Portable hybrid ED-XRD and XRF system for non invasive study of cultural Heritage

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SAN GERÓNIMO DE LA HABANA

ICTP, 17 July, 2015

Subjects

- **A Non invasive physical approach to the study of Cultural Heritage**
- **Requirements for the development of Portable multitechnique X-ray based system**
- **Development of Portable hybrid ED-XRD and XRF system for non invasive study of cultural Heritage.**
- **Applications –importance of emphasizing archaeometrical results for cultural heritage studies**

From Science Institution to a Multidisciplinary cultural heritage environment

Havana's Archaeometry Laboratory

- 1995, CNIC-OHCH collaboration
- 1999-00, Project OHCH: Portable XRF
- 2001, Creation of Archaeometry laboratory at Havana's Historian Office (OHCH)
- 2010 Archaeometry laboratory, at Colegio Universitario San Geronimo de La Habana

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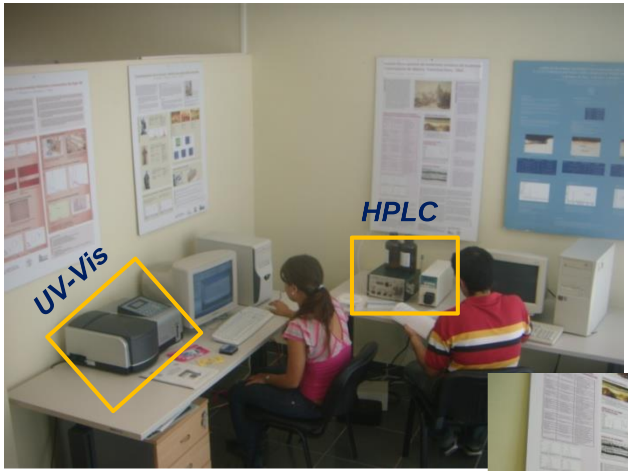
CNIC: National Center for Scientific Research, Havana, Cuba

Archaeometry Laboratory



Expertise:
Physicist, chemist, biochemist, geologist, .., archaeologist, art historian, restaurateurs

Analytical facility: Optical microscopy (**OM**), polarized microscopy
X ray Fluorescence (**XRF**) , X ray diffraction (**XRD**), **radiography**
Ultraviolet-Visible spectrometry (**UV-Vis**), High Performance Liquid Chromatography **(HPLC**)

Multidisciplinary environment

" Archaeology Cabinet"

" Conservation and restoration Cabinet"

•Workshop for paper
• Workshop for ceramic
• Workshop for polychrome
• Workshop for metals
• Workshops for easel painting
• Workshop for wall paintings
•…..

• Laboratory of Chemistry
• Laboratory of Microbiology

Physical methods for Cultural heritage

Non invasive | ***Non invasive Physical approach*** | **Non destructive**

1 Non invasive analysis

without sampling

2 Non destructive microanalysis

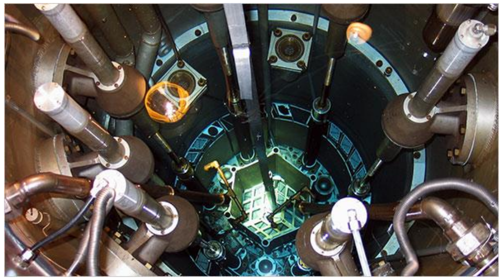
minimum sampling

3 Destructive microanalysis

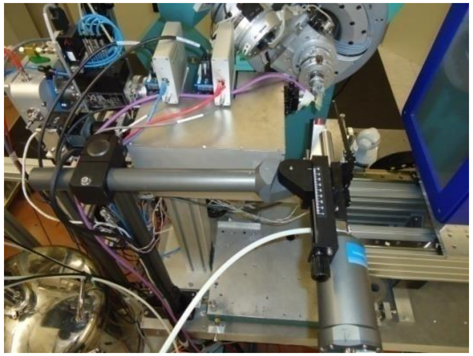
minimum sampling

sample is destroyed

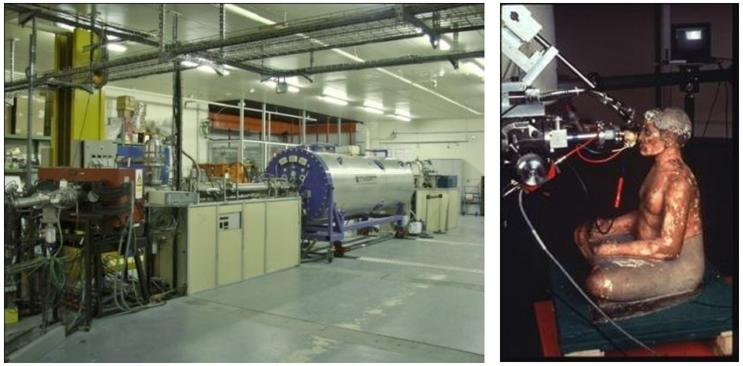
* Microanalysis - micro area analyzed
(non invasive and/or non destructive)



NAA



SXRD, Elettra



PIXE, Louvre

Non invasive analysis

“Suppose that we are studying Neolithic axes made of **jade**, and that we have a few specimens which arrived to us intact. The idea of drilling a hole of one centimeter in diameter in order to characterize the stone and even get information on the provenance is obviously not acceptable. In fact, we have to consider the enormous steps forward that modern techniques are making every day in the direction of rendering the analytical interventions less destructive. So, even **if today we do not have at our disposal a non-invasive method, this may very well be found in a few years.** We are compelled to wait longer in order to satisfy our curiosity, and leave the object intact”.

-It may be more difficult to make a decision when the information we are looking for is vital to establish the correct way to intervene in the conservation process of an object which is in serious danger of destruction.

Reflection of Giacomo Chiari (crystallographer and head of Conservation Department at Gety Museum) in 1999 published on

“The role of science for the conservation of cultural heritage. Definition and importance of Non-destructive and Micro-destructive methods: advantages, limits and field application. Systematic approach to conservation problems”

A non invasive Physical approach

Material punctual analysis

XRF* pigments, inks, and minerals

Non invasives

XRD minerales

Microanalysis

Organic materials

UV inks, organic dye stuff

FTIR pigments, binders

GC/HPLC-MS

Object's structural analysis

Non invasives

Photography of UV reflectance

Infrared reflectance

Radiography

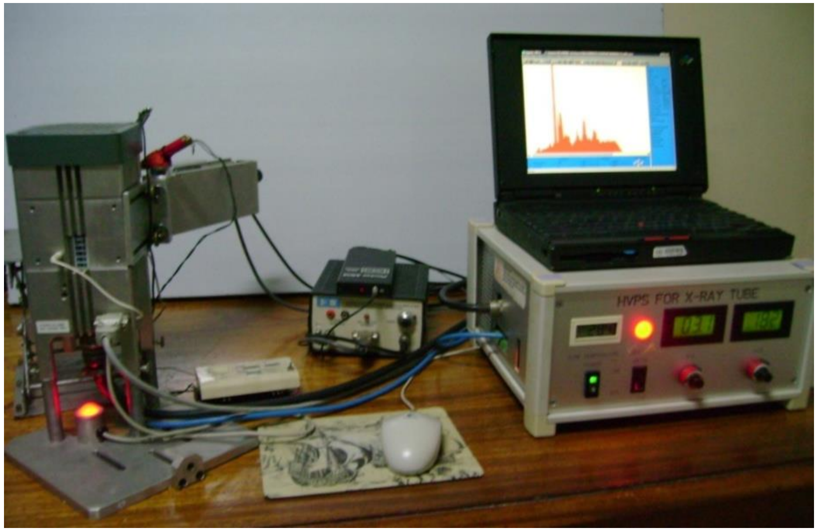
Tomography

* **Elemental and stratigraphical microanalysis μ–XRF, μ–PIXE, SEM-EDX**

Laboratory-developed portable X-ray analyzer

- Development of new technology -

- **X- Ray Fluorescence (XRF)**
  chemical elements (atoms)
- **X-Ray Diffraction (XRD)**
  Chemical compound, crystalline
- **Radiography**
  internal structure of object

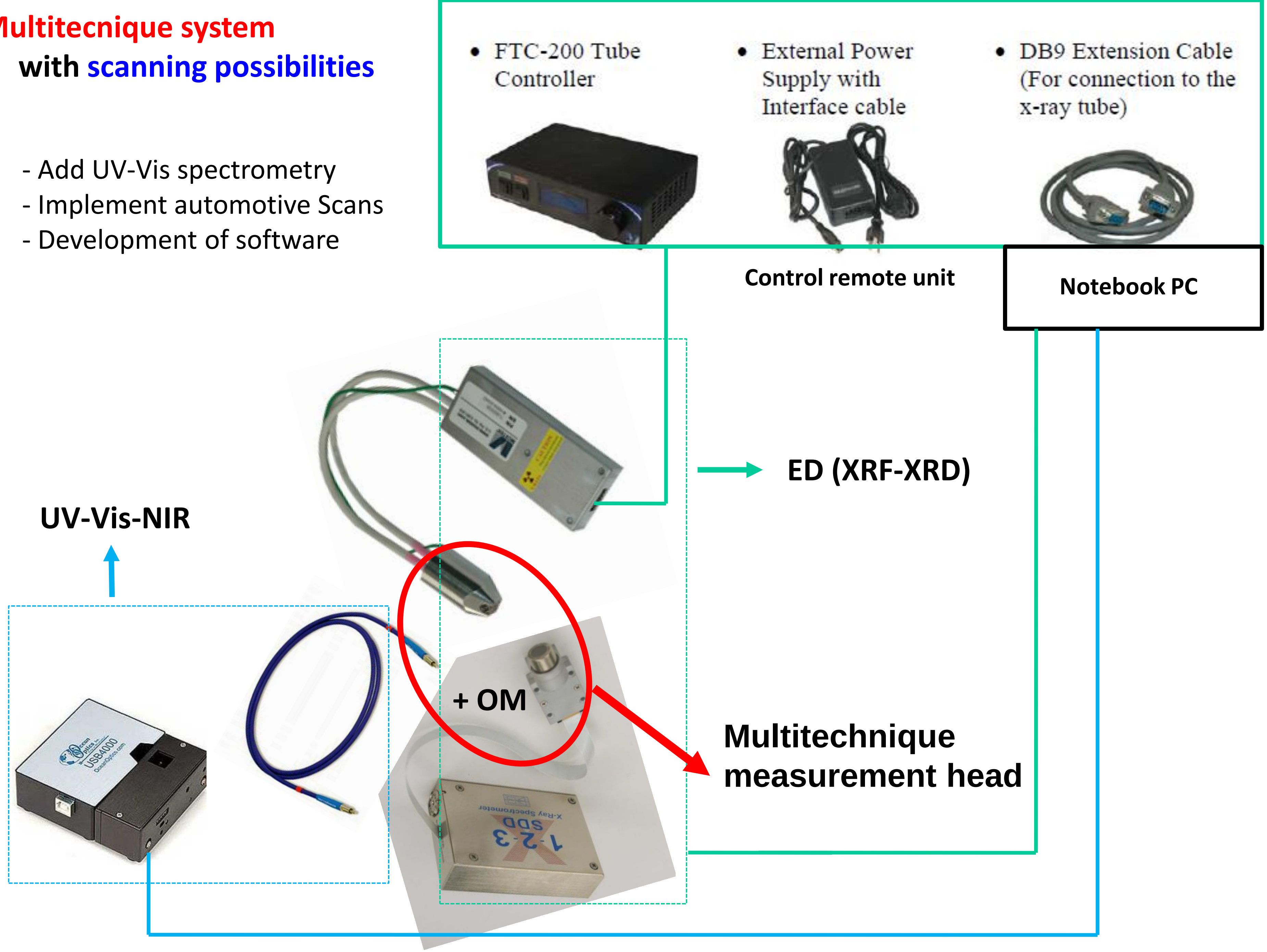


UV-Vis, FTIR

molecular composition

Multitecnique system with scanning possibilities

- Add UV-Vis spectrometry
- Implement automotive Scans
- Development of software



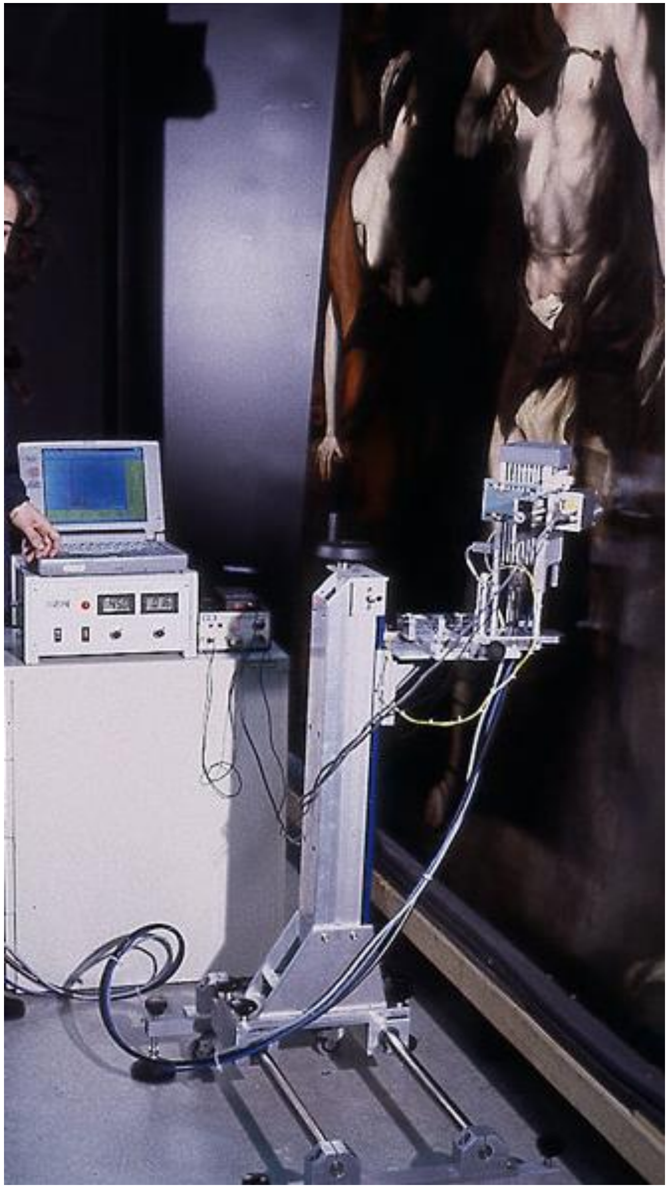
Method for phase identification

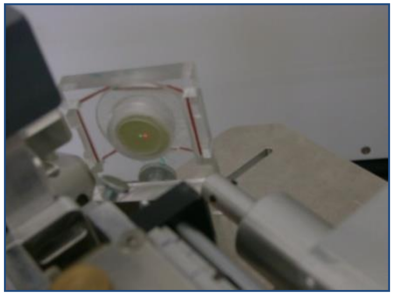
P XRF-XRD ?

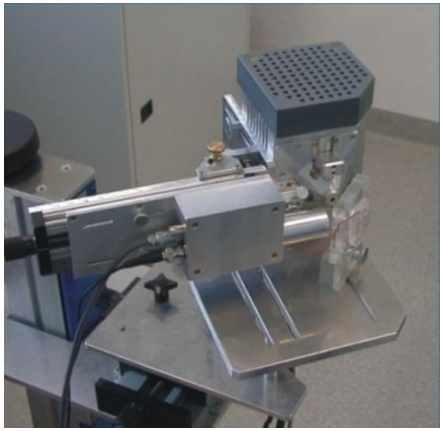
P XRF- Raman ?

Powder XRD	Raman spectroscopy
Sample should be polycristalline, otherwise sampling and pulverization, prior to the measurement is necessary.	Samples do not need pretreatment or preparation prior to the analysis
Information for crystalline materials Not information for amorhous material	Information for crystalline and amorphous materials
Diffraction peaks are broadening and decrease of their intensity when the materials are poorly crystalline.	Data is sensitive to wave lenght of the laser: ex : for the analysis of some blue and green pigment red laser (785 nm) is not suitable or metal object such as gold leaf
Non destructive with respect to the sample	Careful regulation of powder of the laser, which not may destroy sample.
Interpretation of data is straighforward (complete reference data is available)	Interpretation of data is rather difficult
Difractogram can be simulatated from the crystal structure data of material. It has an additive property (principle of superposition)	Spectrum of the mixtures does not agree in a quantitative way with the principle of superposition

Introduction of new technology





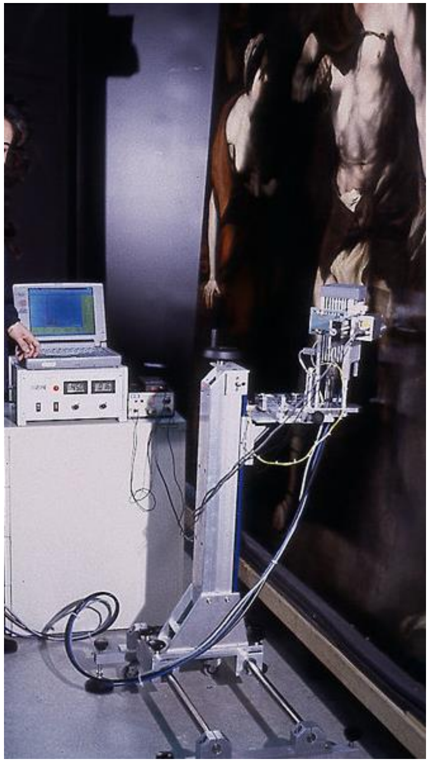


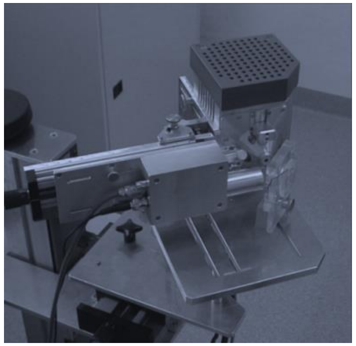
Art x Art

Analytical radiation technique for Art

Project (1999-2000) Development of portable X-ray fluorescence system for the characterization of artistic and archaeological materials

Havana's Archaeometry Laboratory and IAEA

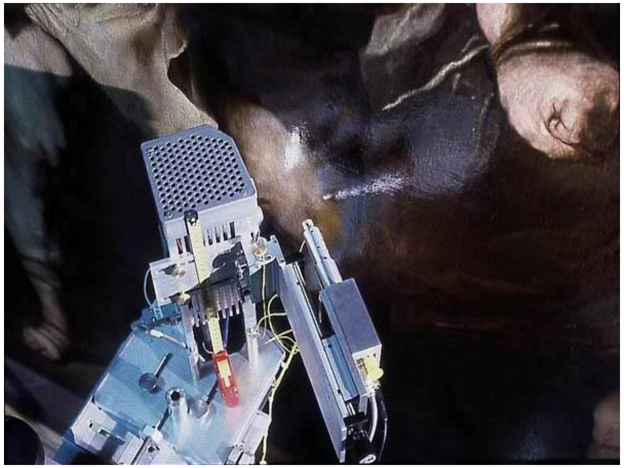




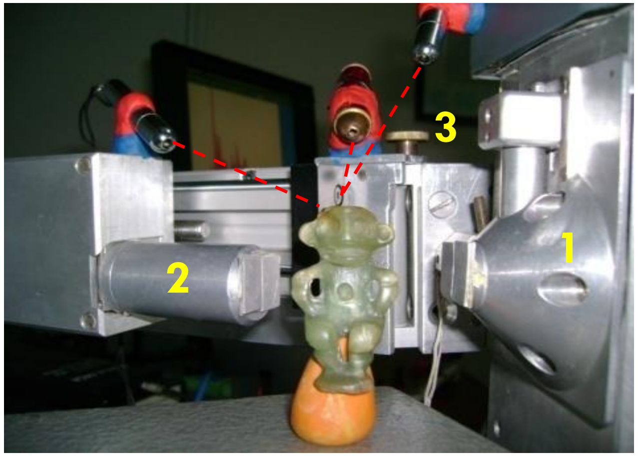
1st prototype
Portable mili (1 , 10 mm) - XRF
at Archaeometery Laboratory, Havana, Cuba

2nd prototype
portable mili (1 , 10 mm) or **micro- XRF**
at IAEA' laboratory, Seibersorf , Austria

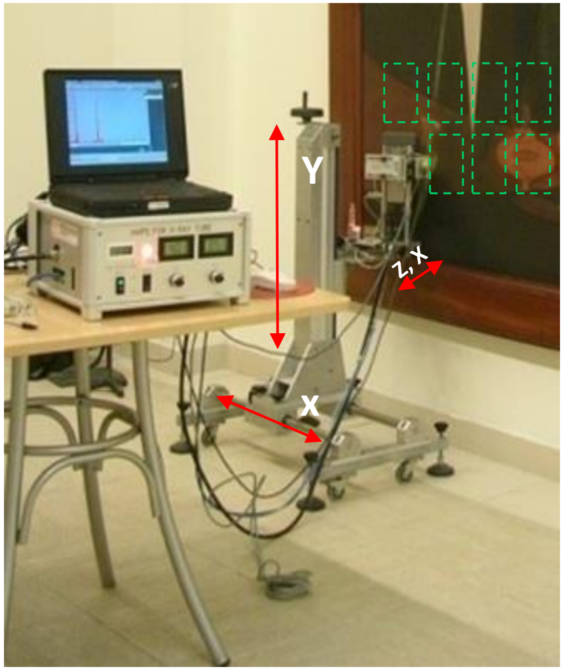
ED-XRF (1999-00)



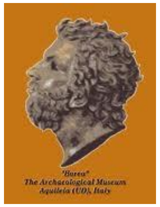
ED-XRD (2004)



Radiography (2006)



Poster
"Development of Portable ED XRF-XRD and Radiograhy for Archaeometry"



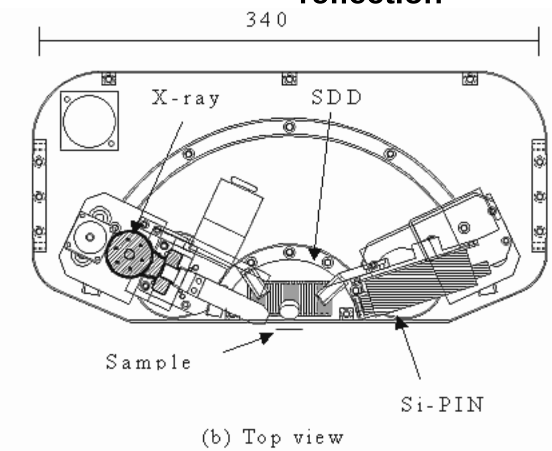
Presented for first time,
International Workshop on Science for Cultural Heritage,
ICTP, 23 - 28 October 2006

A. Mendoza Cuevas , H. Perez Gravié; Portable Energy Dispersive X-ray fluorescence and X-ray diffraction and radiography system for archaeometry, Nuclear Inst. and Methods in Physics Research, A 633, (2011), pp. 72-78, DOI information: 10.1016/j.nima.2010.12.178

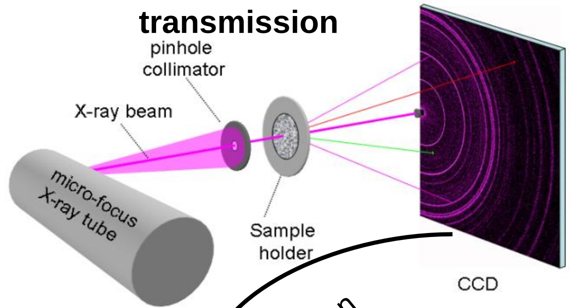
State of Art
Portable XRF-XRD or XRD system

