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Joint ICTP/IAEA Advanced School on in-situ X-ray Fluorescence and Gamma Ray Spectrometry

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Methodology, advantages and limitations of in-situ XRF measurements (including overview of applications)

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Methodology of in-situ EDXRF analysis: Advantages, limitations and applications

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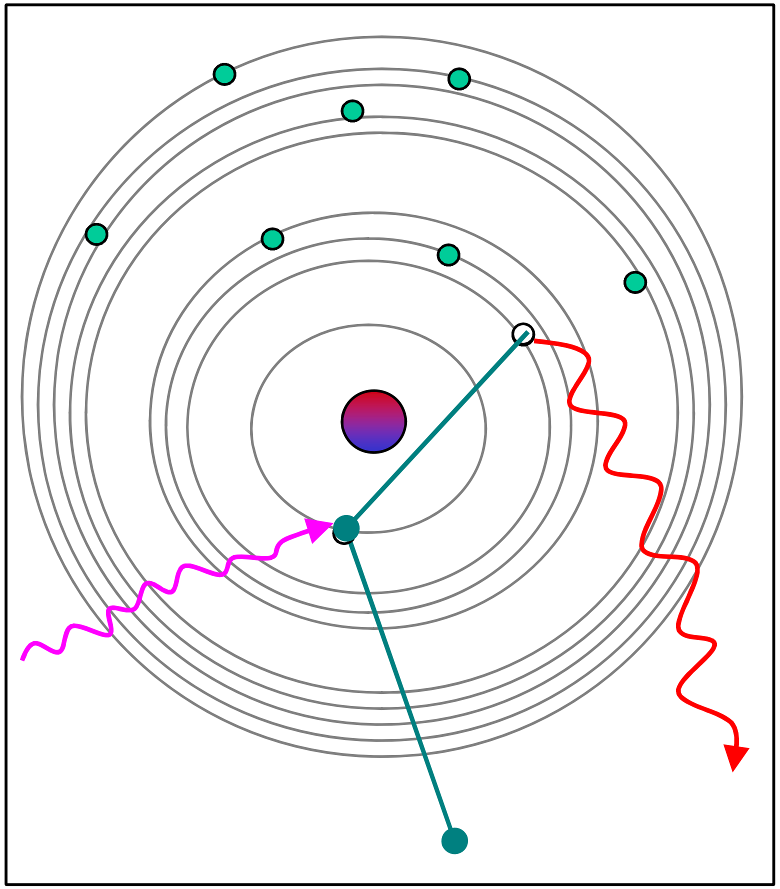
Layout:

- Introduction
  - Fundamentals of XRF analysis
  - IAEA NA XRF laboratory mission
  - Available instrumentation
- Specifics of in-situ EDXRF analysis
  - Advantages
  - Limitations
    - Heterogeneity in effective sample information volume
    - Performance (Trueness, Detection Limits, Uncertainty)
    - Interfering factors, effects and possible corrections
      - Physical nature effects (Particle size, Heterogeneity of particles, Mineralogy heterogeneity, Surface irregularities)
      - Chemical effects (matrix)
- Examples of applications

The origin of characteristic x-rays:



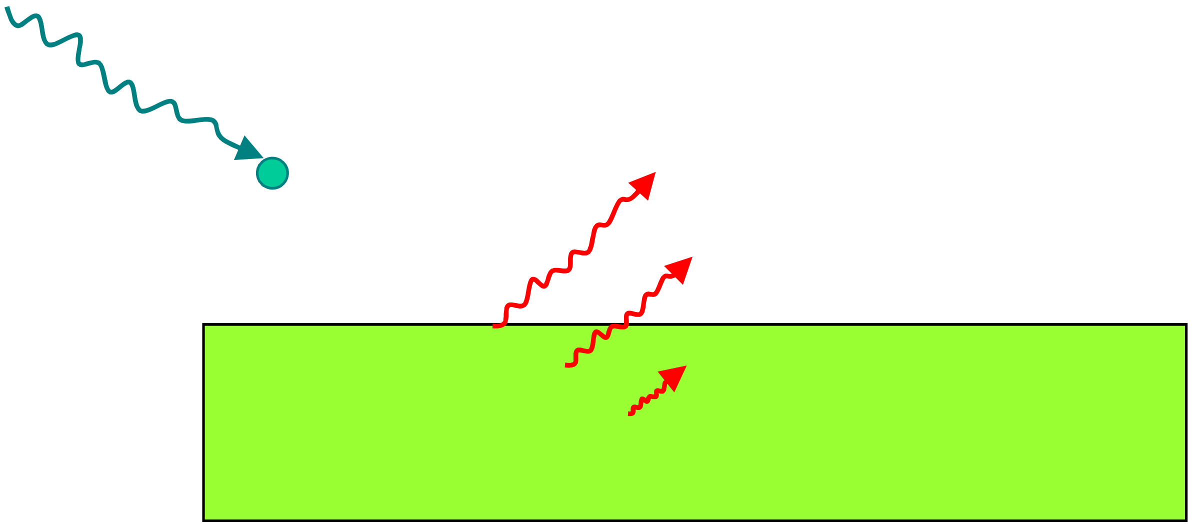
- A particle/photon interacts with an inner-shell electron. If its energy is larger than that of the shell binding energy, the electron is expelled
- An electron from any of the outer shells takes the vacancy recently created
- The excess of energy is released in the form of x-ray

  ➔ Such transitions are allowed by compliance with the principle of exclusion of Pauli

  ➔ CHARACTERISTIC RADIATION

The origin of x-rays: Bremstrahlung

German term for “breaking radiation”

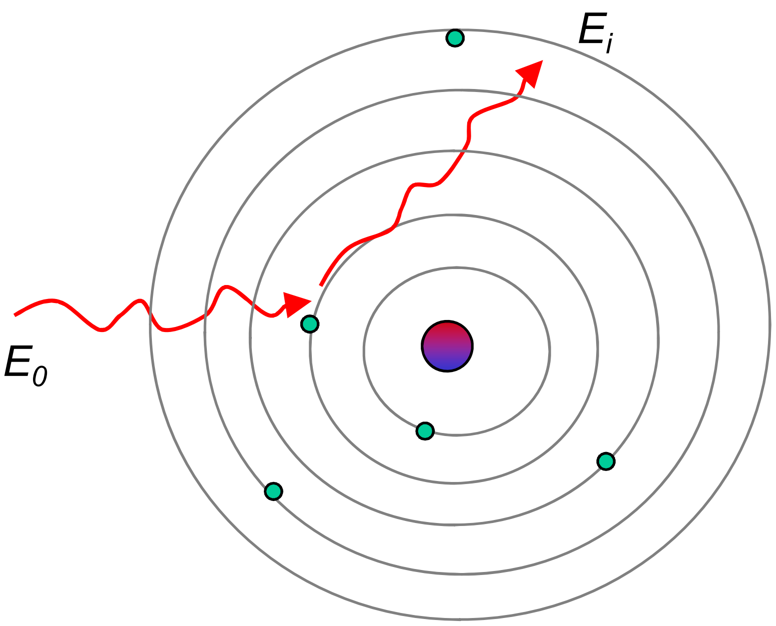


As the electron travels through the matter, it suffers a deceleration process.

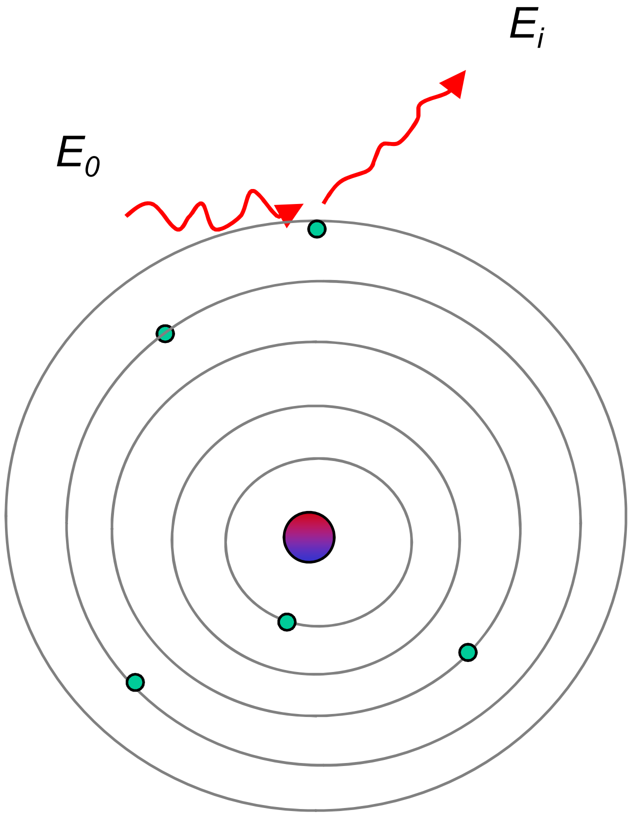
Deceleration is accompanied by the emission of x-rays of variable energy.

