



*The Abdus Salam
International Centre for Theoretical Physics*



1866-5

School on Pulsed Neutrons: Characterization of Materials

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The IAEA's programme on cultural heritage

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The IAEA's Programme on Cultural Heritage

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- Conclusions

Introduction

IAEA role:

- *transfer of technology for peaceful application of nuclear techniques in key areas of national importance such as food security, human health, water resources management, industry, protection of environmental etc.*


Introduction

Nuclear analytical techniques:

- INAA – instrumental neutron activation analysis
- PIXE – particle/proton induced X-ray emission
- RBS – Rutherford backscattering spectrometry
- XRF – X-ray fluorescence

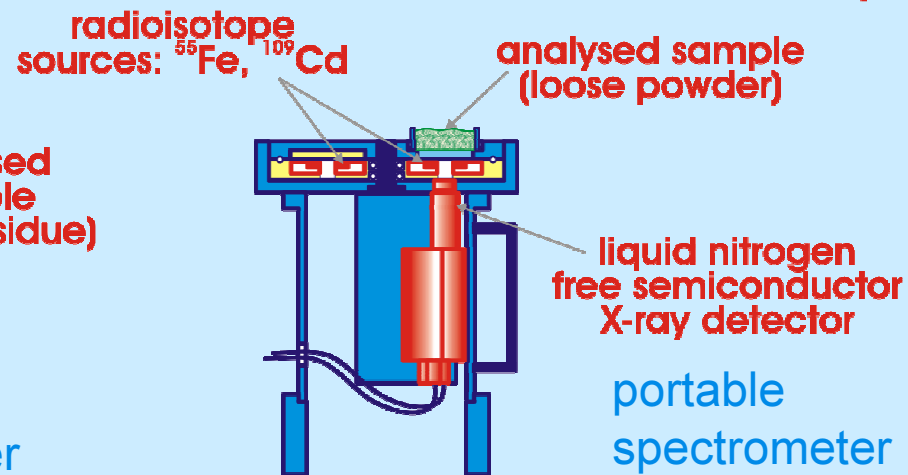
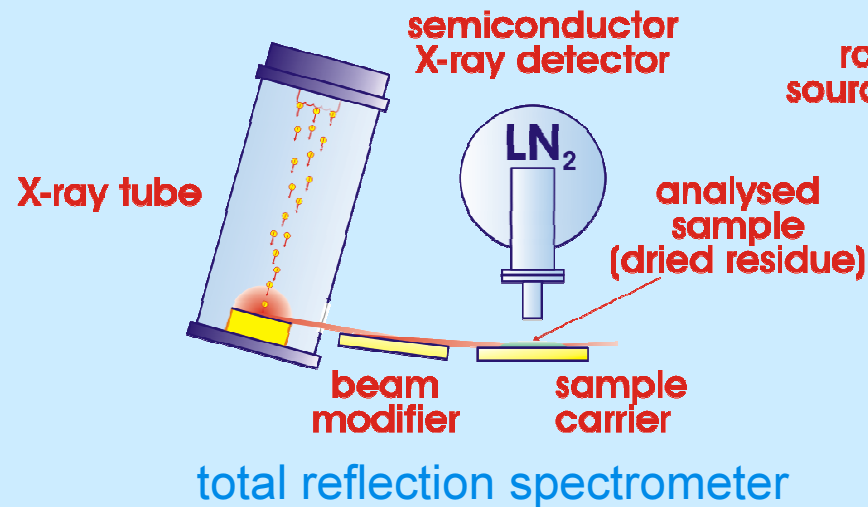
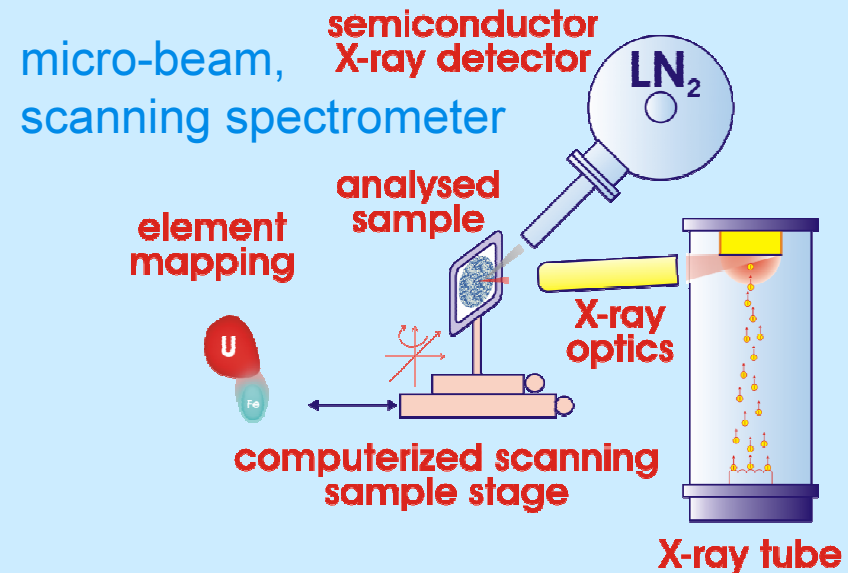
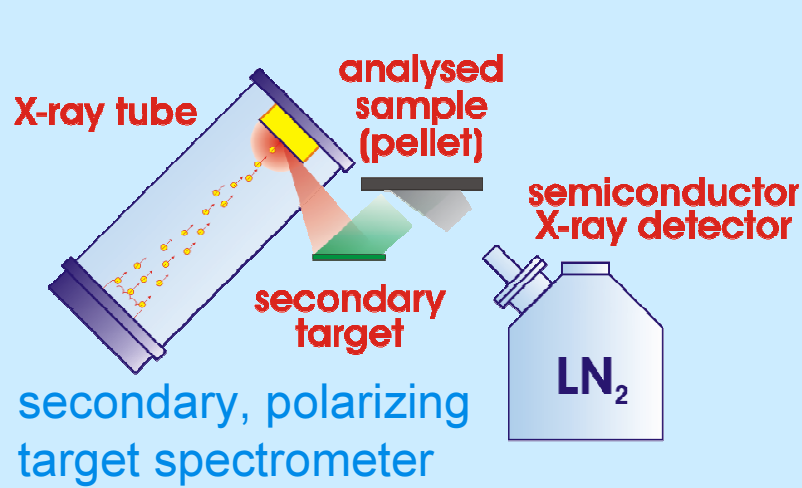
Introduction

Why X-ray fluorescence spectrometry is so useful?

- Simplicity, speed of operation, flexible requirements for sample preparation
 - Immediate analytical results (important for interactive measurement programmes, e.g., study of contaminated sites, remediation activities)
 - Non-destructive analysis (e.g., museum samples, works of art, archaeological samples)
 - Multi-elemental capabilities
 - Good sensitivity
 - Local and bulk analysis
 - Portability
- 

