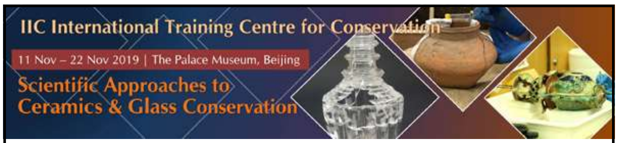


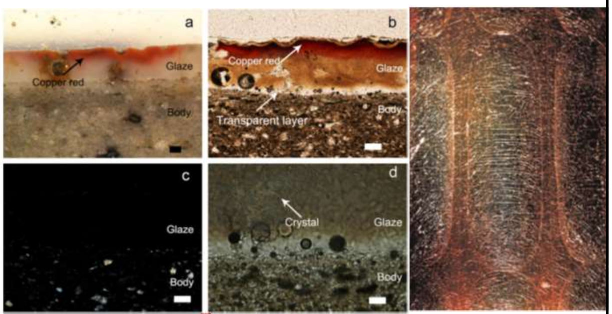
In situ analysis of Glass and Ceramics

12 November 2019

Austin Nevin

INTERNATIONAL INSTITUTE FOR CONSERVATION OF HISTORIC AND ARTISTIC WORKS

What key analytical questions do you have for scientific analysis?



Rainer W. Richter & Christian Neelmeijer (2012) The Waldenburg Beakers andJohann Kunckel: Analytical and technological study of four corner-cut coloured glasses, Studies in Conservation, 57:sup1, S234-S243, DOI: 10.1179/2047058412Y.0000000033

http://dx.doi.org/10.1016/j.ceramint.2016.02.072

INTERNATIONAL INSTITUTE FOR CONSERVATION OF HISTORIC AND ARTISTIC WORKS

Key concepts and Goals

- Chemical background
- Many techniques can be used for analysis of ceramics and glass
  - PIXE, PIGE, EBA, ICP-OES, SEM-EDX, Petrography
- **Non-destructive Elemental Analysis**
  - X-ray Fluorescence (XRF) Spectroscopy
- **Non-destructive Molecular Analysis**
  - X-ray Diffraction
  - Fourier Transform Infrared Spectroscopy (FTIR)
  - Raman Spectroscopy

INTERNATIONAL INSTITUTE FOR CONSERVATION OF HISTORIC AND ARTISTIC WORKS

Glass and Ceramic

- – Amorphous or Crystalline?
- – What is the composition?
- – What is chemical changes may influence composition or surface vs. bulk?
- – What do you need to know for conservation?
- – Bulk vs. Inclusions vs. Surface?

Glass and Deterioration

- initial stage, incipient crizzling, full-blown crizzling, advanced, crizzling and fragmentation stages

Jerzy J. Kunicki-Goldfinger (2008) Unstable historic glass: symptoms, causes, mechanisms and conservation, Studies in Conservation, 53:sup2, 47-60, DOI: 10.1179/sic.2008.53.Supplement-2.47

Material and Chemical Properties

- Cermaics and Glass have low porosity and similar density
- Porcelain: porcelian-clay, flux and filler + glaze
  - – Typically quartz, mica, feldspar, kaolin
  - – Variations include Spanish clays (high Mg)
- Glass: silica, flux
- Multilayered?
- Many different recipes, additives, lime, alkali metals, bone, talc

Elements typically found in glass and ceramics

- Oxides of:
  - Na, Mg, Al, Si, P, K, Ca, Ti, Mn, Fe, Sn, Pb

X-Ray Fluorescence (XRF) Spectroscopy

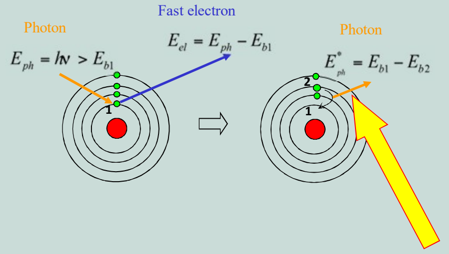
- Suitable as it yields elemental information about raw materials, processing techniques, and physical properties
- Provenance/authenticity
- Note: beam size is large, compared to microscopic techniques (SEM-EDX)

Theoretical Background: XRF

- A **low power** X ray beam is delivered to the sample
- Every chemical element in the sample emits characteristic X –rays give a fingerprint of the element
- An **energy sensitive** detector measures the **energy spectrum** of the emitted X rays
- The analysis of the peaks of the X fluorescence spectrum allows the detection of **elements contained in the sample**
  - In portable detectors (Silicon Drift Detectors), especially useful for the analysis of cultural heritage, the lighter detectable atom is usually sodium $_{11}Na$
  - The limit of detection of lighter elements is given by the presence of Ar in air and by the entrance window of the detector, which is usually made of a low atomic number element (Be)

X ray fluorescence emission mechanism

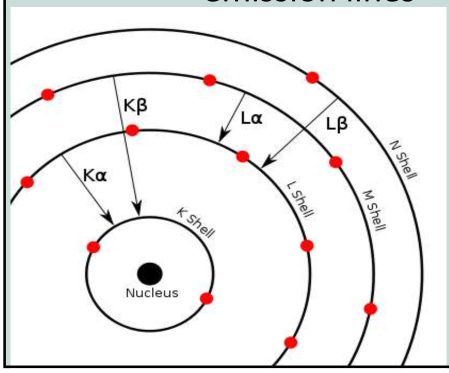
Photoelectric effect



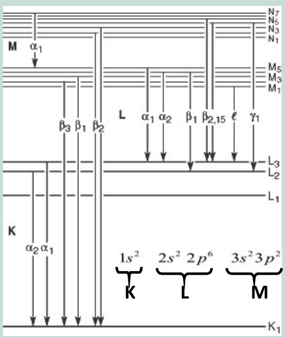
We are interested in this X-ray:
X-ray fluorescence