Main interactions of x-rays with matter

- ✓ photoelectric absorption
- ✓ x-ray scattering

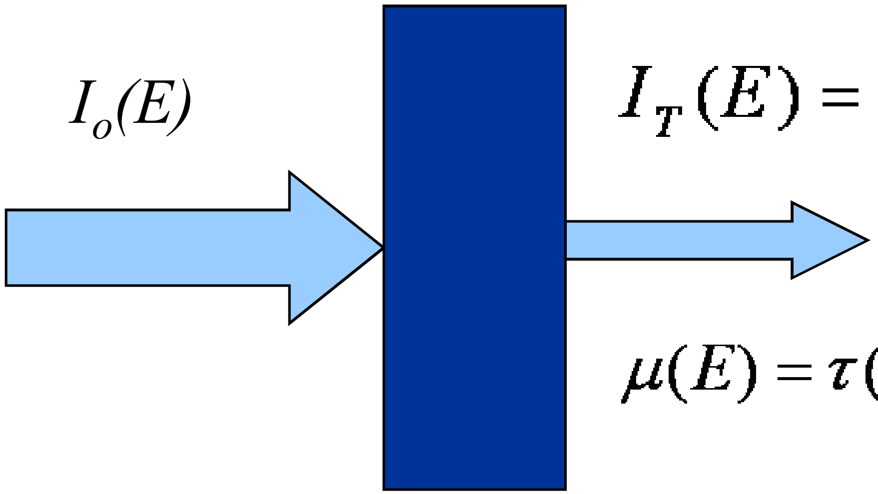


$E_i=E_0$: Coherent (Rayleigh)
mostly with inner $^-$e



$E_i < E_0$: Incoherent (Compton)
mostly with outer $^-$e

Attenuation of x-rays in the matter



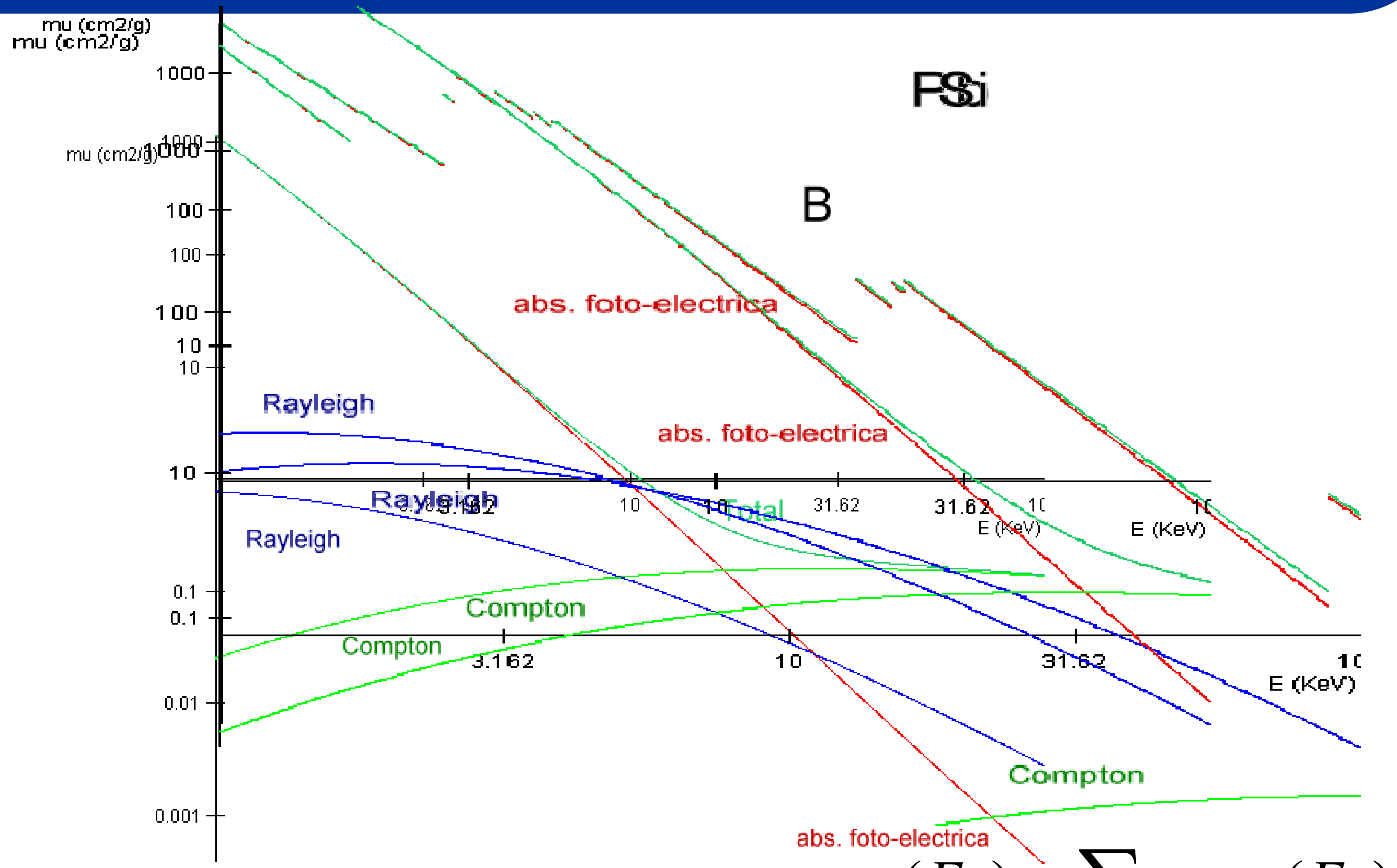
$I_o(E)$

$$I_T(E) = I_0(E)e^{-\mu(E)\rho d}$$

$$\mu(E) = \tau(E) + \sigma_R(E) + \sigma_C(E)$$

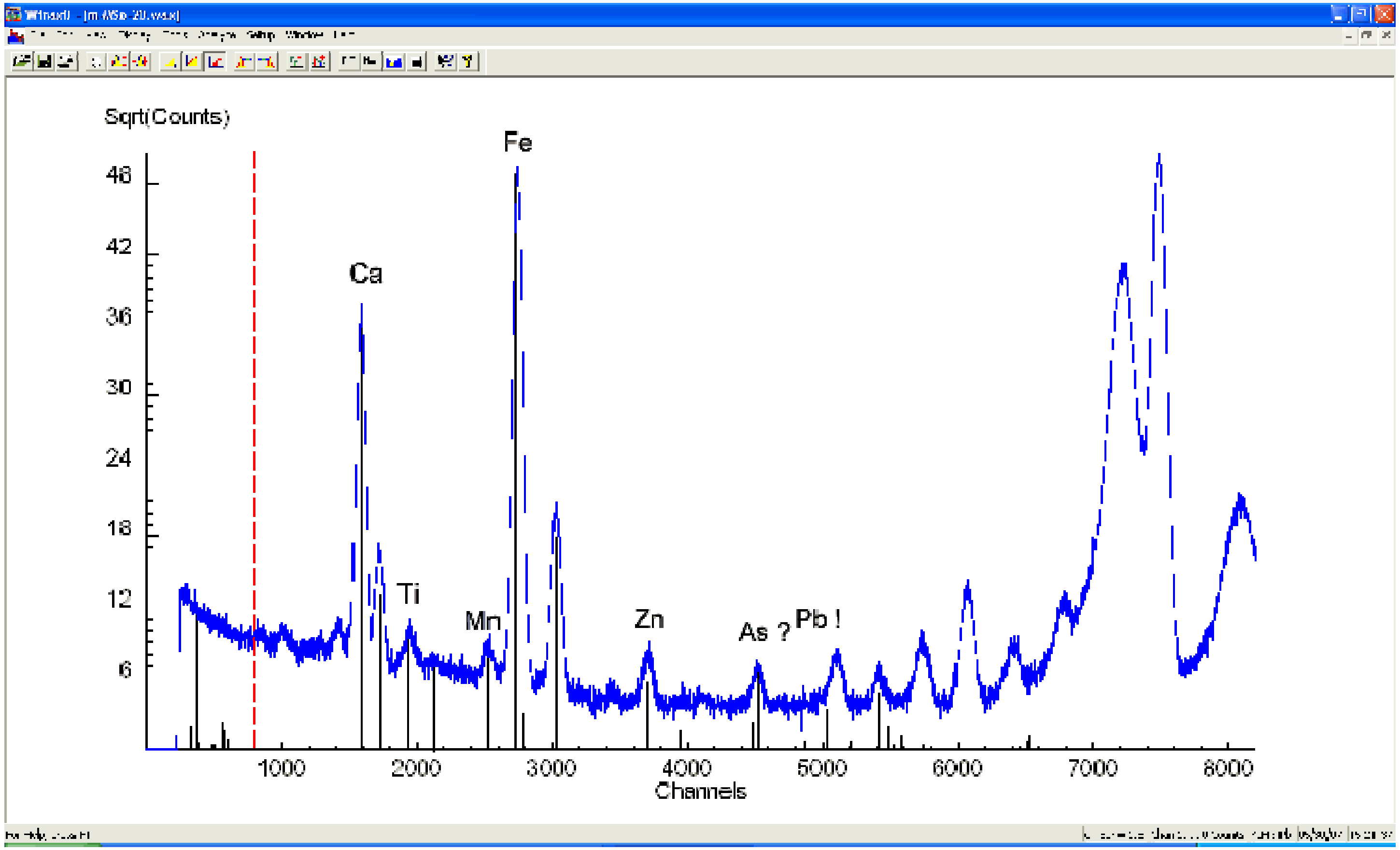
- ⇨ **τ (E)** – photo-electric absorption cross section
- ⇨ **σ_R (E)** – elastic scattering cross-section
- ⇨ **σ_C (E)** – inelastic scattering cross-section