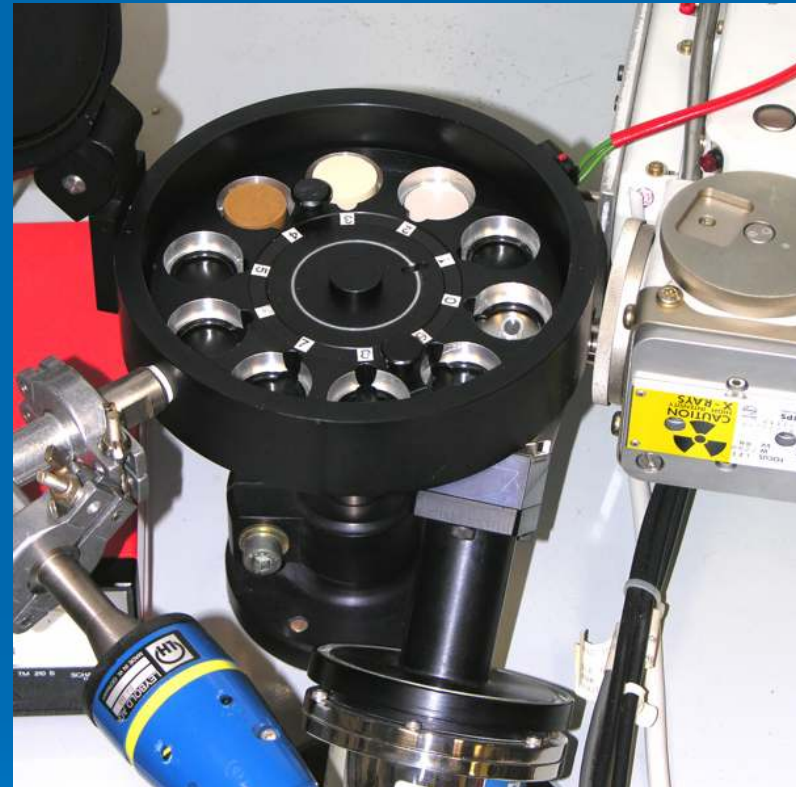
Introduction

Energy dispersive X-ray fluorescence spectrometers



Laboratory XRF spectrometers

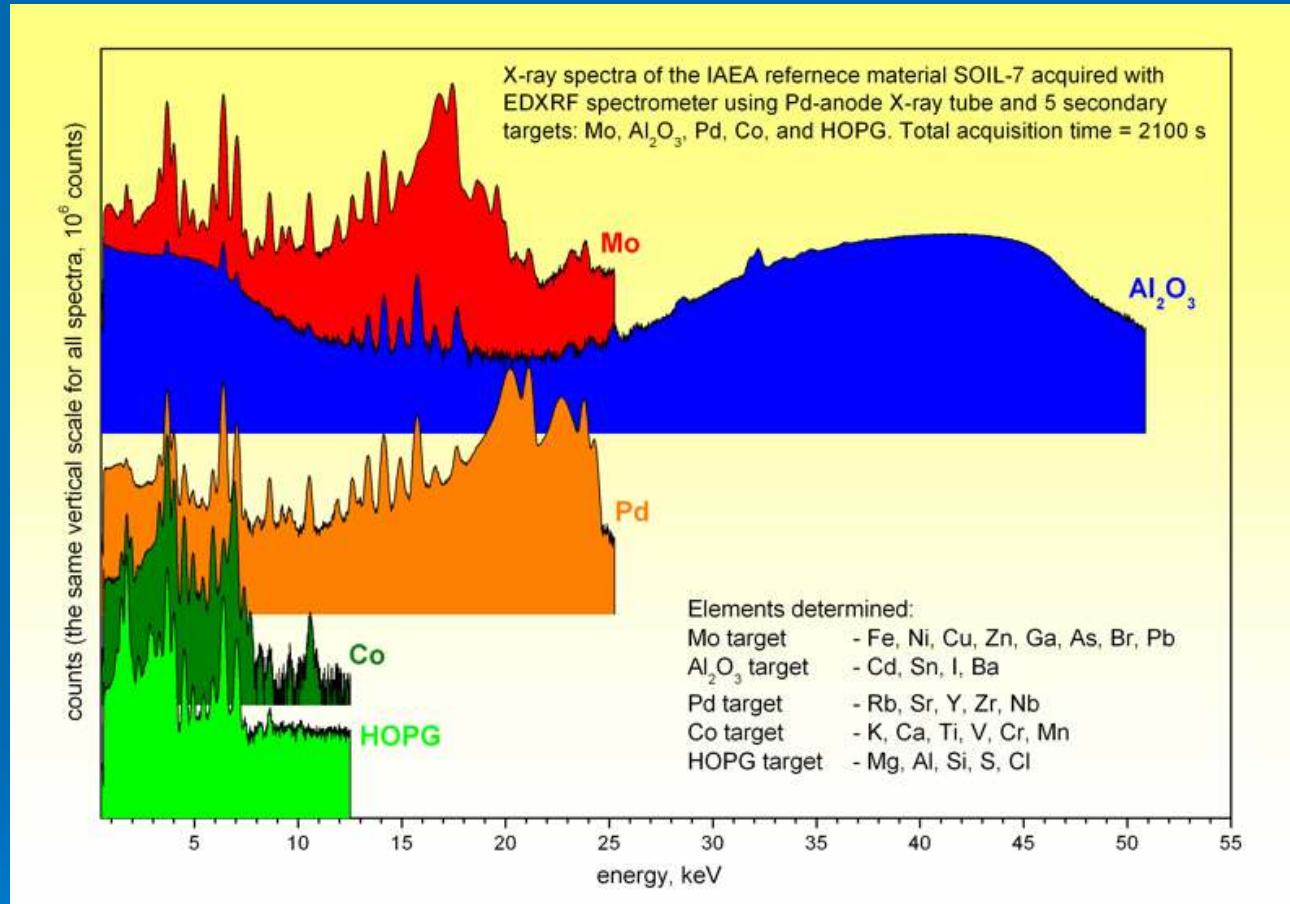
Secondary, polarizing target spectrometers



Left: heavy-duty, fully software controlled EDXRF spectrometer (Pd-anode X-ray tube) utilizing 5 secondary targets (Pd, HOPG, Co, Mo, Al_2O_3); right: in-house assembled EDXRF spectrometer (Cr-, Fe-, Cu-, Mo-, Rh-, Ag-, W-anode), manual selection of secondary targets (Mo, Rh, Ti in use, any other solid target possible)

Laboratory XRF spectrometers

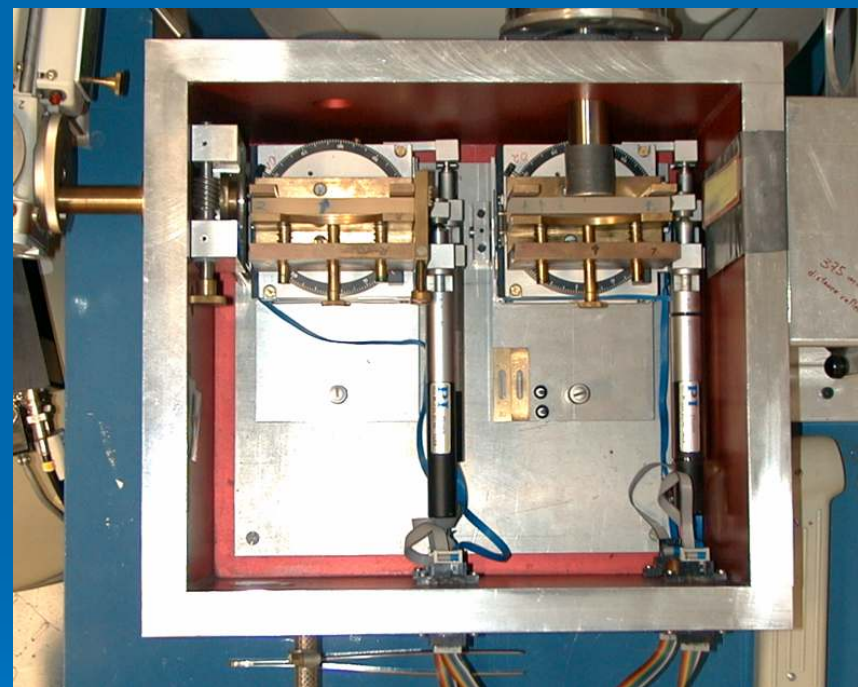
Comparison of X-ray spectra



X-ray spectra of a “thick” pellet sample made of Soil-7 reference material excited in the EDXRF secondary target spectrometer.

Laboratory XRF spectrometers

Total reflection X-ray fluorescence spectrometers

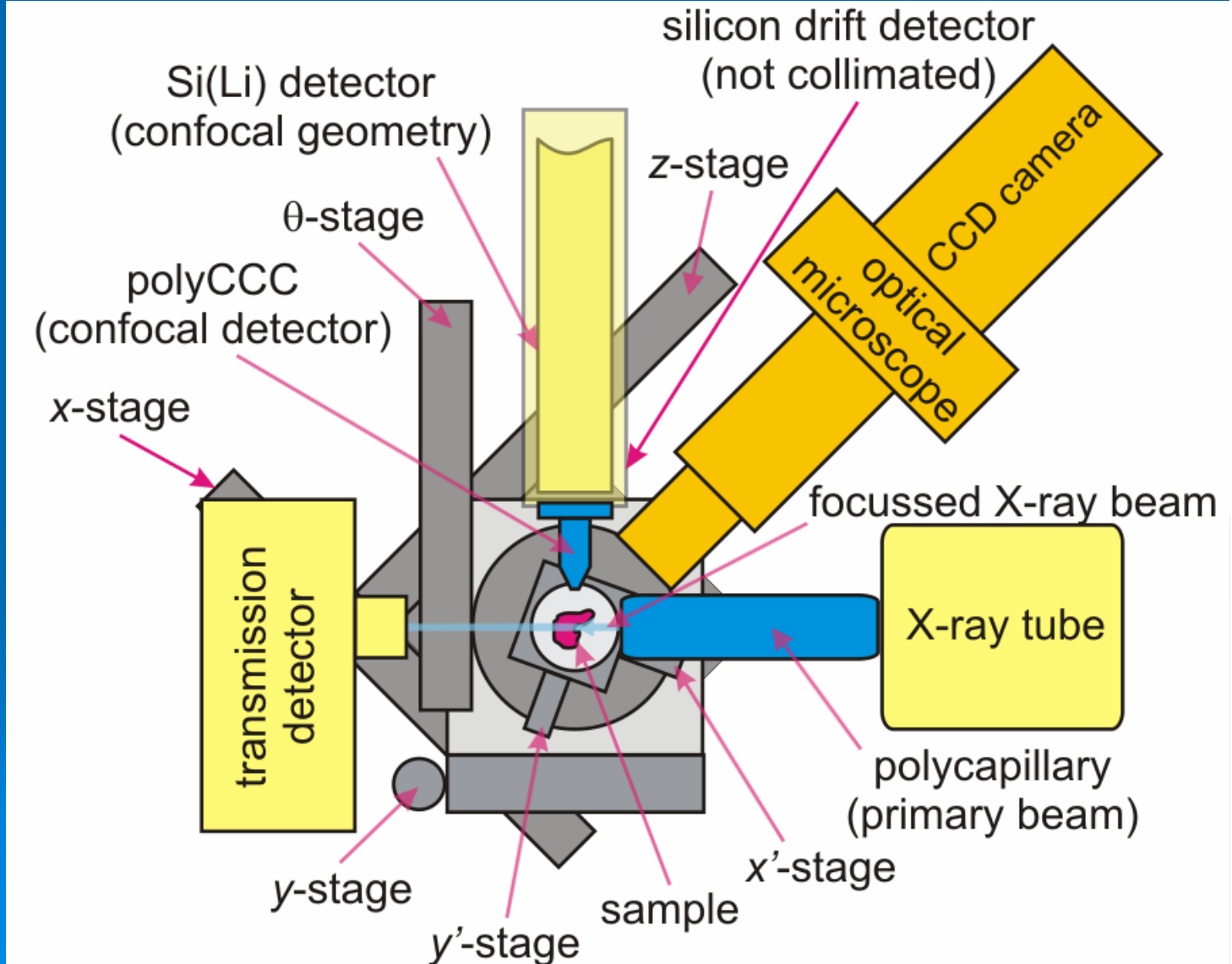


TXRF spectrometers, left: with 12-position sample changer; right: with motorized beam modifier and sample reflector stages