*

X-ray fluorescence: multiple emission lines



Spectral lines



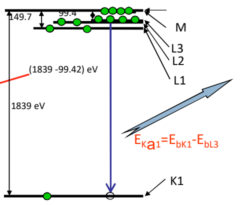
Element	Kα1	Kα2	Kβ1	Lα1	Lα2	Lβ1
3 Li	0.0543					
4 Be	0.1085					
5 B	0.1833					
6 C	0.2770					
7 N	0.3924					
8 O	0.5249					
9 F	0.6768					
10 Ne	0.8486	0.8486				
11 Na	1.0410	1.0410	1.0711			
12 Mg	1.2536	1.2536	1.3022			
13 Al	1.4867	1.4863	1.5575			
l4 Si	1.7400	1.7394	1.8359			
15 P	2.0137	2.0127	2.1391			
16 S	2.3078	2.3066	2.4640			
17 Cl	2.6224	2.6208	2.8156			
l8 Ar	2.9577	2.9556	3.1905			
19K	3.3138	3.3111	3.5896			
2OCa	3.6917	3.6881	4.0127	0.3413	0.3413	0.3449
21 Sc	4.0906	4.0861	4.4605	0.3954	0.3954	0.3996
22 Ti	4.5108	4.5049	4.9318	0.4522	0.4522	0.4584
23V	4.9522	4.9446	5.4273	0.5113	0.5113	0.5192
24Cr	5.4147	5.4055	5.9467	0.5728	0.5728	0.5828
25 Mn	5.8988	5.8877	6.4905	0.6374	0.6374	0.6488
26 Fe	6.4038	6.3908	7.0580	0.7050	0.7050	0.7185
27Co	6.9303	6.9153	7.6494	0.7762	0.7762	0.7914
28Ni	7.4782	7.4609	8.2647	0.8515	0.8515	0.8688
29 Cu	8.0478	8.0278	8.9053	0.9297	0.9297	0.9498
3OZn	8.6389	8.6158	9.5720	1.0117	1.0117	1.0347

*

X emission lines of elements (eV)

X-Ray Data Booklet Table 1-2. Photon energies, in electron volts, of principal K-, L-, and M-shell emission lines.

Element	Kα1	Kα2	Kβ1	Lα1	Lα2	Lβ1	Lβ2	Lγ1	Mα1
3 Li	54.3								
4 Be	108.5								
5 B	183.3								
6 C	277								
7 N	392.4								
8 O	524.9								
9 F	676.8								
10 Ne	848.6	848.6							
11 Na	1,040.98	1,040.98	1,071.1						
12 Mg	1,253.60	1,253.60	1,302.2						
13 Al	1,486.70	1,486.27	1,557.45						
14 Si	1,739.98	1,739.38	1,835.94						
15 P	2,013.7	2,012.7	2,139.1						
16 S	2,307.84	2,306.64	2,464.04						
17 Cl	2,622.39	2,620.78	2,815.6						
18 Ar	2,957.70	2,955.63	3,190.5						
19 K	3,313.8	3,311.1	3,589.6						
20 Ca	3,691.68	3,688.09	4,012.7	341.3	341.3	344.9			
21 Sc	4,090.6	4,086.1	4,460.5	395.4	395.4	399.6			

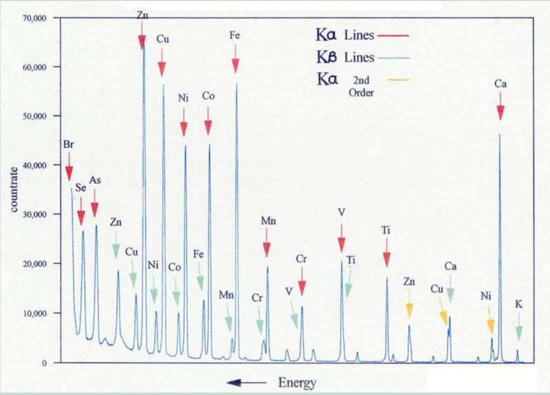


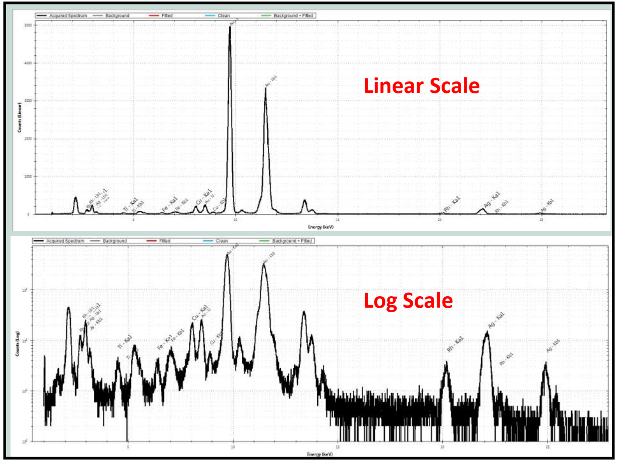
http://xdb.lbl.gov/Section1/Table_1-2.pdf

X emission lines of elements (eV)

Table 1-2. Energies of x-ray emission lines (continued).

