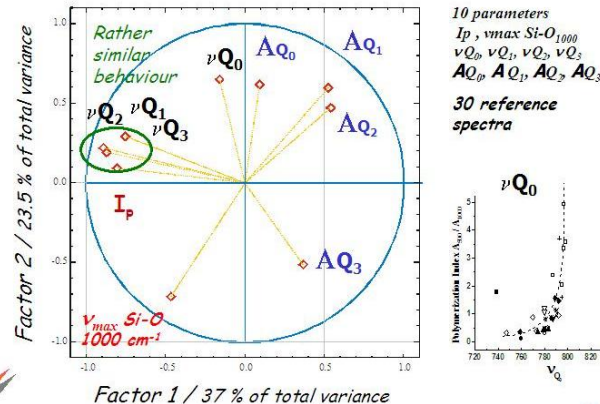
Fits



parameters

Multivariate analysis PCA + Hierarchical classification

PCA Principal Component Analysis : selection of pertinent parameters



17

Application to stained glass window (composition, corrosion)

P. Coloban, A. Tournié, On-site Raman Identification and Dating of Ancient/Modern Stained Glasses at the Sainte-Chapelle, Paris. J. Cultural Heritage 8 [3] (2007) 242-256.

Application to Iznik/Kütahya pottery (provenance)

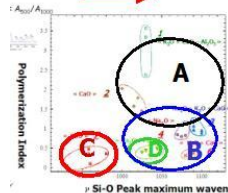
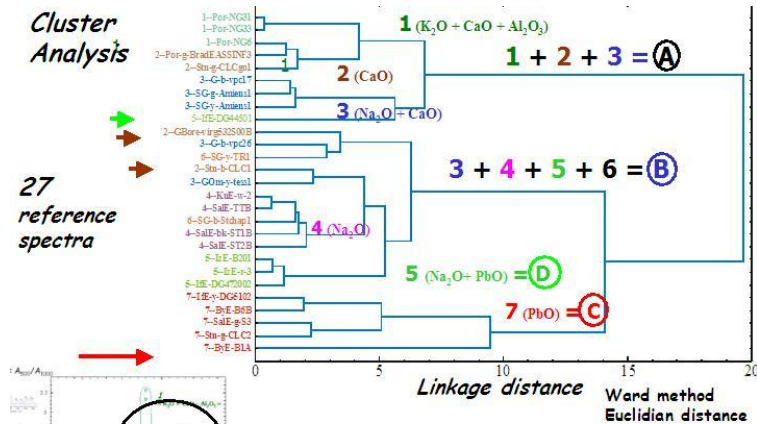
P. Coloban, Recent Case studies in the Raman Analysis of Ancient Ceramics: Glaze Opacification in Abbasid Pottery, Medici and 18th century French Porcelains, Iznik and Kütahya Ottoman Fritwares and Unexpected Lapis Lazuli Pigment in Lajvardina Wares Proc. of MRS 2004 Fall Meetings, 29th November–3 December 2004, Boston, USA, Symposium OO, vol 852, P. Vandiver, J. Mass & A. Murray Eds, 153-160.

Application to Qing dynasty porcelain (ingredient provenance)

J. Burlot, D. Vangu, L. Bellot-Gurlet, P. Coloban, Raman identification of pigments and opacifiers: Interest and limitation of multivariate analysis by comparison with solid state spectroscopical approach J. Raman Spectrosc. 2023, submitted.