Laboratory XRF spectrometers

Micro-beam X-ray Setup Scheme

spatial
resolution:
15 - 40 μm



Micro-Beam X-ray Scanning Spectrometer

Si drift detector
(fluorescence)
on a stage

optical
microscope

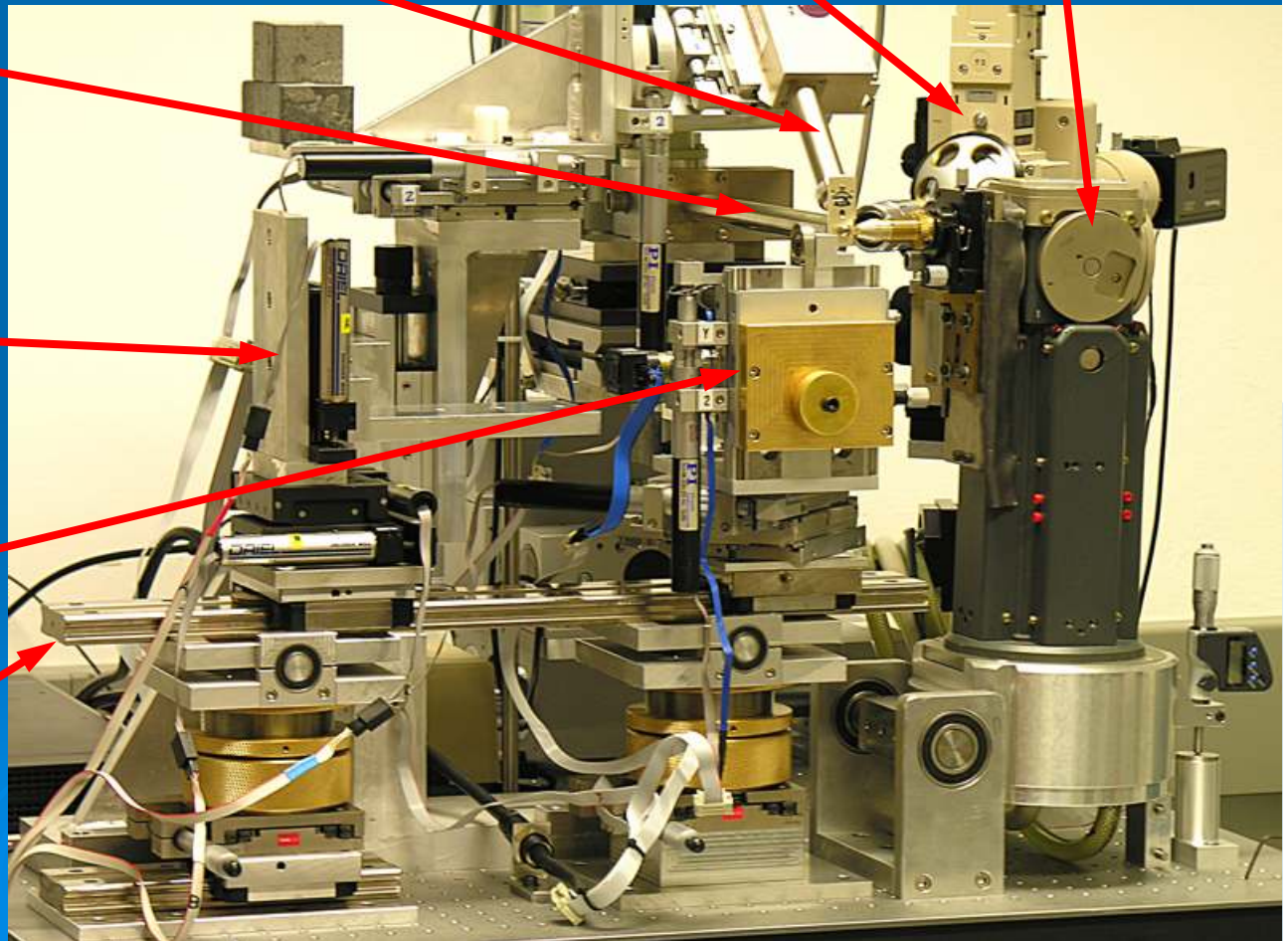
X-ray tube

Si(Li) detector
(confocal)

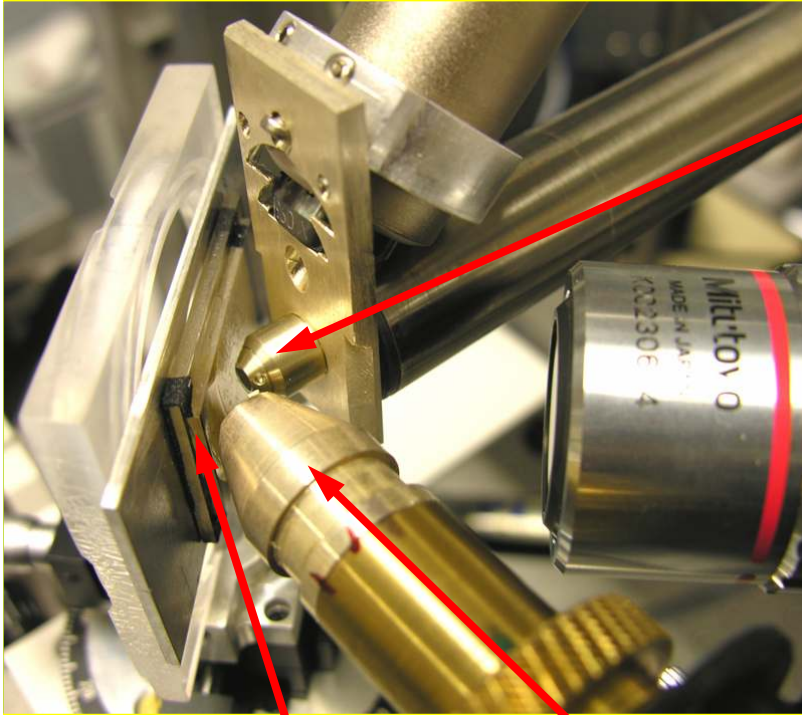
transmission
detector stage

sample stage

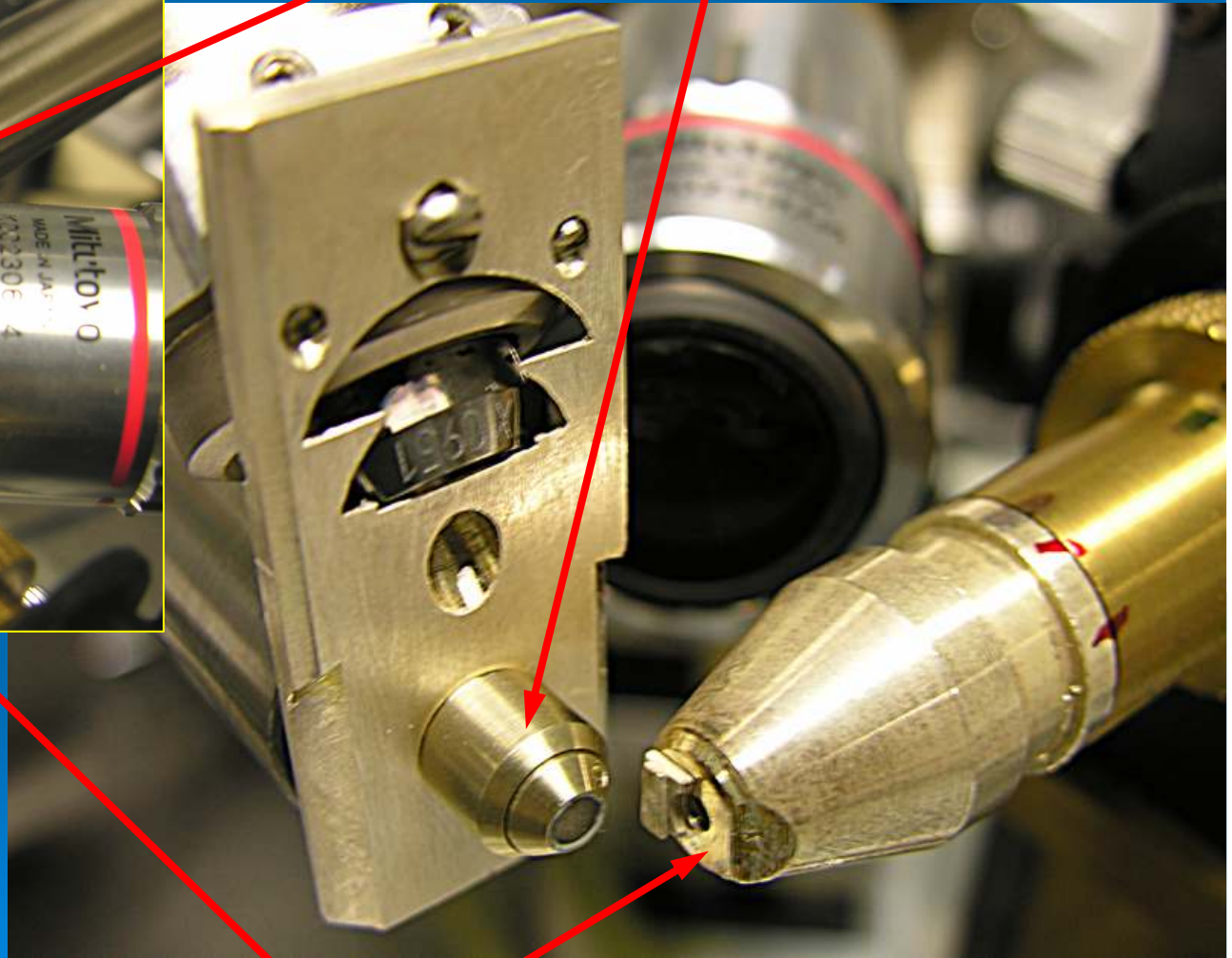
optical bench



Measuring geometry polyCCC (confocal detector)



sample in measuring position



polycapillary (primary beam)

Portable XRF spectrometers

DESIGN CRITERIA - Excitation sources

Radioisotope	Half-live (years)	X- or γ -ray energy (keV)	Photons per disintegration
^{55}Fe	2.7	MnK x-rays (5.9, 6.5)	0.28
^{109}Cd	1.3	AgK x-rays (22, 25)	1.07
		88	0.04
^{241}Am	433	59.5	0.36

Portable XRF spectrometers

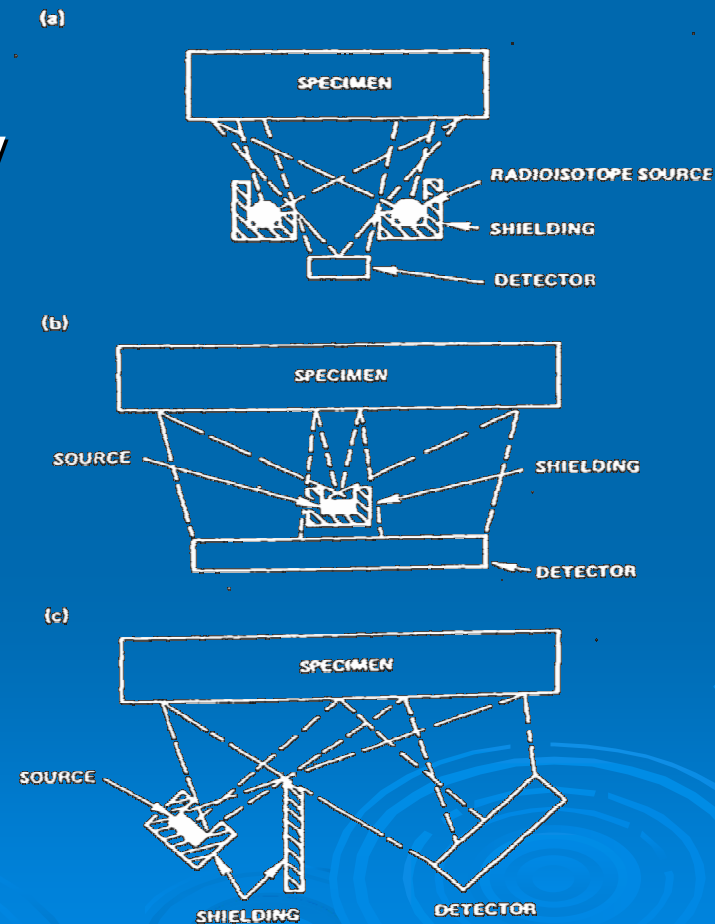
DESIGN CRITERIA - Excitation geometries

Three geometries for
radioisotope-excited X-ray
fluorescence analysis:

a) annular source

b) central source

c) side source



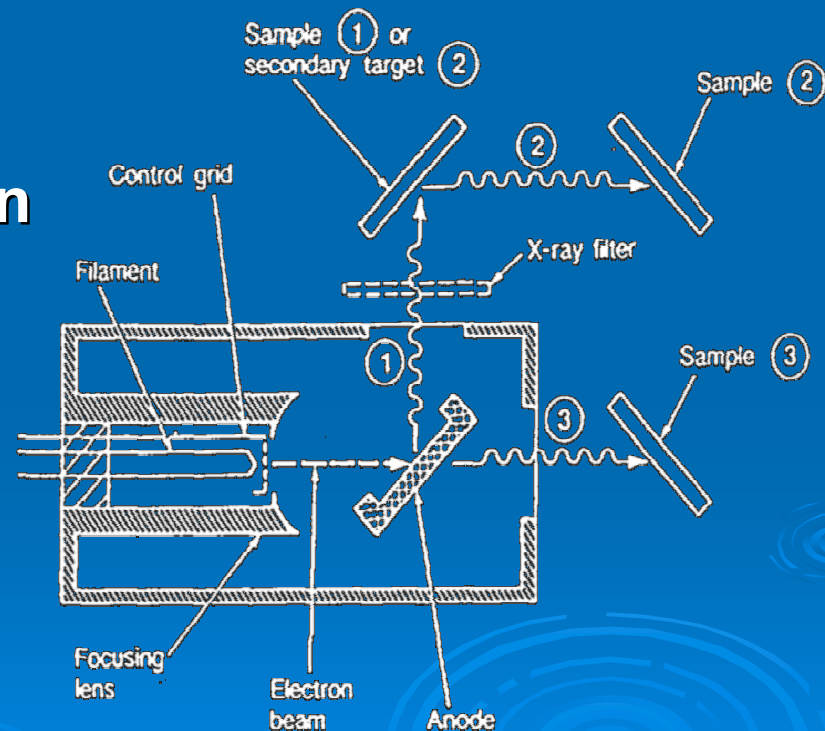
Portable XRF spectrometers

DESIGN CRITERIA - Excitation sources

Typical excitation geometries

for an X-ray tube:

- 1) direct excitation
- 2) secondary target excitation
- 3) transmission geometry



Portable XRF spectrometers

DESIGN CRITERIA - Detectors

- Room temperature and Peltier-cooled semiconductor detectors:

HgI₂

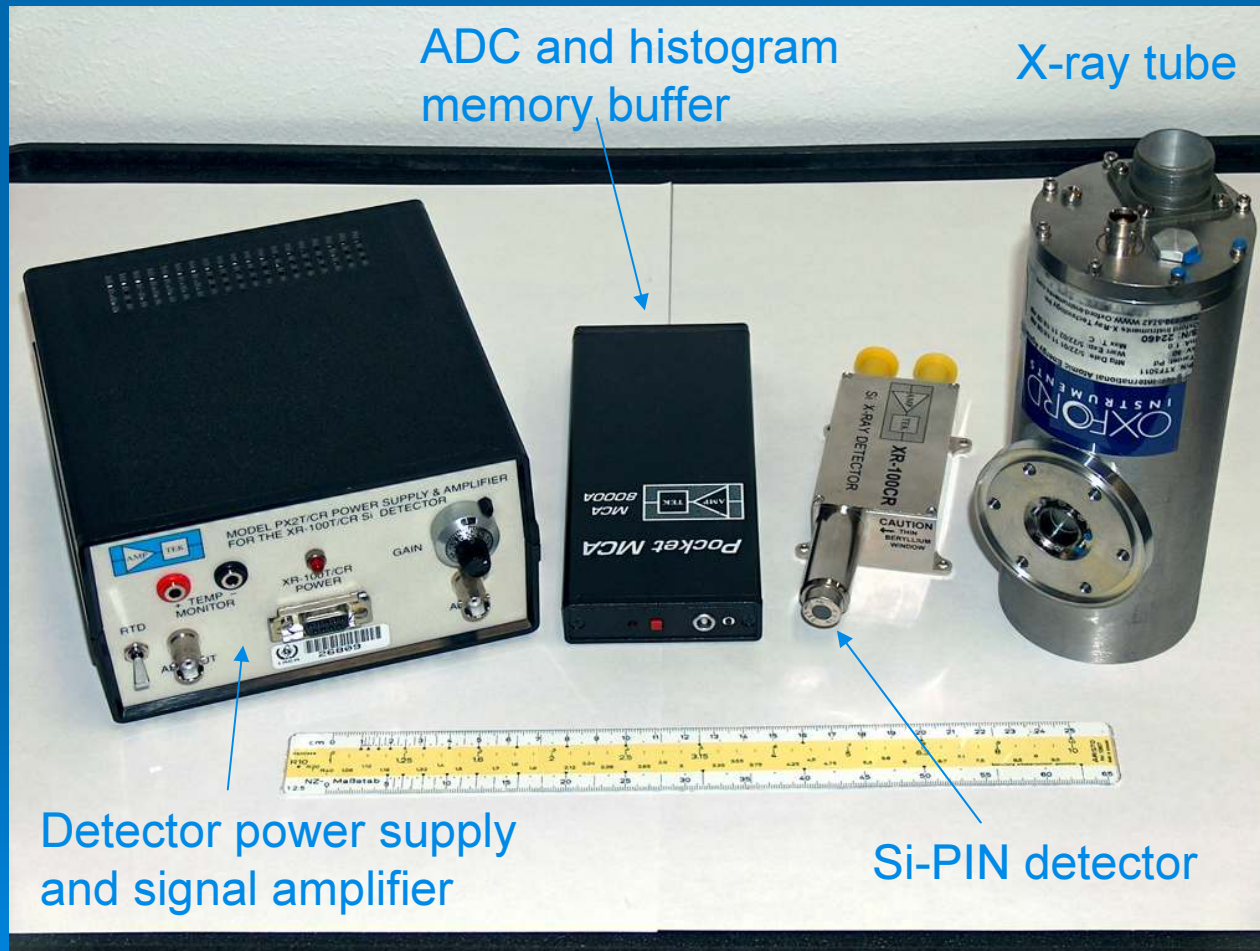
Si-PIN

Si-drift

CdTe

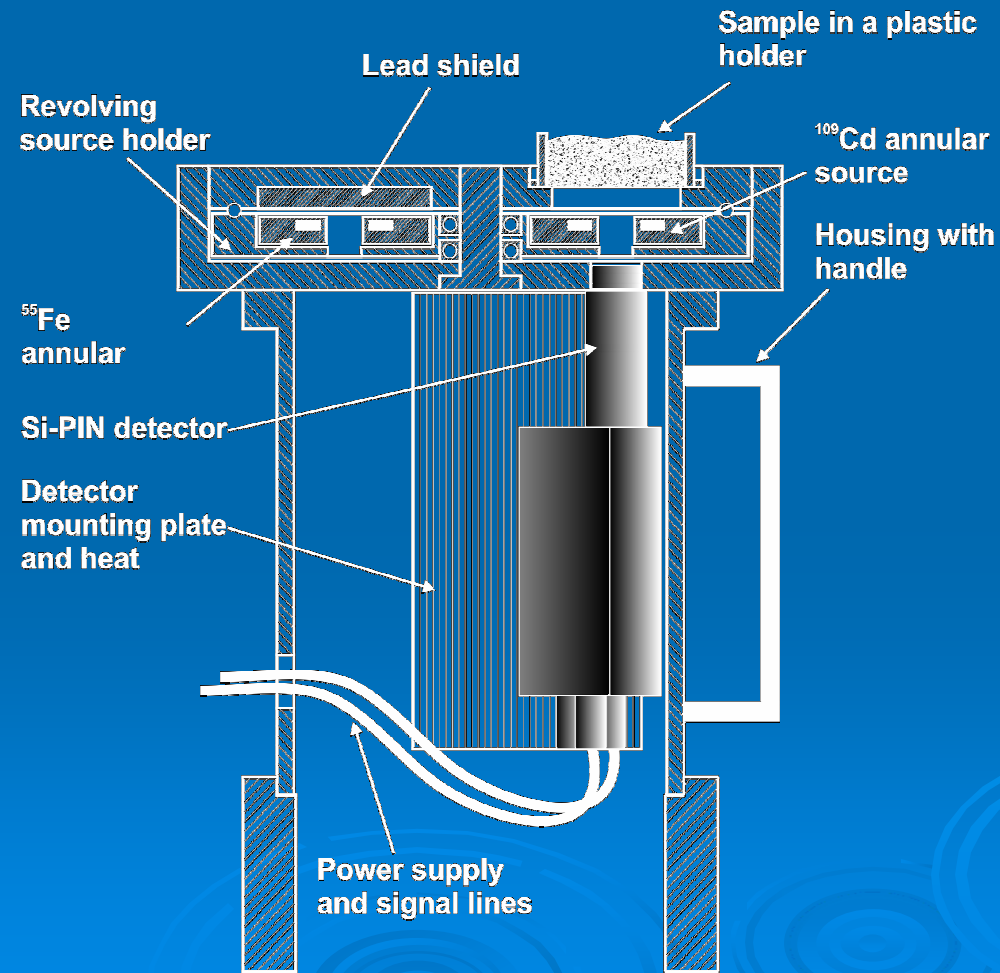


Portable XRF Spectrometers



Portable XRF spectrometers

DESIGN CRITERIA - Development



EXAMPLES of FPXRF SYSTEMS

- Portable XRF unit with thermoelectrically cooled Si-PIN detector

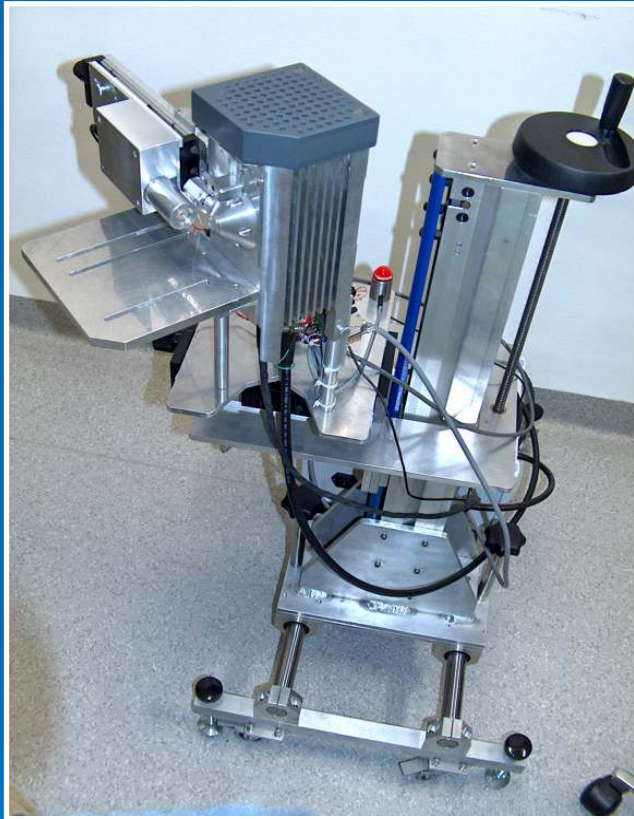


EXAMPLES of FPXRF SYSTEMS

- Portable XRF unit with liquid nitrogen cooled Si(Li) (or HpGe) detector



EXAMPLES of FPXRF SYSTEMS



Direct/secondary excitation in air, Si-PIN detector, pinhole collimator

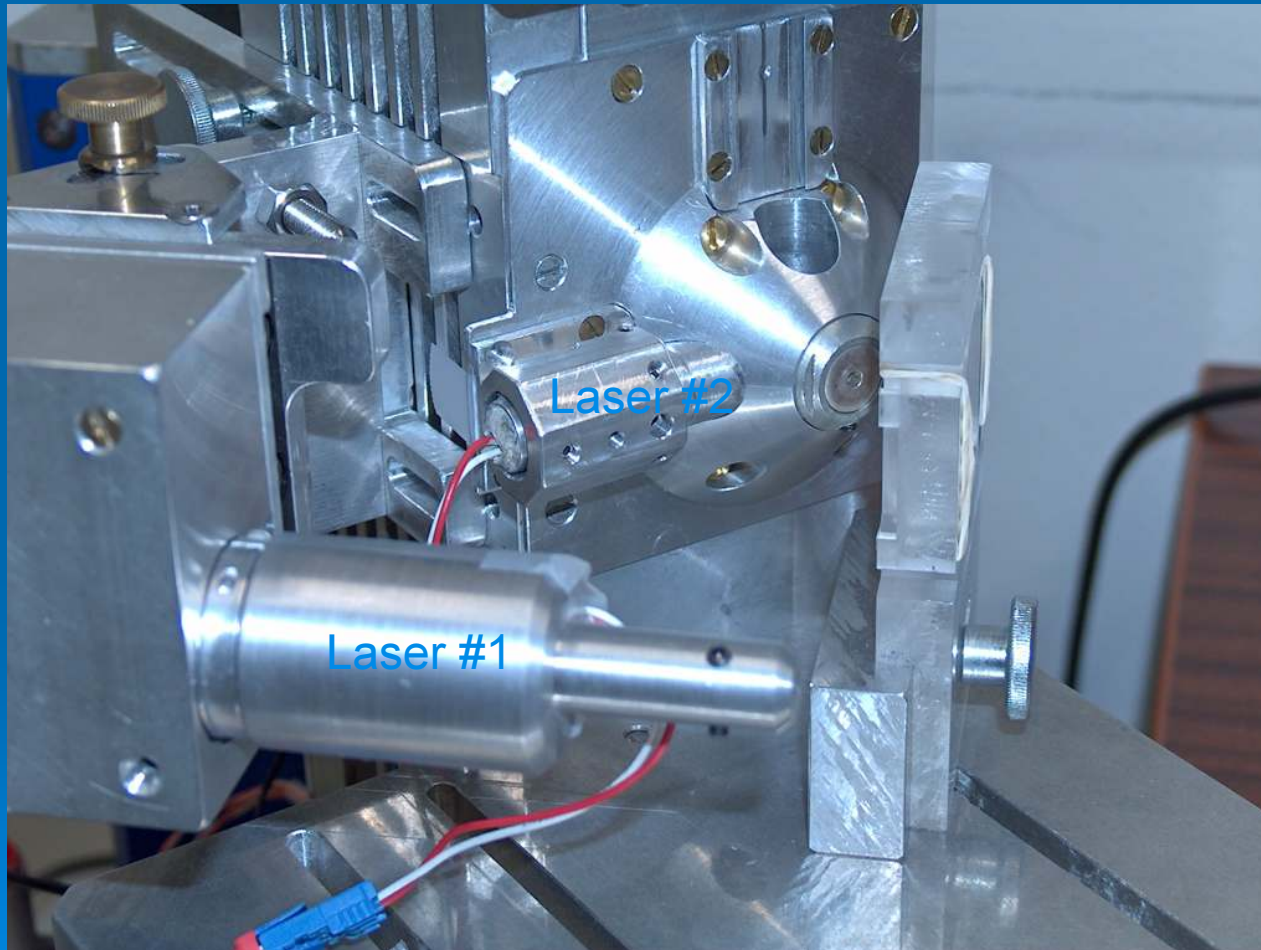


Direct excitation, vacuum attachment, SD detector, polycapillary optics/collimator