Effective attenuation coefficient $\mu(E)$

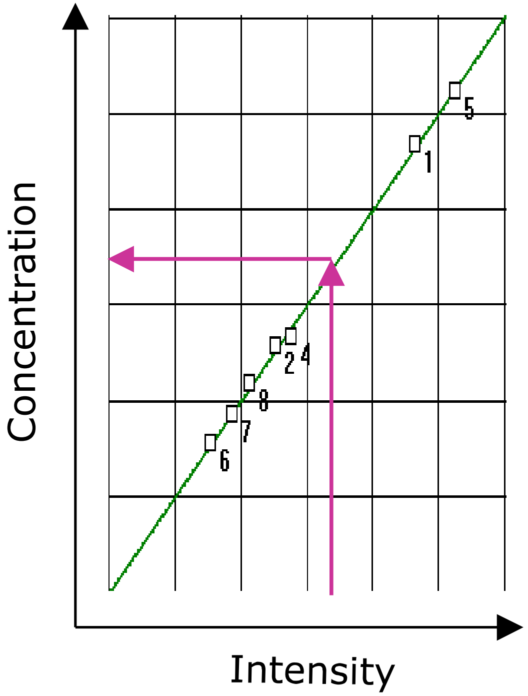


Sample effective attenuation coefficient $\mu_m(E_0) = \sum_j w_j \mu_j(E_0)$

Qualitative analysis: Characteristic x-rays allow unambiguous elemental identification!



Quantitative analysis



XRF is a reference method, standards are required for both, calibration procedure and to assess the quality of the quantitative results.

Standards are measured, intensities obtained, and certain calibration (intensities vs. concentration) is established.

Commercial XRF instruments usually compare the spectral intensities of unknown samples to those of known standards.

ADVANTAGES

- Multi-elemental capability
- Simple sample preparation
- Low contamination risks
- Non-destructive or minimal sample alteration
- Short term delay in obtaining the results
- Relatively low investment and operational costs

The major difficulty for EDXRF quantitation…

$$\boxed{I_i} = \varepsilon(E_i)\boxed{w_i} \int_{E>E_i^{ab}}^{E_{\max}} GK_i A(E_0,E_i) R_i(E_0,E_j) I_0(E_0)\,dE_0$$

- It is a non-linear (on w_i) dependence, since…

$$A(E_0,E_i) = \frac{[1-\exp(-\chi_i \rho_S x)]}{\chi_i}$$ ➡ attenuation within the sample depends on the sample effective attenuation coefficient χ_i and on sample aerial density $\rho_S x$ (mass per unit area, gcm^{-2}]

$$\Rightarrow \quad \chi_i = \frac{\mu_S(E_0)}{\sin\varphi} + \frac{\mu_S(E_i)}{\sin\phi} = ????$$

$R_i(E_0,E_j)$ ➡ enhancement effects are difficult to estimate, and also require of knowledge on elemental composition

$$\Rightarrow \quad R_i(E_0,E_j) > 1 \;\left|\; \begin{array}{l} w_j > 0.01 \\ E_j > E_i^{ab} \end{array}\right.$$

Mission of the IAEA NA XRF Lab:

Assisting Member States in introducing and extending the use of X-ray spectrometry techniques

- Training
- Research aimed to improve analytical performance and to extend applicability
- Provision of analytical services

Instrumentation available at the IAEA XRF Lab:

Commercial EDXR spectrometer
SPECTRO 2000 (excitation using Pd-anode x-ray tube +
ST and polarizers)

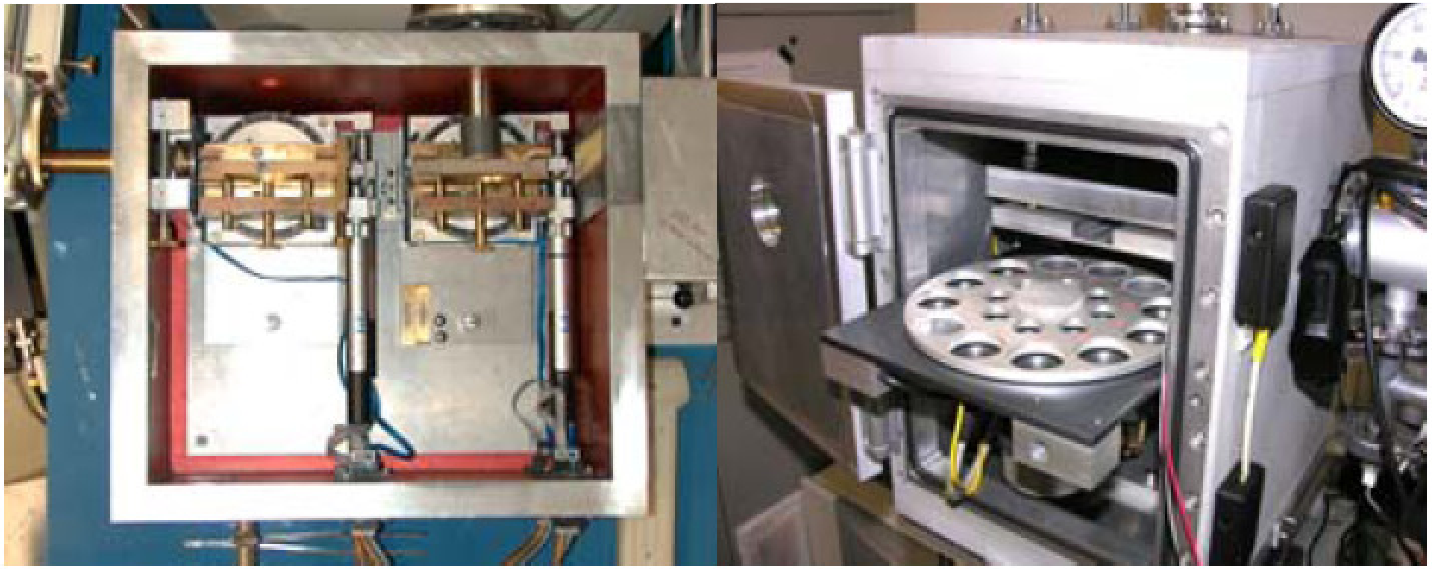
Instrumentation available at the IAEA XRF Lab:

Commercial bench-top EDXR spectrometer
Mini-PAL 4 (excitation using x-ray tube + filters)

Instrumentation available at the IAEA XRF Lab:

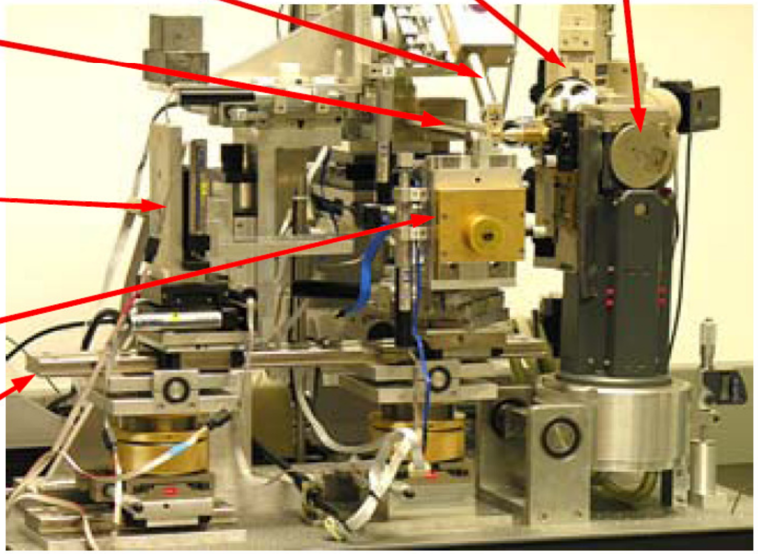
In-house assembled (modular) x-ray spectrometers