Cluster Analysis

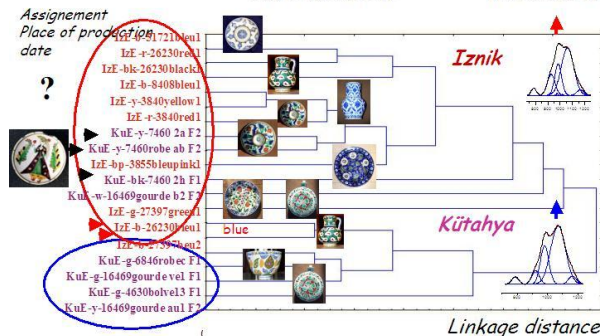
27 reference spectra



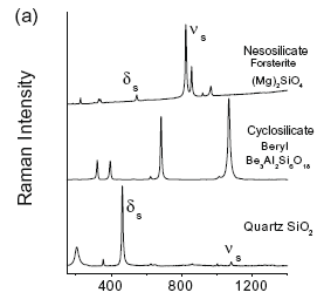
16

10 parameters : I_p , $v_{max\ Si-O_{1000}}$, ν_{Q_0} , ν_{Q_1} , ν_{Q_2} , ν_{Q_3}
 A_{Q_0} , A_{Q_1} , A_{Q_2} , A_{Q_3}

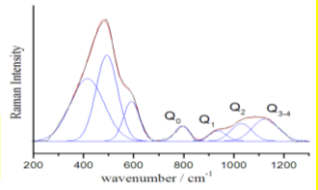
Ward method
Euclidian distance



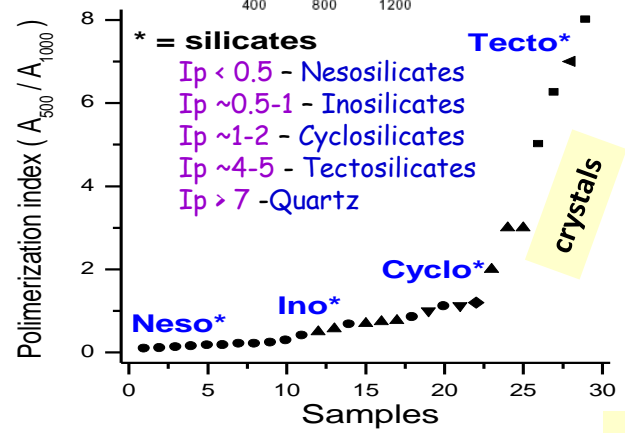
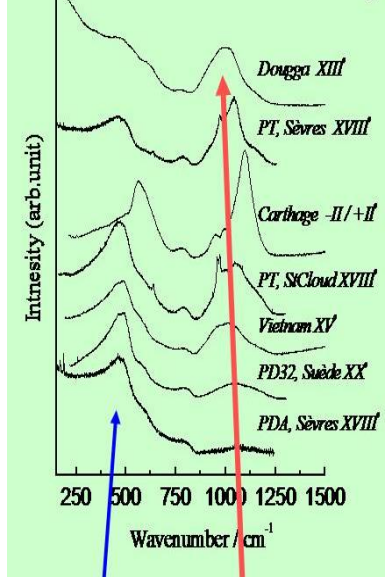
Raman intensity ratio A_{500} / A_{1000} : technology (Tf, etc.)



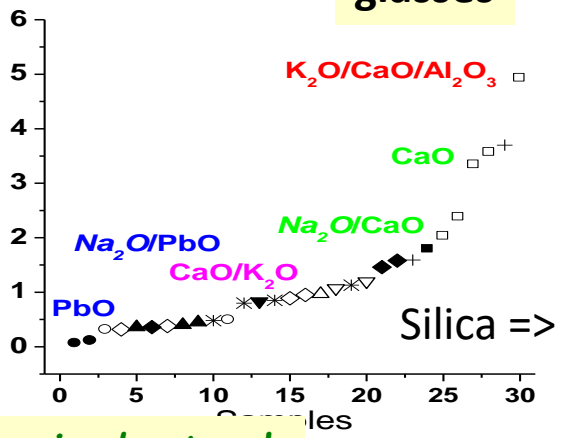
full polymerized network



Melting temperature =>



quartz
Melting temperature =>



de-polymerized network

same for crystalline and amorphous phosphates !