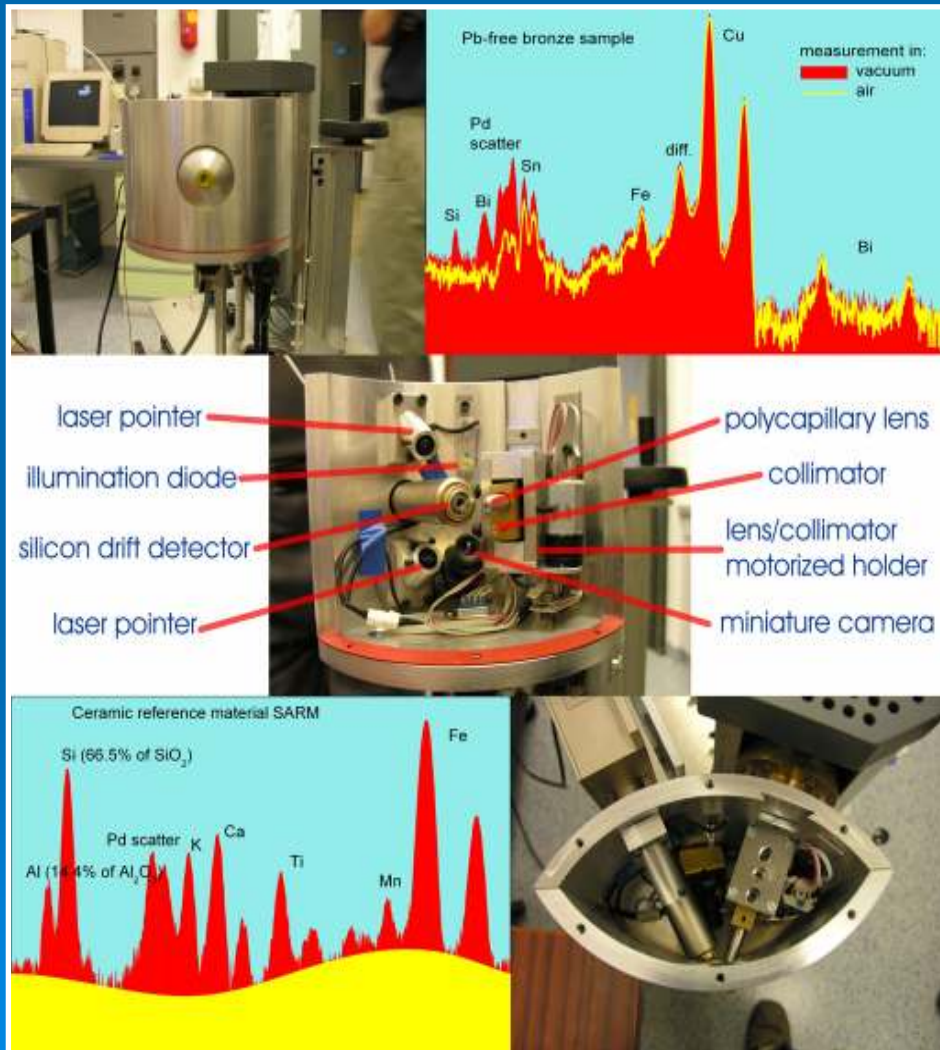
Measuring Geometry



Laser Pointers

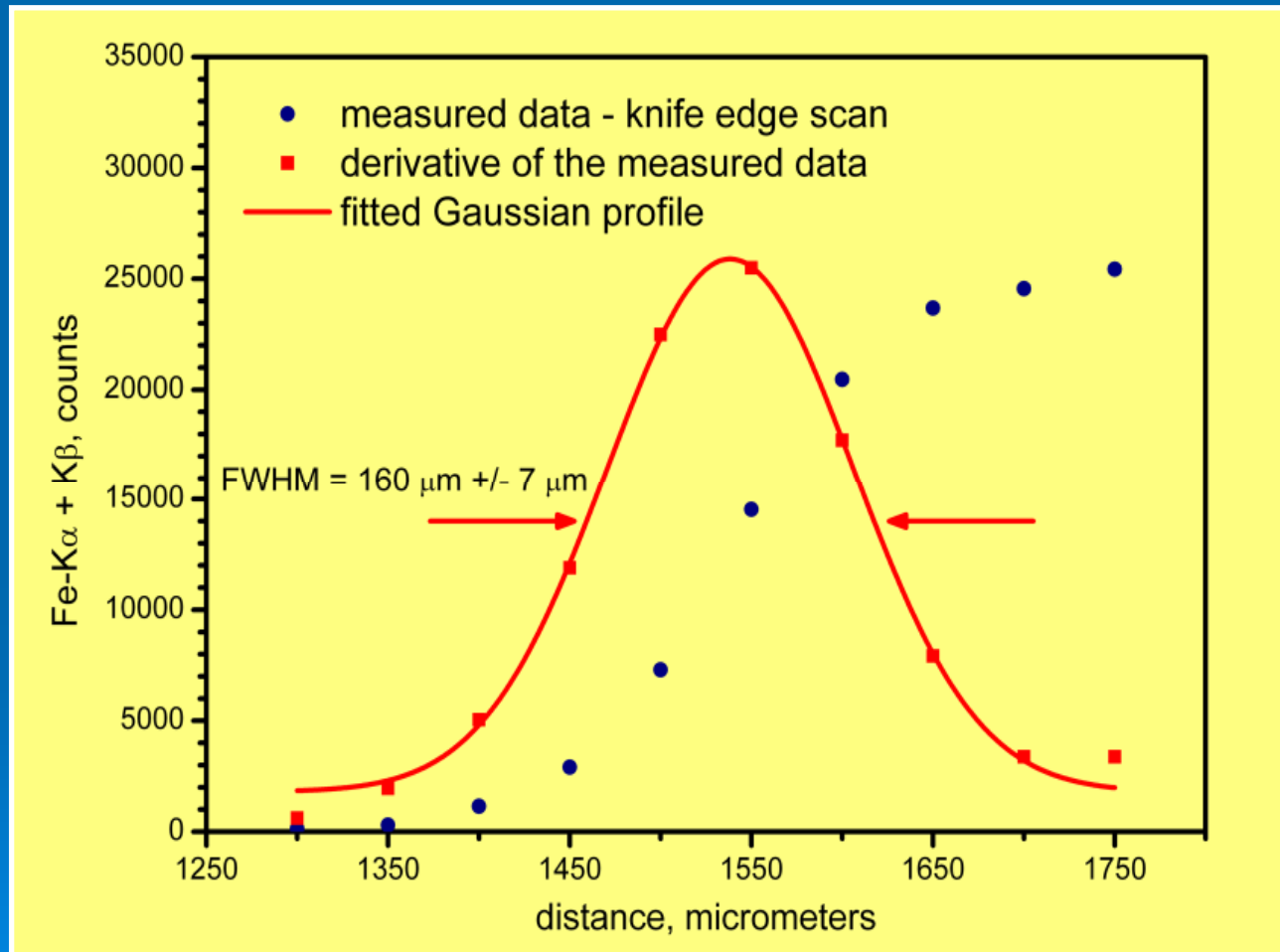


EXAMPLES of FPXRF SYSTEMS

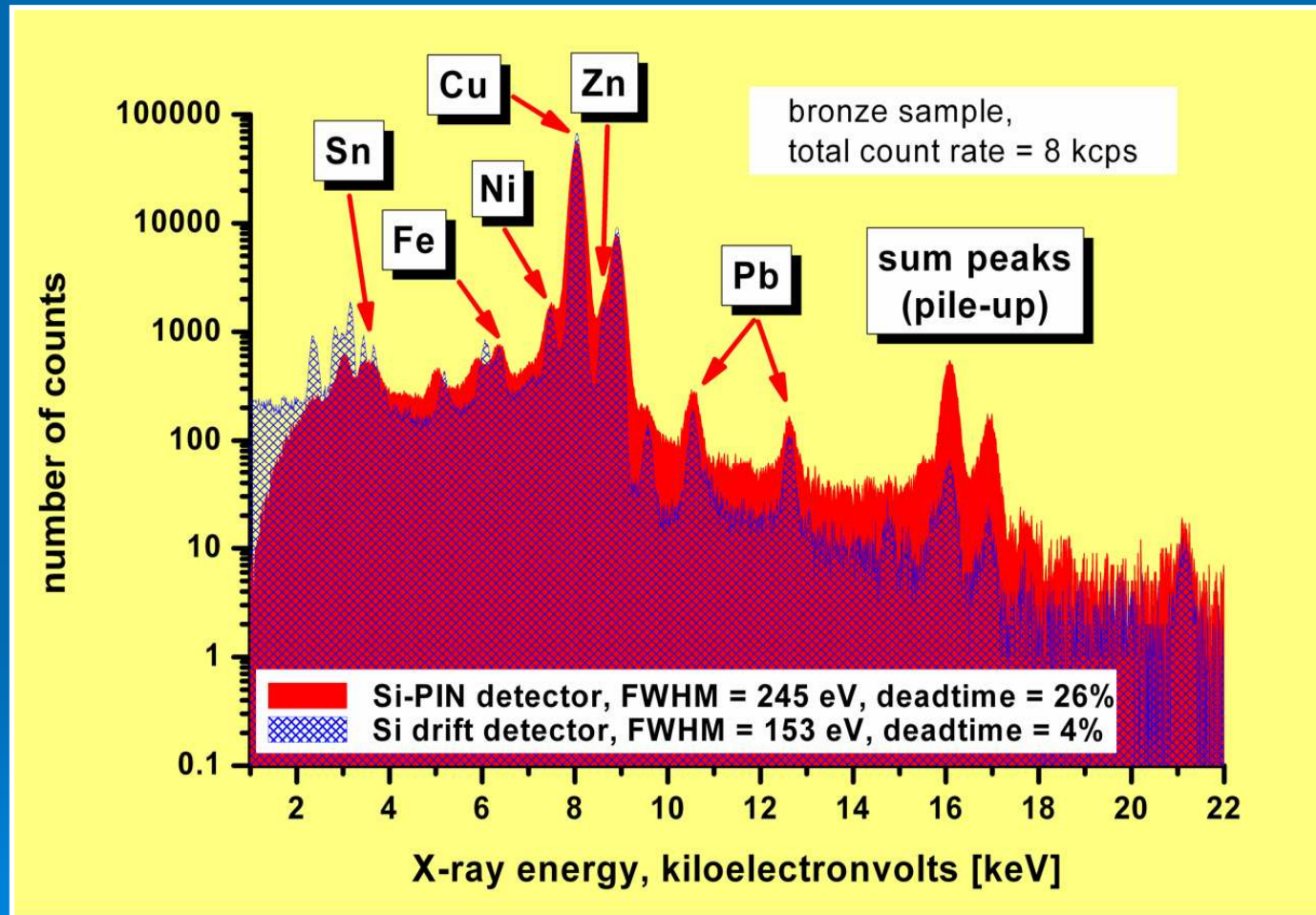


- Pd-anode X-ray tube (50W), direct excitation in vacuum or air
- polycapillary lens and brass collimator,
- silicon drift detector, thermoelectrically cooled, 10 mm² active area, 300 micrometers nominal thickness, 140 eV FWHM at 5.9 keV, 1 microsecond shaping,
- 2 laser pointers,
- CMOS camera with
- mechanical positioning system