XRF-XRD

reflection



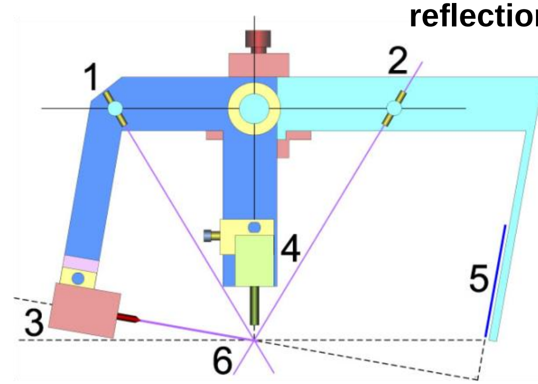
transmission



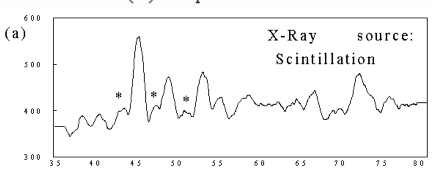
Integration software

2005

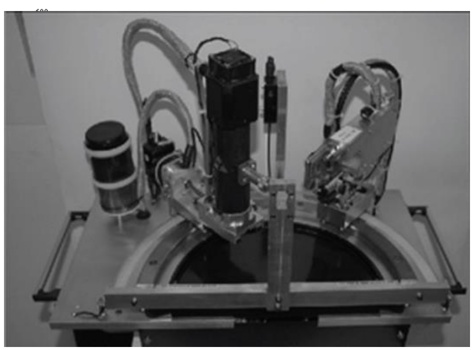
reflection

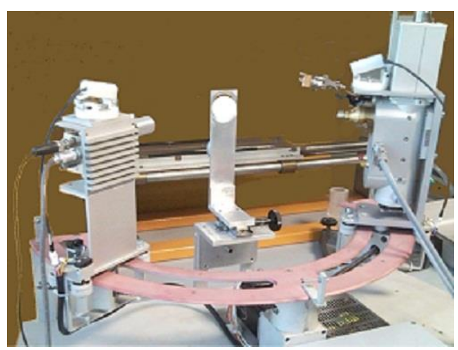


2008, 2010



XRD





2009, 2010

2 D detector	Goniometer
IP 20-60º CD 20-50º	0 - 90º 0 - 120º
tm IP- 15-40 min. CD 8.3 h integration (20-50°)	tm = 32.4 h (20 – 90°)
weight IP 6 kg + 18 kg IP reader ~10 kg CD 7kg + 12 kg unknown weight for support	15, 25, 27 kg unknown weight for support
Positioning with respect to the objects is critical	

Non invasive and in situ XRD

Angle Dispersive X-ray diffraction

Energy Dispersive X- Ray Diffraction

Conventional diffractometer

$\lambda = 2\ d\ sen\ \theta$

(XRD monochromatic beam)

Bragg Law

$E\ d\ sen\ \theta = 6.19926\ keV\ Å$

(XRD polychromatic beam)

State of art (2005-15)

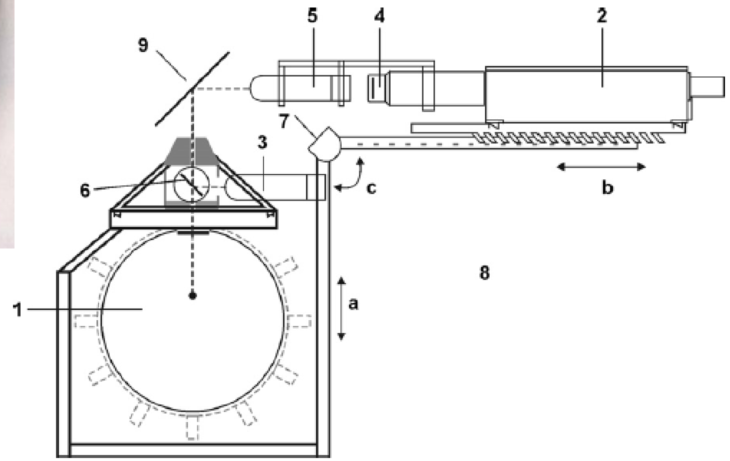
XRF-XRD	Proposal (2004, 2009-15)
Fe, Cr, Cu anode, low X ray penetration	Pd, Ag anode, higher X-ray penetration
Monochromatic and parallel beam	Polychromatic and parallel beam
Angle dispersive detection -> longer tm	Energy dispersive detector -> shorter tm
Two detector (energy and area detector) or one (2D) detector	One ED detector
Weak XRF X-ray excitation	Intense XRF excitation (minor and some trace analysis)
	Higher energy penetration
	a wider accessible region of the reciprocal space (q) $\Delta q = q_{max} - q_{min} = aE_{max} \sin\theta_{max} - aE_{min} \sin\theta_{min}$

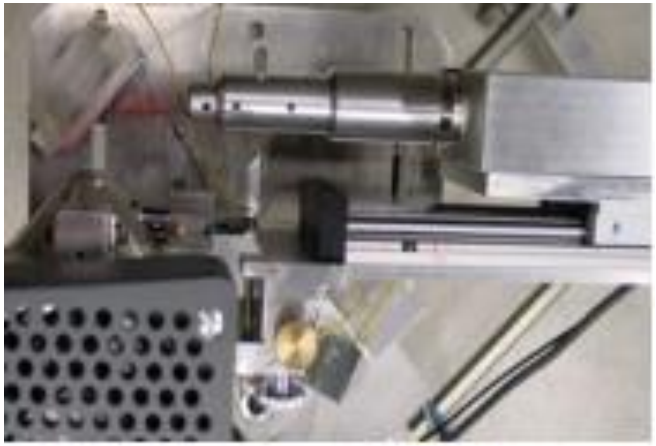
Prototypes XRF – XRD	Proposal XRF- XRD
Cu anode with selective blank (W, Ag y Cr) (D2) Rotatory anode: Cr, Cu and W (D3) or Co and Cu (D5). Fe, Cr o Cu anode (D1, D4) -> low penetration of X rays and weak XRF excitation	Pd, Ag and Rh anode – higher penetration of X rays and good XRF excitation
Weak excitation of XRF -> detection of mayor elements (D1, D2, D3, D4, D5)	Intense XRF excitation -> detection of major, minor and trace elements
(quasi) monocromatic and parallel beam	Pollycromatic and parallel beam
Angle dispersive detection -> longer tm (D1, D2, D3, D4, D5)	Energy dispersive detection principle -> shorter tm
Measurement time (tm) for geometry $\theta - \theta$: aprox. 30 min (D2, D3) using 2D detector 20-50°): CD 8.3 h (D4), IP 15-40 min (D5).	Measurement time (tm): 5-10 ^{1} s for obtaining first difractogram and in the orden of 10^2 s for collecting higher intensity of counts
Two detectors (energy dispersive detector (Si-PIN or Si-drift) or 2D area detectors (D2, D3, D4) -> more weigh, less compact and higher economic cost. (D1, D5).	One energy dispersive detector -> less weight, more compact and lower economic cost.
Critical positioning with respect to the analyzed object.	Flexible positioning adequated to the geometry of analyzed object. A light with the shape of beam is visualized on the object's surface.

D1: Advances in X-ray analysis, Vol. 48 (2005)
D2: http://www.ndt.net/article/apcndt01/papers/1175/1175.htm
D3: Bunseki kagaku58, Japón, 2009
D4: www.interscience.wiley.com, WO2008125450, Francia 2008
D5: URL: http://www.getty.edu/conservation/science/about/portable_xrd_xrf.pdf, Estados Unidos, 2008

Review Portable X-ray powder diffractometer for the analysis of art and archaeological materials, Izumi NAKAI and Yoshinari ABE, 2011

Proposal XRF-XRD analyzer setup





Features (XRF)

Miniaturized X-ray tube (50 kV, 1 mA, Pd anode)

Si-PIN detector with energy resolution of 250 eV.
(Peltier cooling)

Selective source collimation
(submilimiter or 1 cm irradiated spot)

Polychromatic and divergence beam

versatile geometry
(X-ray tube-sample- detector distance and angle (0-90)

Modifications (XRD)

- **Wider angle range (2θ: 0-180)**
- **Selective slit source and detector collimation**
- **polychromatic and parallel beam**
- **Changes on positioning device**
- **idea of detection principle by ED XRD**

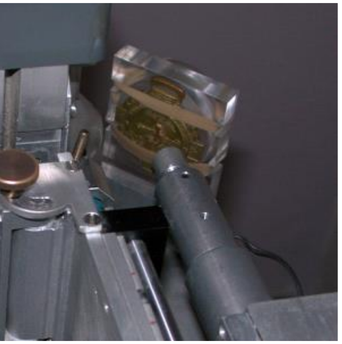
Non invasive and in situ X-ray analysis (2000-15)

XRF *

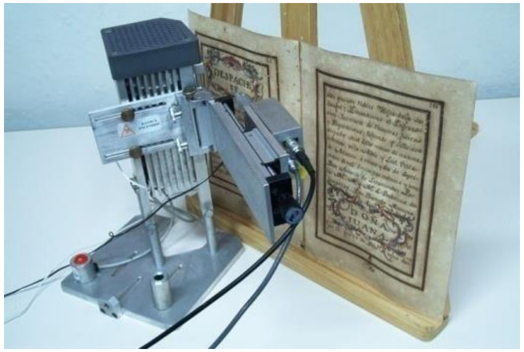
Sevres porcelain

Lam's easel paintings at Havana's Fine Art Museum

polychromes



medals

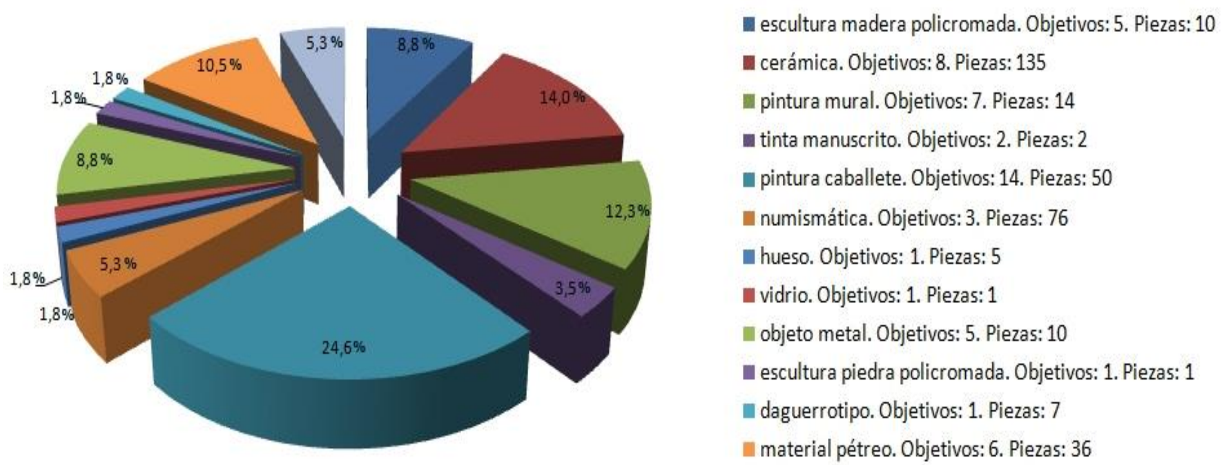


manuscripts

Minerals sculpture

daguerreotypes

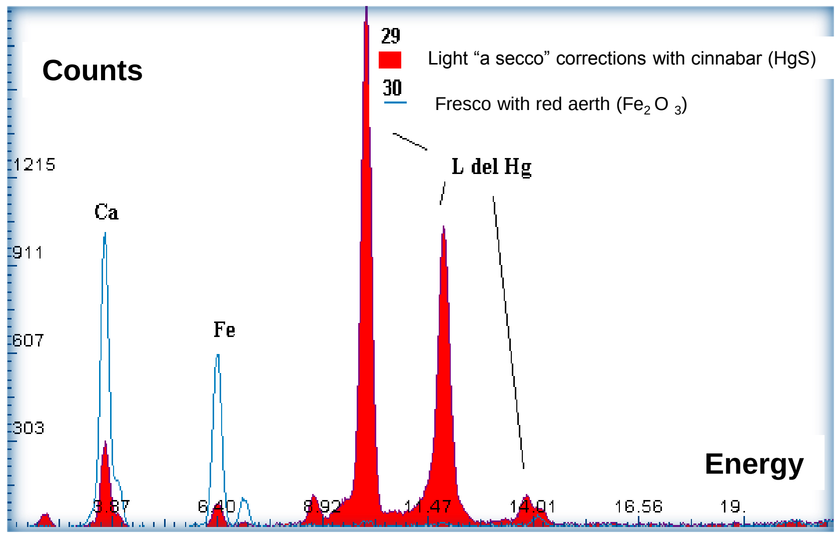
From selected comun applications we'll deduce aditional requirements for the development of new advanced multitechnique Portable X-ray system



Pigments and artistic technique

Ca intensity

- High **Fresco**
- Attenuatted **Seco**



Binder

Microanalysis (ovoalbumine) -> Egg tempera

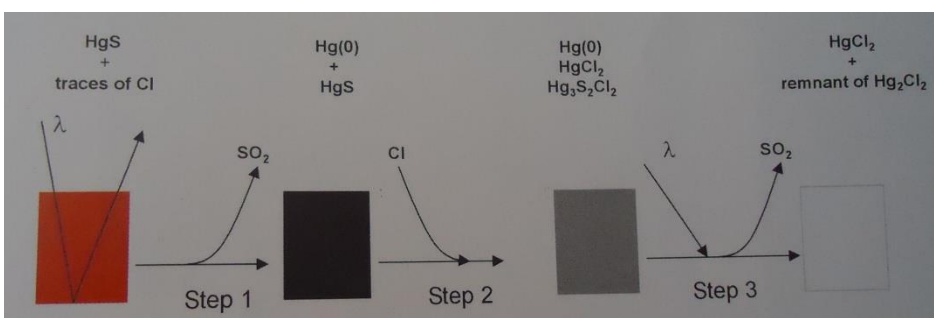
HPLC

A.Mendoza Cuevas, G. Rodríguez, J. Nazco, Tacón 12 a la luz de la investigación Arquemétrica", Revista Opus-Habana, Vol. VI No. 3/2002, 58-67, 2002

Digital restoration

Wall paintings

with original color



K.Kaune, 2005

- **Elemental distribution -> 2D Scanning (X, Y)**
  fine mov. (0.1 mm)

Other applications:
Non legible pictorial art or
writing of historical manuscript

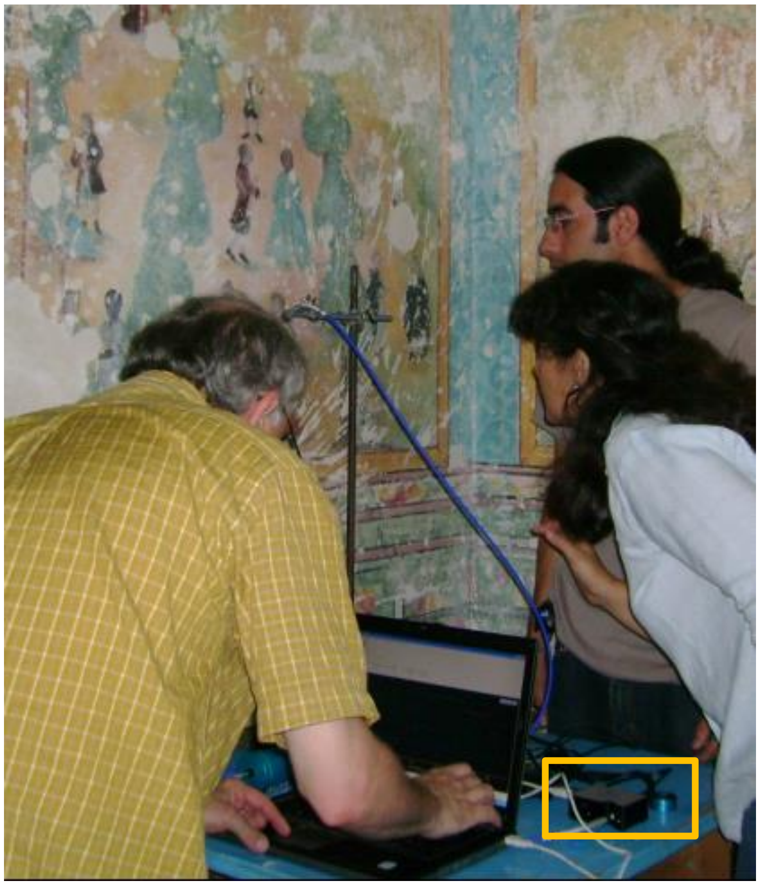
Artistic appreciation

Ultramarine $Na_{8-10}Al_6Si_6O_{24}S_{2-4}$

Wall paintings

Portable UV-Vis-NIR spectrometer

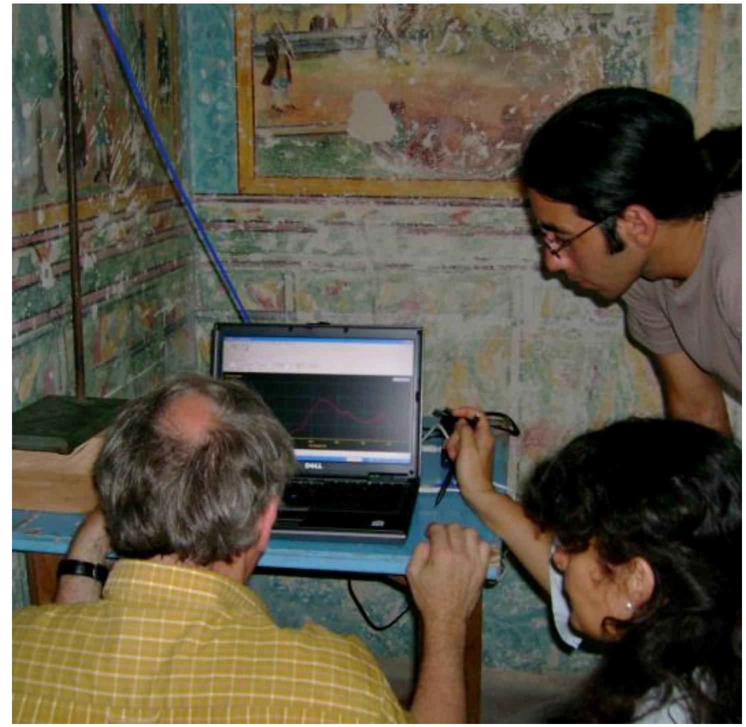
Complementary analysis



Si- XRF

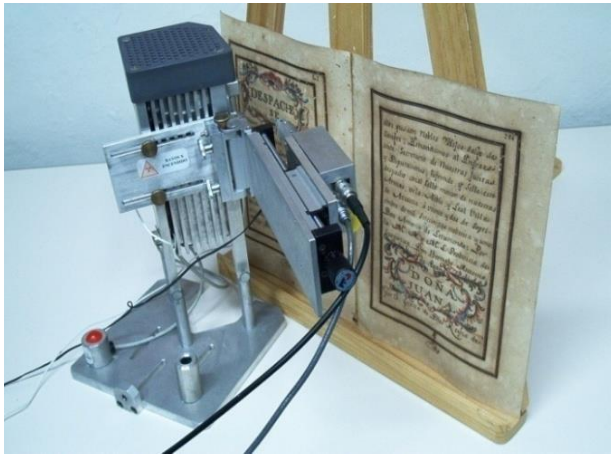
- Light element determination

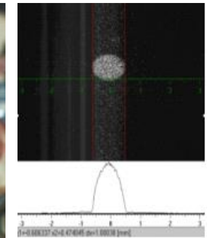
Ultramarine identification



Identification of organic pigment

Manuscripts



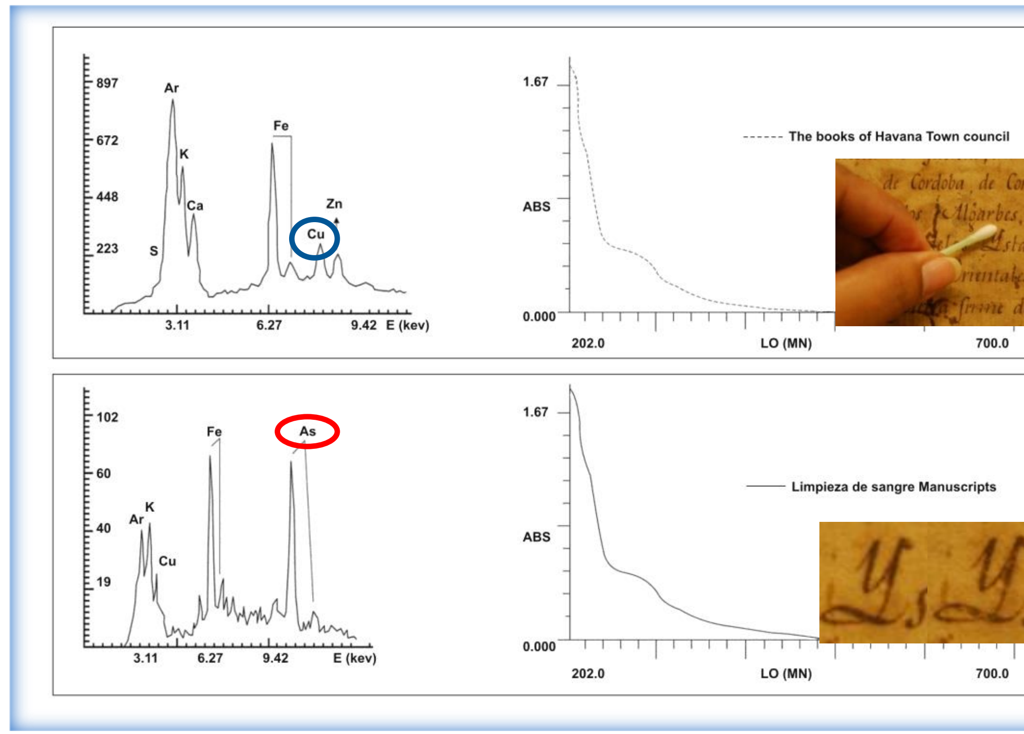


0.2-0.3 mm

Irradiated spot

Positioning /Reproducibility

UV Microanalysis



Iron-gall ink

- Treatment with phytates

Iron-gall inks with Cu

- Treatment with ammonium tetrabutyl bromide

As presence

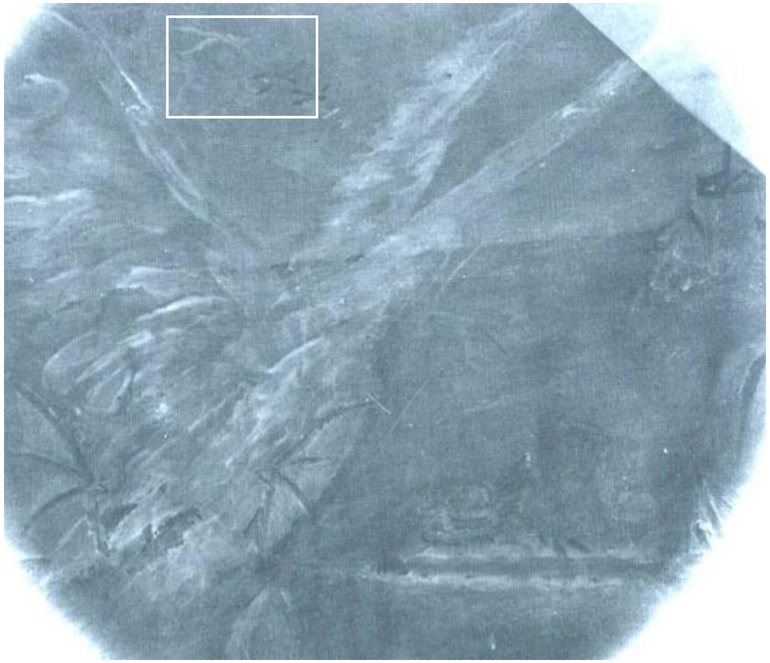
- Use of gloves and safety masks.