Element	Kα1	Kα2	Kβ1	Lα1	Lα2	Lβ1	Lβ2	Lγ1	Mα1
22 Ti	4,510.84	4,504.86	4,931.81	452.2	452.2	458.4			
23 V	4,952.20	4,944.64	5,427.29	511.3	511.3	519.2			
24 Cr	5,414.72	5,405.509	5,946.71	572.8	572.8	582.8			
25 Mn	5,898.75	5,887.65	6,490.45	637.4	637.4	648.8			
26 Fe	6,403.84	6,390.84	7,057.98	705.0	705.0	718.5			
27 Co	6,930.32	6,915.30	7,649.43	776.2	776.2	791.4			
28 Ni	7,478.15	7,460.89	8,264.66	851.5	851.5	868.8			
29 Cu	8,047.78	8,027.83	8,905.29	929.7	929.7	949.8			
30 Zn	8,638.86	8,615.78	9,572.0	1,011.7	1,011.7	1,034.7			
31 Ga	9,251.74	9,224.82	10,264.2	1,097.92	1,097.92	1,124.8			
32 Ge	9,886.42	9,855.32	10,982.1	1,188.00	1,188.00	1,218.5			
33 As	10,543.72	10,507.99	11,726.2	1,282.0	1,282.0	1,317.0			
34 Se	11,222.4	11,181.4	12,495.9	1,379.10	1,379.10	1,419.23			
35 Br	11,924.2	11,877.6	13,291.4	1,480.43	1,480.43	1,525.90			
36 Kr	12,649	12,598	14,112	1,586.0	1,586.0	1,636.6			
37 Rb	13,395.3	13,335.8	14,961.3	1,694.13	1,692.56	1,752.17			
38 Sr	14,165	14,097.9	15,835.7	1,806.56	1,804.74	1,871.72			
39 Y	14,958.4	14,882.9	16,737.8	1,922.56	1,920.47	1,995.84			
40 Zr	15,775.1	15,690.9	17,667.8	2,042.36	2,039.9	2,124.4	2,219.4	2,302.7	





Glazes and Enamels

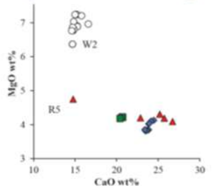
- Elements may suggest different additives or opacifiers and include:
  - Sb, Sn, Pb, Zn, As (modern Zr)
  - Naples Yellow (Pb, Sb) or Lead-tin yellows (Pb, Sn)
  - Hematite (Fe)
  - Cobalt (Co) and Fe/Zn/Mn

INTERNATIONAL INSTITUTE FOR CONSERVATION OF HISTORIC AND ARTISTIC WORKS

Stained glass

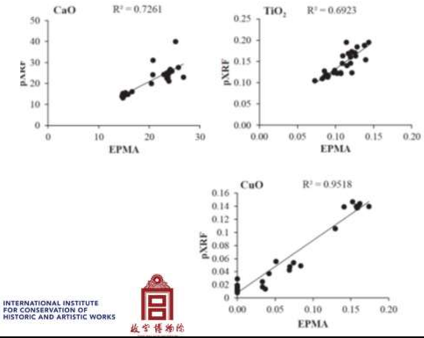
EPMA	White	Blue	Red	R5	Green/ Yellow	Rel. Acc. %
Na_2O	2.22	1.11	1.32	0.40	1.50	8.9
MgO	6.94	3.94	4.19	4.75	4.21	-5.2
Al_2O_3	1.32	1.62	1.64	1.86	1.64	-1.2
SiO_2	57.63	51.27	50.12	51.47	46.18	0.4
P_2O_5	3.37	2.92	3.37	3.81	4.04	1.4
SO_3	0.18	0.15	0.22	0.18	0.26	-2.9
Cl	0.33	0.04	0.05	0.35	0.04	0.9
K_2O	10.13	11.41	10.83	18.99	15.81	0.4
CaO	15.14	23.83	25.14	14.78	20.61	-2.2
TiO_2	0.09	0.12	0.12	0.13	0.14	13.7
MnO	1.43	1.20	1.17	1.11	1.46	-5.5
Fe_2O_3	0.48	0.89	0.53	0.37	2.70	-6.2
CoO	<0.03	0.08	<0.03	<0.03	<0.03	BD
CuO	0.04	0.16	0.08	0.05	0.06	-4.1
ZnO	0.04	0.14	0.04	<0.03	0.04	-25.4
PbO	0.07	0.19	0.20	<0.03	0.06	-7.0
Total	99.71	99.55	99.47	98.77	99.23	

	White	Blue	Red	R5	Green/ Yellow	Rel. Acc. %
Ti	708	1020	829	1102	1070	7.9
Co	25	768	49	53	155	-8.1
Ni	53	66	47	69	49	3.4
Cu	120	1123	465	187	338	-0.5
Zn	393	1379	1379	206	319	-0.9
Rb	225	323	300	283	363	3.3
Sr	491	693	735	524	594	-10.0
Zr	59	114	108	71	113	5.0