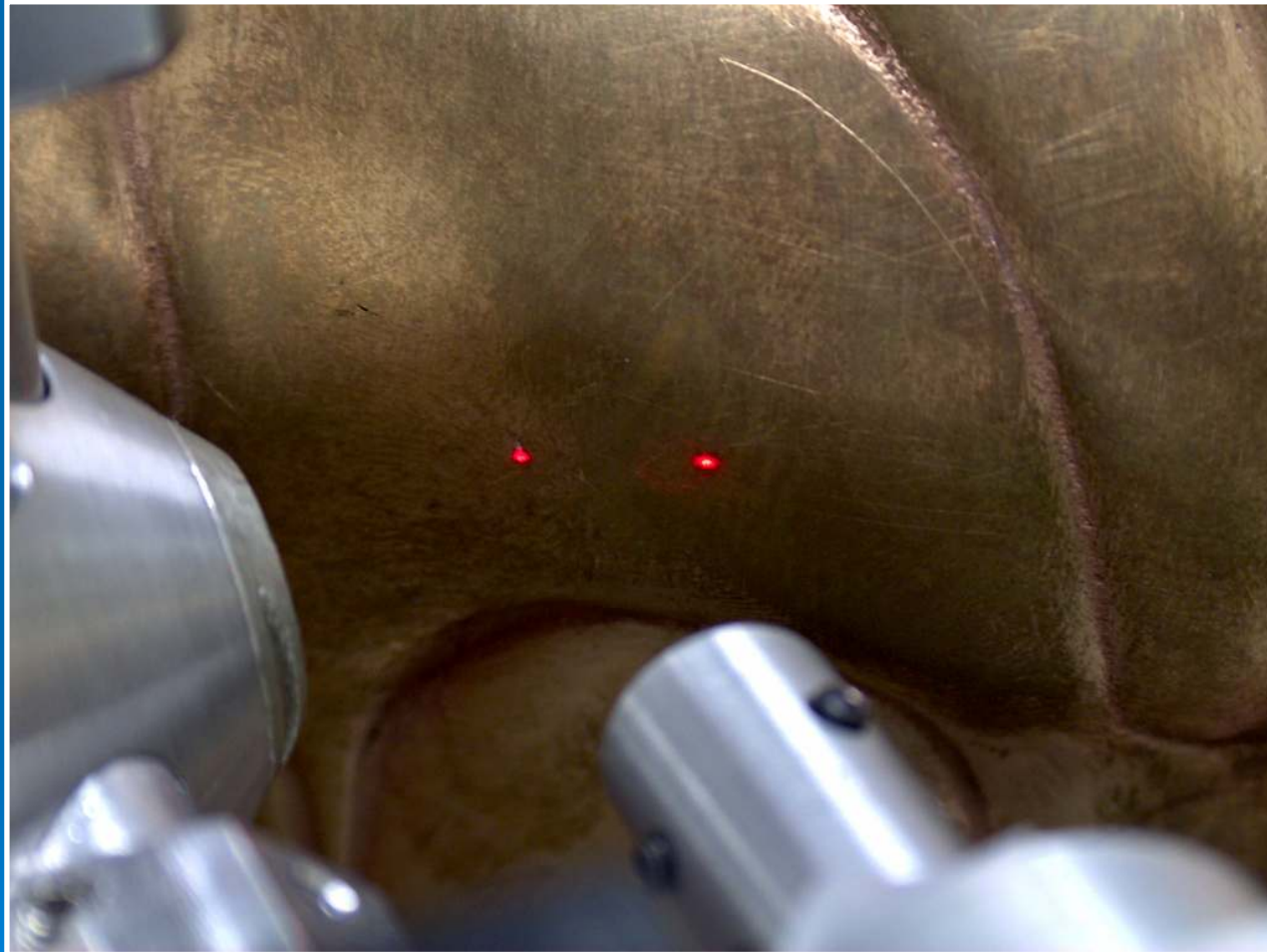
X-ray beam profile, polycapillary



X-ray detector performance

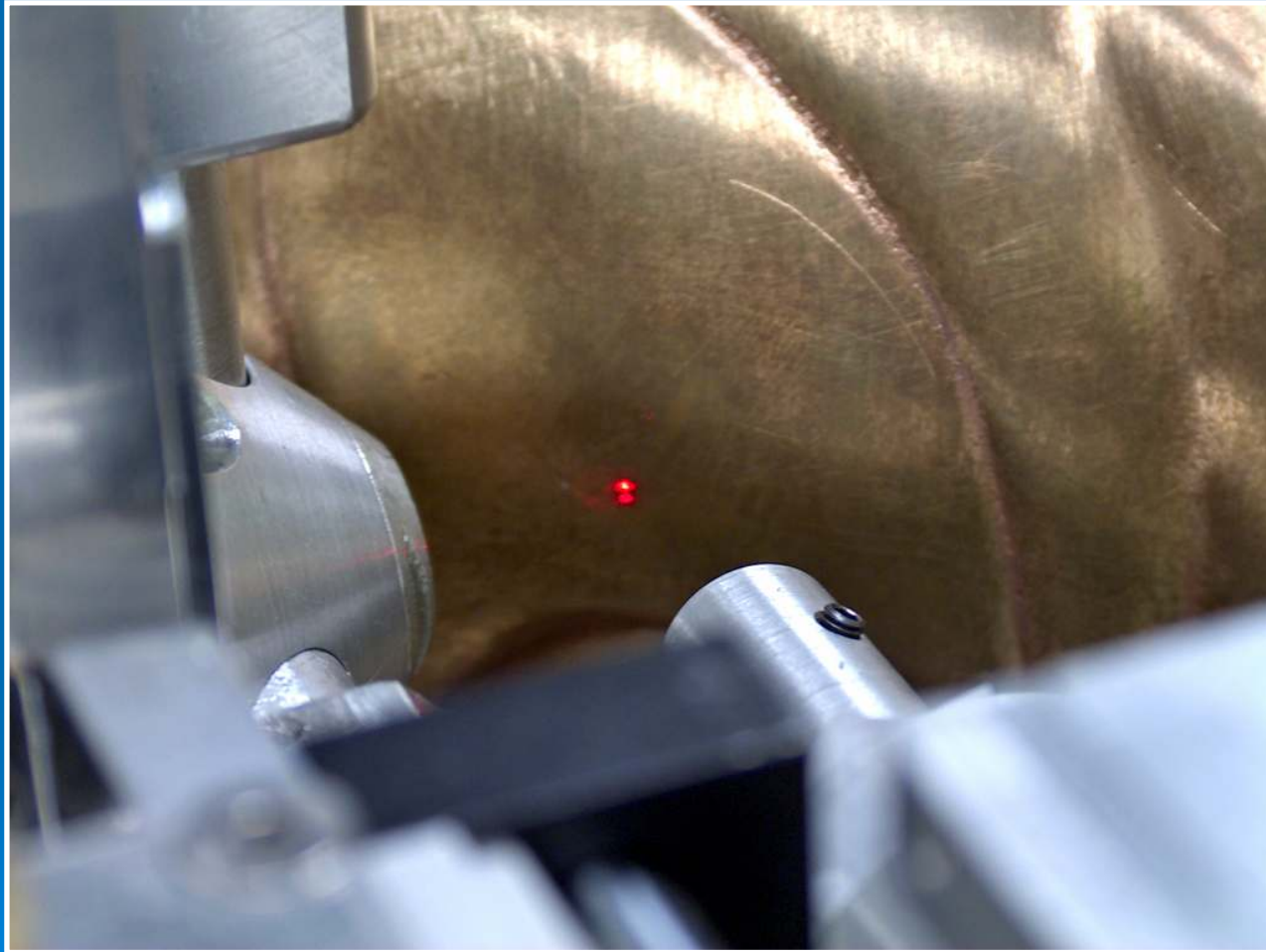


Measuring “difficult” samples



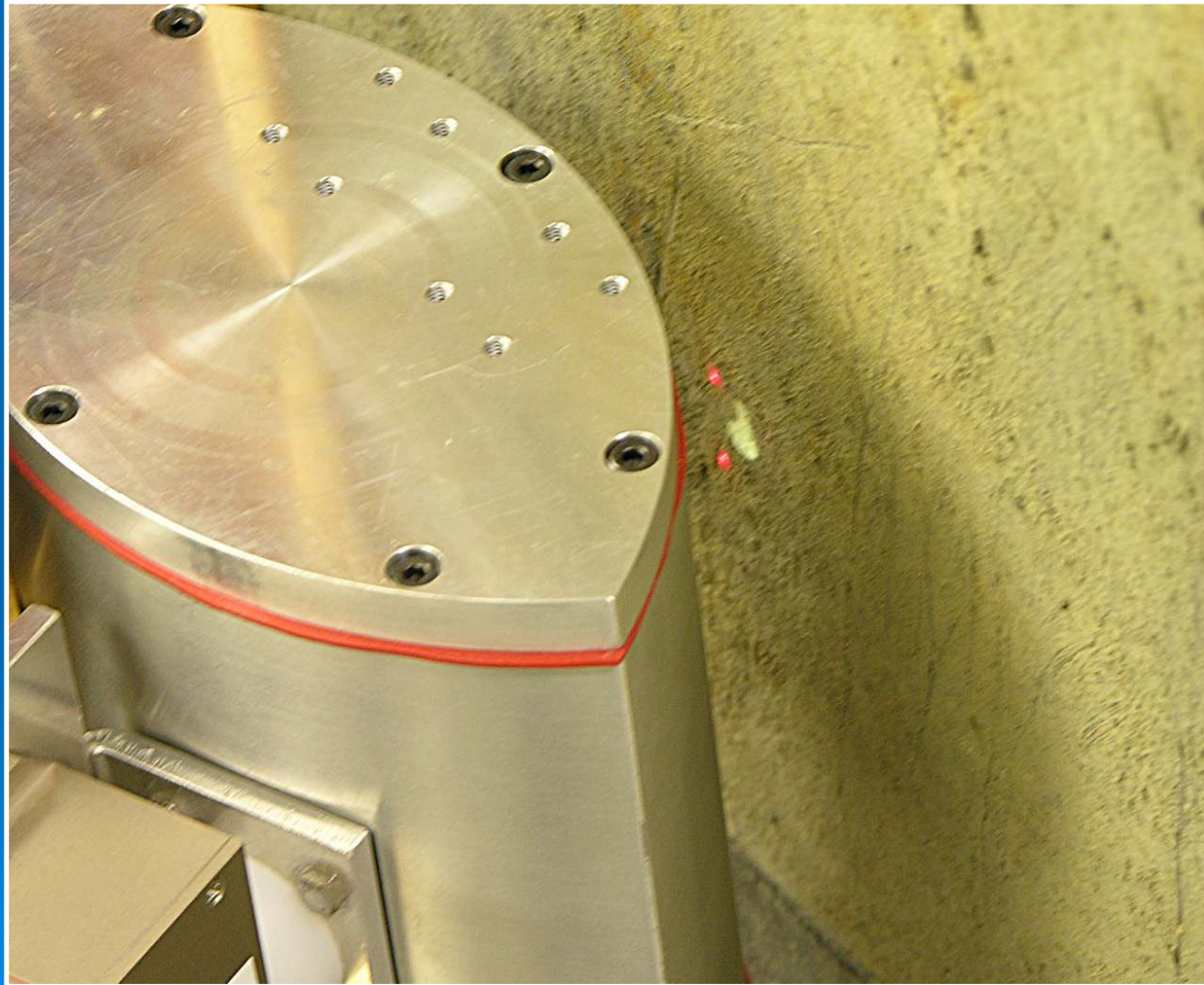
Object not in the optimum measuring position

Aligning the instrument

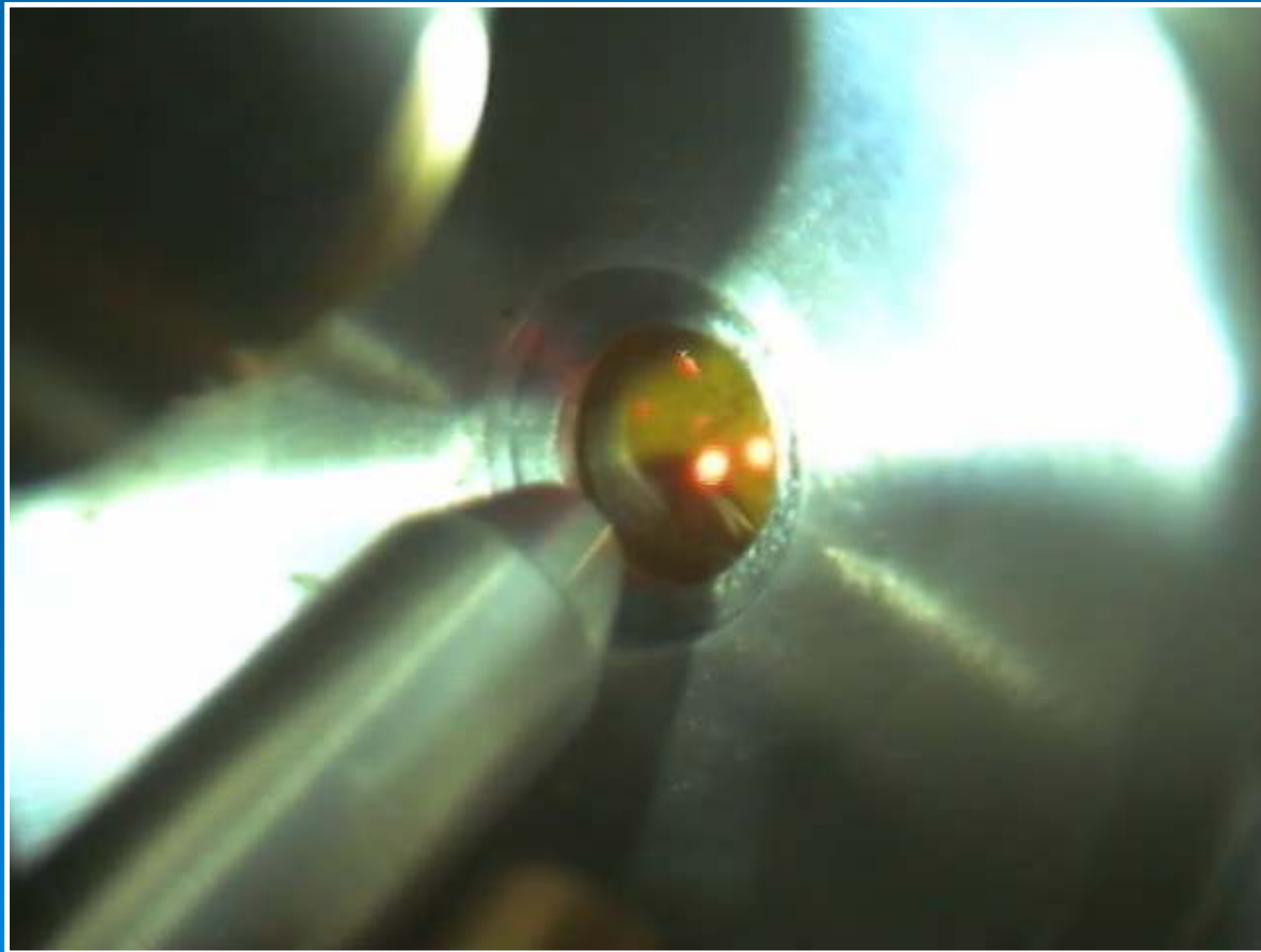


Object in the optimum measuring position

Vacuum chamber – adjustment by lasers



Vacuum chamber – precise adjustment with a CMOS camera



Portable XRF spectrometers

ANALYTICAL PERFORMANCE

- capable of detecting chemical elements with the atomic number ≥ 11 (sodium)
- detection limits in the PPM range
- beam spot diameter: 0.2 mm, 1 mm
- local and bulk analysis capability

PARAMETERS OF (in-situ) XRF MEASUREMENTS

- Critical penetration depth (information depth)
“Sample thickness from which 99% of a fluorescence signal originates”

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

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

PARAMETERS OF (in-situ) XRF MEASUREMENTS

Element	Information thickness, μm	
	$\bar{Z} = 12.5$	$\bar{Z} = 15$
P	12	79
Ca	50	32
Zn	540	340
Pb	930	570

PARAMETERS OF (in-situ) XRF MEASUREMENTS

- 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

PARAMETERS OF (in-situ) XRF MEASUREMENTS

Accuracy

- Analysis of standard reference materials
- Analysis of confirmatory samples by using the reference (confirmatory) laboratory method considered as standard analytical method (minimum 10 % of total number of analyzed samples)

if r^2 between 0.7 and 0.9 – screening level

if $r^2 > 0.9$ PXRF and confirmatory data equivalent

PARAMETERS OF (in-situ) XRF MEASUREMENTS

Detection Limit

Interference-free detection limit not fully adequate for *in-situ* applications

- A. Precision-based DL determined as 3 times st. dev. of the results for replicate analyses of low-concentration samples (5-10 x estimated DL):
 - (i) site specific calibration standards, (ii) appropriate SRMs, and (iii) clean sample matrix spiked with low concentration of target analytes

- B. Field or performance-based DL – analysis of low concentration outliers on data cross plots for log transformed PXRF results vs. log transformed confirmatory results – DL where the linearity disintegrates