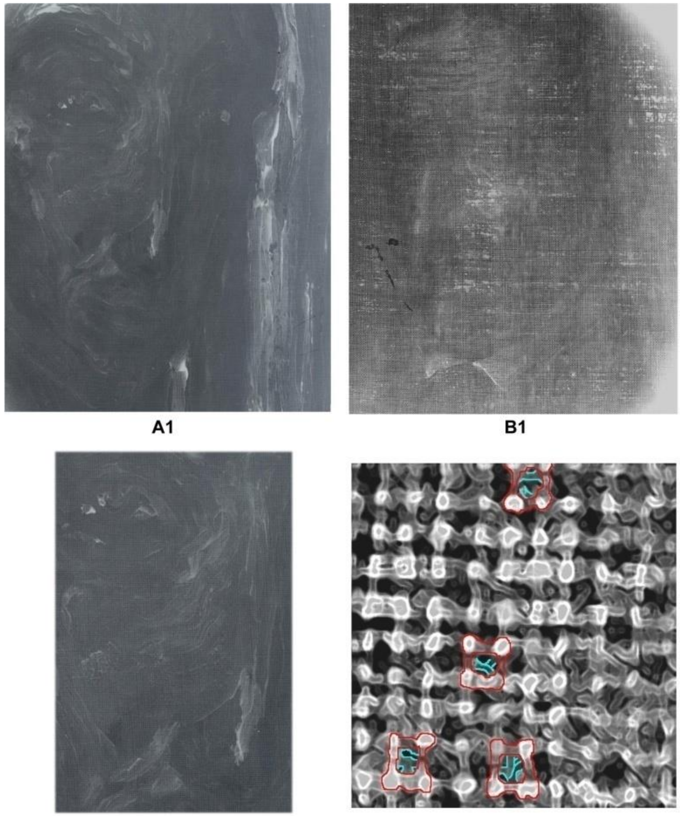
XRF + UV

A. Mendoza, M. Correa, Identificación de tintas metalo-gálicas en manuscritos históricos mediante análisis ni destructivo combinado de espectrometría de fluorescencia de rayos-X y ultravioleta visible", Revista cubana de Química, Vol. XXI, Nº 1, 2009

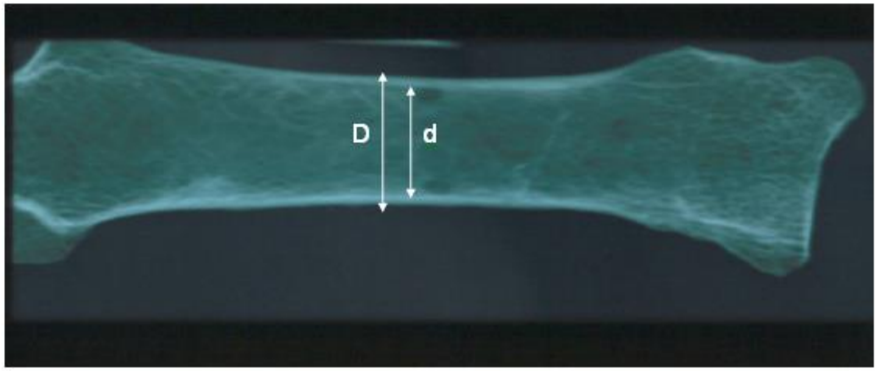
Conservation and restoration

Radiography





Paintings



Archaeological human second metacarpial bone

Radiogrametry

Cortical index = [(D-d)/D] x 100

- **2D Scanning (X, Y)**
  gross mov.

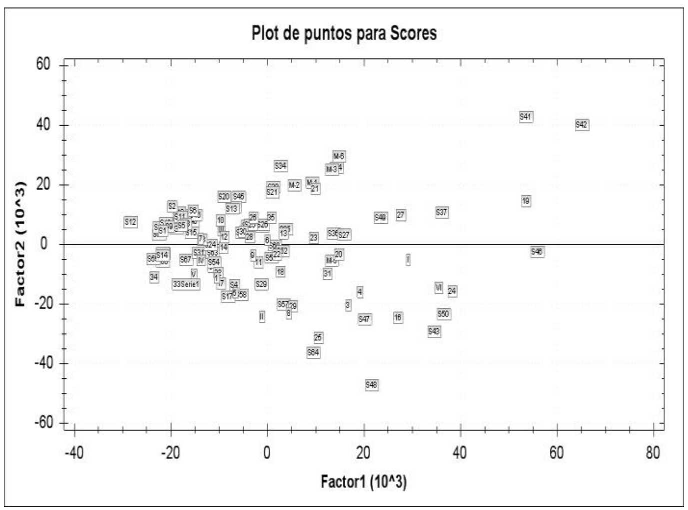
Mexican Red archaeological ceramic

(after prehispanic Azteca Roja, 1570-1780)

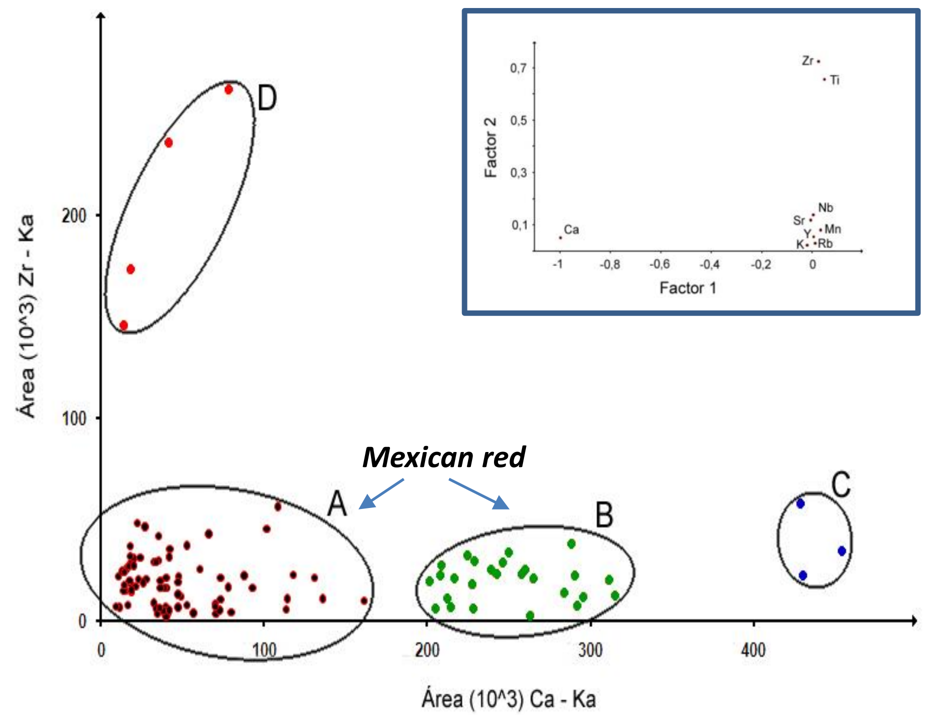
Provenance study

Multivariate analysis (HCA – PCA)

- **Non homogeneus paste (1cm irradiated spot)**
- **Reproducible object sample positioning**



trace elements



K, Ca, Ti, Mn, Rb, Sr, Y, Zr, Nb

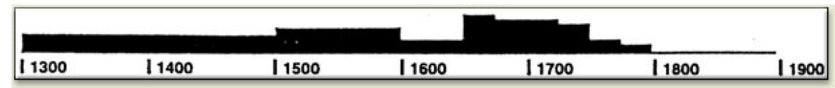
A. Mendoza Cuevas, L. Velázquez Maldonado, A. Rodríguez Vega, Y. Hidalgo Navarro, M. Zamora Barrabí, Caracterización de pasta cerámica con un sistema de Fluorescencia de rayos X Portátil. Estudio de la cerámica “Méjico Rojo”: hallazgo arqueológico en el Convento Santa Teresa en el Centro Histórico de Ciudad de La Habana, simposio del 53 International Congress of americanist, Taller: Nuevos aportes de las técnicas de Arqueometría en el estudio y caracterización del patrimonio cultural, aceptado2010

XVII century

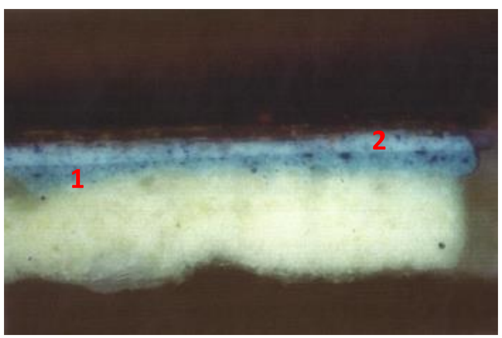
Polychromes

Attribution of (Indirect) dating

Natural ultramar (< 1828 >)

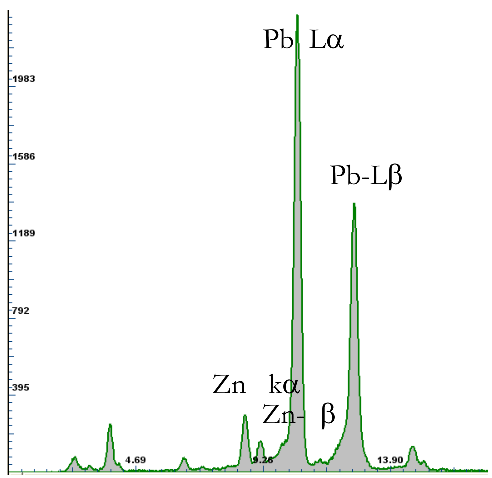


Ultramar $Na_{6-10}Al_6Si_6O_{24}S_{2-4}$

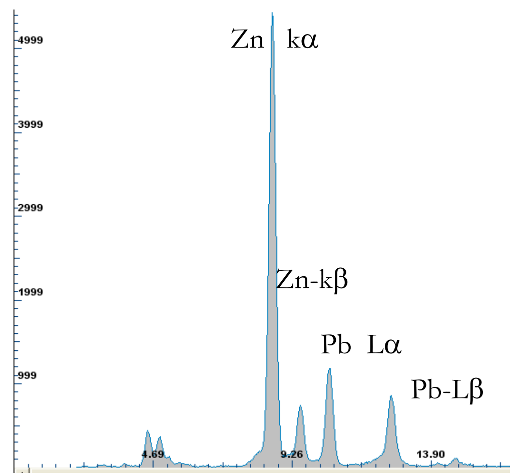


Stratigraphical analysis

Non invasive PXRF



1



2

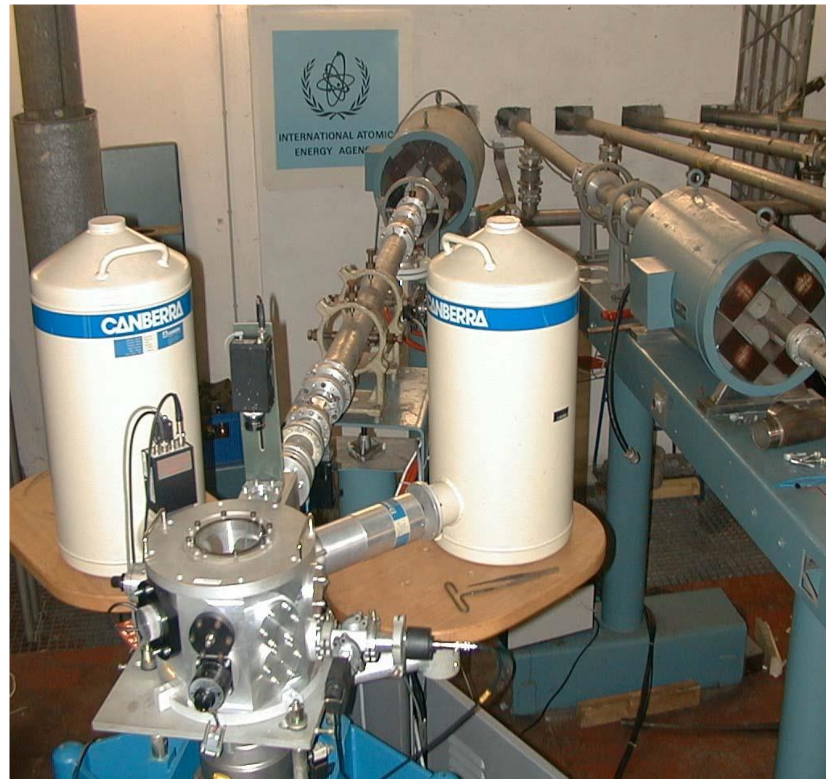
Original color ?

A. Mendoza Cuevas, Microanálisis de capas pictóricas en esculturas policromadas, revista Nucleus, No. 44, 2008

Stratigraphical non destructive microanalysis

μXRF

μPIXE



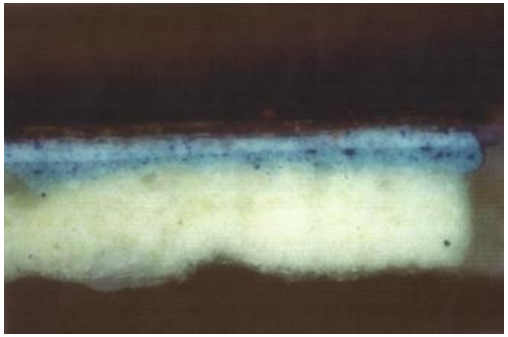
Test the potentiality of μXRF on the study of <u>paint layers</u> in cross section samples of polychrome sculpture

- **μXRF is improving its spatial resolution and X ray optics can be iinstalled n conventional laboratory tube based XRF system.**

μXRF: micro X ray Proton Ray Fluorescence

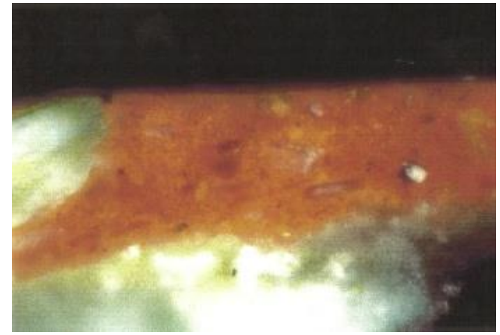
μPIXE: micro Proton Induced X-ray Emission

μ XRF



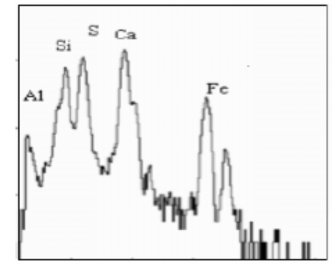
Smalt blue (Si, tr Co)

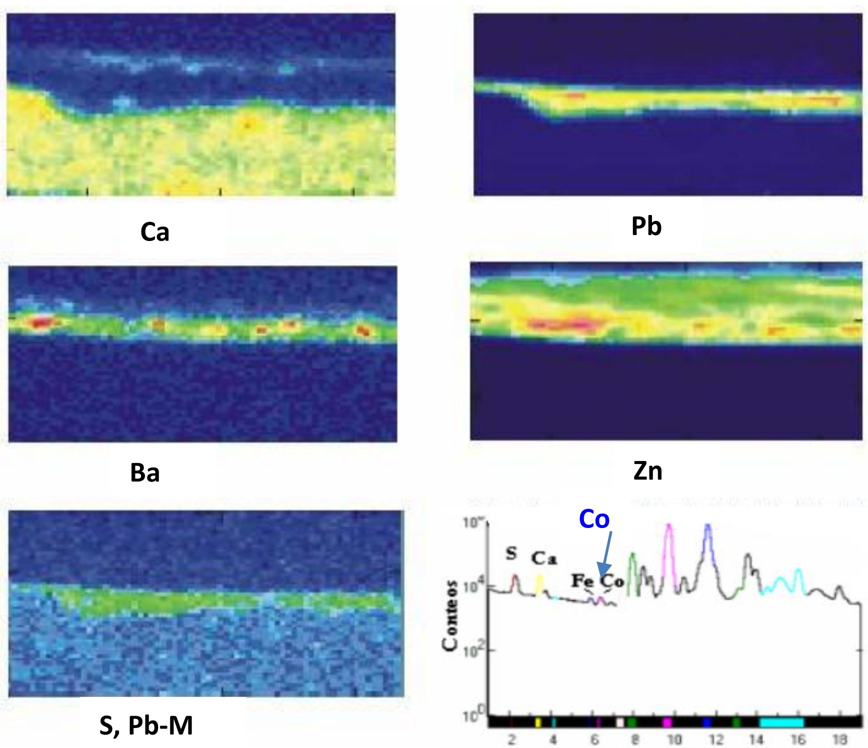
μ PIXE

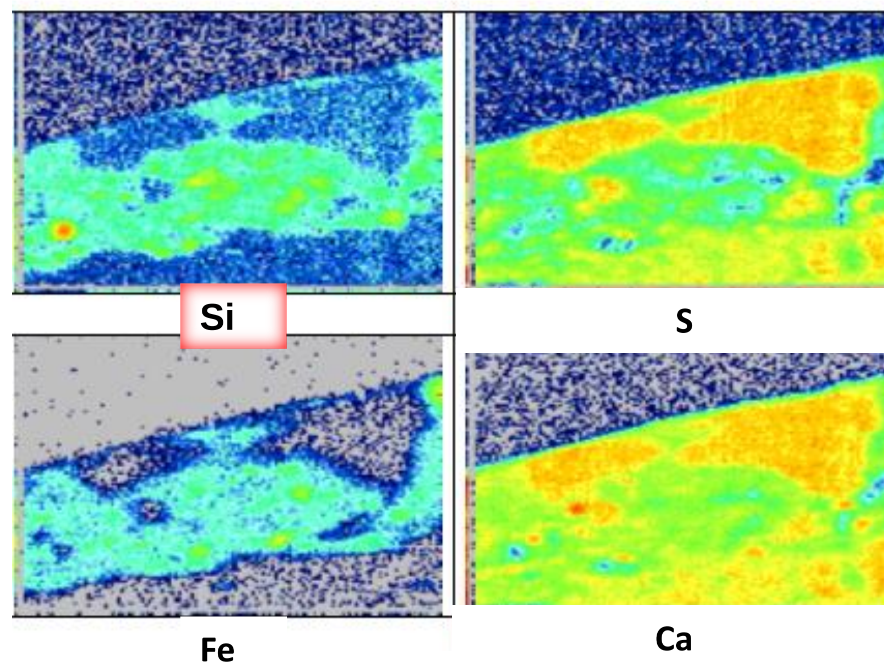


Red, Armenian bol (Fe*, Al, Si)

RBS







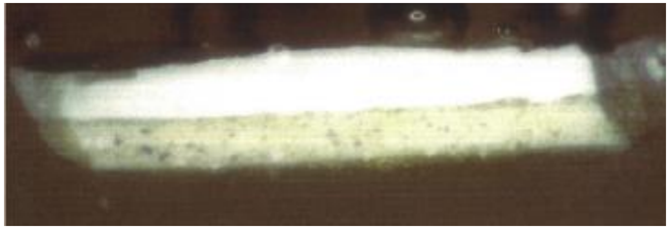
A. Mendoza Cuevas, Microanálisis de capas pictóricas en esculturas policromadas, revista Nucleus, No. 44, 2008

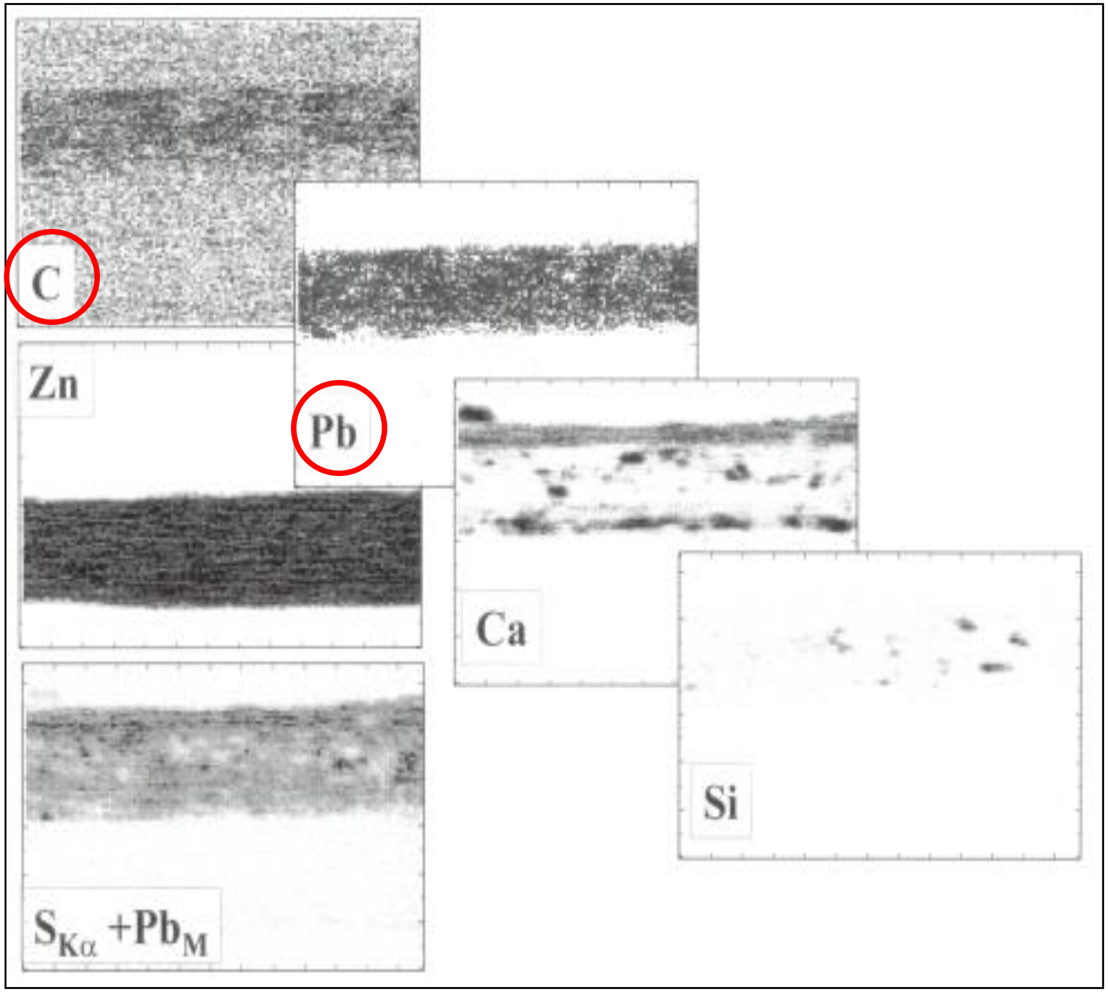
It would be good if PXRF system reach to detect light elements !