DOI: 10.1557/adv.2017.233

XRF vs. Electron beam analysis



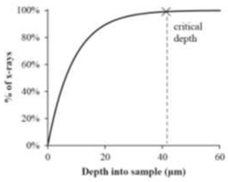
INTERNATIONAL INSTITUTE FOR CONSERVATION OF HISTORIC AND ARTISTIC WORKS

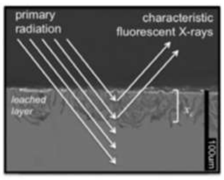
故宮博物院

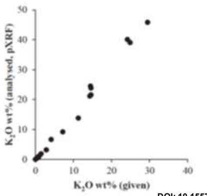
DOI: 10.1557/adv.2017.233

Critical Depth

I_x/I_0	K	Ca	Rb	Sr	Zr
99%	41.3	41.3	872	999	1325
90%	20.6	20.7	436	500	662
75%	12.4	12.4	262	301	399
50%	6.2	6.2	131	150	199
25%	2.6	2.6	54.4	62.4	82.8







DOI: 10.1557/adv.2017.233

Critical: Depth resolution

- Multi-layered samples vs. Bulk
- Depth of penetration of X-rays
- Attenuation of photons in glaze, that depends on glaze composition
- Glaze may account for K lines of Mg-Fe
  - Lime-alkali glazes have Ca/(Na+K) >1
  - Alkali-lime have Ca/(Na+K)<1
- Glazes containing Pb (L line) can be easily detected
- With thick glaze layers, signals from Rb, Sr, Y and Zr are from bulk

Critical: Trace elements

- XRF for trace element analysis is complicated by the different penetration of X-rays, attenuation of emitted photons, and intrinsic limitations of instrumentation and detection
- Still for glass Zr, Rb and Sr are most useful in classifying glasses
- Careful optimisation of instrumentation to collect data from bulk and trace elements may be needed (especially for samples that are thinner than critical depth of analysis)

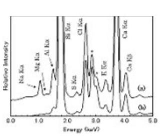
Useful quotation

- When pXRF is used without the benefit of sampling for laboratory analysis, it will be **difficult to interpret** glass types without the major element concentrations and it will be **impossible to compare** to other published data without a database of trace elements
- The analysis of trace elements by pXRF provides a way to study the **different sources** of glass and glassmaking technology, and to identify non-original glass

INTERNATIONAL INSTITUTE FOR CONSERVATION OF HISTORIC AND ARTISTIC WORKS

DOI: 10.1557/adv.2017.233

Case study: pXRF (vacuum) and Roman Glass



Na_2O content ranges mainly between 14 and 22 wt%,

Vacuum 500 Pa → light element detection
MOXTEK AP3.3 polymer window (vs. Conventional Barium) → light element detection, Pd source @ 40 kV

X-Ray Spectrom. **2009**, *38*, 121–127

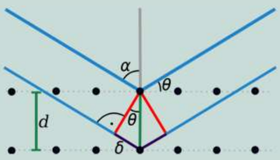
Critical Aspects: Calibration standards

- Calibration standards are needed for the quantification of concentrations of different elements in ceramics and glasses
  - Light vs. Heavy elements
- Quantification requires comparision between XRF and complementary (ICP-OES) techniques
  - Many glass standards are available for calibration
  - Fewer porcelain standards

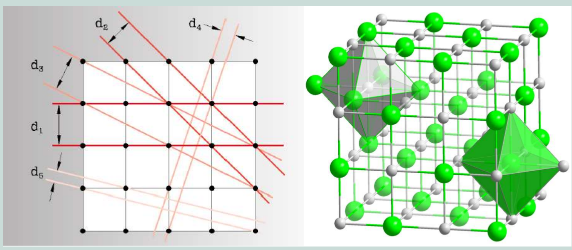
Phase Analysis: X-ray Diffraction

- Diffraction of crystalline materials is extremely powerful for material identification
- Based on Bragg´s Law:

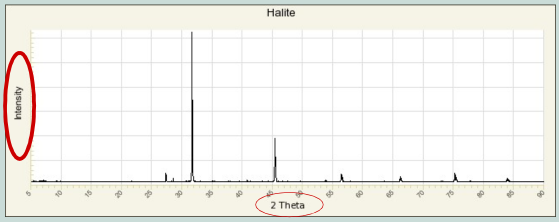
$$n \lambda = 2 d \sin \theta$$



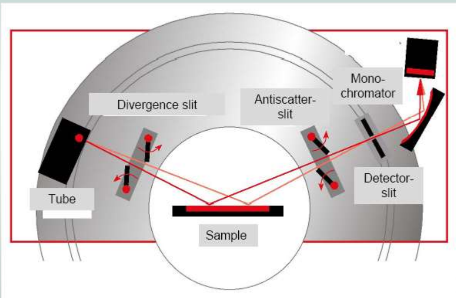
For Cubic systems



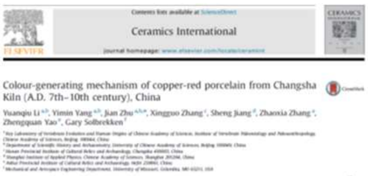
Typical XRD Spectrum from a pure sample



Typical setup for XRD



Case study: SR Micro-XRD Analysis of glazes

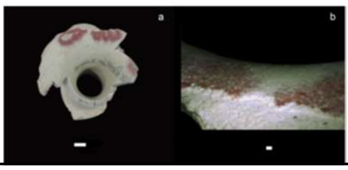

Contents lists available at ScienceDirect

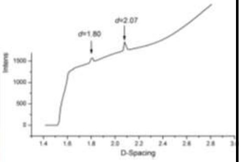
Ceramics International

journal homepage: www.elsevier.com/locate/ceramint

Colour-generating mechanism of copper-red porcelain from Changsha Kiln (A.D. 7th–10th century), China