- $Ip < 0.3 - 0.8$ - Pb rich silicates ~ 600°C
- $0.8 < Ip < 1.1$ - Na rich silicates ~ 1000°C
- $1.1 < Ip < 2.5$ - Ca rich silicates ~ 1200°C
- $Ip > 2.5$ - K rich silicates => +1400°C

working/melting temperature

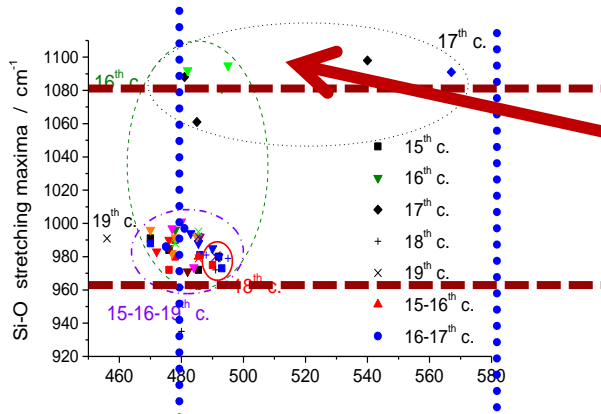
Ph. COLOMBAN
 Polymerisation Degree and Raman Identification of Ancient Glasses
 used for Jewellery, Ceramics Enamels and Mosaics
 J. Non-Crystalline Solids 323 [1-3] (2003) 180-187.

Chinese cloisonnés



Kangxi paravent

PbO



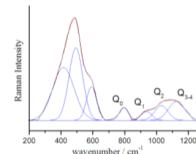
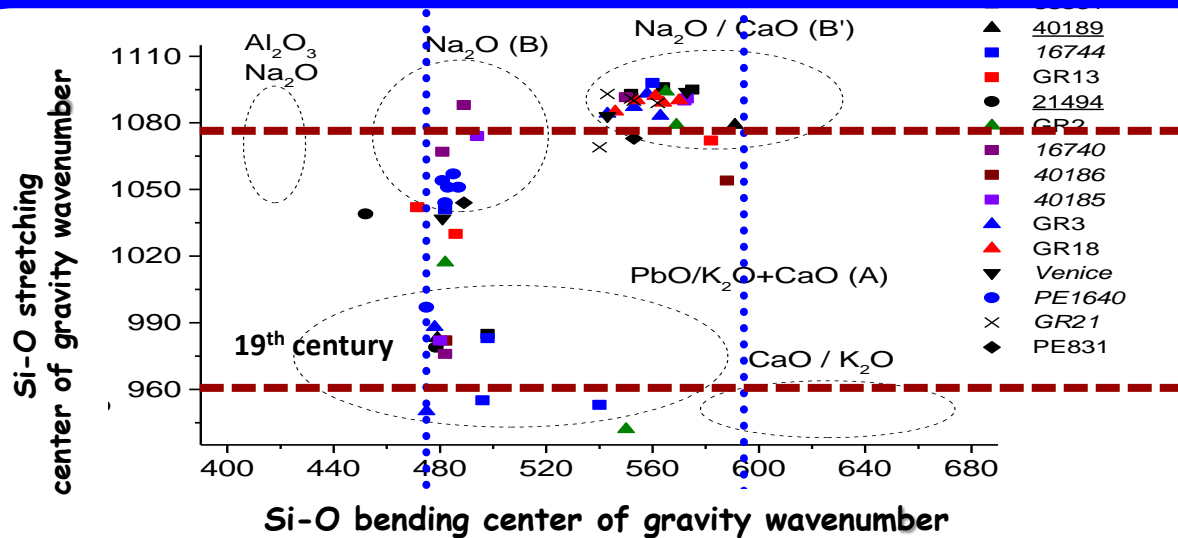
except
for some 17th productions
"French technology"

China Court Jesuits

Lead-based enamels
15 to 19th century
Very narrow distribution
especially for 18th c. one
→ Same workshop?