μ PIXE - μ RBS

correlation

With sampling





Lead white $Pb_3 (CO_3)2(OH)_2$
(Albayald)

A. Mendoza Cuevas, Microanálisis de capas pictóricas en esculturas policromadas, revista Nucleus, No. 44, 2008

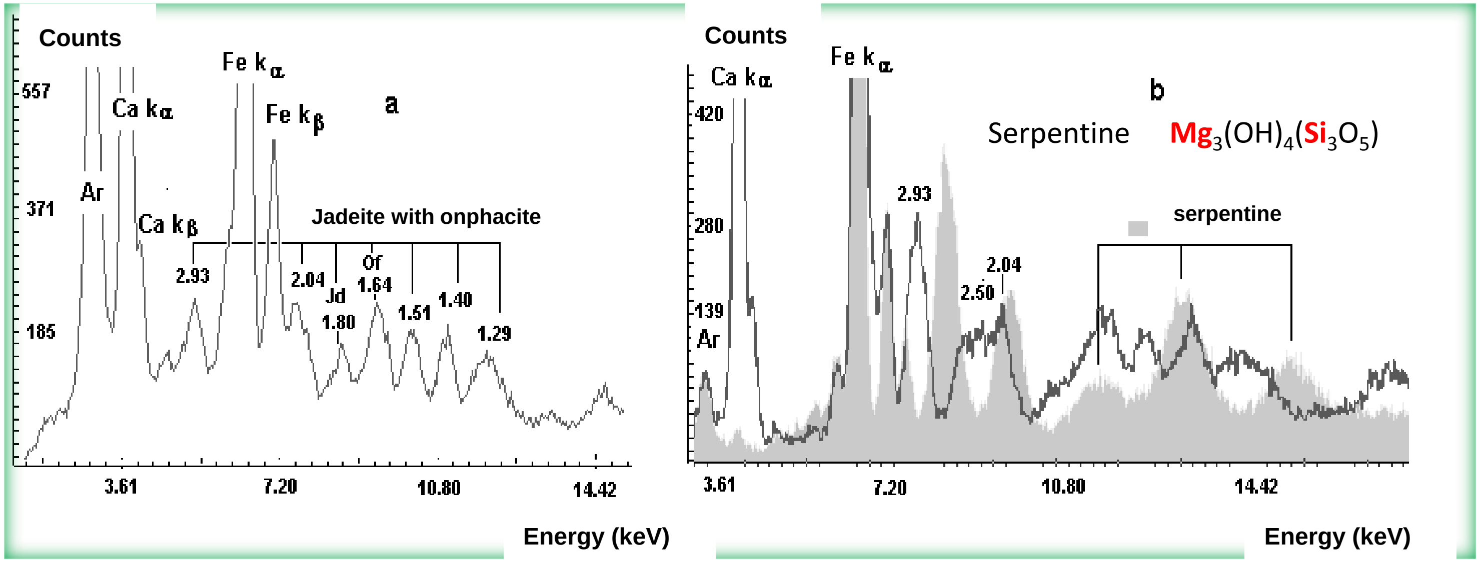
Jadeite **$NaAlSi_2O_6$** or $Na(Al,Fe^{3+})Si_2O_6$
Nephrite $Ca_2(Mg,Fe)_5Si_8O_{22}(OH)_2$
Omphacite $Ca_{0.6}Na_{0.3}Mg_{0.6}Al_{0.3}Fe^{2+}_{0.1}Si_2O_6$

Identification of gemstone and other minerals

ED - XRD

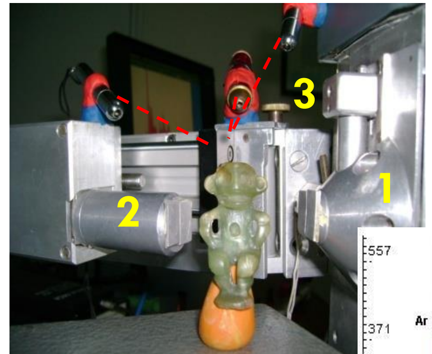
- **XRD as complementary analysis to XRF**

Non invasive XRD



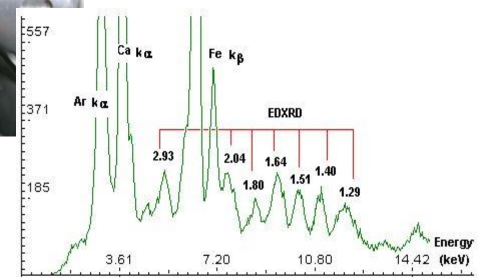
A. Mendoza Cuevas, H. Pérez Gavié, A. Rodríguez Vega, A. Quevedo, Identificación no destructiva e in situ de Jade en objetos arqueológicos con un nuevo sistema portátil de Difracción de rayos X y Fluorescencia de rayos X. Primeros análisis de objetos en piedra verde de la cultura aborigen Taína, **Libro Taller de Jade y Piedras verdes,** del 53ICA, México, accepted in 2010

Project (2004-06): Portable X-ray system for the non destructive characterization of artistic and archaeological material, Havana's Archaeometry Laboratory



XRD

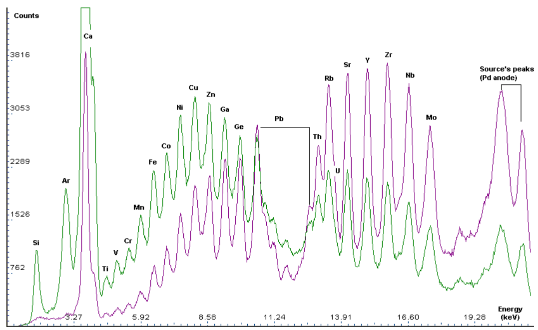
XRD in archaeological jade objects (Taino's aborigine idols and axes)



Identification of **jadeite and onphacite**

XRF

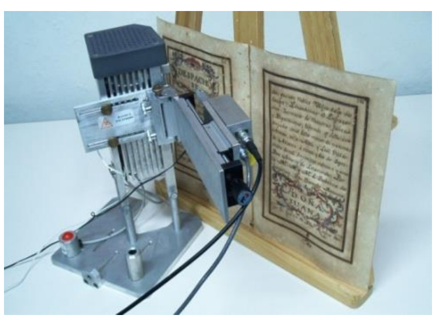
mayor, minor and trace

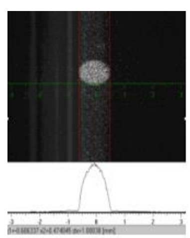


500 ppm glass (SRM: NBS610)

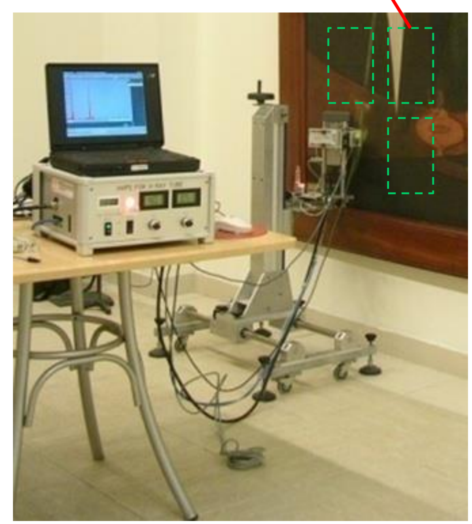
Beam dimensions

sub-mm beam for XRF analysis of manuscript's ink
or 1 cm beam for non homogeneous samples as archaeological ceramics





2D scanning - **Radiography**



A. Mendoza Cuevas , H. Perez Gravié; Portable Energy Dispersive X-ray fluorescence and X-ray diffraction and radiography system for archaeometry, Nuclear Inst. and Methods in Physics Research, A 633, (2011), pp. 72-78, DOI information: 10.1016/j.nima.2010.12.178

Conclusions

Requirements for new developments of XRF-XRD-Radiography system

Low cost, compact and light apparatus

- Use of EDXRD detection principle to combine XRF-XRD.
- Spatial resolution: submilimeter for fine details or 1cm beam for non homogeneous sample.
- Improve Energy resolution and count rate: Si-PIN- Si drift for EDXRD.
- XRF should reach good analytical performance for minor and trace element analysis with proposed XRF-XRD-Radiography system
- Easy an reproducible positioning of measurement head with respect to object.
- Detection of light elements (F, Na, Mg, Al, Si), Si, Mg, Na …) is necessary for provenance studies (ex. archaeological ceramics and stone tools)
- Combined XRF, XRD, UV-Vis-NIR analysis for pigment identification (multitechnique portable)
- Development of a compact and light measurement head allows

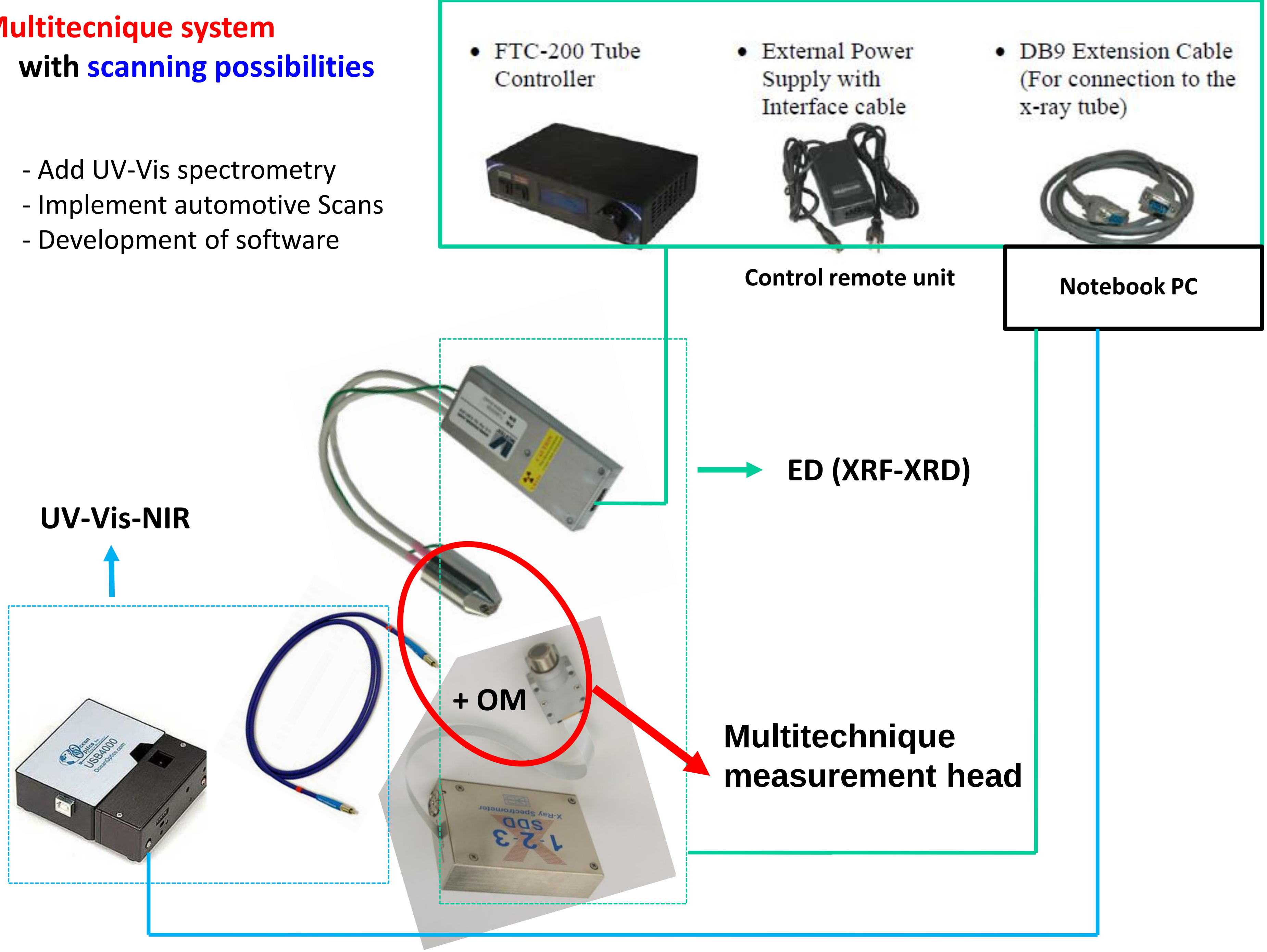
  2D (X,Y) scanning for a non invasive and in situ elemental distributions
  Automatic angular scanning   for hybrid XRD
  Non invasive and in situ depth profiles (z) is necessary for multilayer system studies..

NEW

- Versatile support to move the measurement head for large or complex geometry object.
- Development of methodology (and subroutines) for specific problems of cultural heritage *studies* (**Archaeometry)**

Multitecnique system
with scanning possibilities

- Add UV-Vis spectrometry
- Implement automotive Scans
- Development of software



EXACT project

Elemental **X**-ray **A**nalysis and **C**omputed **T**omography

Coordinator: Prof. C. Tuniz

- **Micro-Tomography**

- **Portable X-ray system**

Multidisciplinary Laboratory, ICTP
A.Mendoza, F. Bernardini, C. Zanolli
M. Crespo, A. Cicuttin, I. Birri, M. Dos Santos
Stanka

Elettra
D. Dreossi, L. Mancini,
A. Gianoncelli, G. Tromba

Funded by Friuli-Venezia-Giulia Region and ICTP

X-ray tube

very small and light

small and medium light

USB

< 280 g

Amptek
(10–40 kV, 200 μA, 2mm)

Moxtek 500 g
(10–50 kV, 200 μA, 400 μm)

1816 g

Oxford (50kV, 1 mA, max. 200μm)

Detector

USB

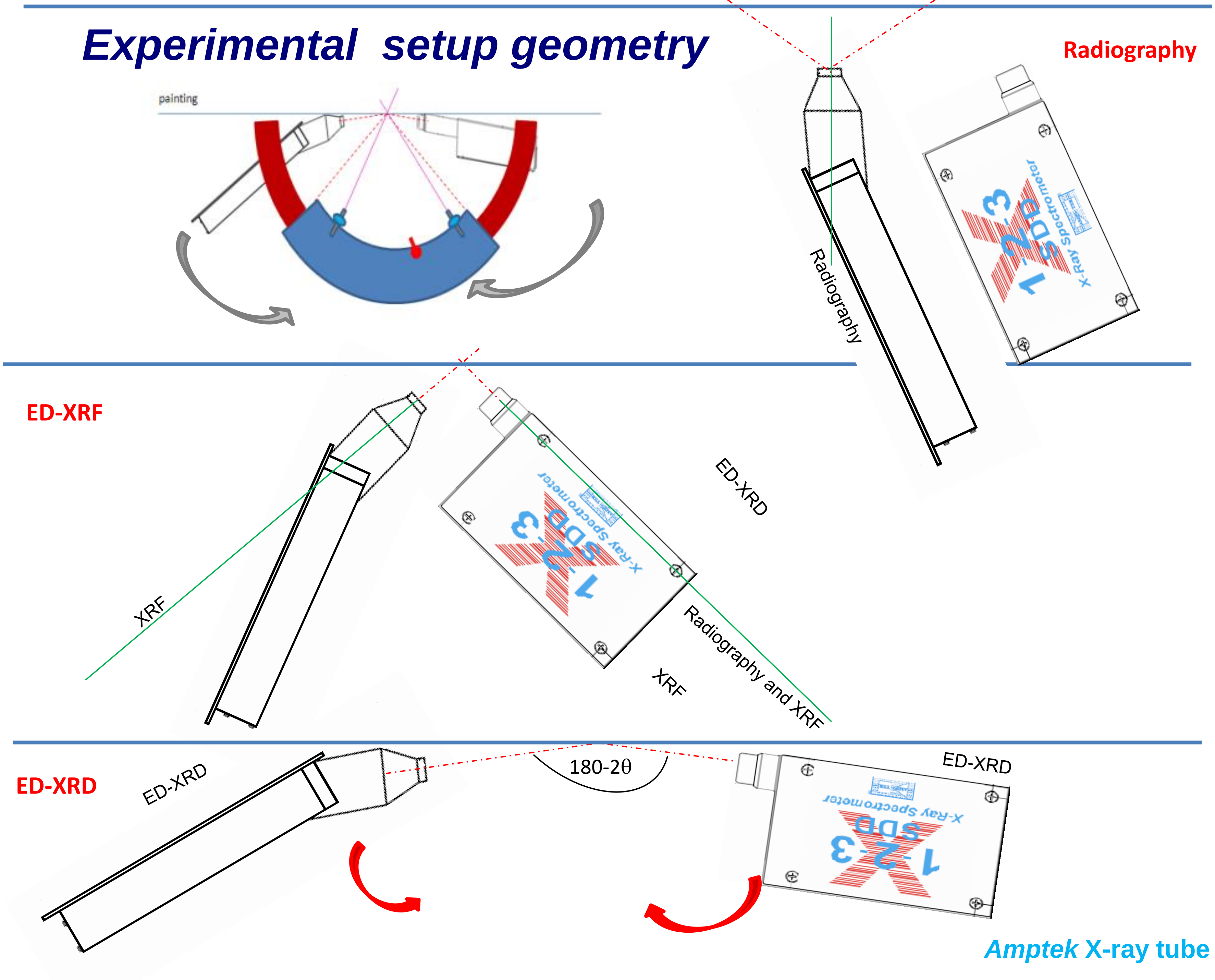
Amptek Si-drift detector
(7 mm^2 X 450 μm, 136 e V)

Ag or Pd anode
2 mm, 400 μm, 200 μm (spot)
max. voltage 40-50 kV
max. current: 200 μA. 400 μA, 1mA
energy resolution: 127 eV (light element's detection)

Construction of X - ray tube controller

Mlab

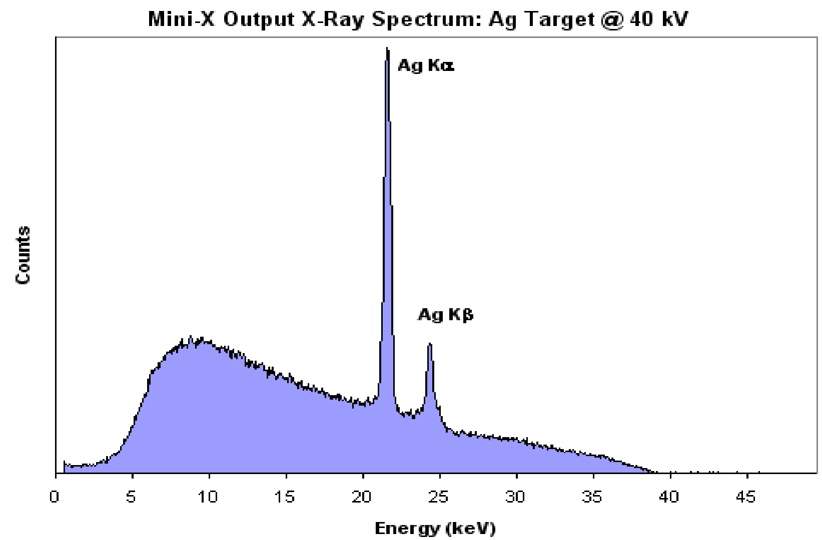
Experimental setup geometry

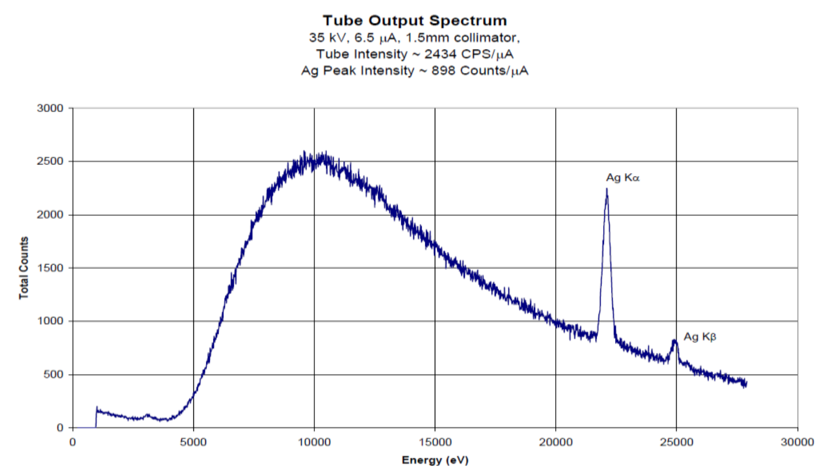


XRD signal intensity depend on the energy, influenced by the primary beam and absorption effects.

Amptek

Moxtek

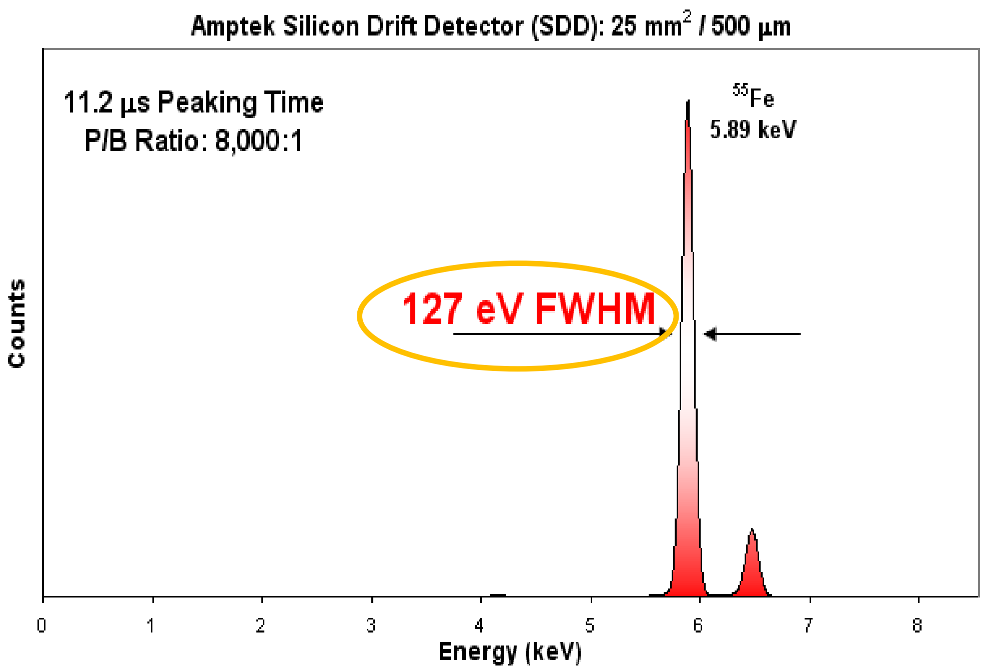




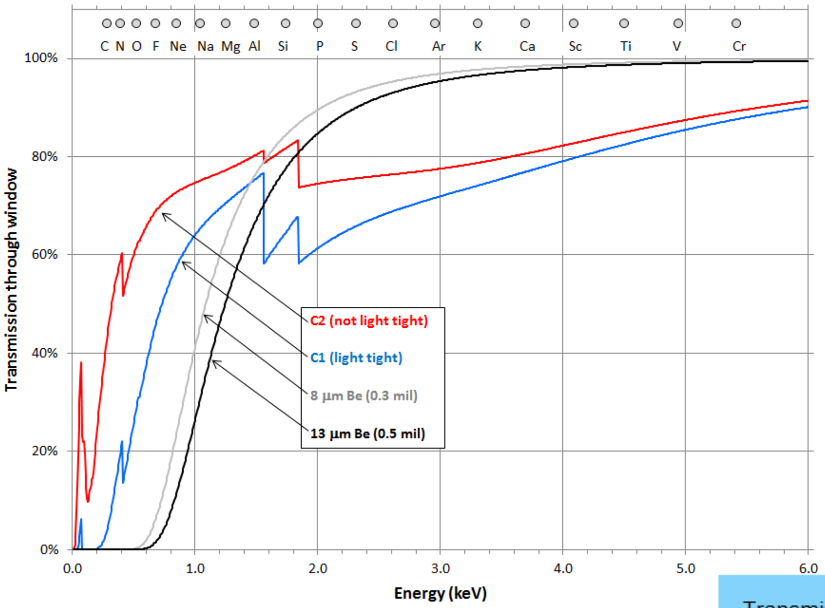
Low incident angle and scanning possibilities

Amptek SDD

Super SDD!
Silicon Drift Detector (SDD)
25 mm^2 x 500 µm



Amptek C-Series Low Energy X-Ray Windows



C1 Windows:
light-tight so it can be used in normal ambient room light.