Yuanqiu Li, Yimin Yang, Jian Zhu, Xingguo Zhang, Sheng Jiang, Zhaoxia Zhang, Zhengquan Yao, Gary Solbrekken



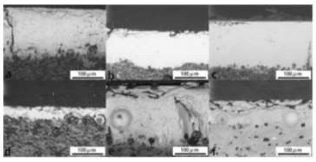


Case Study: Western Han Dynasty

RESEARCH ARTICLE

A technological combination of lead-glaze and calcium-glaze recently found in China: Scientific comparative analysis of glazed ceramics from Shangyu, Zhejiang Province

Yue Wang, Yihang Zhou, Zhefeng Yang, Jianfeng Cui*
School of Archaeology and Museology, Peking University, Beijing, China
* cuijianfeng@pku.edu.cn



DOI:10.1371/journal.pone.0219608.g003

XRD: a key to understanding firing temperature

- Co Source, voltage: 30kV, current: 300uA
  Angle range: 5˚-55˚ (2θ), step: 0.04˚(2θ).
- The formation of mullite requires a temperature higher than 1200˚C, which means the samples No.19 and 24 were fired at a high temperature. The firing temperature of the sample No. 04 and 23 are much lower since no mullite signal was detected

Table 4. The XRD test results of the ceramics bodies (wt.%).

No.	Sample group	Quartz	Rutile	Mullite
04	Medium-lead	86.1	8.1	
19	Low-lead	72.2		21.2
23	High-lead	85.5	8.9	
24	Medium-lead	67.3		24.9

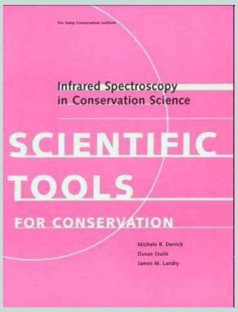
INTERNATIONAL INSTITUTE FOR CONSERVATION OF HISTORIC AND ARTISTIC WORKS

故宫博物院

DOI:10.1371/journal.pone.0219608.g003

Vibrational Spetroscopy

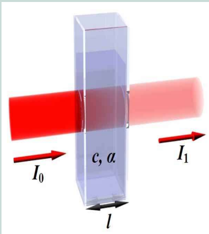
- Common technique used for the analysis of inorganic and organic materials
- A very powerful tools for the assessment of degradation and conservation materials
- In IR absorption, frequencies which match the natural vibrational frequencies of molecules may be absorbed
- In Raman spectroscopy, frequencies which match vibrational frequencies may be scattered

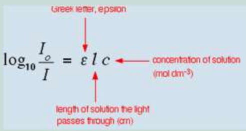


INTERNATIONAL INSTITUTE FOR CONSERVATION OF HISTORIC AND ARTISTIC WORKS

故宫博物院

Absorbtion: Beer Lambert Law

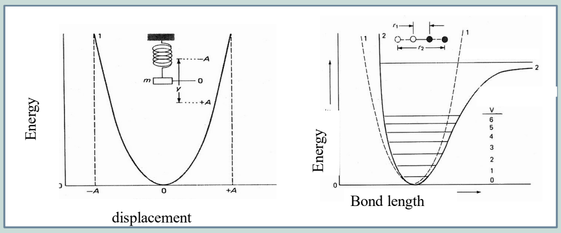




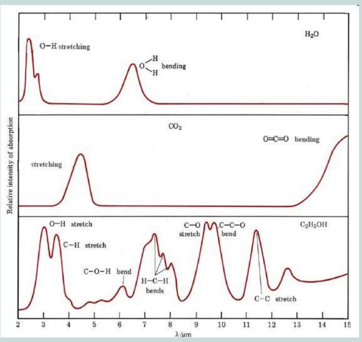
FTIR sensitivity: approximately 1 %*

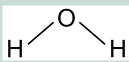
Simple model of infrared absorption

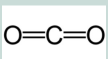
- In molecules, the chemical bond exerts an elastic force between atoms
- Absorption takes place only for discrete frequencies that correspond to the energy separation of vibrational levels

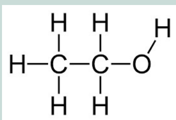


FTIR spectroscopy of simple molecules



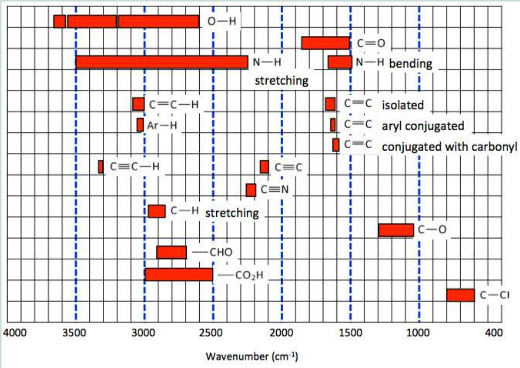






Functional Groups are key to spectral **interpretation**

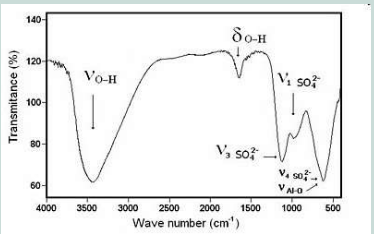
Extra Information: IR Vibrational Frequencies



Si-O vibrations

Band, cm^{-1}	Assignment
3435	Absorbed water
1632	H–O–H str.
1082	Si–O–Si, SiO str.
1175	Si–O–Si str.
797	Si–O sym.str.
778	Si–O sym. str.
694	Si–O of SiO_4 sym. bend.
516	Si–O–Al asym. bend.
475	Si–O–Si asym. bend.