China cloisonné - Painted Limoges enamels comparison of glassy matrices



Limoges painted enamels
15th up to 18th century
sodium-based enamels

Qing Dynasty Imperial huafalang painted enamelled artefacts

(18th century : Kangxi to Qianlong reign)

Identification of artefacts with painted enamels prepared with Ingredients imported from Europe

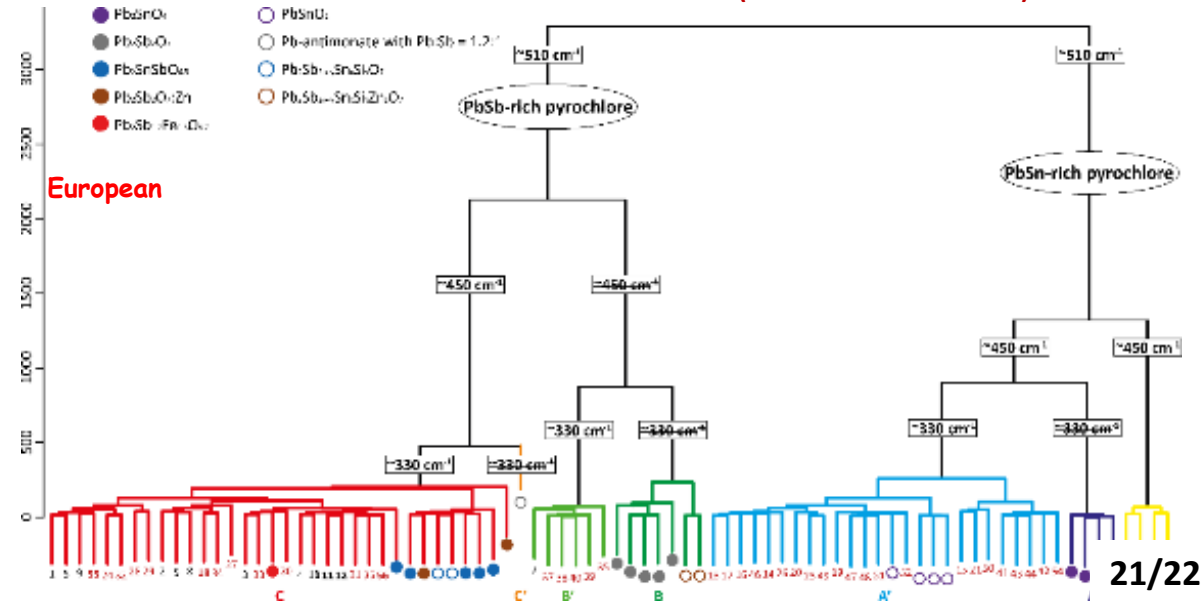
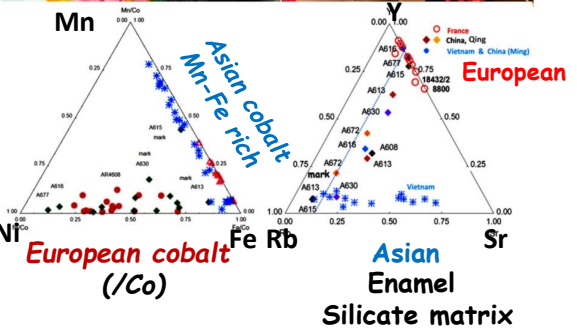
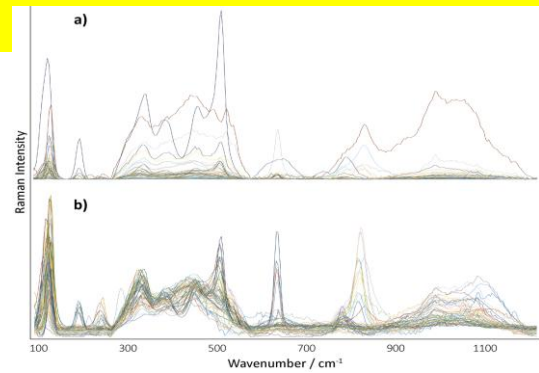
Yellow (and green) enamels
3 different structures both for Sn- and Sb-based Naples yellow (pyrochlore-like) pigments

Variables: wavenumbers, band width & area of pigment signature (silicate matrix excluded)



pXRF

Raman



J. Burlot, D. Vangu, L. Bellot-Gurlet, P. Colombar, Raman identification of pigments and opacifiers: Interest and limitation of multivariate analysis by comparison with solid state spectroscopical approach J. Raman Spectrosc. 2023, submitted.