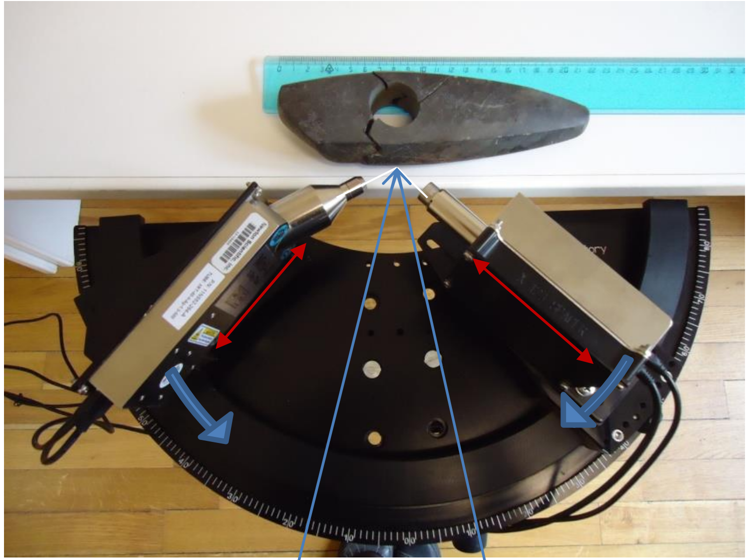
C2 Windows:
Vacuum applications and EDS (EDX) in scanning

Transmission for Low Z Elements | Specifications

Element	C1	C2	8 µm Be (0.3 mil)	12 µm Be (0.5 mil)
Li	0%	29%	0%	0%
Be	0%	13%	0%	0%
B	0.06%	19.7%	0%	0%
C	4.3%	43.9%	0%	0%
N	20.2%	59.2%	0%	0%
O	29.4%	62%	0%	0%
F	46.1%	69%	4%	1%
Ne	58.1%	72.9%	20%	9%
Na	65.4%	75.1%	40%	27%
Mg	70.6%	77.3%	59%	47%
Al	75.4%	80.3%	73%	64%
Si	64.7%	81.8%	82%	75%

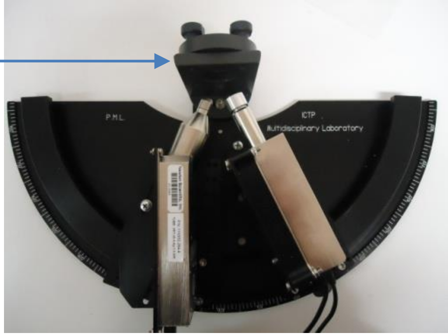
First prototype for laboratory test

Measurement head: Setup for X-ray tube and detector



Positioning Lasers **6.69 kg**

sample holder for calibration

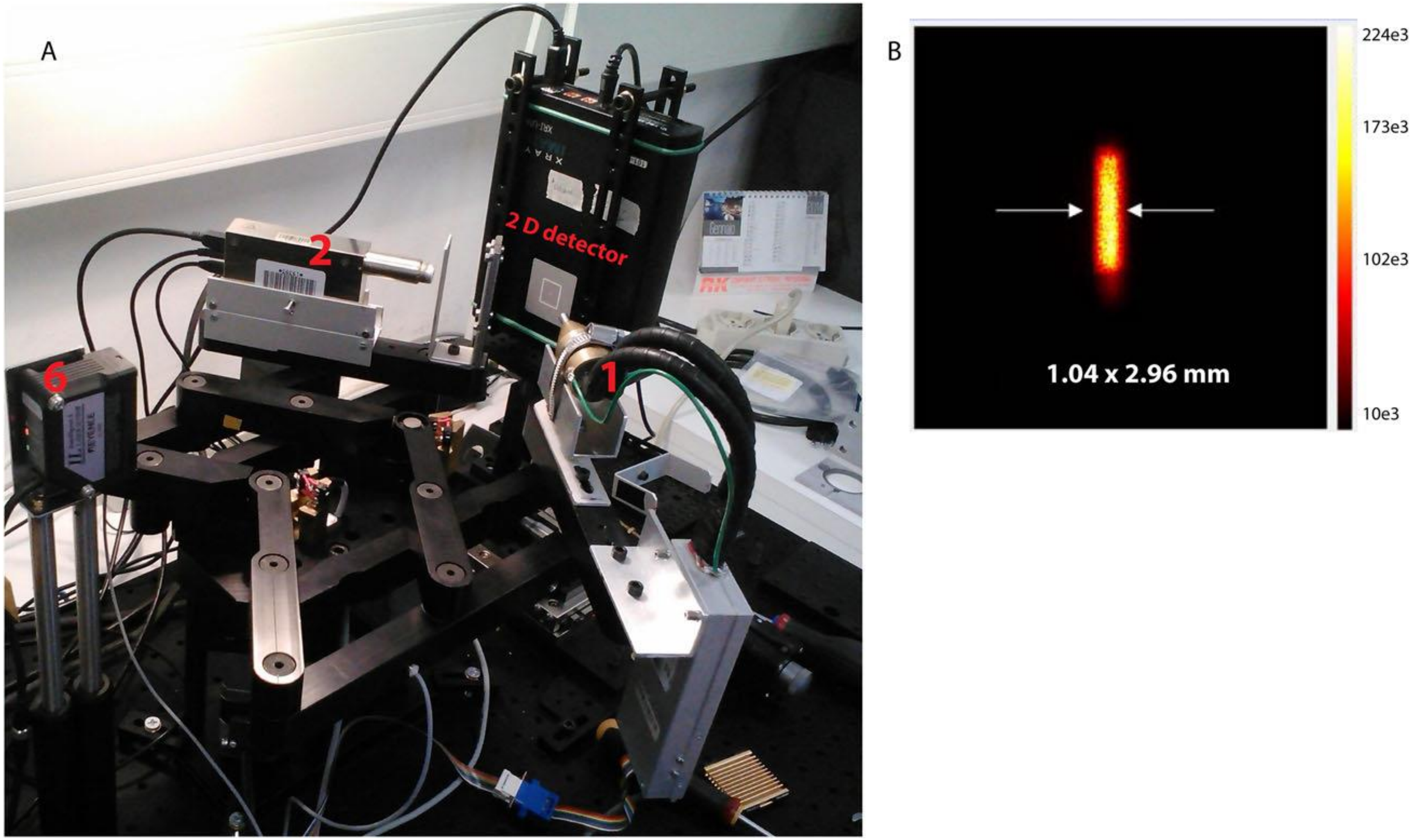


Setup for “in situ” analysis

set of collimators

XRF: selective pinhole collimator
XRD: variable slit collimator

high (max =170 cm , min = 11.5 cm) total weight = 9.82 kg



(A) Experimental setup of the second prototype during the measurement of beam spot using a 2D detector (Medipix).
(B) Details of the beam shape (as measured from Medipix) used for XRD measurements.

wileyonlinelibrary.com/journal/xrs

X-Ray Spectrom. **2015**, *44*, 105–115

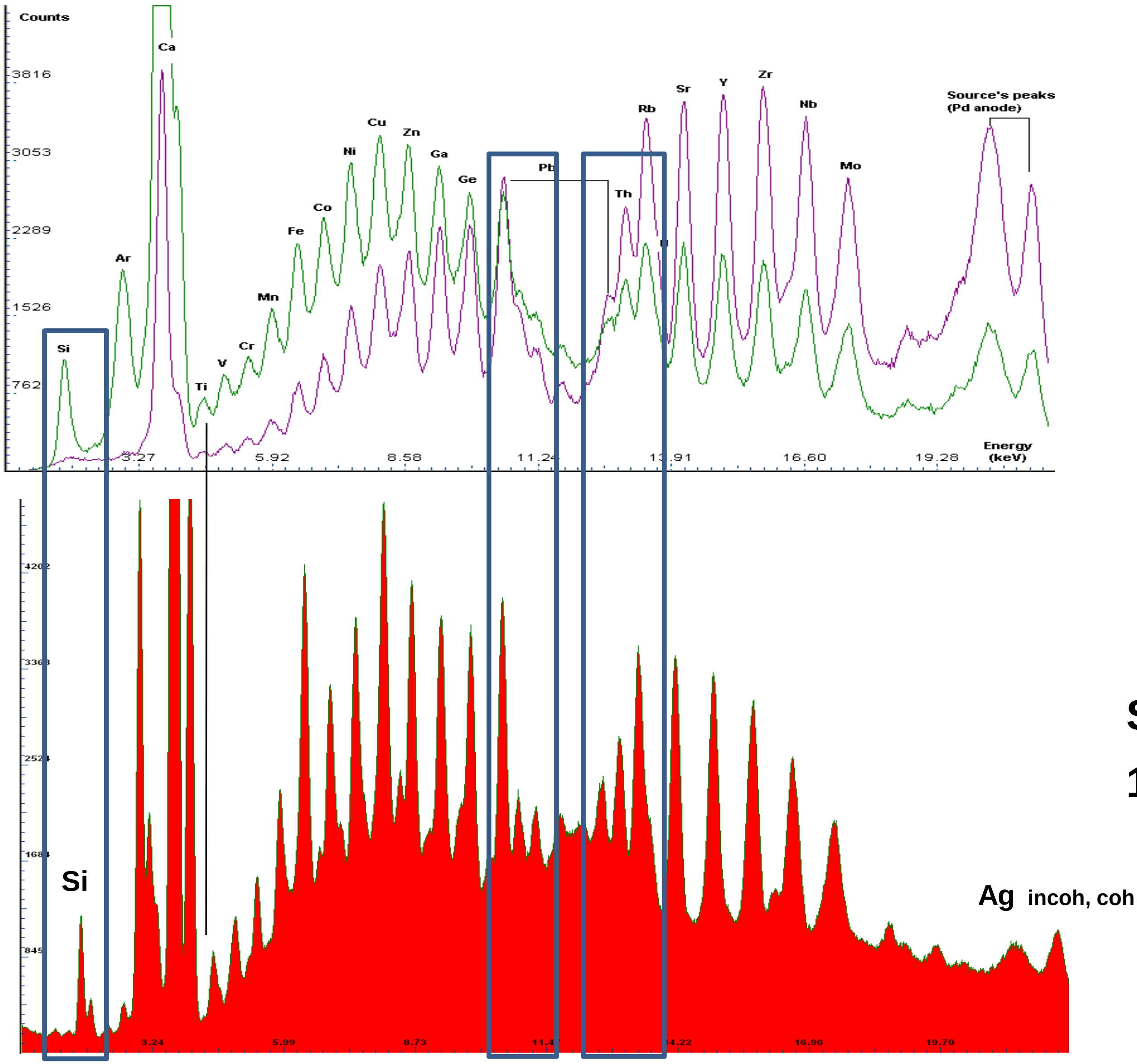
Energy dispersive X-ray diffraction and fluorescence portable system for cultural Heritage applications, A. Mendoza e col.

Table 1. Portable EDX XRF-XRD systems specifications

Main features and parameters	First prototype	Second prototype (motorized)
X-ray tube anode (minimum–maximum voltage, maximum current, anode spot)	Ag (10–40 kV, 100 μA, 2 mm)	Ag (10–50 kV, 200 μA, 400 μm)
Weight (g)	360	500
Maximum energy range	Polychromatic beam (0–40 kV)	Polychromatic beam (0–50 keV)
Output power (W)	8	10
Beam size (source slit collimator)	1.2, 0.8 mm (selective slit collimator)	0–0.5 mm (variable slit collimator)
Detector (energy range, Mn −kα FWHM resolution, active area, Be window)	Si-drift (1–120 keV, 125 eV, 27 mm^2, 500 μm)	Si-drift (0.5–120 keV, 136 eV, 9 mm^2, 450 μm)
Detector slit collimation	0.6 × 3.8 mm	0–1 × 0–4 mm variable slit collimation
Weight (g)	190	190
Goniometer type (minimum step)	Reflecting manual goniometer/ED detector (0.25)	Reflecting automated goniometer/ED detector (0.003)
2 scan range (2 = $_1$ + $_2$)	3–85° ($_1$ = $_2$ =) 0–90°(independently $_1$ and $_2$)	0–73° 0–90° (independently $_1$ and $_2$)
Measurement head weight	6 kg (goniometer can be lighter)	7 kg (goniometer can be lighter) 0.4 kg (X-ray tube power supply and controller)
Total weight	9.82 kg (measurement head + tripod) + notebook	7 kg (associate electronic of motors) 14.4 kg (measurement head + associate electronic) + PC

ED, energy dispersive; EDX, energy dispersive X-ray; FWHM, full width at half maximum; XRD, X-ray diffraction; XRF, X-ray fluorescence

Analytical performance



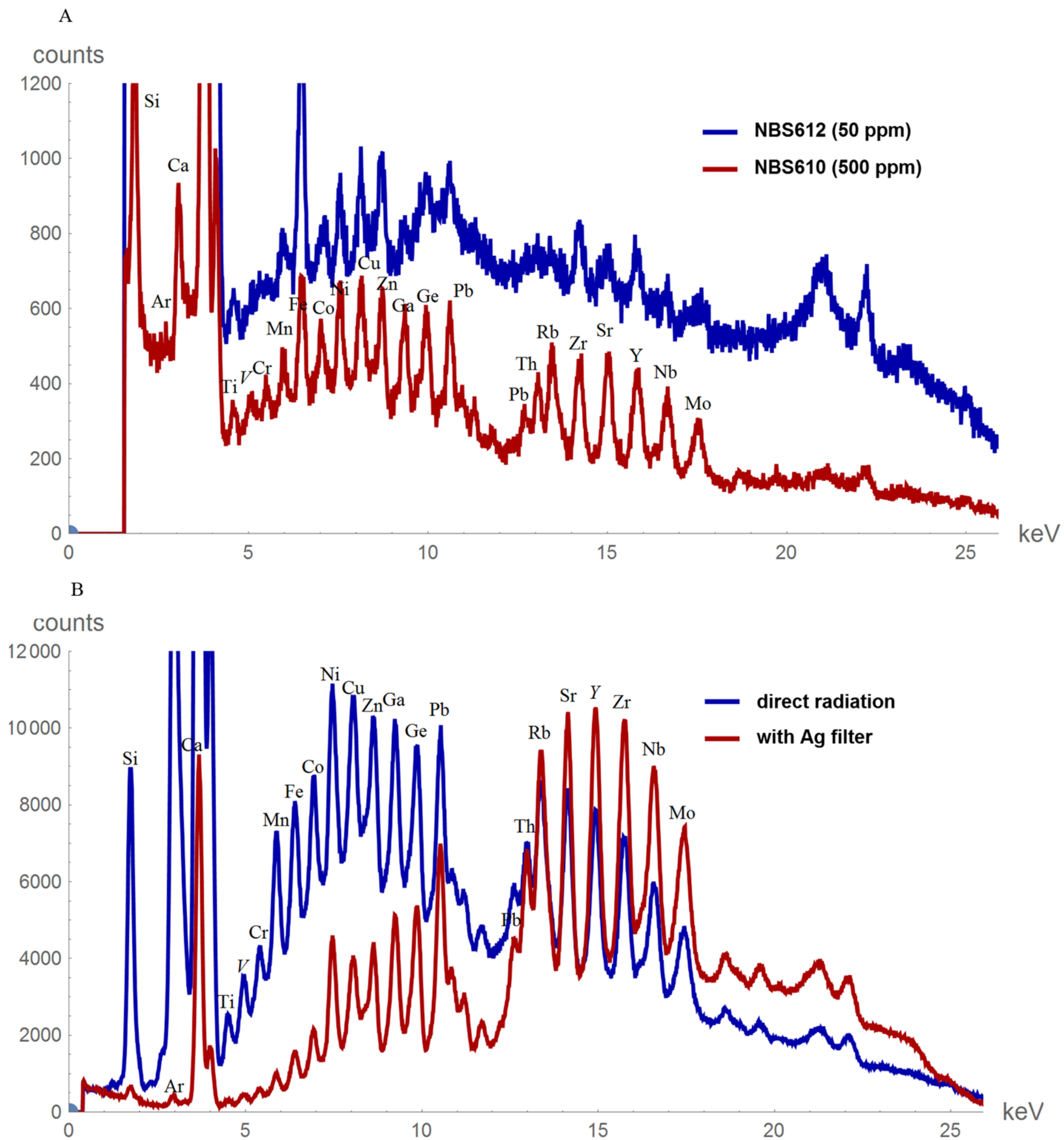
Si-PIN

250 eV

Si-Drift

136 eV

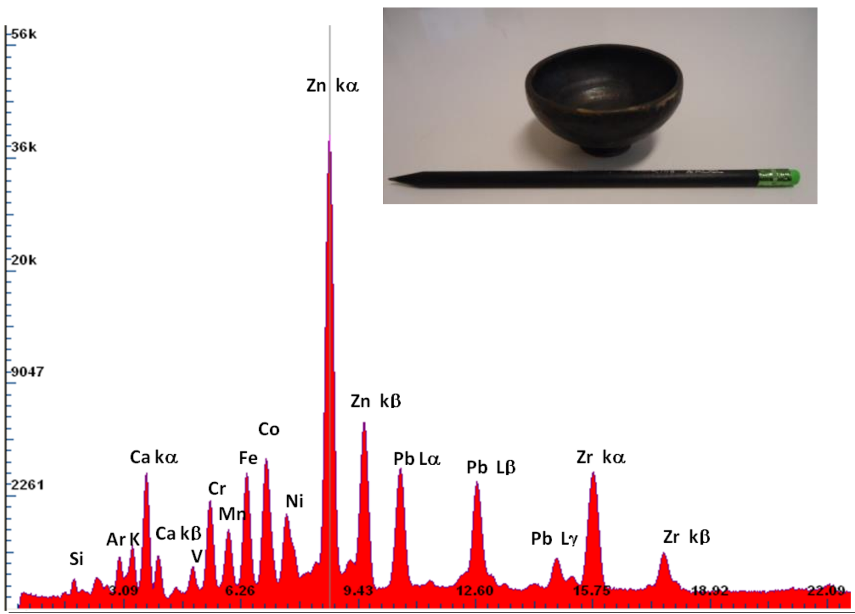
NBS 610 ~ 500 ppm



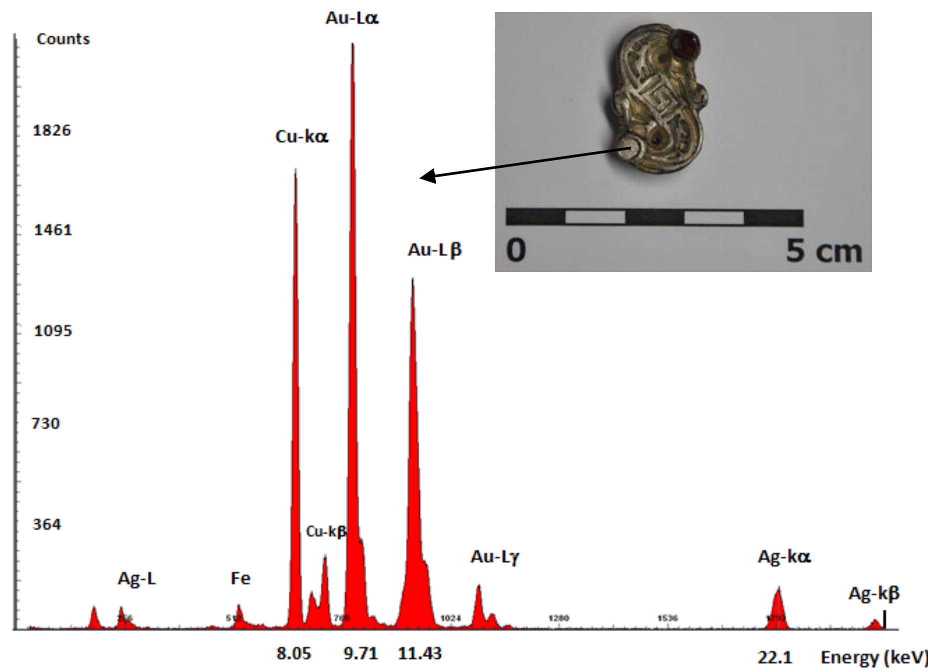
A - XRF spectra of reference glasses: NIST 610 (500 ppm) and NBS 612 (50 ppm) using first prototype.
B - XRF spectra of NBS 610 with direct and filtered radiation taken using the second prototype

Study of real objects

XRF spectra



Private collection, Stanka Tanaskovic



Kyjov, Czech Republic (480 AD)

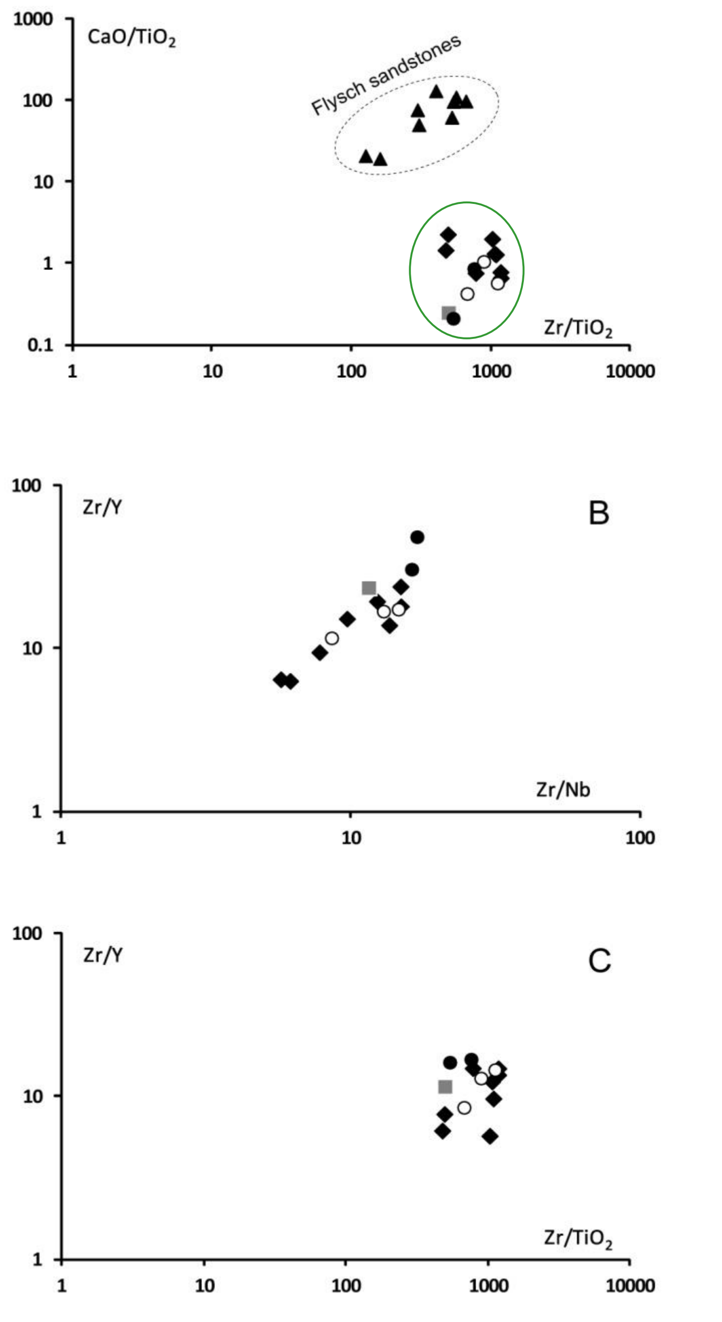


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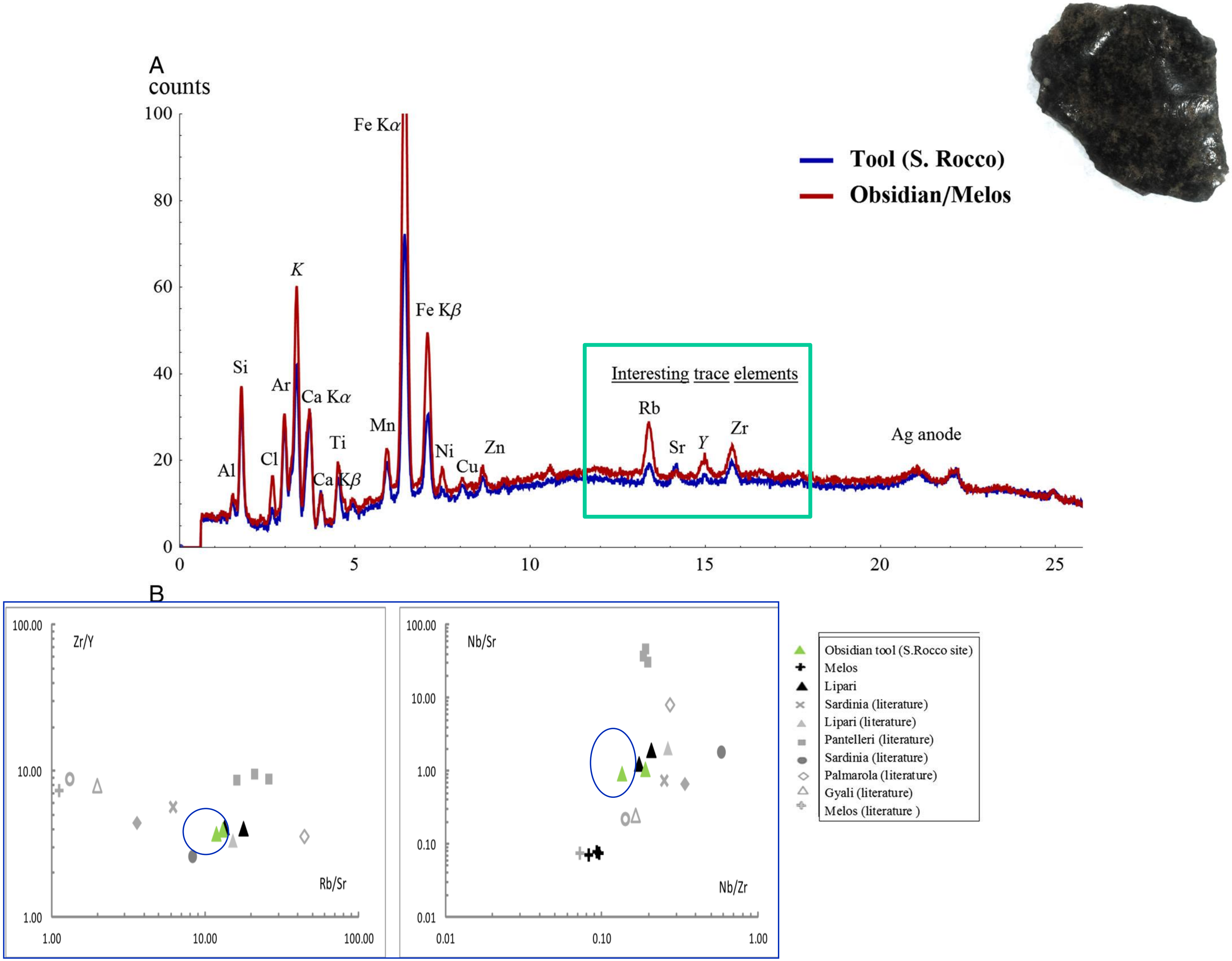
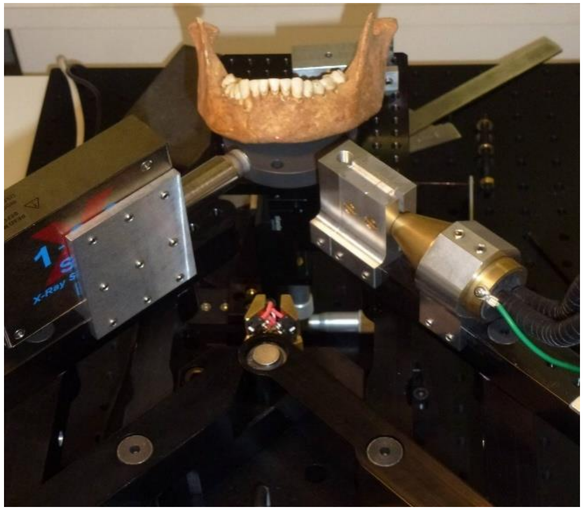
Table 4. Quantitative XRF analysis ISO2 (Bronze Age whetstone)		
Analyte	PXRF	ICP*
Fe_2O_3%	2.25 ± 0.25	2.39 ± 0.02
MnO%	0.02 ± 0.005	0.02 ± 0.001
TiO_2%	0.42 ± 0.03	0.75 ± 0.01
K_2O%	1.52 ± 0.21	1.48 ± 0.02
Rb ppm	45 ± 5	48 ± 5.2
Sr ppm	49 ± 7.3	59 ± 3.0
Y ppm	25 ± 8.3	23 ± 3.1
Nb ppm	18.2 ± 6.4	11.7 ± 1.6