- Rh-anode x-ray tube + ST
- Radioisotope excitation
- TXRF (Atominstitut design)



Instrumentation available at the IAEA XRF Lab:

In-house assembled μ–XRF spectrometer



Si drift detector (fluorescence) on a stage

optical microscope

X-ray tube

Si(Li) detector (confocal)

transmission detector stage

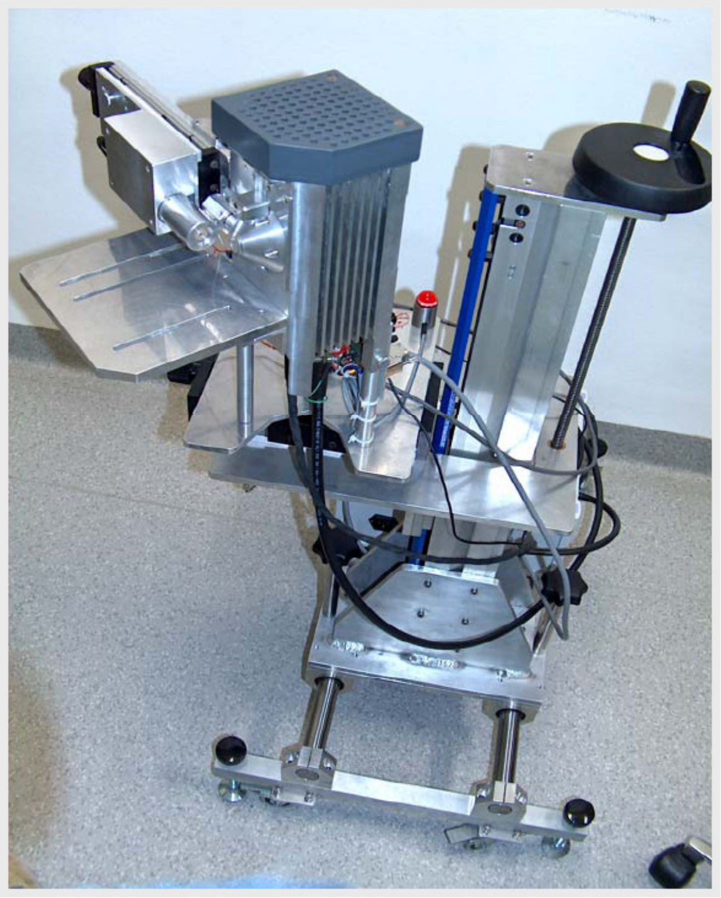
sample stage

optical bench

Instrumentation available at the IAEA XRF Lab:

Portable spectrometer (excitation using ^{55}Fe, ^{109}Cd,^{241}Am)

Instrumentation available at the IAEA XRF Lab:



Trans-portable
spectrometer (V 1)
Excitation using
Ag-anode 50 W x-ray tube

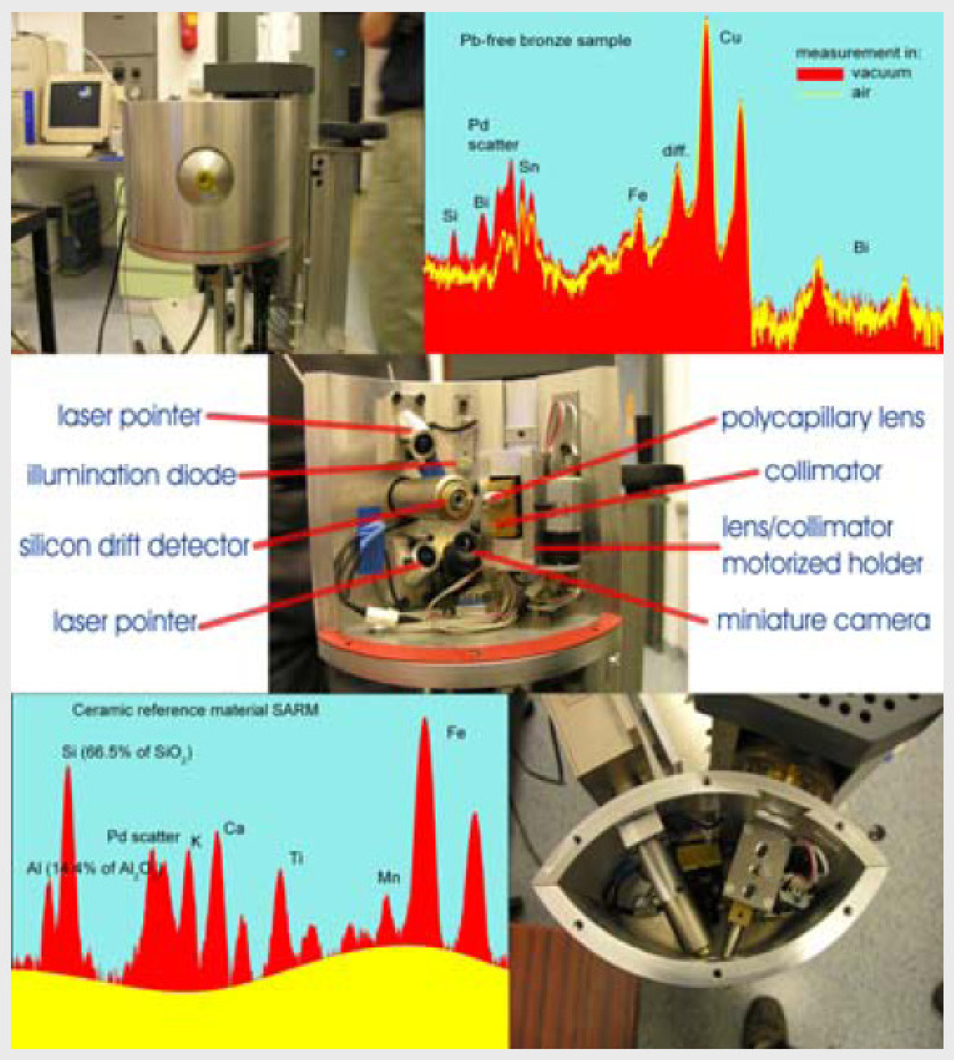
- Collimation, or
- ST excitation
- Air path

Instrumentation available at the IAEA XRF Lab:

Trans-portable spectrometer (V 2)
Excitation using
Ag-anode 50 W x-ray tube and

- Poli-capillary lens (~ 30 μm)
- Vacuum path

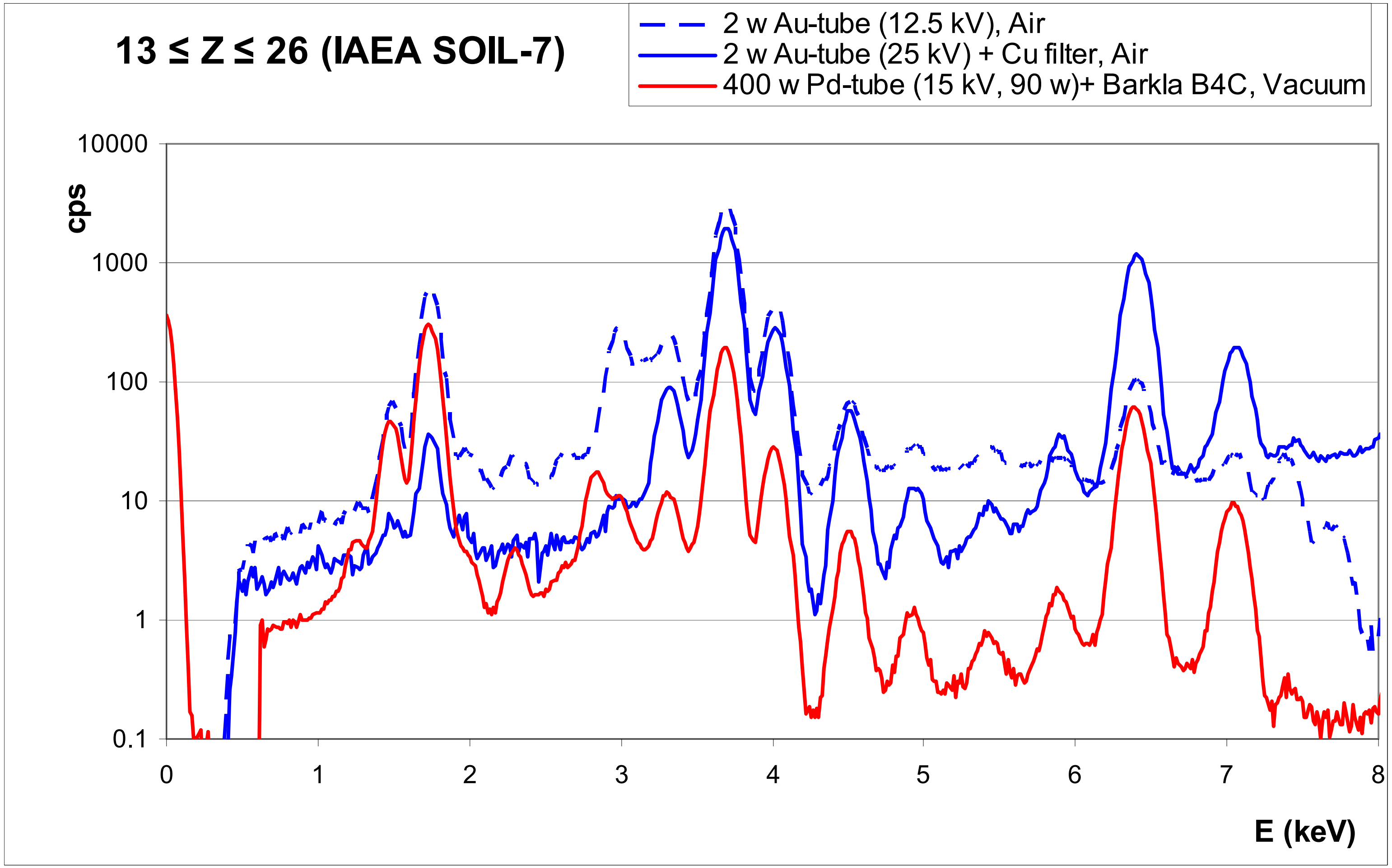
Instrumentation available at the IAEA XRF Lab:



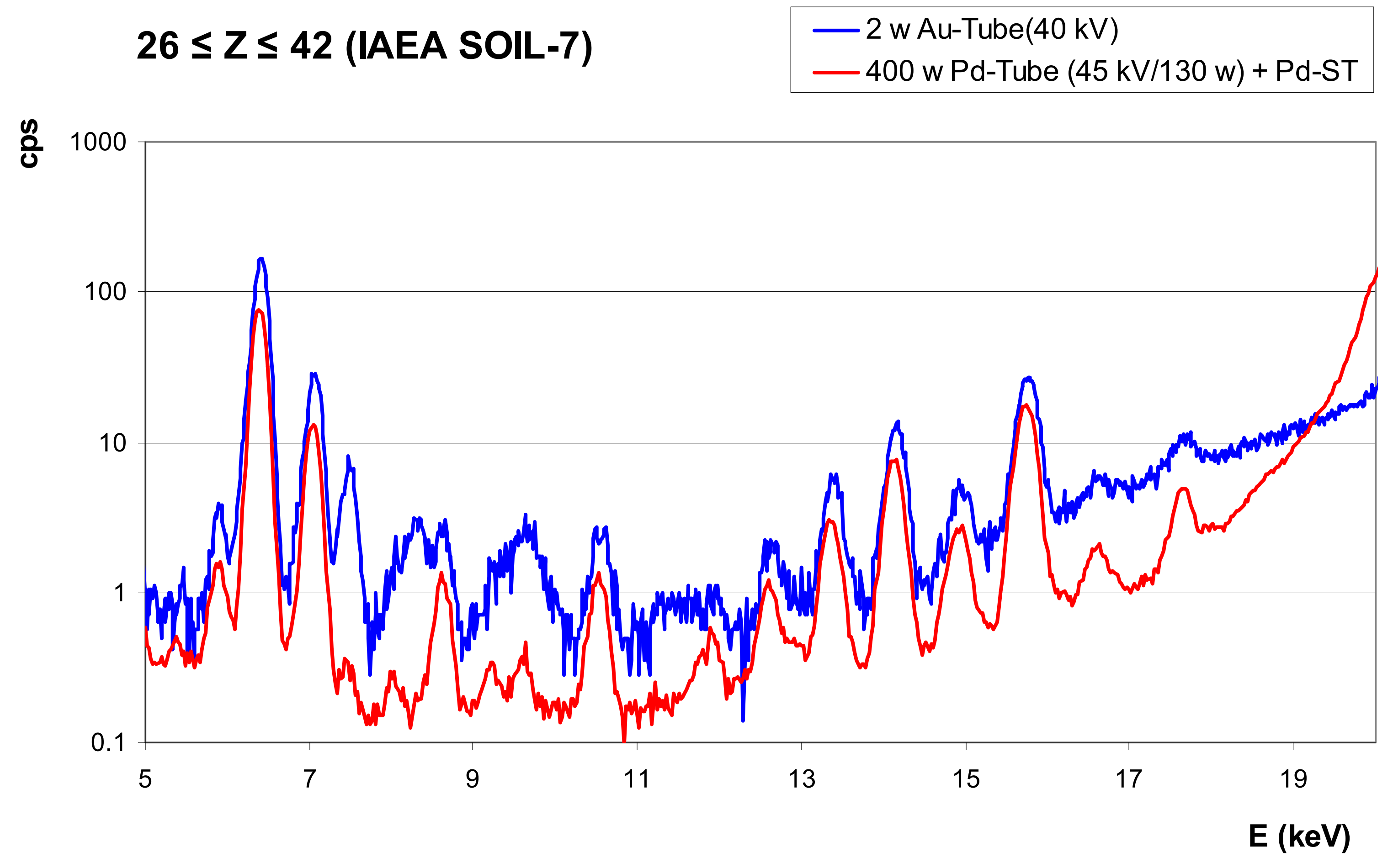
ADVANTAGES OF IN-SITU XRF ANALYSIS

- Multi-elemental capability
- Non-destructive
- Short term delay in obtaining the results
- Relatively low investment and operational costs
- State of art instrumentation offers comparable instrumental sensitivity (although higher DL)

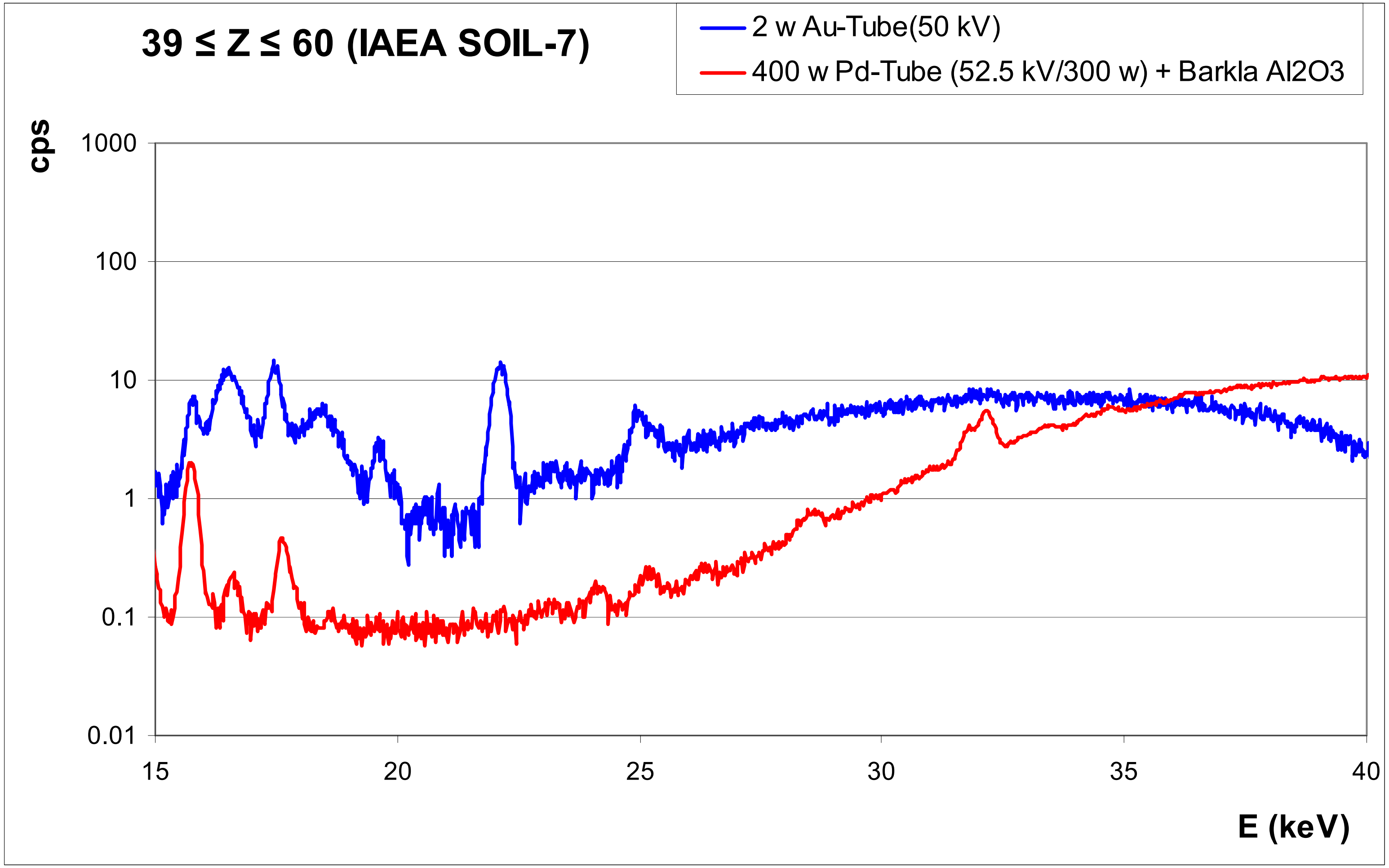
Comparison: Secondary Target Vs Filter



Comparison: Secondary Target Vs Filter



Comparison: Secondary Target Vs Filter



GENERAL LIMITATIONS IN XRF ANALYSIS

- Strong matrix effects must be considered (attenuation, enhancement)
- Impossible to measure radiation from all elements
- Complex relationship between the measured signal and the measurand (concentration or mass fraction)
- Radiation exposure precaution
- Requires specialized training and concern

