ETH
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DCHAB
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Pigment Analysis

Study of a painting

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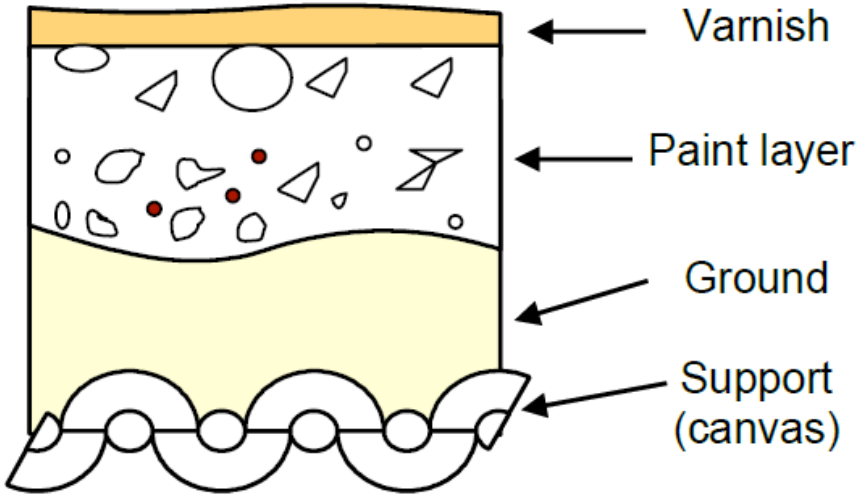
Original preparation study discovered?

The Battle of Anghiari

Structure of paintings

- Cross-section of a painting



- Material identification
  - Inorganic pigments and natural minerals
  - Binding materials

Pigments

- Organic or inorganic
- Usually distinguished from a dye by its insolubility in the vehicle
- Most are dry colorants

Blue pigments used in history

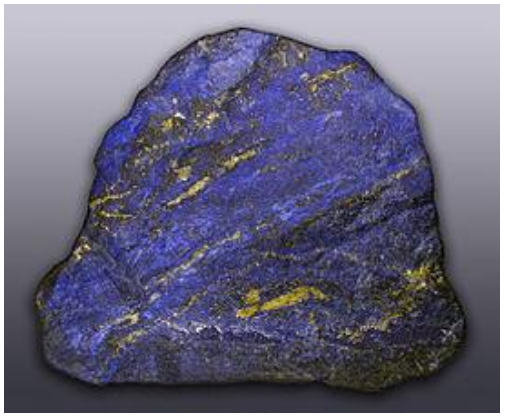
Pigment	Formula	Production	Date of introduction
Woad/Indigo	$C_{16}H_{10}N_2O_2$	Plant leaves	Ancient times/13th century
Han Blue	$BaCuSi_4O_{10}$	Synthetic	Ancient China
Egyptian Blue	$CaCuSi_4O_{10}$	Synthetic	Ancient times
Ultramarine	$Na_{8-x}[AlSiO_4]_6[S_3, S_2]_{2-2x}$ (different formulae possible)	Natural (from lapis lazuli) or synthetic	Natural: 6th century Synthetic: 19th century
Azurite	$Cu_3(CO_3)_2(OH)_2$	Ground mineral	15th century
Smalt	SiO_2(65%) + K_2O (15%) + Al_2O_3 (5%) + CoO (10%)	Synthetic	1584
Prussian Blue	$Fe_7(CN)_{18}$	Synthetic	1724
Cobalt Blue	$CoAl_2O$	Synthetic	1802
Cerulean Blue	$CoO \cdot nSnO_2$	Synthetic	1821
Copper phthalocyanine	$C_{32}H_{16}CuN_8$	Synthetic	1935

Blue pigments

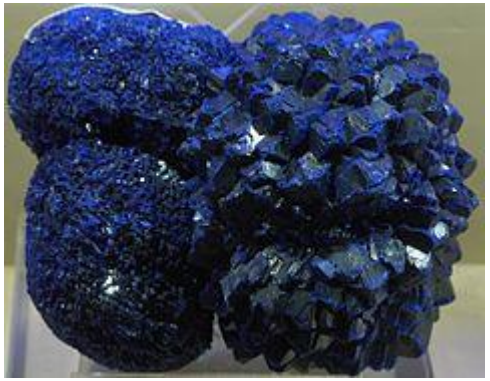
Indigo

Woad

Smalt



Lapis lazuli



Azurite

Analytical approach

- Non-destructive
  - no sampling required
- Non-invasive
  - sample is not destroyed
- No vacuum
- Sensitive
- Multi-elemental
- Fast

Sampling location

- Where pigments are expected
  - Blue area (minimal interferences)
  - Green area
- Avoid restored areas
  - Study painting under UV light (dark spots) and X-radiography