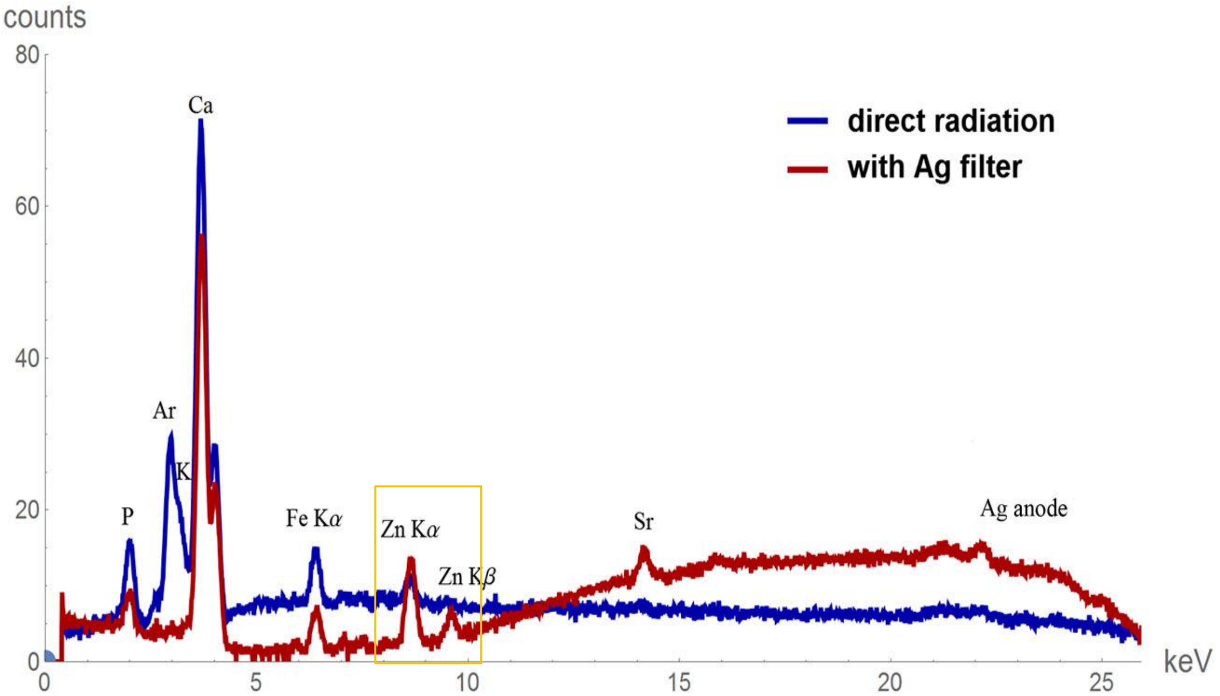
PXRF, Portable X-ray fluorescence instruments; XRF, X-ray fluorescence
* ICP-ES (major elements, %) and ICP-MS (trace elements, ppm)



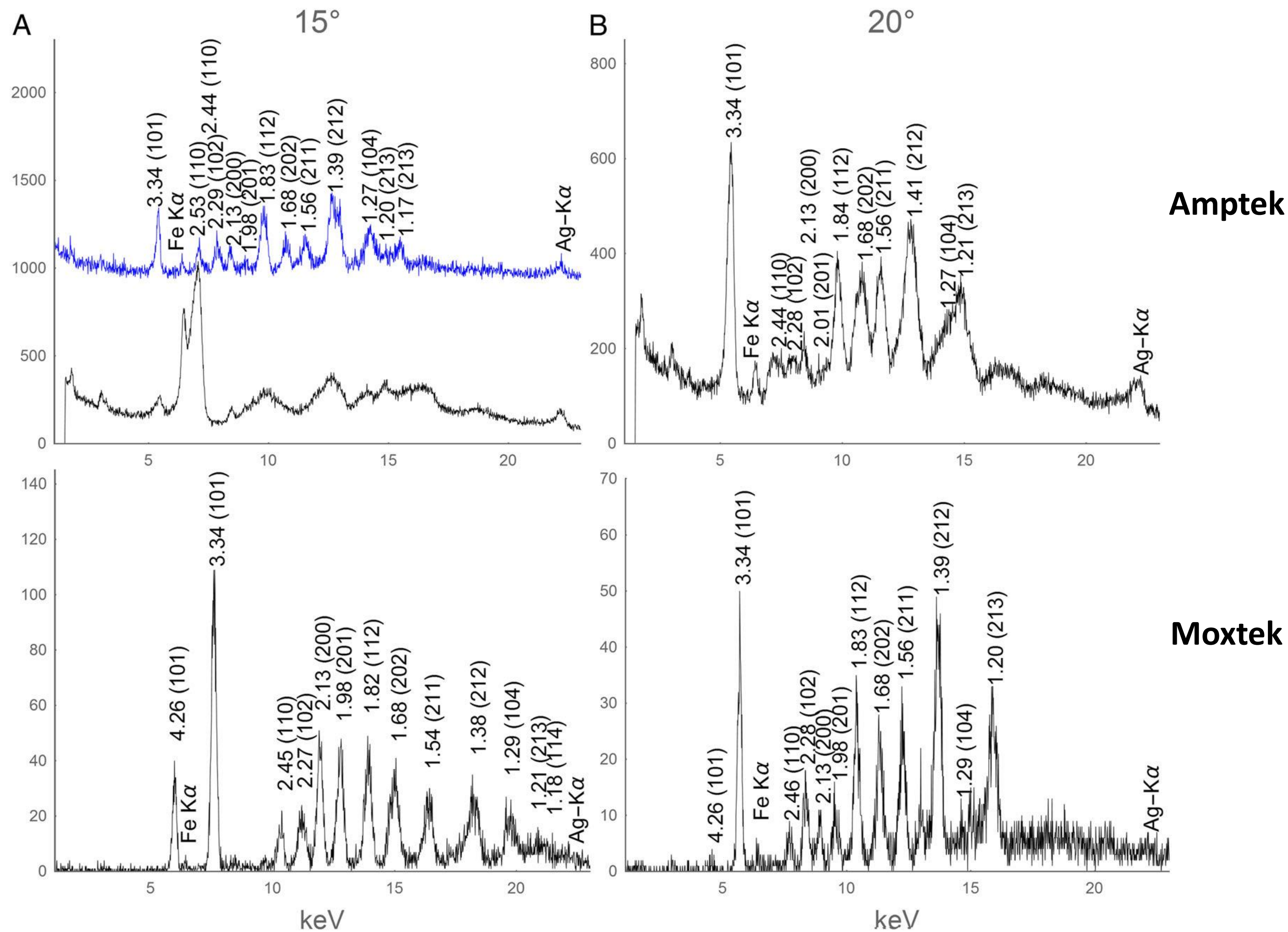
A
counts
100
80
60
40
20
0
0
5
10
15
20
25
Fe Kα
Fe Kβ
K
Si
Ar
Ca Kα
Ti
Mn
Al
Cl
Ca Kβ
Ni
Cu
Zn
Tool (S. Rocco)
Obsidian/Melos
Interesting trace elements
Rb
Sr
Y
Zr
Ag anode
B
100.00
Zr/Y
10.00
1.00
1.00
10.00
100.00
Rb/Sr
100.00
Nb/Sr
10.00
1.00
0.10
0.01
0.01
0.10
1.00
Nb/Zr
Obsidian tool (S.Rocco site)
Melos
Lipari
Sardinia (literature)
Lipari (literature)
Pantelleri (literature)
Sardinia (literature)
Palmarola (literature)
Gyali (literature)
Melos (literature)

The XRF spectra of an archaeological tooth measured with direct and filtered radiation





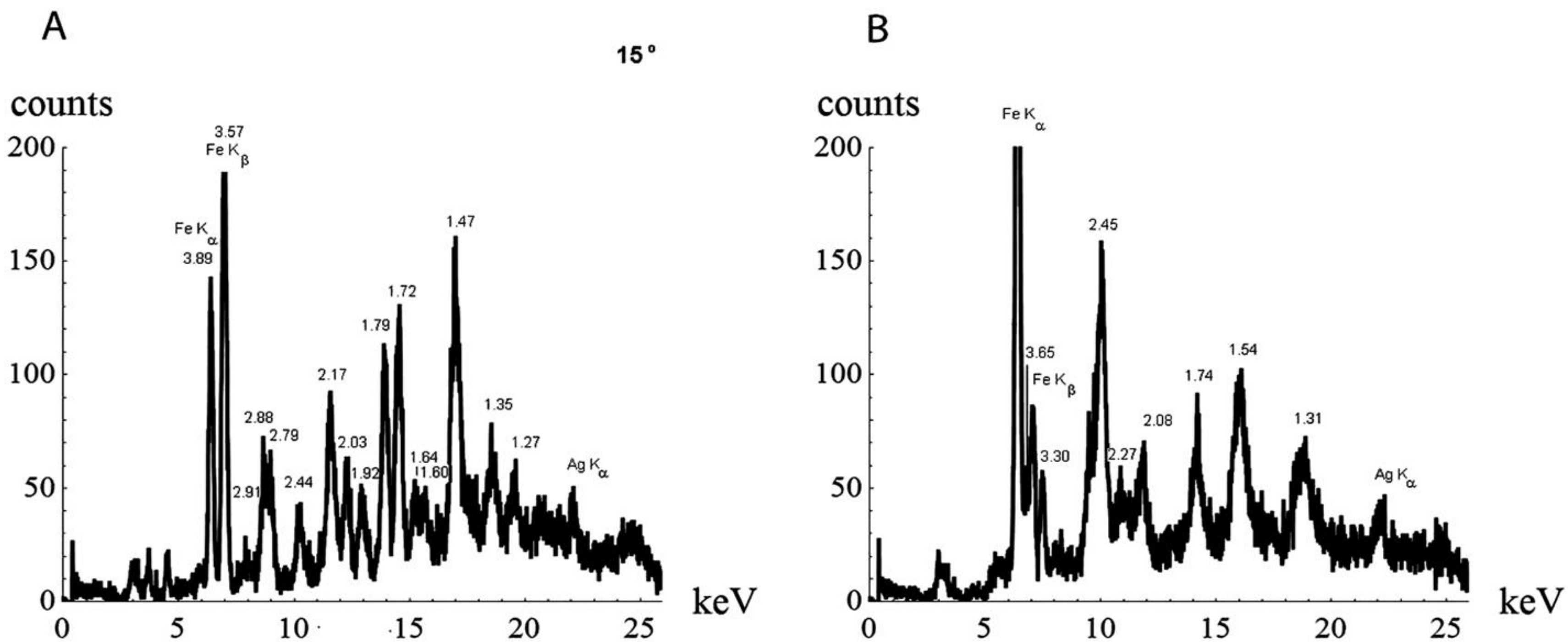
Zn, Interesting for paleodiet is emphasized



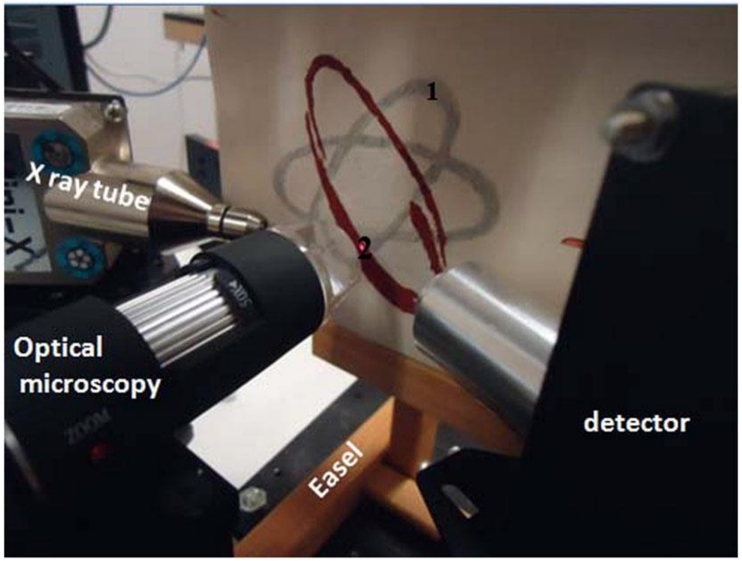
EDXRD diffractogram of powdered quartz acquired with the first (A) and the second (B) prototypes acquired for 400 s (28 kV, 142 μA) and 300 s (28 kV, 300 s), respectively at scattering angles (15° and 20°).

Table 2. X-ray diffraction data at 15° (with the second prototype) and reference data of quartz

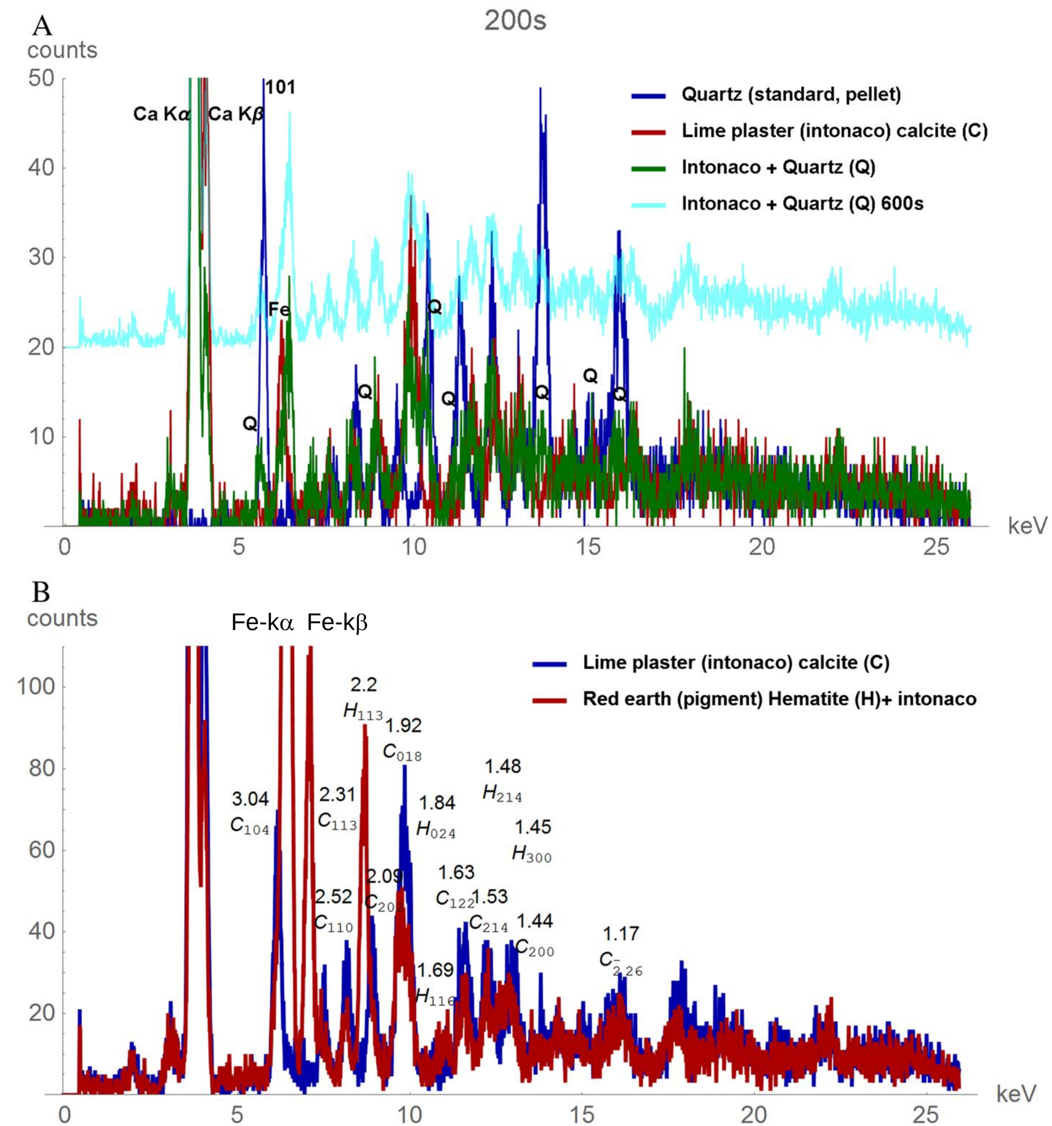
	Quartz (15°)	Ref. PDF: 33–1161
h k l	d_{obs}/Å (I_{obs})	d_{ref} /Å (I_{ref})
1 0 0	4.25 (37)	4.2570 (17)
1 0 1	3.34 (100)	3.3420 (100)
1 1 0	2.45 (20)	2.4570 (11)
1 0 2	2.27 (22)	2.2820 (12)
2 0 0	2.13 (46)	2.1270 (9)
2 0 1	1.98 (41)	1.9792 (7)
1 1 2	1.82 (46)	1.8179 (26)
2 0 2	1.68 (36)	1.6719 (8)
2 1 1	1.54 (27)	1.5418 (20)
2 1 2	1.38 (24)	1.3752 (17)
		1.3718 (19)
1 0 4	1.29 (21)	1.2880 (5)
2 1 3	1.21 (13)	1.1999 (6)
		1.1978 (3)



XRF-XRD spectra of jadeite (A) and serpentine (B) taken in XRD mode for **600** s.



Identification of the crystalline phase is carried out in the shortest time so far reported, nearly comparable to the fastest ADXRD portable system using X-ray optics.



Advantages of EDXRD

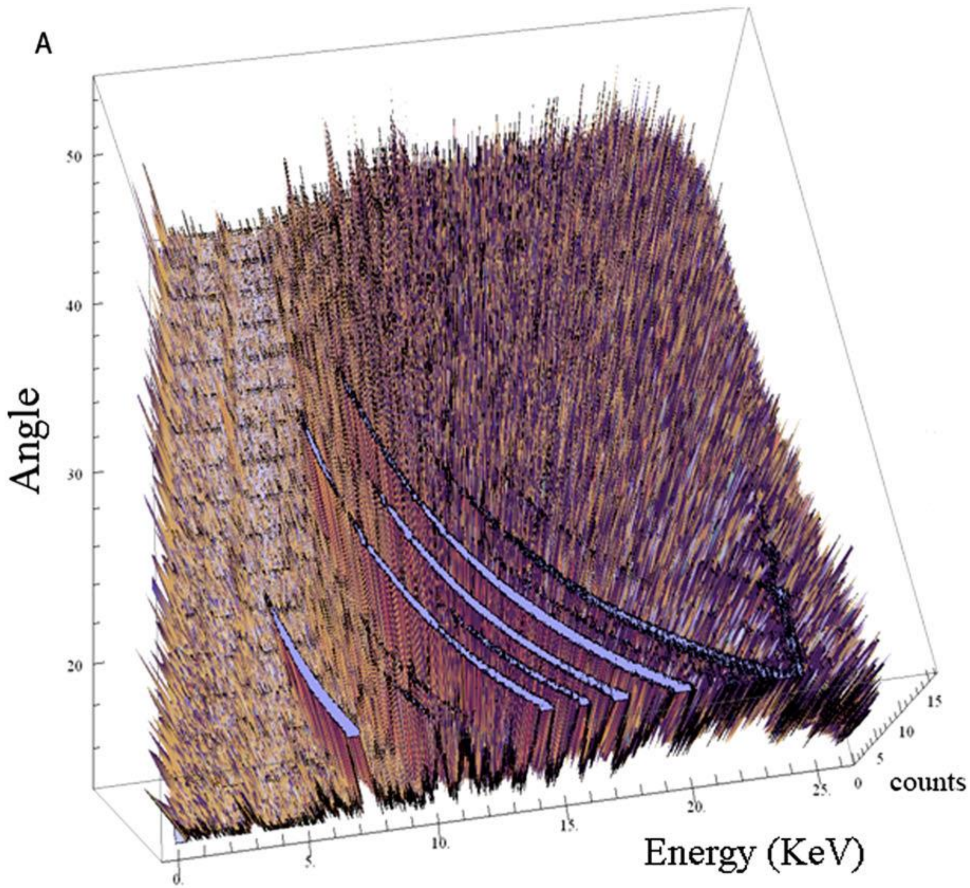
- faster data acquisition times (by one or two orders of magnitude with respect to ADXRD)
- simultaneous collection of diffraction lines, for a fixed angle (without mechanical movements of detector or X-ray source).
- a wider accessible region of the reciprocal space (q) may be obtained.