4. Conclusions & Perspectives

On-site non-invasive identification of amorphous and crystalline phases

- ⇔ Authentication (anachronisms, characteristic phases, ...)
- ⇔ Conservation (corrosion)
- ⇔ Datation (very surface protonation increases with centuries)

Requirements

Convenient laser source (color and power 100 to 300 mW)

High energy, good resolution spectrometers.

High magnification advanced optics

Deep understanding of the light-matter interaction and modeling
to extract information (statistical comparison, Raman is not a standard
analytical technique)

Prospects

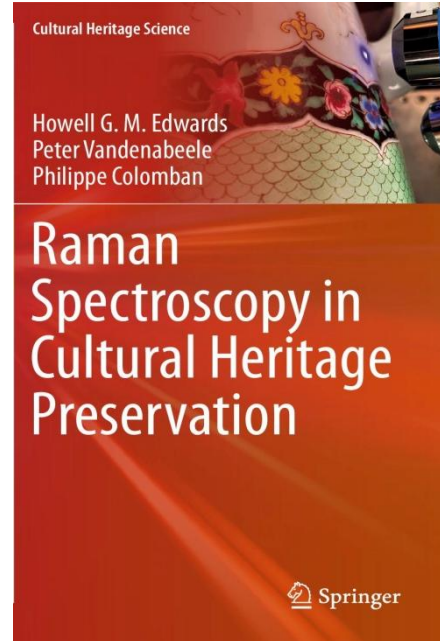
Compact spectrometer with blue laser

On-site Raman mapping

Higher performance CCD (pixel resolution)

Stand-off set-up (telescope, pulsed laser)

On-site SERS measurement, etc.



Thanks for attention

S_3^- chromophore Lapis lazuli already observed in



- **Ptolemaic glass, 1st c BCE**
'Begram Hoard', Afghanistan
Coll. Musée national des arts asiatiques - Guimet
(Caggiani et al., Anal. Methods 2013)
- **Ptolemaic enamelled faience (Pompei)**
(A. Mangone, G. E. De Benedetto, D. Fico, L. C. Giannossa, R. Laviano, L. Sabbatini, I. D. van der Werf, A. Traini, New J. Chem., 2011, 35, 2860-2868)
- **Roman Lübsow chalice**
S. Greiff, J. Schuster, J. Cult. Herit. 2008, 9 Suppl., e27
- **14th c. Swabian-Normand-Islamic pottery (Sicilia, Apulia)**
(R.J.H. Clark, C. Laganara et al., Bari University)
- **13th-14th c. Swabian-Normand-Islamic enameled glass**
(M.C. Caggiani, A. Mangone et al., Bari University)
- **14th c. Lajvardina pottery**
(Ph. Colomban)** *in combination with ~2% Co !!*
- **14th-15th c. Mamluk glass** (some time in combination with Co)
- **18th Böttger porcelain (Saxony)** : *lapis as whitening agent of the glaze*



OA
7352



Lamp bearing
the name of *Sayf al-Din Tankizbughâ*
Body : circa 1362
Egypt or Syria (Europe for foot)
Foot : 19th c. restoration Ph.J. Brocard

Comparison of coloring agents in Europe and China
in the 17th - 18th centuries in
glass/enamel (*Qing Dynasty*)

The phases detected by Raman micro-spectroscopy
are in bold, those whose elements are detected
by mobile XRF fluorescence are in italics.
In red underlined the imported recipes.