How to Examine a FTIR and Raman spectrum



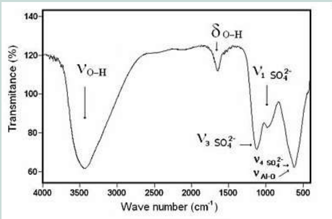
Trasmittance vs. Wavenumber (cm^{-1})
Absorbance vs. Wavenumber (cm^{-1})
Reflectance vs. Wavenumber (cm^{-1})

Crucial differences in applicability and results

Spectral properties

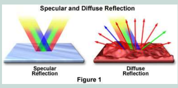
Bands

- **Position/frequency**
  - Depends on the bonds
- **Shape**
  - Reflects the purity of the sample, and the presence of similar bonds in a sample
- **Relative intensity**
  - Number of molecules in a sample (concentration)

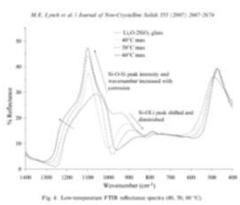


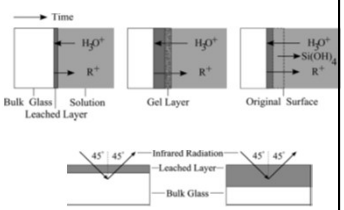
Reflectance Analysis

- Specular Reflection (smooth surfaces)
  - measurement of thin layers or monolayers
  - coatings
- Diffuse Reflection (DRIFTs) (rough surfaces)
  - structural information is from the bulk matrix



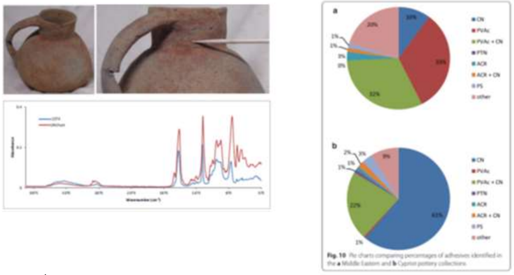
FTIR of Glass and Corrosion





doi:10.1016/j.jnoncrysol.2007.05.012

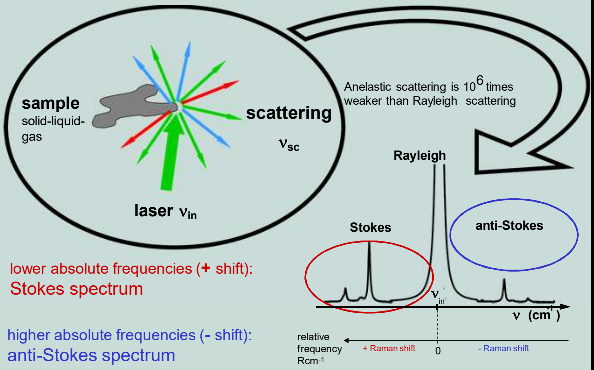
FTIR for studying adhesives: well established



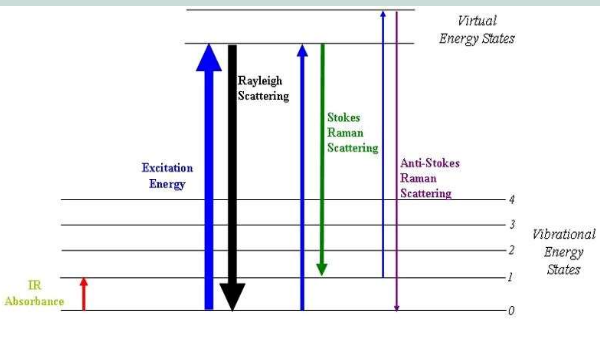
DOI 10.1186/s40494-016-0116-z

INTERNATIONAL INSTITUTE FOR CONSERVATION OF HISTORIC AND ARTISTIC WORKS

Raman Spectroscopy: Basic Principle

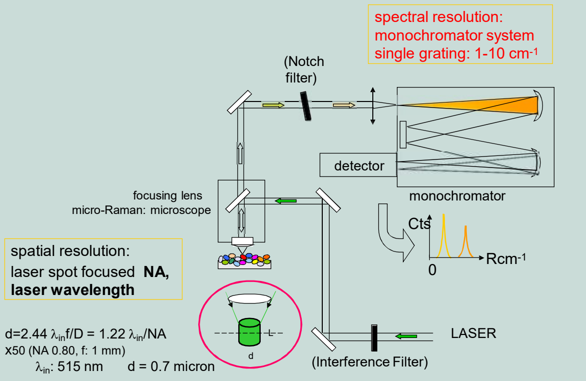


Energy diagramme



INTERNATIONAL INSTITUTE FOR CONSERVATION OF HISTORIC AND ARTISTIC WORKS

Micro-Raman Setup

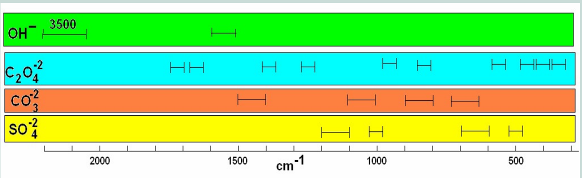


Complexity of Raman Spectroscopy: Experimental Parameters

- Spectral Resolution (grating, laser)
- Spectral Range
- Calibration
- Number of acquisitions
- Time for each acquisition
- Laser parameters:
  - Wavelength
  - Power density
  - Fluence (energy/ spot size)
- Microscope parameters
  - Magnification, focal distance, aberrations