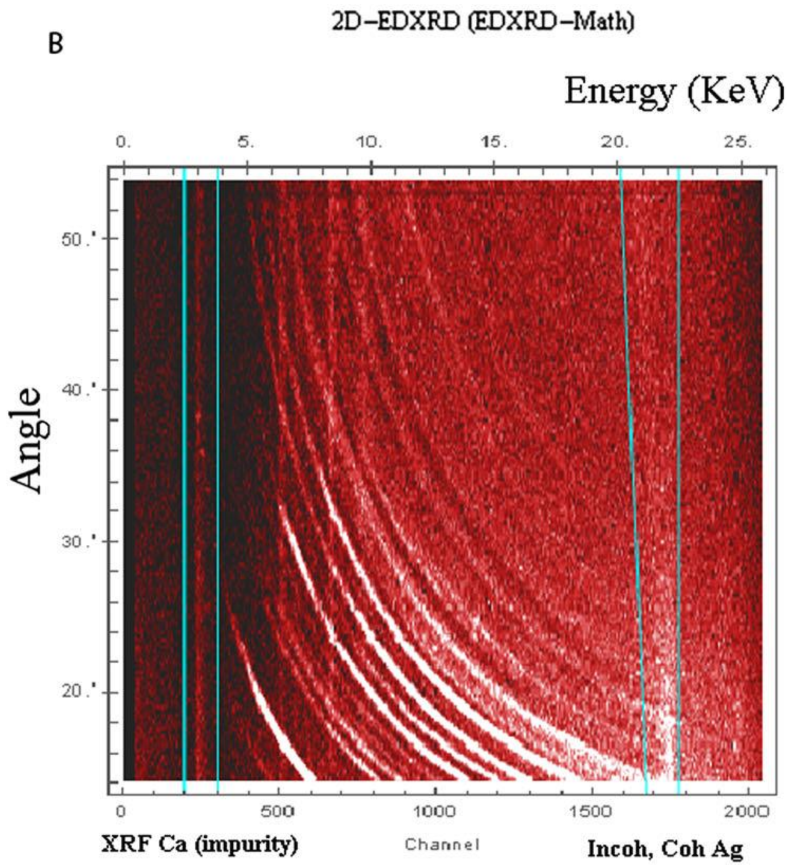
  $\Delta q = q_{max} - q_{min} = aE_{max} \sin \theta_{max} - aE_{min} \sin\theta_{min}$
- EDXRD measurements can be performed with the commercially available miniaturized low-power X-ray tubes commonly used for portable XRF.
- the same sample point can be simultaneously analyzed by both techniques because only one detector is used.
- The higher energy used in EDXRD (compared with conventional Cu anode ADXRD) allows a deeper penetration of X-rays (as it occurs in XRF) in multilayered objects, which is useful for rock arts, paintings, and polychrome sculptures studies.

Problems

- XRD and XRF peaks appear in the same spectrum, sometimes overlapping, (which can be avoided by changing the detection angle)
- quantitative analysis is much difficult than ADXRD because the quantities that modulate the scattered intensity in an EDXRD measurement depend on the energy, and the q, d resolution depends also on the detector energy resolution

Angle scanning ED-XRD system (Hybrid XRD)



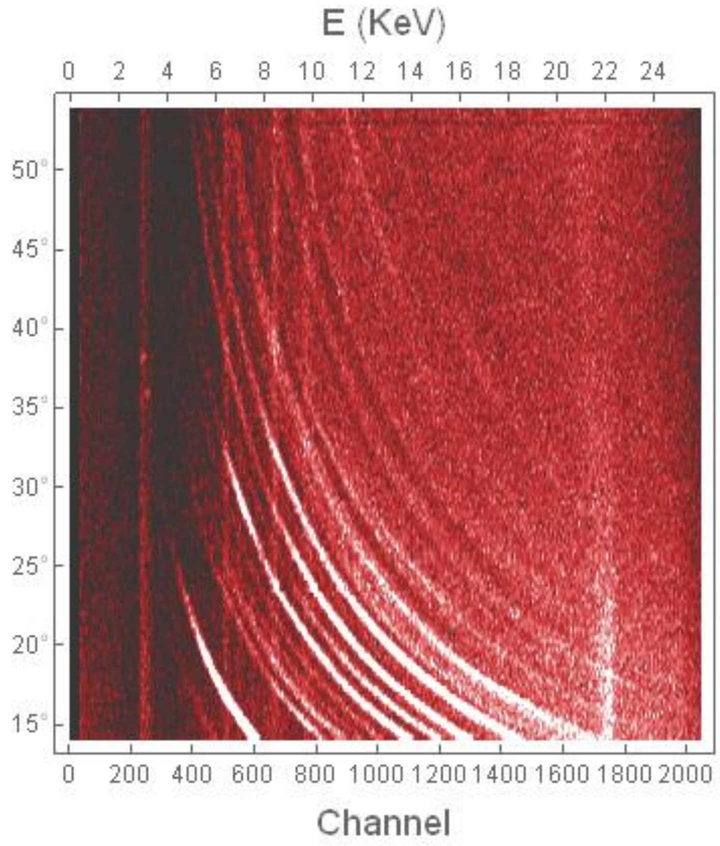


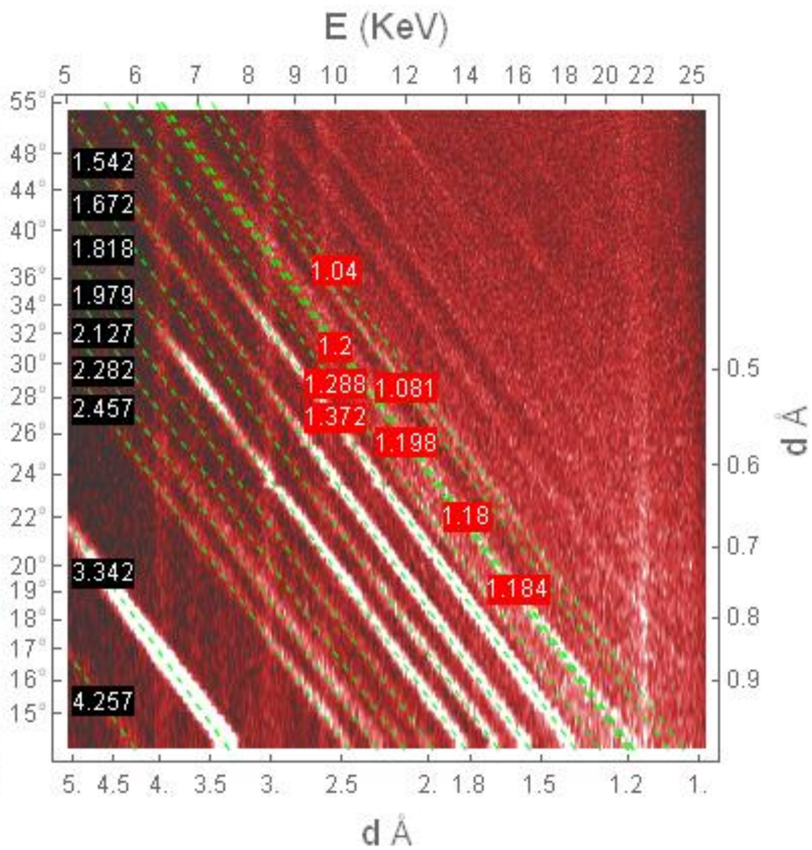
d- crystal interplanar spacing

The 3D diffractogram obtained by plotting angle scan EDXRD diffractograms (A) and its density plot Energy versus Angle (B) where Iso-**d** curves are observed. EDXRD, energy dispersive X-ray diffraction; XRF, X-ray fluorescence

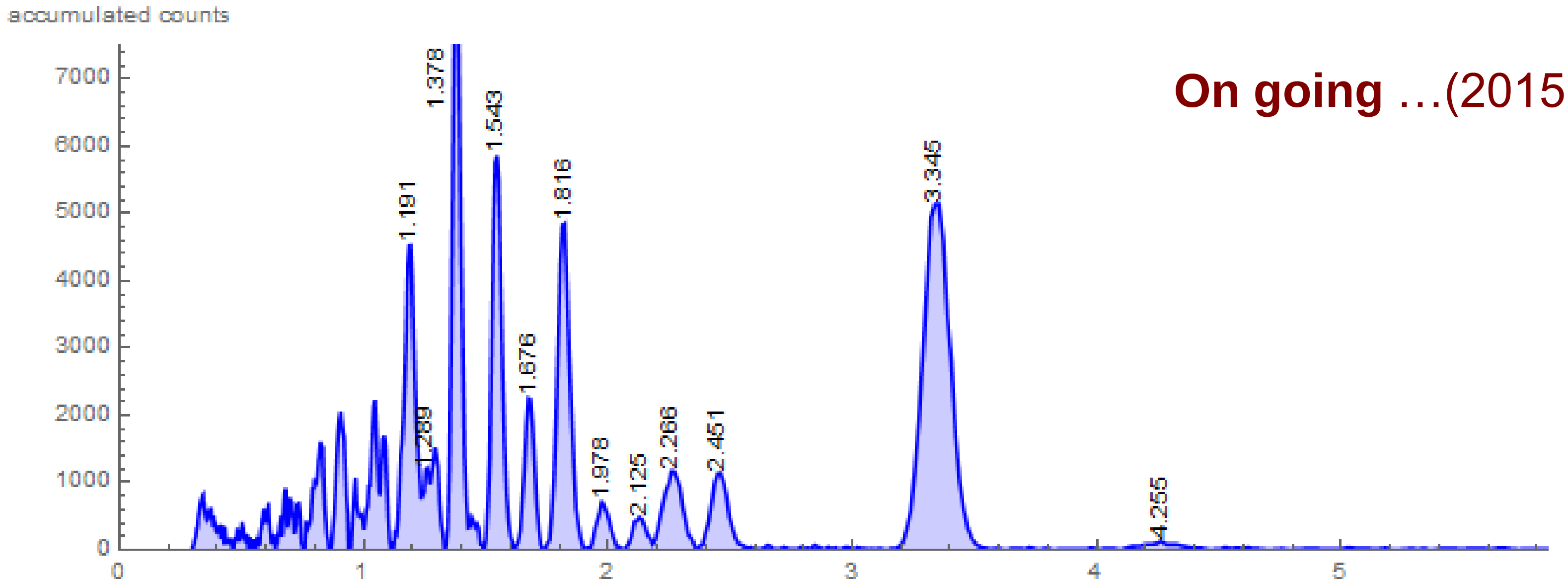
Data processing of hybrid data

On going …(2015)





Hybrid diffractogram

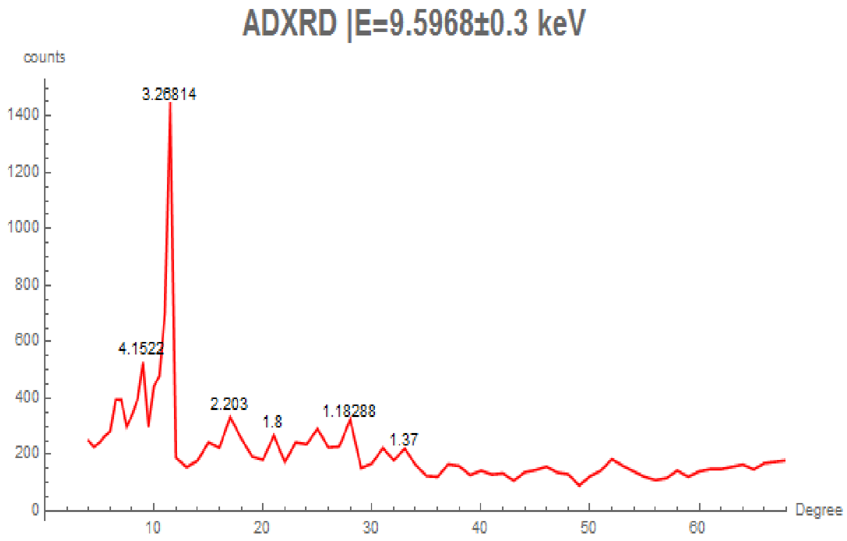


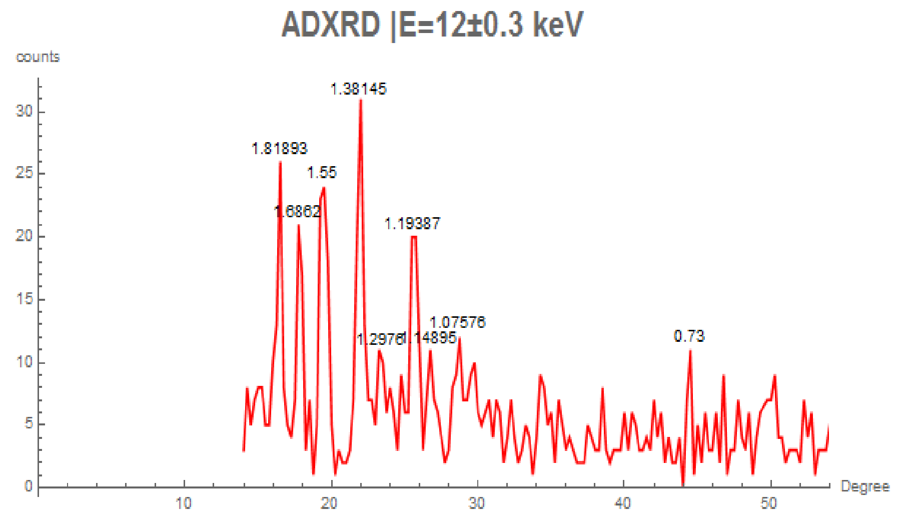
On going …(2015)

h k l	D_{ref} Å (I_{ref})	D_{obs} Å (I_{obs}) at 15 °	D_{obs} Å (I_{obs}) hybrid	hybrid outperform EDXRD $\theta = 15°$
2 1 3	1.1999 (6)	1.21 (13)		
	1.1978 (3)		1.191 (50)	X
1 0 4	1.288 (5)	1.29 (21)	1.289 (13)	X
2 1 2	1.3752 (17)	1.38 (21)	1.378 (100)	X
	1.3718 (19)			
2 1 1	1.5418 (20)	1.54 (27)	1.543 (65)	X
2 0 2	1.6719 (8)	1.68 (36)	1.676 (25)	X
1 1 2	1.8179 (26)	1.82 (46)	1.816 (54)	X
2 0 1	1.9792 (7)	1.98 (41)	1.978 (8.14)	
2 0 0	2.1270 (9)	2.13 (46)	2.125 (5.41)	X
1 0 2	2.2820 (12)	2.27 (22)	2.266 (13.01)	
1 1 0	2.4570 (11)	2.45 (20)	2.451 (12.63)	X
1 0 1	3.3420 (100)	3.34 (100)	3.345 (57.11)	
1 0 0	4.2570 (**17**)	4.25 (37)	4.255 (1.48)	X

Virtual angle dispersive diffractogram

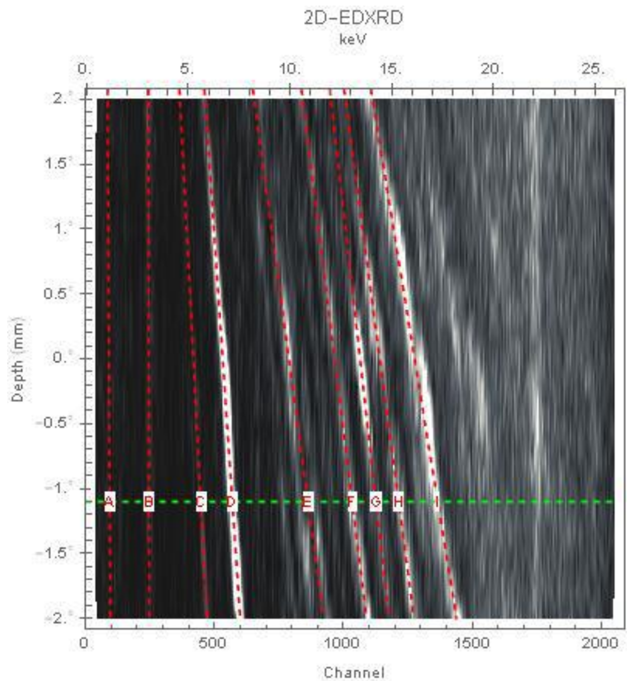
On going …(2015)

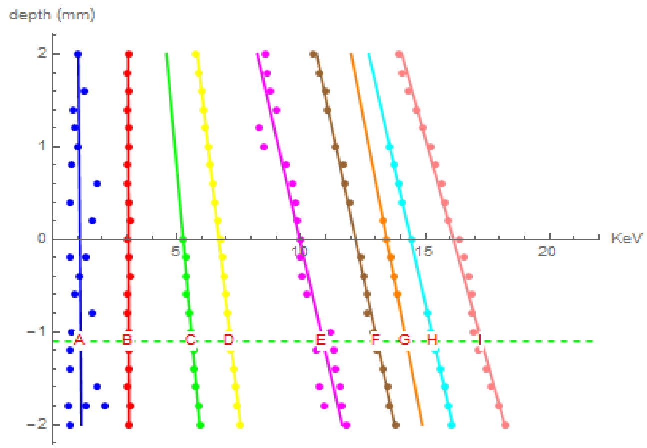


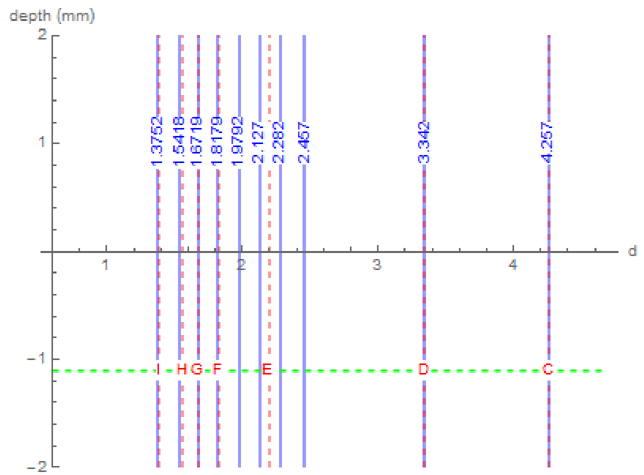


AD diffractograms of powdered quartz sample power for E = 9.6 keV , from 4° to 68, step 1° (left) and E = 12.0 keV, from 15° to 55°, step 0.25° (right)

Determination of correct positioning







A plot of Intensity vs. Position and Energy show the shift of XRD signals due to position of the sample.

Method of positioning and identification

1. Positioning sample using laser
2. Measure the sample positioned at various distance.
3. Create a list of the putative components/mineral of the sample under study as candidate composition.
4. Select from reported databases the prominent inter-planar distances of the candidate.
5. Detect by image processing the peaks arranged in lines along diffractogram measured at different distance. Of those lines register the slope and intercept or equivalent descriptors.
6. For each candidate evaluated, the lines observed are extended so as to fit with the d reported, a score is assigned according to the fitting.
7. The remaining unassigned d, are reevaluated over the image for detecting further lines with weaker signals.

8 The score value is assigned according the total number of line and proximity.

Advantages of Hybrid XRD

- Angle scanning ED-XRD system (Hybrid XRD) take the advantages of both, EDXRD (shorter time and higher energy penetration) and ADXRD (higher inter-planar distance resolution).
- The use of logarithmically modified density plots (Angle vs E) facilitate direct reading of d-spacing, and fluorescence lines becomes more contrasted, which make easier background estimation and substraction in the hybrid diffractogram.
- The obtention of a single diffractogram that resume the 3D hybrid data allows fast and reliable identification of all detected lines in ED-diffractogram at multiple angles and improve the accuracy of interplanar distance determination and its resolution with respect to the values obtained from individual ED-diffractogram.
- AD-diffractogram extracted from the 3D hybrid data can be conveniently utilized for specific d range and higher energy.
- In particular **the Hybrid method is suitable for non invasive analysis of Cultural Heritage object using a compact and economic setup with Energy dispersive detection for simulataneus XRF and XRD analysis.**

Remarks

•Most of the applications chosen focus the qualitative analysis for material identification, which address the typical questions in cultural heritage. Exceptions are the study by XRF of obsidian provenance and the composition of bronze-age ax, which involved a quantitative analysis of intensities.

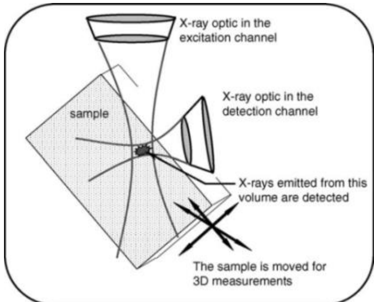
•In the cases of XRD analysis, it is far more difficult to handle intensities using EDXRD than with ADXRD. A current disadvantage in the portable system for XRD, is that intensity depend on the energy, influenced by the primary beam and absorption effects. Also, for this instrument (reflection geometry) the optical path in the sample dependent on the photon energy.

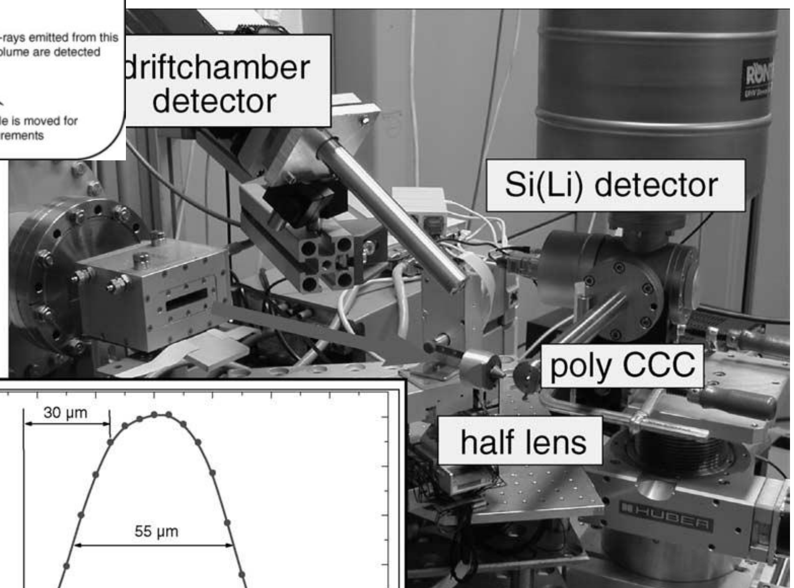
•For quantitative analysis of unknown or uncertain composition, as is the case in cultural heritage, **future development** of models of the hybrid data that combine the physics behind the technology, the results of XRF analysis, and the available ADXRD databases is required.