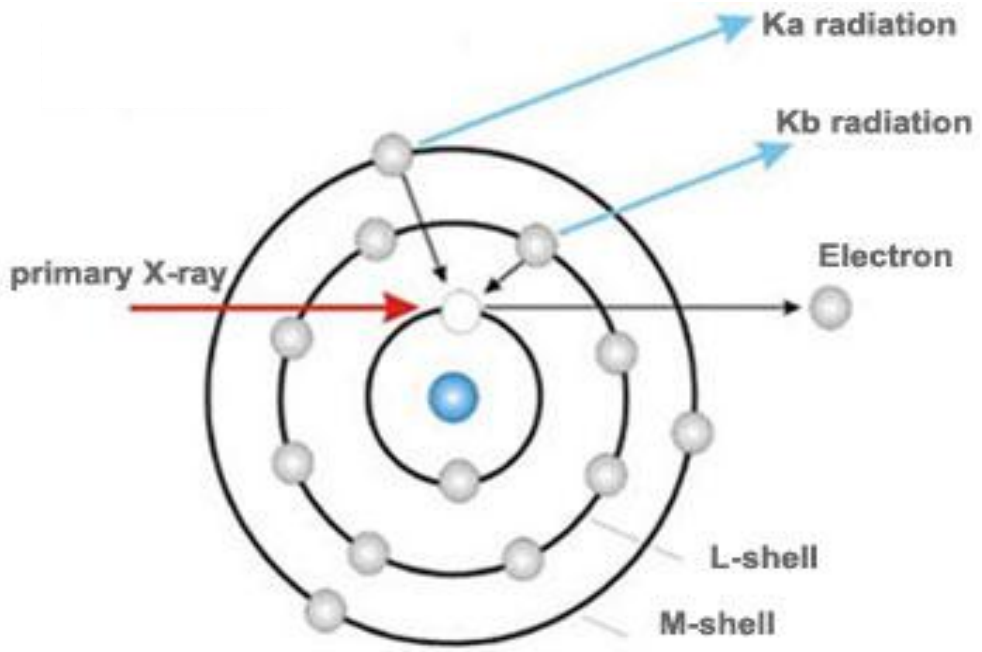
Madonna Suckling the Child, artist of the Ferrarese School from the early 16th Century, oil paints on a wooden panel shown under normal (left) and UV light (right)

X-ray spectroscopy

- Determines elemental composition
- Characterization of materials by using x-ray excitation

X-ray spectroscopy

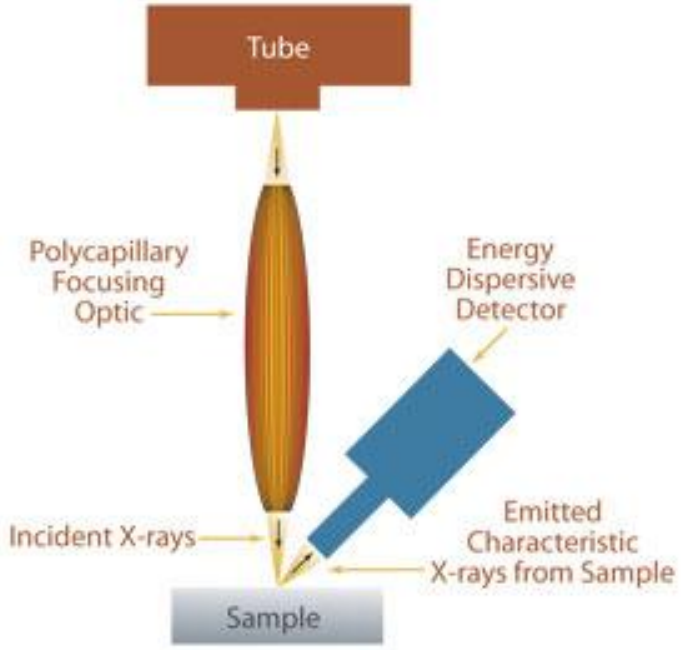
- Principle
  - Energy-dispersive X-ray spectroscopy (EDXRF)
  - Wavelength-dispersive X-ray spectroscopy (WDXRF)



http://www.vesindia.org/KnowledgeCenter.aspx

Mirco X-ray fluorescence (µXRF)