17世纪在欧洲和中国玻璃/珐琅着色剂的比较。
通过便携显微拉曼光谱检测的晶体粗体显示
通过移动XRF荧光检测到的元素 以斜体书写
红色下划线表示为进口配方

Color 颜色	Europe 欧洲 (name/ formula) (物质名称/化学式)	Date (post quem) century 发明使用时间 (世纪)	Chine 中国 (特征物质/化学式) (characteristics/formula)	Date d'innovation/usage (Dynastie) 发明使用时间 (王朝)
White 白色	<i>Cassiterite (SnO₂)</i> 锡石	<5 th 5世纪之前	<u>Imported 进口的</u>	
			Fluorite (CaF ₂) 萤石	> Song 自宋朝
	<i>K, Ca – Pb Arsenates</i> 砷酸盐 钾、铅和砷酸钙 <i>Na_{1-x-2y}K_xCa_yPb₄(AsO₄)₃</i> <i>(Ca₃(PO₄)₂) phosphate</i> 磷酸钙	~16 th 16世纪之前	<u>Imported 进口的</u>	
Blue 蓝色	<i>Arsenic-rich cobalt</i> 富砷钴矿	~16 th - 19 th 从16世纪到19世纪	<i>Mn-rich cobalt</i> 富锰钴矿 (Han blue 汉蓝) <i>Arsenic-rich cobalt</i> 富砷钴矿	Yuan – Ming “元”、“明” 时期
	<i>Pb₂Sn₂O₆ - Pb₂Sb_{2-x}M_xO_{7-d}</i> <i>M= Fe, Si, Zn (Naples Yellow)</i> (烧绿石固溶体) <i>pyrochlore</i>	Antiquity (Sn) 古代 (15 th) 15世纪 文艺复兴时期 (Sb-Sn,Si,Zn,Fe)	<i>Fe²⁺/Fe³⁺ ions</i> <i>Fe²⁺ / Fe³⁺ 离子</i>	>Han 汉代以来
Green 绿色	<i>Cu²⁺</i>	Antiquity 古代	<i>Cu²⁺离子</i>	>Han 汉代以来
	<i>Blue + Yellow</i> 蓝色+黄色	Renaissance	<u>Imported 进口的</u>	
Red 红色	<i>Hematite (Fe_{2-x}M_xO₃)</i> 赤铁矿	Roman 罗马帝国	<i>Hematite (Fe_{2-x}M_xO₃)</i>	> Ming 自明朝
	<i>Hercynite (Fe_{2-x}M_xO₃)</i> 海长岩	Roman 罗马帝国		
	<i>Cu⁰ nanoparticles</i> 铜纳米粒子	Celtic 凯尔特人	<i>Cu⁰铜纳米粒子</i>	> Yuan 自元朝
	<i>Au⁰ nanoparticles</i> 金纳米粒子	Roman (?) 罗马帝国 Renaissance (15 th)	<u>Imported 进口的</u>	

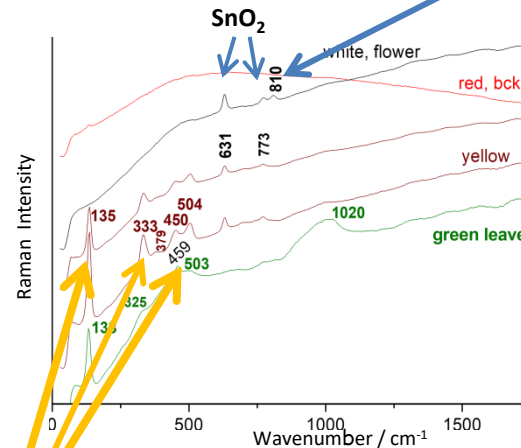
Qing Dynasty Imperial *huafalang* bowl (18th century : Kangxi to Qianlong reign)