CONSIDERATIONS FOR IN-SITU XRF ANALYSIS

- Sample effective information layer

Sample thickness from which 99% of a fluorescence signal originates

$d_{crit} = m_{thick}/\rho = 4.61/(\rho\mu_{tot})$

$\mu_{tot} = \mu(E_0)\csc\Psi_1 + \mu(E_i)\csc\Psi_2$

Characteristic radiation (Energy, keV)	Penetration depth, μm	
	$\vec{Z}=12.5$	$\vec{Z}=15$
P, Kα (2.01)	12	9
Ca, Kα (3.69)	50	32
Zn, Kα (8.62)	540	340
Pb, Lα (10.51)	930	570

CONSIDERATIONS FOR IN-SITU XRF ANALYSIS

- Sample effective information layer

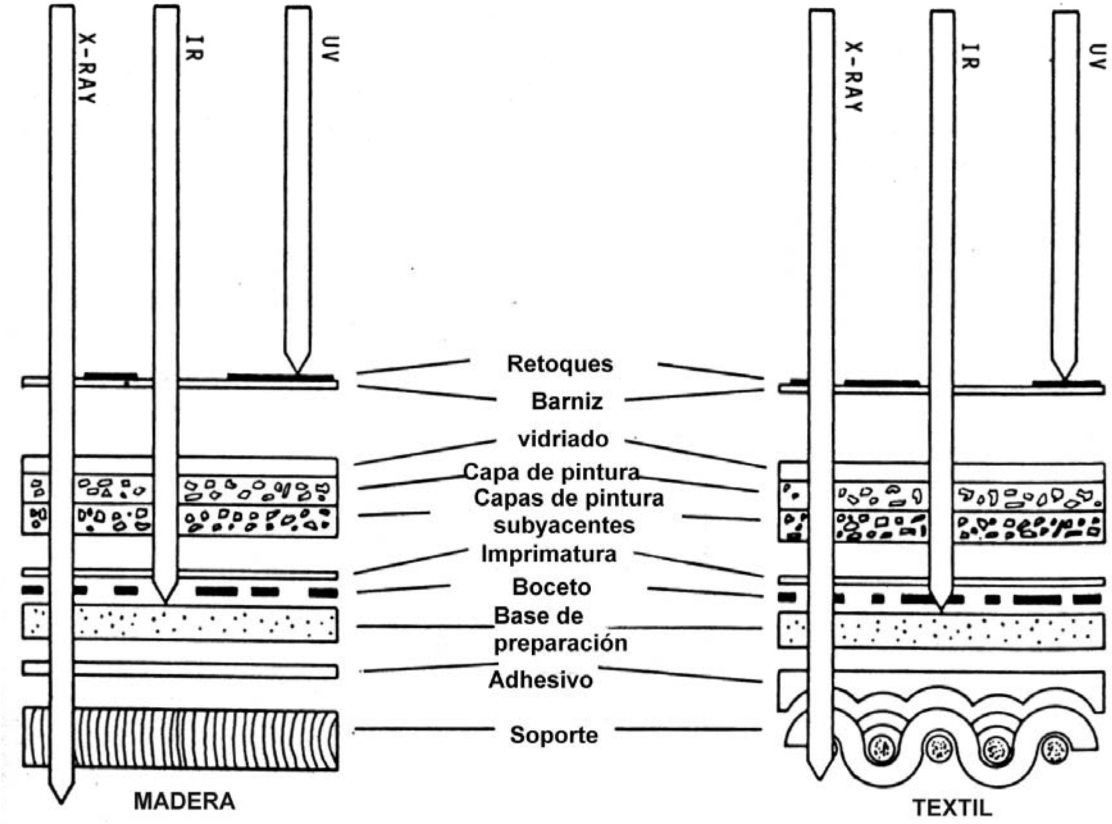
50 % of d_{crit} $\Rightarrow$ 90% of fluorescence signal
35 % of d_{crit} $\Rightarrow$ 80% of fluorescence signal
15 % of d_{crit} $\Rightarrow$ 50% of fluorescence signal

Essential in the analysis of heterogeneous samples (mineralogy effects), samples of irregular surface or with surface contamination

CONSIDERATIONS FOR IN-SITU XRF ANALYSIS

- Heterogeneous cross-section profile of the information volume

  (e.g. cross section of a painting)



CONSIDERATIONS FOR IN-SITU XRF ANALYSIS

Assessment of the trueness of the results

- Absence of suitable CRM

→ Comparison with results obtained by a reference (laboratory) method

  → $0.7 < r^2 < 0.9$ – screening level

  → $r^2 > 0.9$ – results are of commensurable trueness

CONSIDERATIONS FOR IN-SITU XRF ANALYSIS

Assessment of Detection Limits

DL are never interference-free

- Options:

→ Precision-based approach:

DL = 3 x SD of results of low concentration samples

- 'low' ~ 5 times de value of expected instrumental sensitivity DL
- use of appropriate CRM or spiked clean samples

→ Field of performance-based:

DL = disintegration of linearity in the correlation between log values of results obtained by in-situ and by laboratory reference method

CONSIDERATIONS FOR IN-SITU XRF ANALYSIS

Assessment of uncertainty of the results

Main sources contributing:

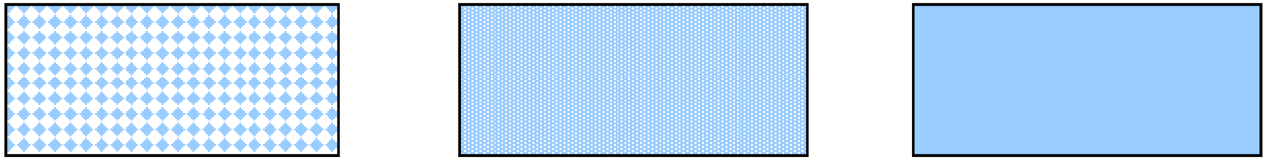
- Due to sample heterogeneity in effective inspected volume
- Departures from assumptions during sample measurement
- Sample handling / preparation
- Inherent to the analytical model

Physical Factors, Effects and possible procedures for correction

Particle size effects and compactness:

- Different size of particles of the same composition

Illita: $2K_2O \bullet 3(Mg,Fe)O \bullet 8(Al,Fe)_2O_3 \bullet 24SiO_2 \bullet 12H_2O$



Air: 15 % volume, 5 % volume , 0 % volume

Attenuation correction (E_0=17.44, E_i)

Al-Kα (1.48)	0.000437	0.000433	0.000432
Si-Kα (1.74)	0.000571	0.000557	0.000550
K -Kα (3.31)	0.001967	0.001843	0.001787
Fe-Kα (6.39)	0.009376	0.008664	0.008348

Physical Factors, Effects and possible procedures for correction

Heterogeneity of Particles

(when focus of excitation is comparable with particle size):

- Different shape particles
- Different mineralogy particles

K in:
Illita - $2K_2O \bullet 3(Mg,Fe)O \bullet 8(Al,Fe)_2O_3 \bullet 24SiO_2 \bullet 12H_2O$
K- feldspar - $K[AlSi_3O_8]$
Muscovite - $KAl_2[(OH,F)_2|AlSi_3O_{10}]$

⇨ Average on *n* measurements

n is related to target RSD(%) and average concentration w_{ave} as:

$$n = \left(\frac{100 \times \sigma}{RSD \times w_{ave}} \right)^2$$

Physical Factors, Effects and possible procedures for correction

Surface irregularities:

- Signal from convex or concave surfaces is lower than that originating from flat surface

  - theoretical models to calculate unevenness factor (source-sample distance, surface peak-valley amplitude, frequency number of convex and concave surfaces)