Raman Spectroscopy: fingerprint region

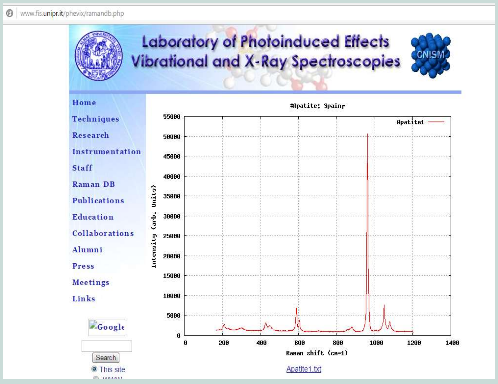
Inorganic molecules



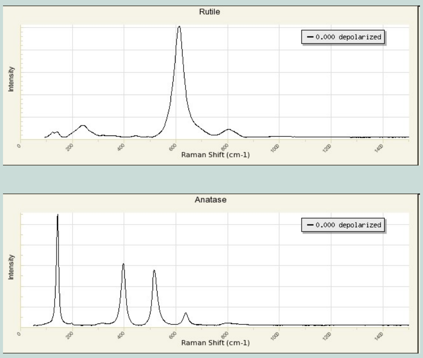
Si-O also Raman active!

Spectral databases: Raman and XRD

–Base de données de spectres Raman (La Société Française de Minéralogie et Cristallographie) (la SFMC)
–Handbook of Minerals Raman Spectra (ENS-Lyon)
–Integrated database of Raman spectra, X-ray diffraction and chemistry data for minerals (RRUFF Project)
–Mineral Raman Database (University of Parma)
–Raman Spectra Database of Minerals and Inorganic Materials (RASMIN) (Ceramics Inst. AIST)
–Raman Spectra of Carbohydrates (Royal Vet. & Agric. Univ.)
–Raman Spectroscopic Library of Natural and Synthetic Pigments (Univ. College London)
-IRUG Database
Minerals:
–http://rruff.info/



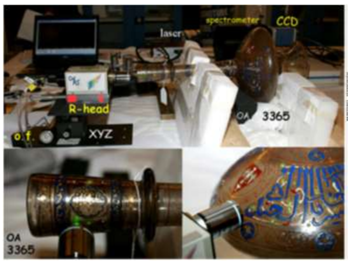
Mineral Polymorphs Raman spectra of Anatase vs Rutile – TiO_2

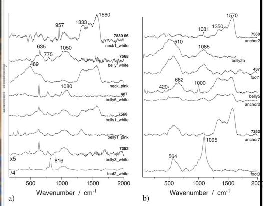


Raman Spectroscopy

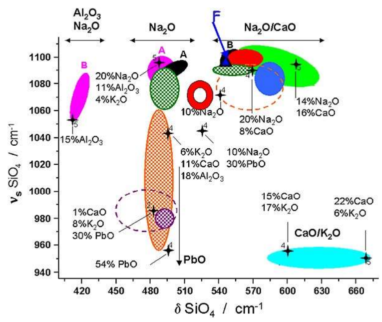
- Pigments and colourants
- Variation in intensity of bending and stretching bands based on composition and degradation
- Si-O-Si bonds have strong signals at 500 and 1000 cm^{-1} (broader in glassy structures), and the ratio of these bands has been used to classify the polymerisation (see Colomban)

Case study: Raman Spectroscopy of Egyptian glass





P. Colomban et al , JRS, 2012



- Classification diagram using the SiO_4 symmetric stretching band wavenumber (νs) versus the bending (δ) for a large glass corpus. Red circle and blue F correspond to Mamluk and 19th century (OA 7352 foot) glass. Representative compositions for the different areas are given (stars).

P. Colomban et al , JRS, 2012

Figure 2: Analysis of epoxy resin adhesive in the roundel by means of the Perkin Elmer RamanFlex 400F instrument with a fibre-optic probe.

INTERNATIONAL INSTITUTE FOR CONSERVATION OF HISTORIC AND ARTISTIC WORKS

Experimental Parameters

- PerkinElmer Raman Flex 400F with a 3 m fibre
- Laser (diode) 785 nm maximum power 300 mW at the laser source, 100 mW at the sample)
- Spectra acquired with a resolution of 2 cm^{-1} from 200-3200 Raman Shift
- Distance from sample: 100 µm
- Acquistion time: 5 to 100 s

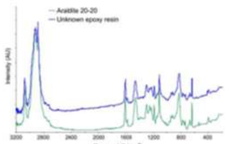


Figure 6: Raman spectra of unknown epoxy resin from roundel and comparative spectrum for Araldite 20-20 epoxy resin.