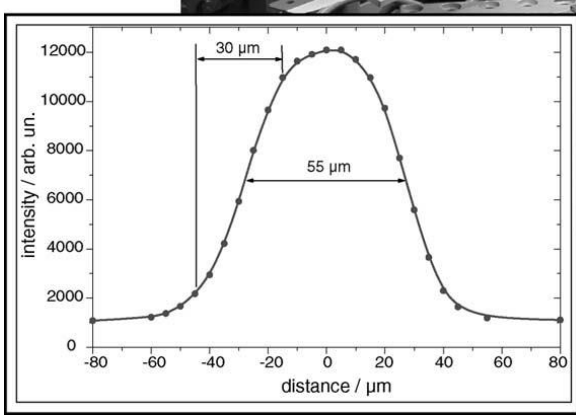
Future works, to add depth profile capability (alternatives...)

to the thybrid XRF-XRD system

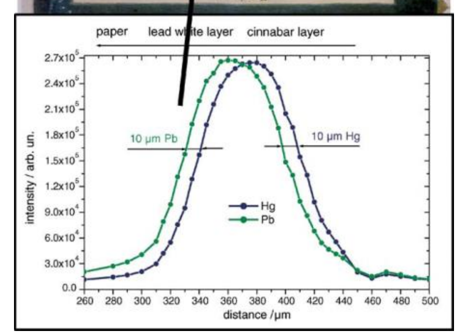
Non invasive stratigraphic study of paint layer







Laboratory μ–XRF



Bi. Kanngießer,2003

Emphasizing archaeometrical results for the study of cultural heritage

to be presented to humanity experts

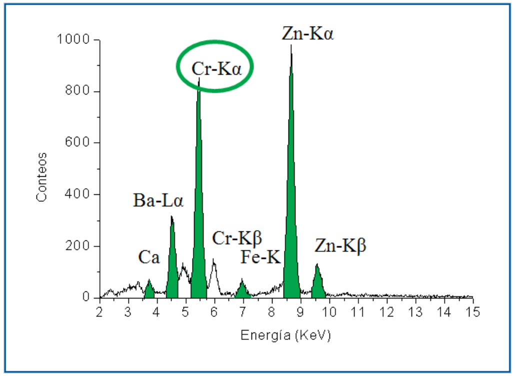
(art historian, arquelogist, conservators and restorators)

Data processing

1. Qualitative analysis

Material Identification or characterization

E - $E_i \ldots E_f$



XRF

2. Multivariate analysis

data classification or material identifications

Methods of Principal component analysis (PCA)

(for provenance or attribution studies)

Mathematical variables (P)

$$P_i = Sum_i\, p_i X_i$$

Real variable

X - $I_i \ldots I_f$

PX = Y

Reduce No. variable

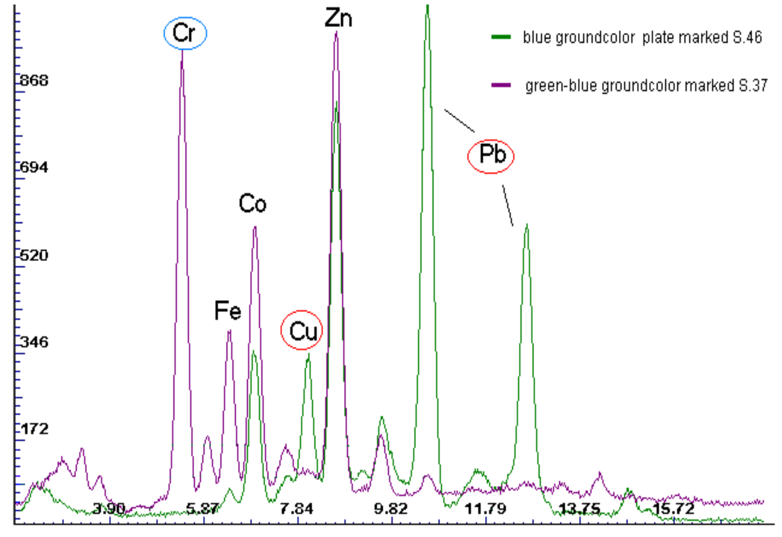
$$PX = \begin{bmatrix} p_1 \\ \vdots \\ p_m \end{bmatrix} \begin{bmatrix} x_1 & \cdots & x_n \end{bmatrix}$$

$$Y = \begin{bmatrix} p_1 \cdot x_1 & \cdots & p_1 \cdot x_n \\ \vdots & \ddots & \vdots \\ p_m \cdot x_1 & \cdots & p_m \cdot x_n \end{bmatrix}$$

Sevres porcelain attribution

Sevres manufacture blue

dark blue or indigo	
Gray fundente	61
Cobalt carbonate	13
Hidratated cinc carbonate	26
Turquoise Blue	
Alumb	92
Cobalt carbonate	6
Cinc carbonate	2
Blue d'azur	
Gray fundent	67
Cobalt carbonate	11
Hidratated cinc carbonate	22
Sky blue	
Gray fundent	79
Cobalt carbonate	7
Hidratated cinc carbonate	14
Green-blue	
Chromium oxide	50
Cobalt carbonate	25
Cinc carbonate	25



- **Background color**

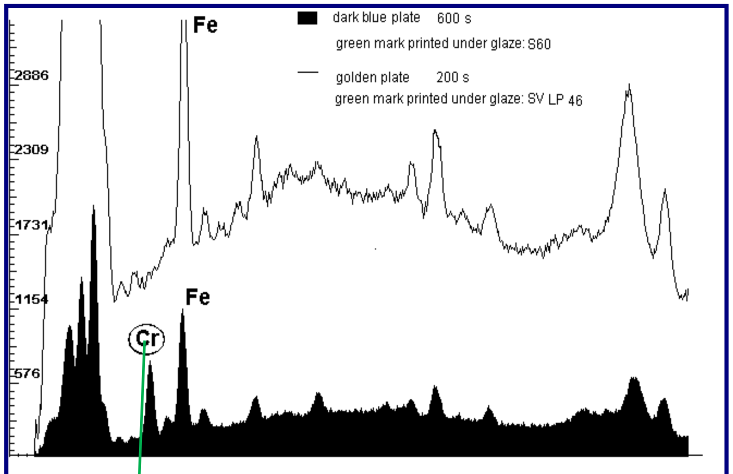
Surdecor ?

mark s46

A. Mendoza Cuevas, J. Nazco – Torres, Exámenes para atribución de porcelanas Sevres por fluorescencia de rayos X en museos habaneros, Revista Nucleus, No. 46, 2009

Sevres porcelain attribution

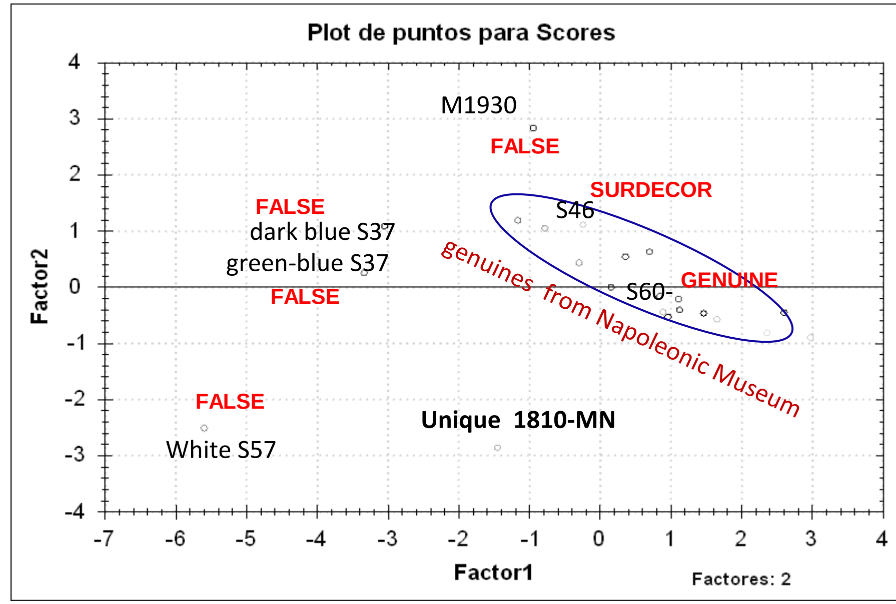
- **Marks**



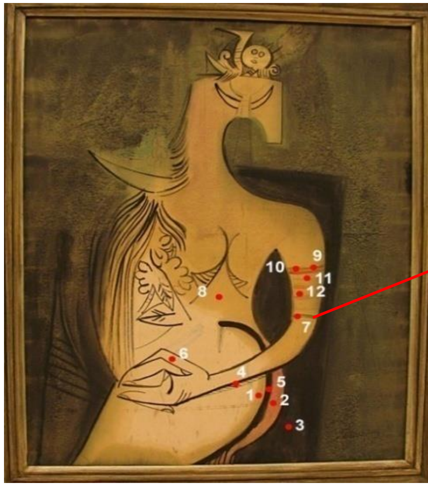
serial mark in Chromium green, 1848

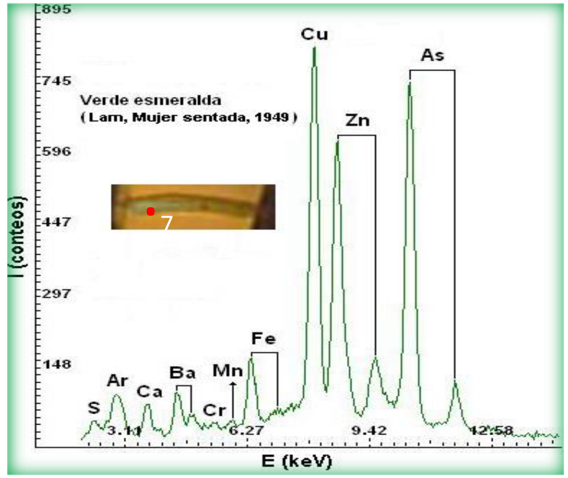
- **Paste**

Multivariate analysis



S46 (surdecor)
S37 s57 Sevres falses

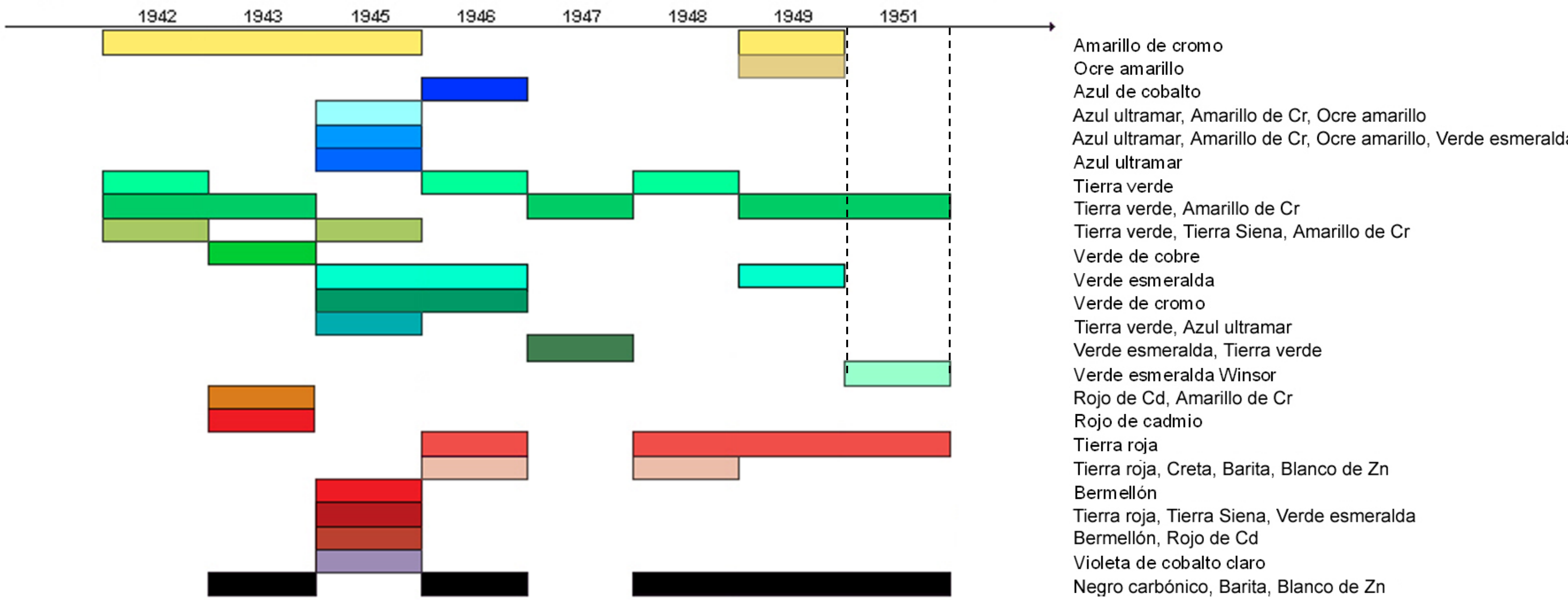




Easel paintings

- Paris green, Emerald green, Veronese or Schweinfurt green
- 1832 (*Winsor and Newton, UK)* - ~1950

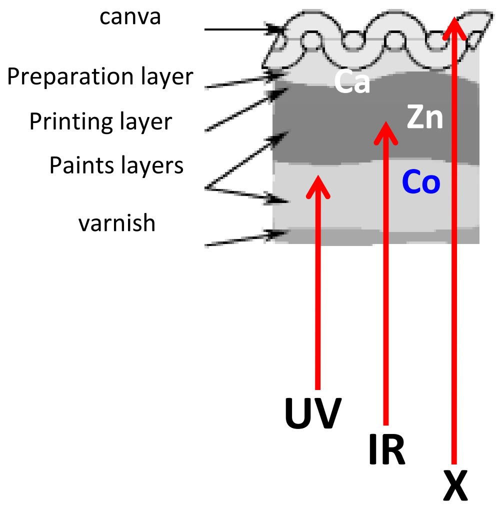
- Emerald phtalocianine green
- 1936- present



Art History and authentication

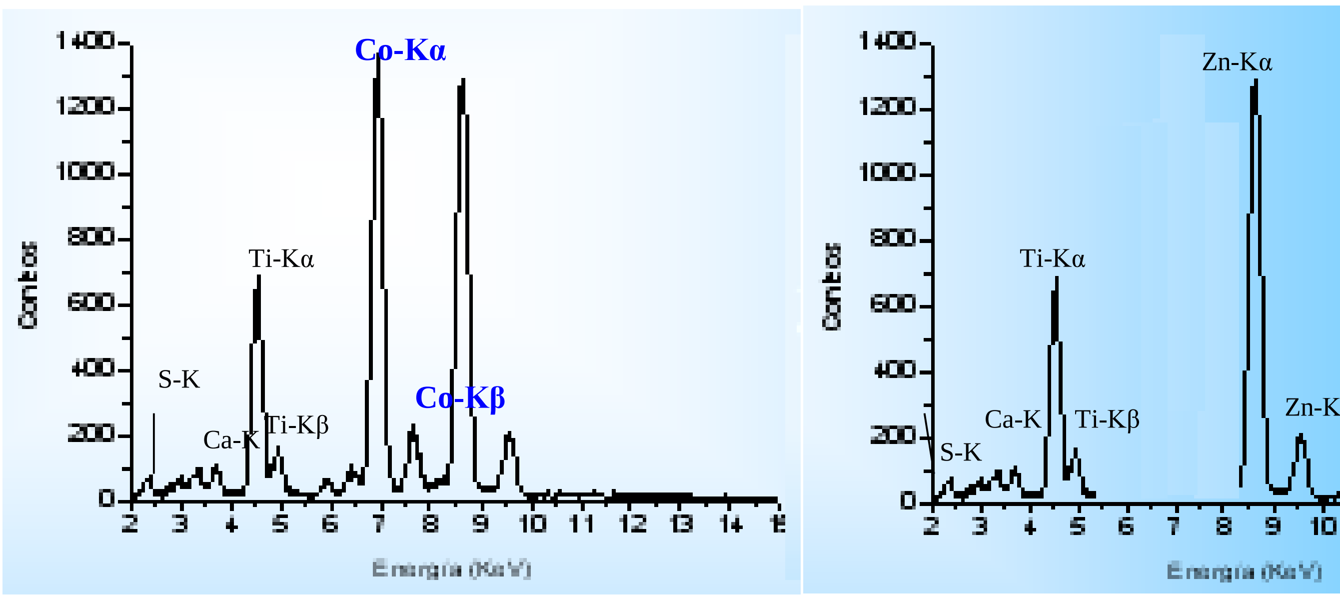
Multilayer system

Development of methodology for non invasive and in situ analysis for *painting* attribution



Incident beam

White target spectrum



Cobalt blue

1.14 keV - 5.09 keV (S, Ca y Ba o Ti)
9.08 keV -10.09 keV (Zn-Kβ)

PXRF data - Multivariate analysis of paintings

Servando Cabrera´s easel paintings

Processing conditions of "white target spectra" data

No. samples	Ranges	Pre-processing
5-10 point x color 28 paintings 492 (25 Servando's paintings) + 178 (16 models paintings) **670 espectra , total**	$E_i \ldots E_f$ *1.14 keV - 5.09 keV (S, Ca y Ba o Ti)* *9.08 keV -10.09 keV (Zn-Kβ)* X - $I_i \ldots I_f$	*Multiscattering*
	PCA parameters *Confidence level: 0.95* *5 Principal componentes (97%):* • *Variance* • *Percent* • *PRESS*	

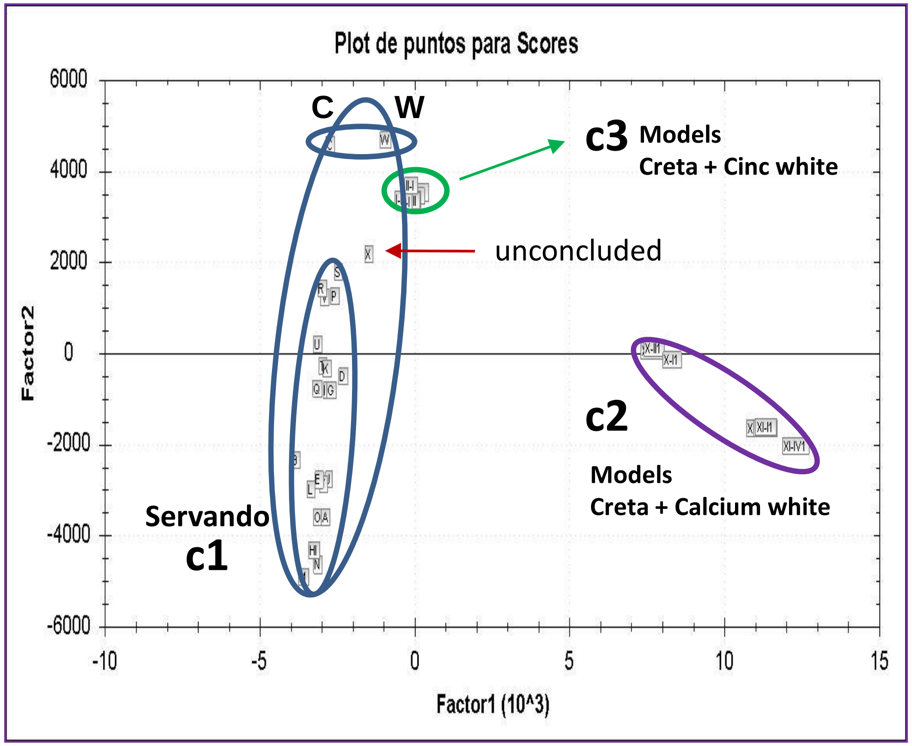
Algoritms fo constructing the classification models

SIMCA: Soft Independent Modeling of Class Analogy

PLS-DA: Partial least square discriminate analysis

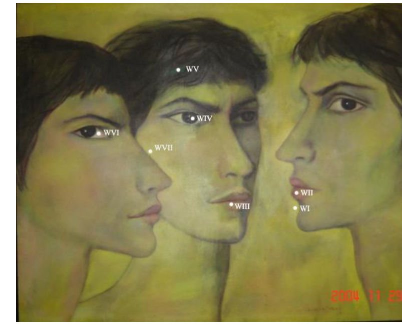
SVM: Support Vector Machine

PCA



with undepainting

W



C

X

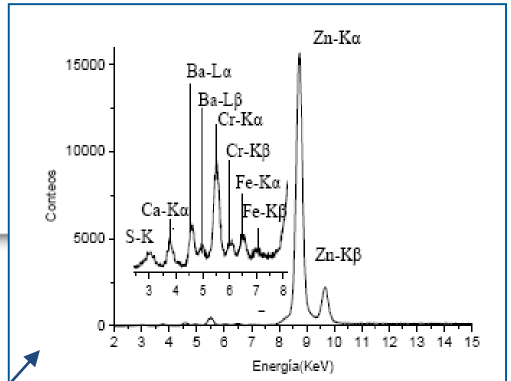
unconcluded

Prediction

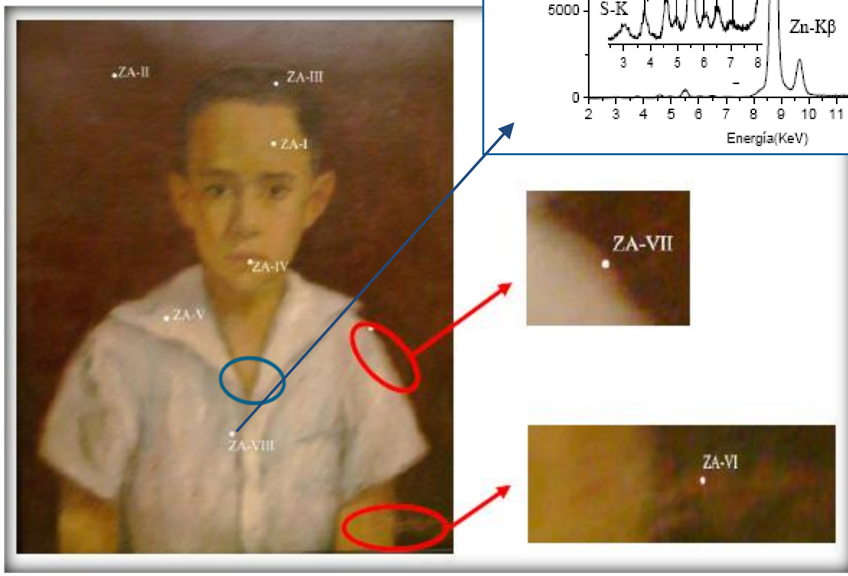
Set 1	SIMCA		PLS-DA			SVM	Set 2	SIMCA		PLS-DA			SVM
	Mejor	vecina	c1	c2	c3	Clase predicha		Mejor	vecina	c1	c2	c3	Clase predicha
E	1	-1	1	0	0	1	C	-1	-1	1	0	0	1
F	1	-1	1	0	0	1	F	1	-1	1	0	0	1
N	1	-1	1	0	0	1	D	1	-1	1	0	0	1
II-I1	3	-1	0	0	1	3	II-I1	3	-1	0	0	1	3
II-III1	3	-1	0	0	1	3	II-III1	3	-1	0	0	1	3
I-V	3	-1	0	1	0	2	I-V	3	-1	0	1	0	2
IX-V	2	-1	0	1	0	2	IX-V	2	-1	0	1	0	2

A. Mendoza , I. Maqueira, Identificación de pigmentos y obtención de un modelo de atribución en pinturas. Estudio de la pintura de Servando Cabrera, revista Cubana de Física, aceptado, 2011

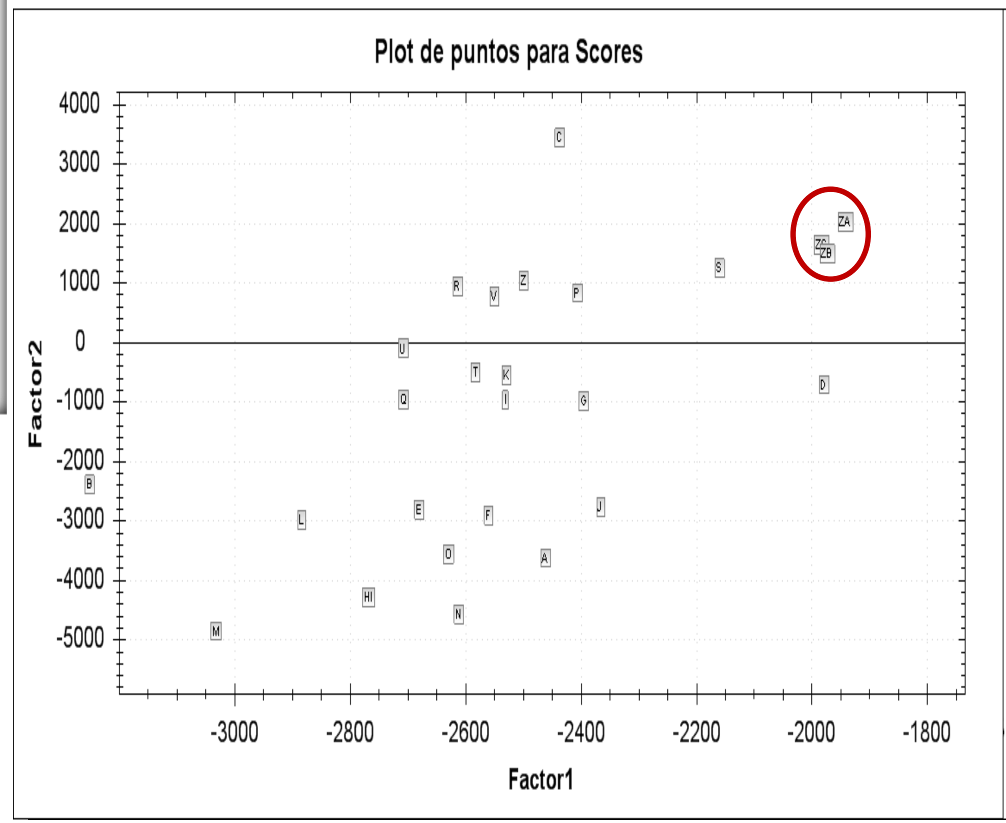
Qualitative analysis



Painting of pending attribution



ZB



Multivariate analysis

Atribution

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- L. R. Velazquez Maldonado, M. Correa Jimenez, colegues at Havana,s Archaeometry Laboratory, Cuba

- restorer, curator,museologist and archaeologist of Havana´s Historian Office, colegues at Archaeometry Laboratory

Thanks for your attention !

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