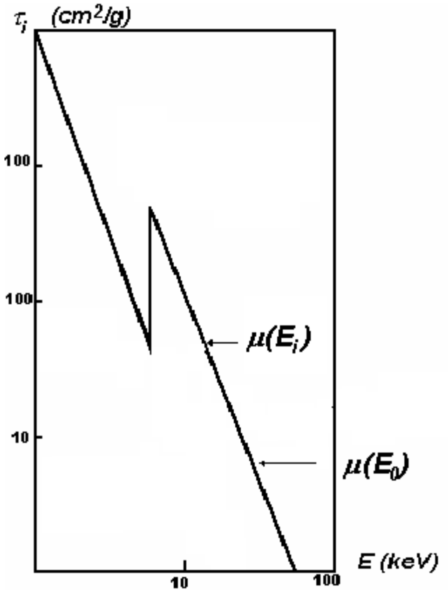
  - use of Compton / Rayleigh scatter

$$N_i = G \times K_i(E_0) \times A(E_0, E_i)\varepsilon(E_i)I_0(E_0)$$

$$\frac{N_i}{N_i^{flat}} = \frac{G}{G^{flat}} \quad \Rightarrow \quad N_i^{corr} = N_i^{flat} = N_i \times \frac{Sc^{flat}}{Sc}$$

Chemical (matrix) effect and possible procedures for correction

Differences in attenuation correction: Use of Compton scatter to correct for differences in matrix composition



$$\log[\mu(E_i)] - \log[\mu(E_0)] = \log\left[\frac{\mu(E_i)}{\mu(E_0)}\right]$$

$$\log(E_i) - \log(E_0) = \log(\frac{E_i}{E_0})$$

$$\frac{\log[\mu(E_i)] - \log[\mu(E_0)]}{\log(E_i) - \log(E_0)} = slope = A \quad \Rightarrow \quad \frac{\mu(E_i)}{\mu(E_0)} = \left(\frac{E_i}{E_0}\right)^A$$

$$\frac{1}{\chi_i} = \frac{\sin\theta_2 \sin\theta_1}{\mu_M(E_i)\sin\theta_1 + \mu_M(E_0)\sin\theta_2} =$$

$$= \frac{\sin\ \theta_2\ \sin\ \theta_1}{\mu_M(E_0)\left(\frac{E_i}{E_0}\right)^A \sin\ \theta_1 + \mu_M(E_0)\sin\ \theta_2} =$$

$$= \frac{\sin\theta_2 \sin\theta_1}{\mu_M(E_0)\left[\left(\frac{E_i}{E_0}\right)^A \sin\theta_1 + \sin\theta_2\right]}$$

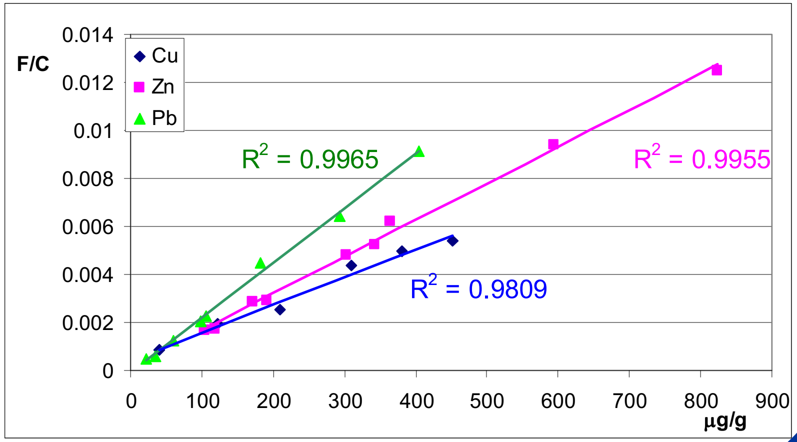
Chemical (matrix) effect and possible procedures for correction

Differences in attenuation correction: Use of Compton scatter to correct for differences in matrix composition

$$I_i = G\varepsilon(E_i)w_i \frac{K_i \sin\theta_2 \sin\theta_1}{\mu_M(E_0)\left[\left(\frac{E_i}{E_0}\right)^A \sin\theta_1 + \sin\theta_2\right]} I_0(E_0)$$

$$I_C = \frac{G_C \varepsilon(E_C)\sin\theta_2 \sin\theta_1}{\mu_M(E_0)\left[\left(\frac{E_C}{E_0}\right)^A \sin\theta_1 + \sin\theta_2\right]} I(E_0)\sum_i \frac{N_0}{A_i} w_i \sigma_{C,i}$$

$$\frac{I_i}{I_C} = \frac{G}{G_C} \times \frac{\varepsilon(E_i)}{\varepsilon(E_C)} \times \frac{\left(\frac{E_C}{E_0}\right)^A \sin\theta_1 + \sin\theta_2}{\left(\frac{E_i}{E_0}\right)^A \sin\theta_1 + \sin\theta_2} \times \frac{w_i K_i}{\sum_i \frac{N_0}{A_i} w_i \sigma_{C,i}}$$



Chemical (matrix) effect and possible procedures for correction

Differences in attenuation correction:

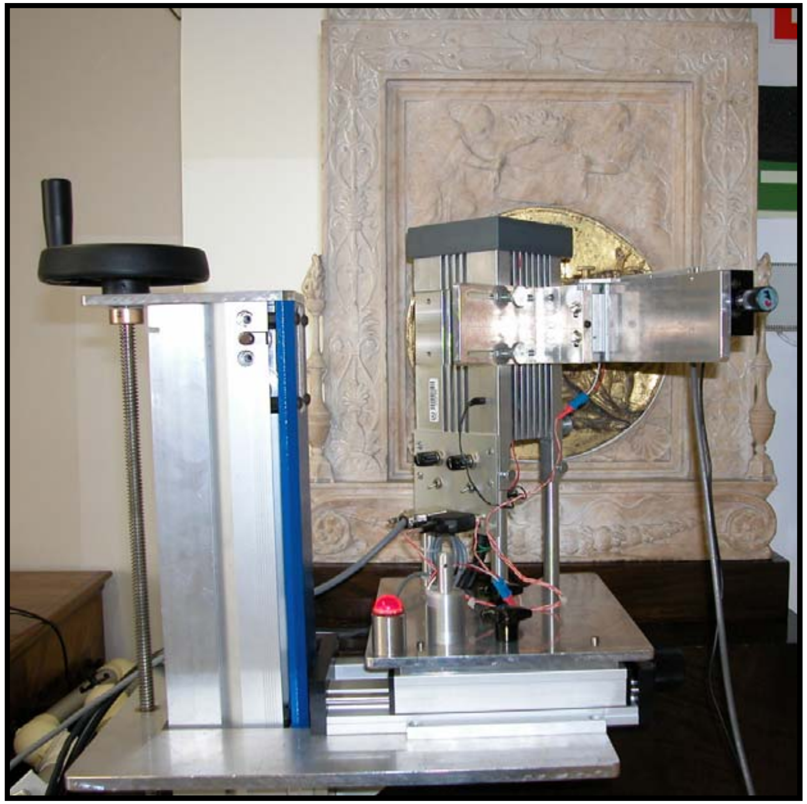
For different matrices

$I_i / (I_{Com})^S$ vs. concentration
(*L.G.Livingstone, X-Ray Spectrometry, 1982, 11, 89*)

For two samples with different matrices *a* and *b*, and the same concentration of the analyte, the optimum *S* from:

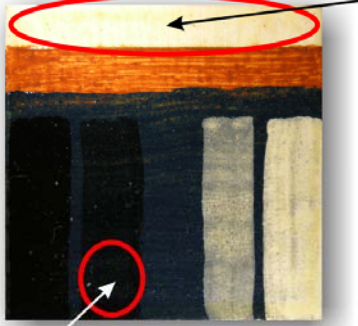
$$(I_{i,b} / I_{i,a}) / (I_{sct,b} / I_{sct,a})^S = 1$$

Applications in cultural heritage studies:
Analysis of bronze objects



“Virgin and Child” by Donatello (Florence 1386 - 1466) - a bronze tondo from Kunsthistorisches Museum’s (Vienna) collection. Average composition of the bronze was used for documentation purposes.