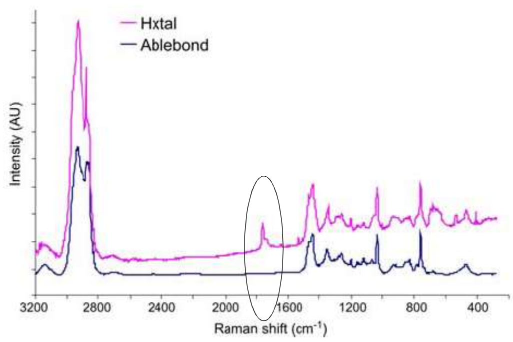
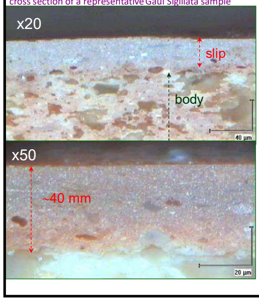


Figure 7: Comparative Raman spectra for Ablebond 342-1 epoxy resin and Hxtal NYL-1 epoxy resin.

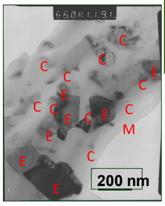
Raman Spectroscopy: ceramics

La Graufesenque (south Gaul, France)
- important production centre of *Sigillata* wares (I century AD)
- ceramic of good quality: brightness and waxy shine of the slip

cross section of a representative Gaul Sigillata sample



TEM

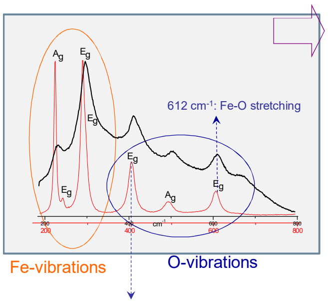


E: hematite
C: corundum
M: glassy matrix
(Si and Al oxides)

DOI 10.1002/jrs.2678

Raman Spectroscopy: ceramics

hematite a-Fe_2O_3 isostructural with corundum;



411 cm^{-1}: O-Fe-O bending (FeO_6 octahedra)

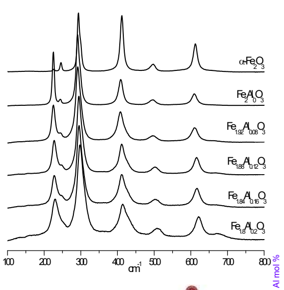
Sigillata slip:
- → luminescence background
- → red shift of Raman bands
- → broeadening of Raman bands
- → weakening of 224 cm^{-1} band
- → band @ 670 cm^{-1}
- → shoulder @ 414 cm^{-1}

disordered structure:
- lattice defects (punctual or extended defects) without changing the symmetry group;
- nano-crystals

DOI 10.1002/jrs.2678

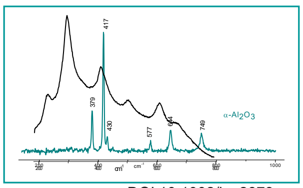
Raman Spectroscopy: ceramics

Raman spectra of Al-doped hematites (calcination at 1000 °C of oxalates)



hematite spectrum still present

effect of Al doping:
- broadening
- red shifting
- appearance of a shoulder at 430 cm^{-1}
- appearance of a signal at 670 cm^{-1}



DOI 10.1002/jrs.2678

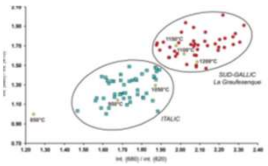
Classfication based on Si vibrations/firing temperatures

Table 1. Mineral compositions determined by XRD of the studied clays, before firing and after firing at 1050 and 1200 °C

Studied clays	Mineral composition: Present phases before firing	Present phases after firing at 1050 °C	Present phases after firing at 1200 °C
ESP4	**Illite, kaolinite**, quartz and hematite	**Hematite, corundum** and spinel ($MgAl_2O_4$)	**Mullite, hercynite**, corundum and hematite
VA7	**Illite, chlorite**, kaolinite (?), quartz, hematite and calcite	**Hematite, spinel** ($MgAl_2O_4$), corundum and anorthite	**Mullite**, anorthite and hematite
MON4	**Illite**, quartz, hematite	**Hematite, corundum** and spinel ($MgAl_2O_4$)	**Hercynite** and corundum
MON7	**Illite, chlorite**, quartz, hematite, albite and dolomite	**Hematite** and **spinel** ($MgAl_2O_4$)	**Hercynite**

The main phases are given in boldface.

X-ray diffraction and microprobe analysis revealed systematic differences between the central Italian (Arezzo) and south Gaul productions (La Graufesenque), both in the elemental and mineral compositions.[6–8]
All the slips contain quartz and hematite:
however, the Gallic ones embody a significant content of corundum nanocrystals, while the Italian productions contained a great proportion of spinel ($MgAl_2O_4$).
In addition, the X-ray diffraction study of the mineral composition of the body indicates that the Italian *sigillata* was fired at lower temperatures than the Gallic ones.



DOI 10.1002/jrs.2678

Conclusions

- **Non-destructive Elemental Analysis**
  - X-ray Fluorescence (XRF) Spectroscopy:
    - Heavy vs. Light elements
- **Non-destructive Molecular Analysis**
  - Fourier Transform Infrared Spectroscopy
    - Corrosion products, organic materials
  - Raman Spectroscopy
    - Different glass signatures, glaze composition, organic materials
  - X-ray Diffraction
    - Phase information, firing temperature

INTERNATIONAL INSTITUTE FOR CONSERVATION OF HISTORIC AND ARTISTIC WORKS

故宫博物院