Pb-Ca/K-arsenate

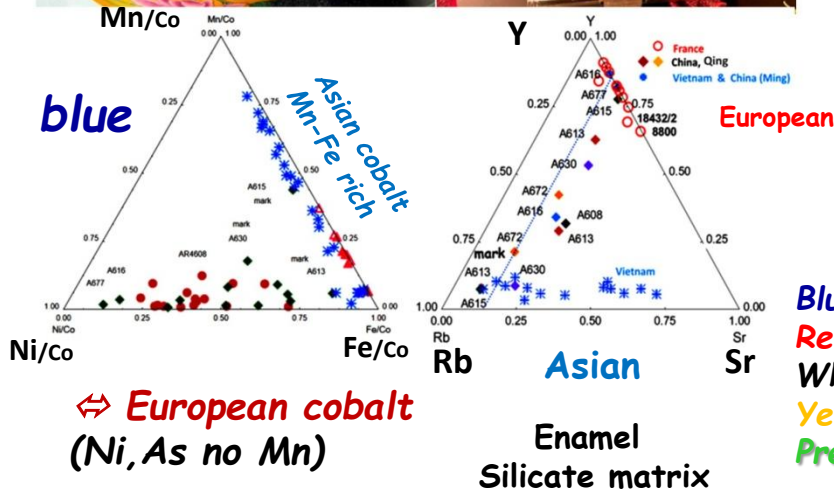


pXRF

pRaman



Red : metal nanoparticle fluorescence (Cu° or Au°)
White: cassiterite SnO_2 + Pb-Ca/K-arsenate
Yellow: Lead stannate/antimonate + cassiterite
Green: idem (+ Cu^{2+})



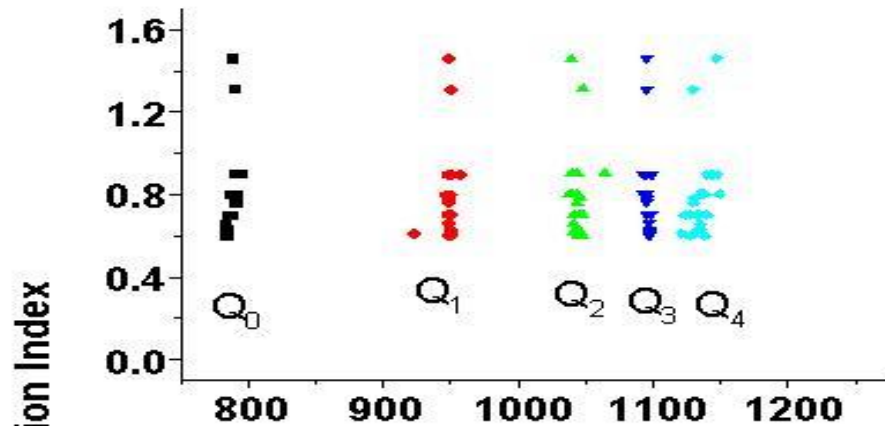
huafalang enamels

Blue: Imported European cobalt under Jesuits guidance

Red: Au° NPs (imported under Jesuits guidance)

White : European recipes

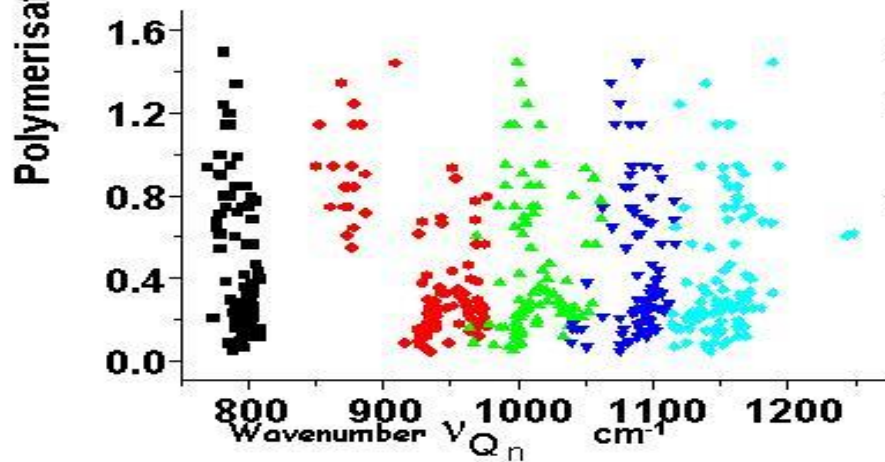
Yellow & green: Chinese recipes already imported from Europe during Previous Dynasty (Ming)



SiO₄ network

Roman glasses :
 an unique signature
 whatever the origin :
 Italy, France, Tunisia

single technology &
 composition



Stained glasses :
scattered signatures

⇒ *Churches, France*
 many workshops &
 many compositions