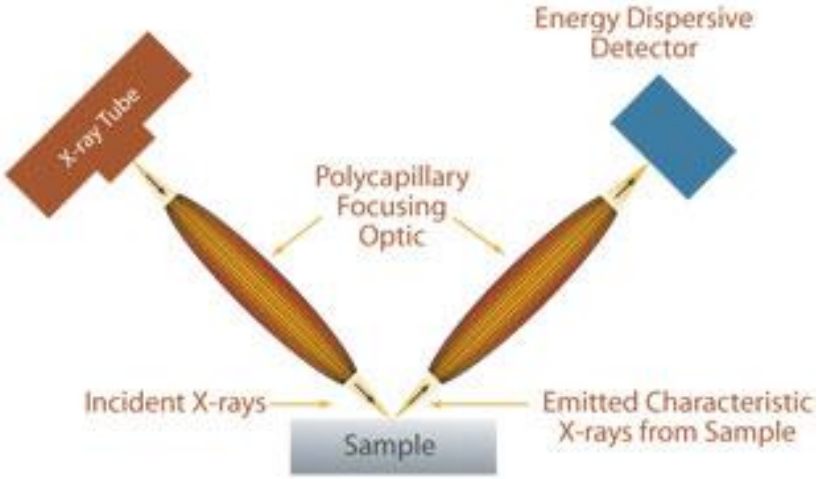
- Often based on EDXRF systems
  - All elements excited simultaneously
  - Fluorescence radiation collected
  - Separate different energies of element characteristic radiation
- Polycapillary focusing optic
  - Spatial resolution in µm range



http://www.xos.com/techniques/xrf/

Confocal μXRF

- depth profiling possible



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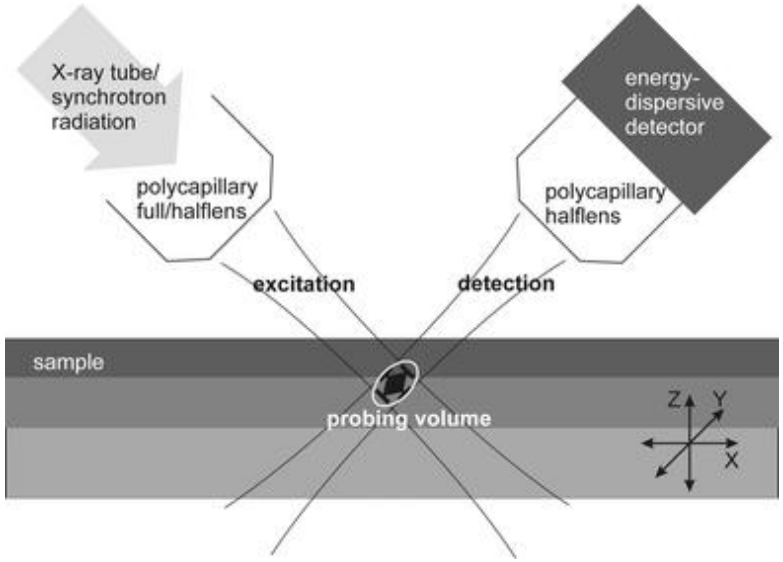
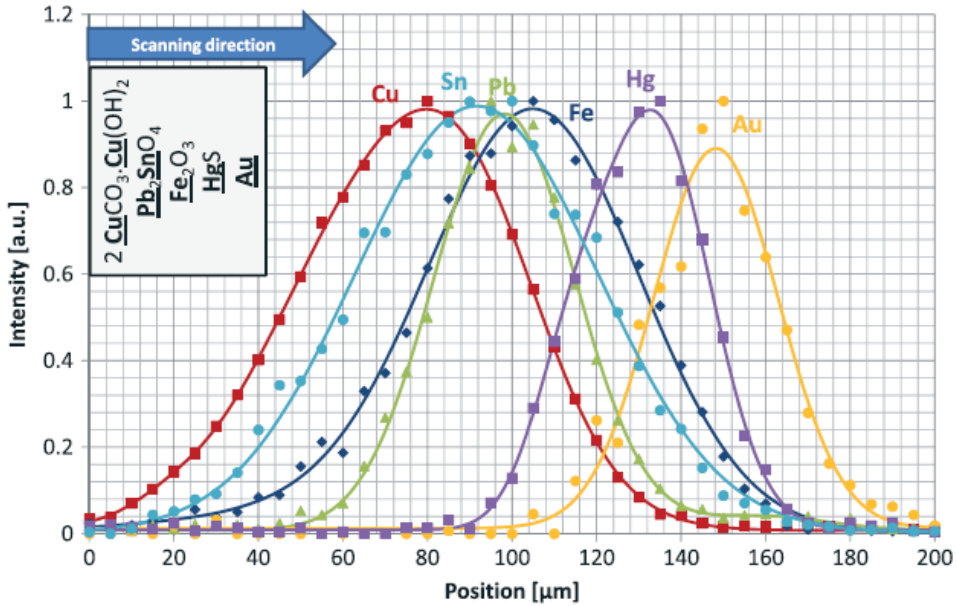


I. Mantouvlou et al., J. Anal At. Spectrom., 2010, 25,544-561

Confocal μXRF - example



S. Smolek et al., X-Ray Spectrom. 2014, 43, 93–101

Advantages (XRF)