Applications in cultural heritage studies:
Identification of pigments



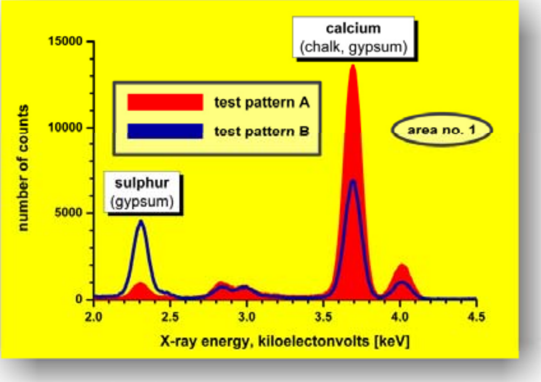
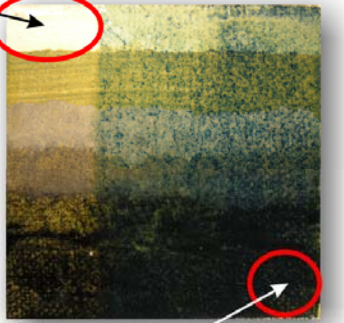


Fig. 1. X-ray spectra, area no. 1



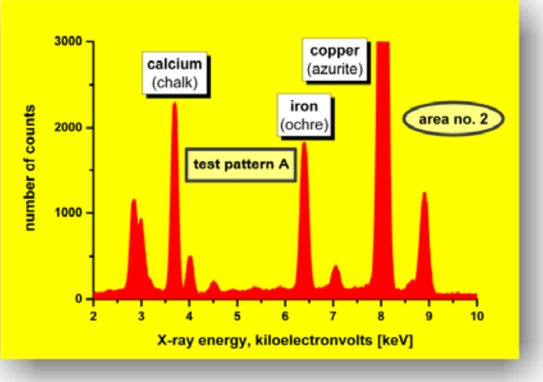


Fig. 2. X-ray spectrum, pattern A, area no. 2

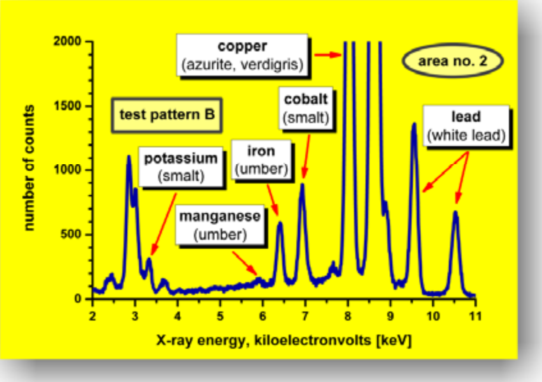
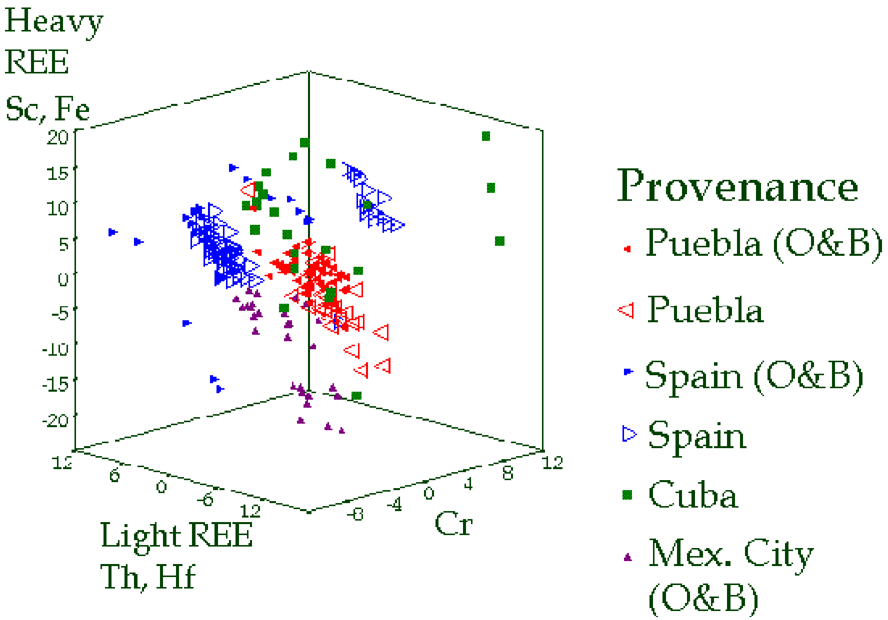


Fig. 3. X-ray spectrum, pattern B, area no. 2

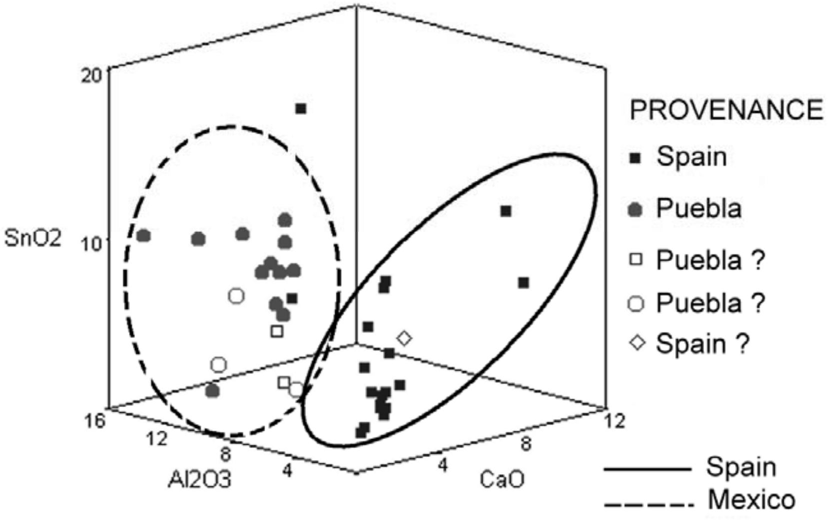
Applications in cultural heritage studies: Compositional classification of ceramics

Ceramic fabric

White glaze



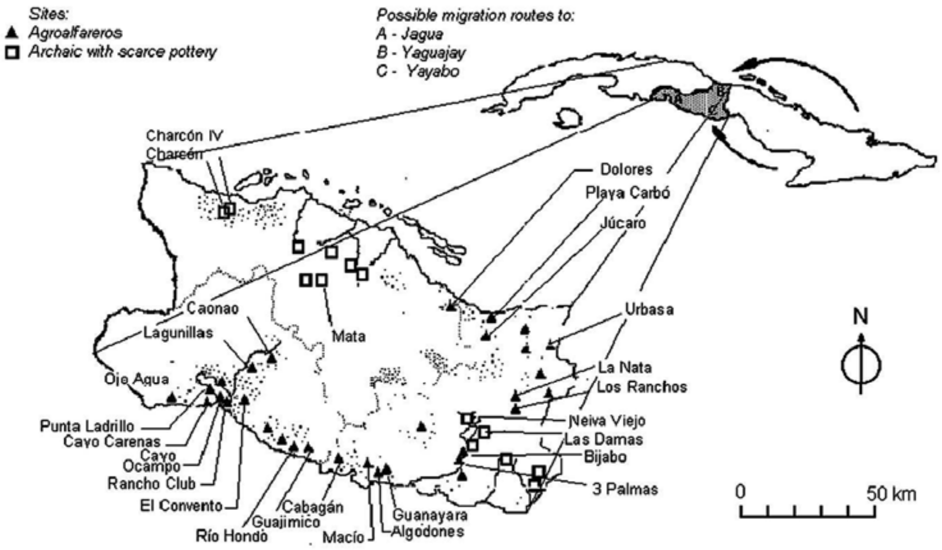
NAA

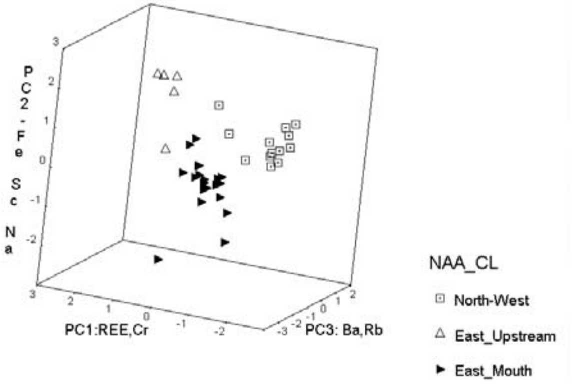


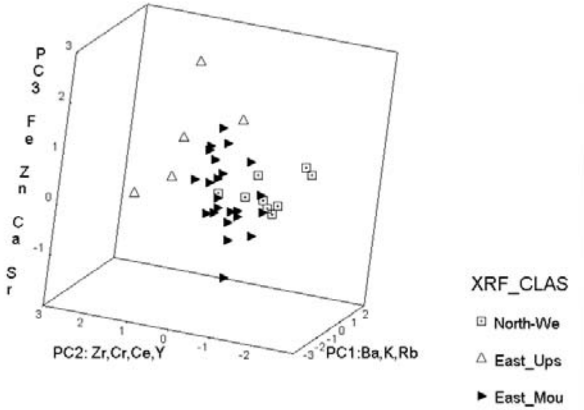
μ-XRF

Ref: *R. Padilla, Schalm O., Van Espen P., Janssens K., Arrazcaeta R. Micro analytical characterization of surface decoration in Majolica pottery. Analytica Chimica Acta 535(2005) 201-211*

Applications in cultural heritage studies: Compositional classification of ceramics







Ref: *Padilla R., Van Espen P., Godo P.P., The suitability of XRF analysis for the classification of archaeological ceramics: A comparison with a previous INAA study, Analytica Chimica Acta, Volume 558, Issues 1-2, 3 February 2006, Pages 283-289*

Applications in environmental pollution screening:

Applications in metal scrap sorting and RoHS identification:

Thanks for your time and attention…