- Small sample area
- Trace element concentration (ppm range)
- Very high sensitivity with monochromatic excitation which eliminates the X-ray scattering background under the fluorescence peaks
- Multi-layer coating thickness analysis possible
- Simple
- Fast
- Vertical positioning (working distance) less crucial

Limitations (XRF)

- Atomic number must be Z > 11
- Cannot distinguish among isotopes of an element
- Only elemental composition, no crystal/ligand structure
- Cannot distinguish ions of the same element in different valence states

Copper containing pigments

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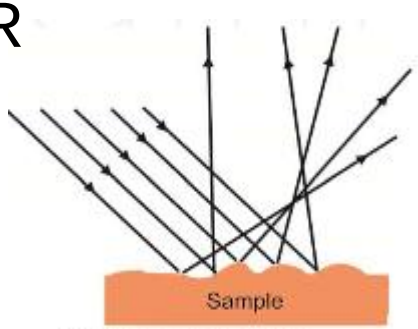
Fourier transform infrared (FT-IR) spectroscopy

- Absorption technology
- IR active transition: change in electric dipole moment
- FTIR-spectrometer has much better signal-to-noise-ratio and needs much less measurement time than a dispersive IR spectrometer
- FTIR spectrometer simultaneously collects spectral data in a wide spectral range
- Diffuse reflectance IR



Diffuse reflection

Advantages (FT-IR)

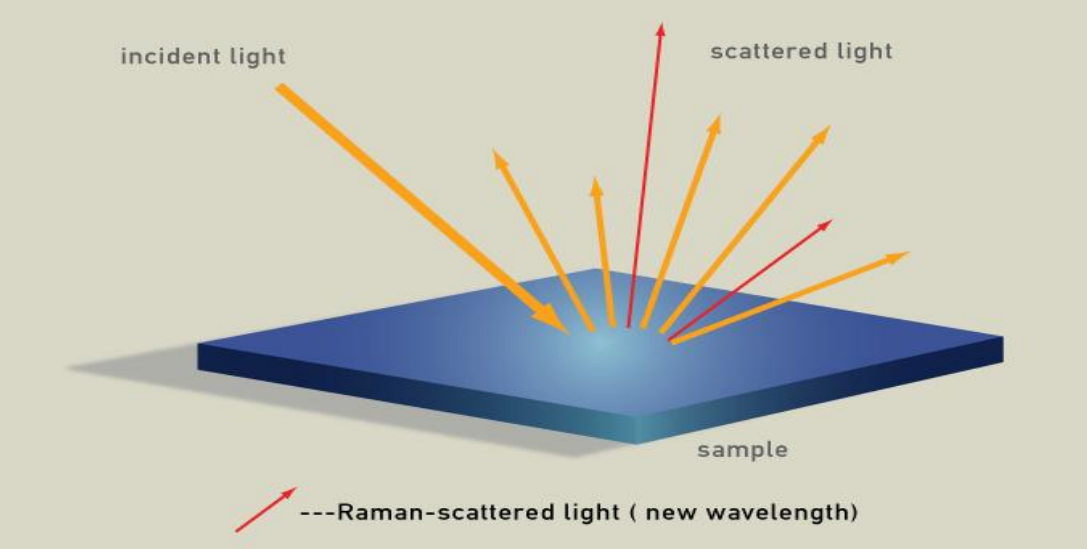
- Detection without contact
- Portable units
- Relatively cheap
- Especially useful in recognizing inorganic mixtures
- Wide application area: pigments as well as organic materials (varnishes, paint media, adhesives, plastics)
- Detects changes in the composition of a material as the result of natural or accelerated aging

Limitations (FT-IR)

- FTIR analysis should be combined with another analytical technique to be reliable
- Lower sensitivity to paint due to other organic material

Raman Spectroscopy

- Light scattering technology
- Approximately one photon out of a million will scatter
- Raman active transition: polarizability of molecule changes



Advantages (Raman)

- Detection without contact
- Location of wavelenghts is independent of the excitation wavelenght: near-infrared region can be used to limit fluorescence to prevent damage to artwork
- Most of the paints can be detected by Raman
- Mobile Raman spectrometers available
- Fast technique
- A few pigments can be analyzed only by Raman and not by FTIR, such as sulfide pigments (eg: cadmium yellow, vermilion) and carbon black pigments of vegetable origin

Limitations (Raman)

- Raman is much less sensitive to organic materials then FT-IR, such as varnishes, binders, and some organic pigments
- Cost of instrumentation is very high
- Low sensitivity
- Competition with fluorescence (doesn't work for anthraquinones and flavonoids)
- In this case SERS is recommended (needs to come in contact with substrate, not allowed in many museums, database not so much established as for Raman)

Thank you for your attention