PARAMETERS OF (in-situ) XRF MEASUREMENTS

➤ Blank samples

1. *Instrument blank*

- to verify that no contamination exists in the spectrometer or on the probe window, e.g., Teflon block, quartz block, clean sand, lithium carbonate
- daily analysis before and after measurements

OK if no concentrations > DL

PARAMETERS OF (in-situ) XRF MEASUREMENTS

2. *Method blank*

- to monitor for laboratory-induced (sample preparation) contaminants or interferences e.g., clean silica or lithium carbonate that undergoes the same sample preparation procedure as analyzed samples
- (at least) daily analysis

OK if a method blank doesn't contain any analyte at a concentration above DL

PARAMETERS OF (in-situ) XRF MEASUREMENTS

Total uncertainty

$$\sigma^2_{\text{tot}} = \sigma^2_{\text{sample representation}} + \sigma^2_{\text{sample collection}} +$$

$$\sigma^2_{\text{sample handling}} + \sigma^2_{\text{sample preparation}} +$$

$$\sigma^2_{\text{analysis}}$$

Interfering effects affecting accuracy of XRF analysis

➤ Physical matrix effects

A. Particle size effects

e.g., Cr in soil: 1 cm² irradiated area,
penetration depth 0.2 mm, DL=200 mg/kg



8.4 μg Cr in the information layer
(single grain of diameter of 135 μm)

Interfering effects affecting accuracy of XRF analysis

Solution: grinding and sieving to a uniform and small particle size fraction

B. Heterogeneity of materials

(preliminary and simple procedure to homogenize the material is recommended – important during validation of XRF results through confirmatory analysis)

Interfering effects affecting accuracy of XRF analysis

C. Surface irregularity effects

- detected X-ray fluorescence intensities are systematically lower than those observed from flat samples
- theoretical model to calculate unevenness factor (source-sample distance, surface peak-valley amplitude, frequency number of convex and concave surfaces)

Interfering effects affecting accuracy of XRF analysis

- D. Mineralogy effects (dependence on mineral assemblage – size, distribution and position of minerals - present in the excited volume (information volume):
- grain size (vs. volume from which the fluorescence signal originates)
 - excitation-detection efficiency

Interfering effects affecting accuracy of XRF analysis

E. Chemical matrix effects

- Absorption
- Enhancement

F. Spectral interferences

- insufficient energy resolution of detector
- overlap of characteristic X-ray lines of two or more elements (first identify all possible spectral interferences and then apply spectrum evaluation software)

Correction procedures for the interfering effects

➤ Physical matrix effects

A. Surface irregularity

1. Use of Compton and Rayleigh scattered primary radiation

$$I_{\text{corrected}} = I_{\text{measured}} \times B_{\text{reference}} / B_{\text{measured}}$$

(for silicate rocks effective correction up to about 3 mm only)

Correction procedures for the interfering effects

2. *Use of a special calibration procedure based on relative instrumental calibration factors*

$$R_{ik} = I_i / I_k$$

i – analyte; k – reference element

Correction procedures for the interfering effects

➤ B. Mineralogy effects

- From experiments for representative (flat) samples the rel. st.dev. of the average concentration (R) is calculated

$$R = 100(\%) (s/n^{0.5}) / C_{\text{mean}}$$



$$n = [(100 \times s) / (R \times C_{\text{mean}})]^2$$

Correction procedures for the interfering effects

➤ Chemical matrix effects

A. Methods based on scattered primary radiation
(reduces also surface irregularity and moisture effects)

I_i / I_{Com} vs. concentration

for synthetic calibration samples or site-specific calibration samples analysed by reference analytical method

Correction procedures for the interfering effects

➤ $I_i / (I_{Com})^S$ 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:

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

Correction procedures for the interfering effects

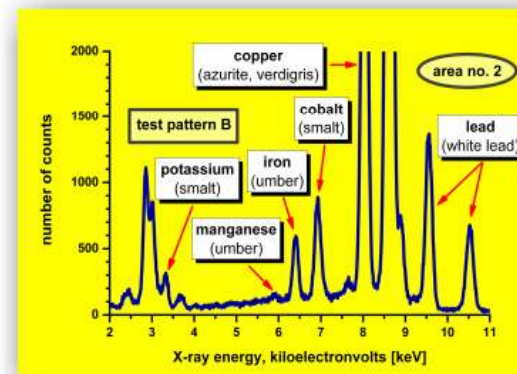
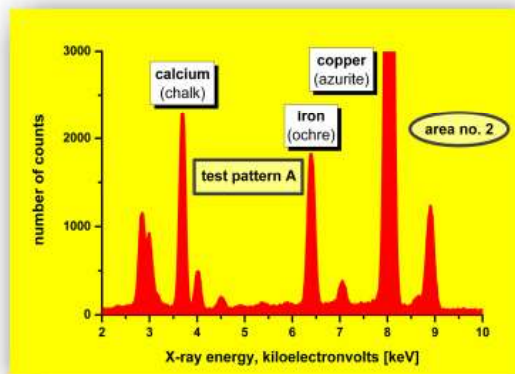
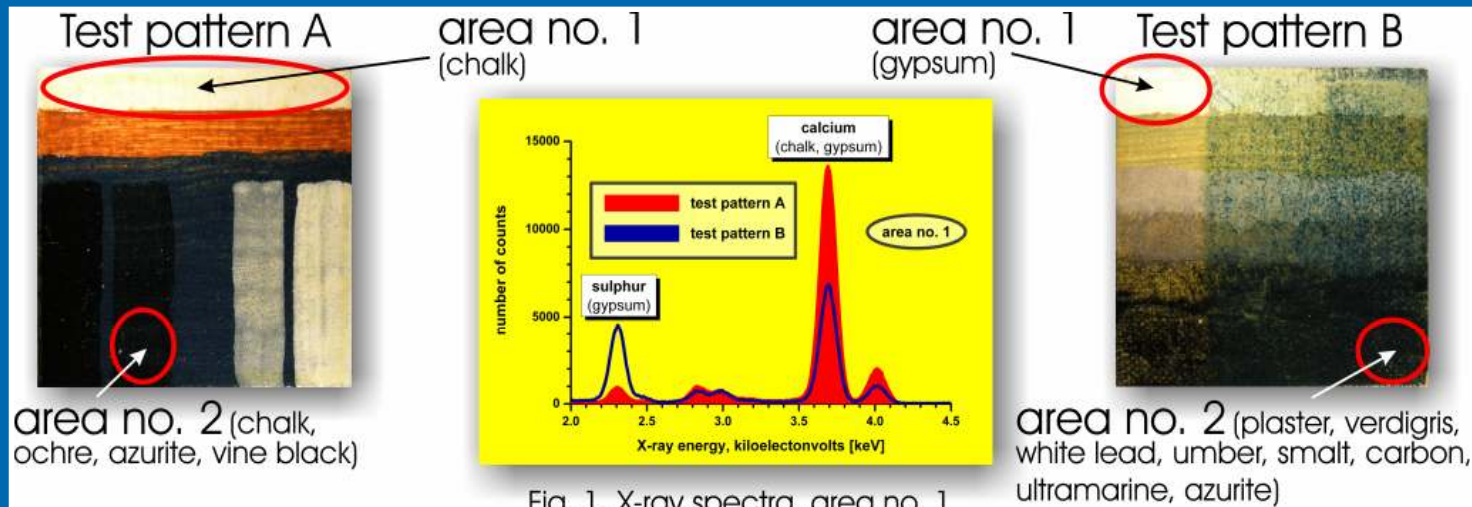
➤ B. Backscatter Fundamental Parameter Method

Q_i , Q_A , and Q_B (element mass per unit area) are unknown:

$$I_i = Q_i K_i(E_0) \frac{1 - \exp\left\{-\left[\sum_j F_j + F_A + F_B\right]\right\}}{\sum_j F_j + F_A + F_B} (1 + F_i^{Enh}) S_i;$$
$$F_j = Q_j \left(\frac{\mu_j(E_0)}{\sin \Psi_1} + \frac{\mu_j(E_i)}{\sin \Psi_2} \right)$$
$$F_{A/B} = Q_{A/B} \left(\frac{\mu_{A/B}(E_0)}{\sin \Psi_1} + \frac{\mu_{A/B}(E_i)}{\sin \Psi_2} \right)$$

EXAMPLES OF APPLICATIONS

(Inorganic pigments)



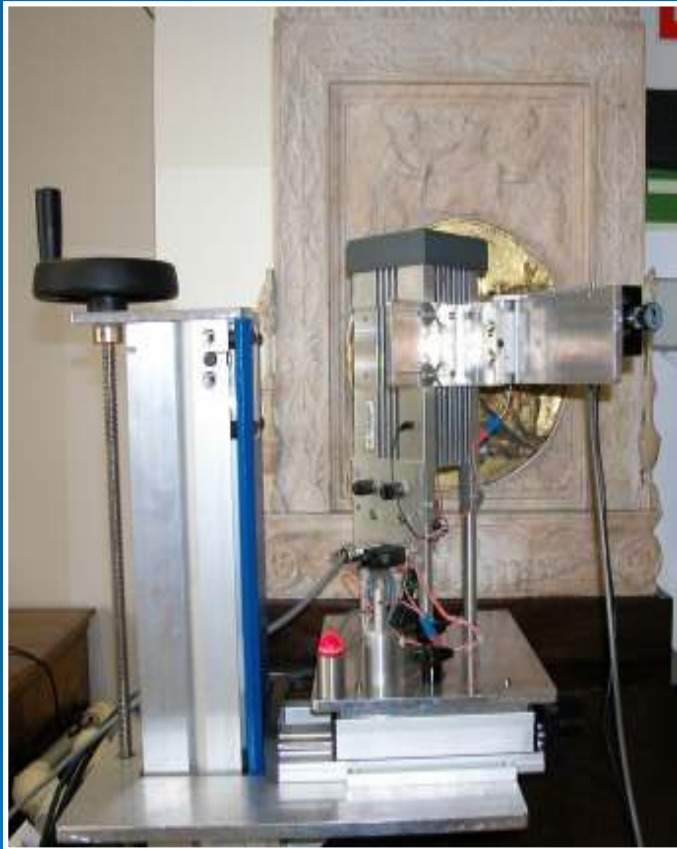
EXAMPLES OF APPLICATIONS

*(Investigation of archeological objects from
Kunsthistorisches Museum, Vienna)*

- Egyptian and Near Eastern Collection: coal pot, small box with lid (galena residue), wooden stele (pigment identification), tweezers (alloy analysis), armlets (alloy analysis)
- Painting gallery: identification of pigments, priming coatings
- Arms and Armour Collection: oriental saddle identification of pigments and metal applications
- Collection of Sculpture and Decorative Arts: bronze tondo, small can, Venice glass (glass composition)
- Museum of Entomology: Benin bronzes (alloy composition)

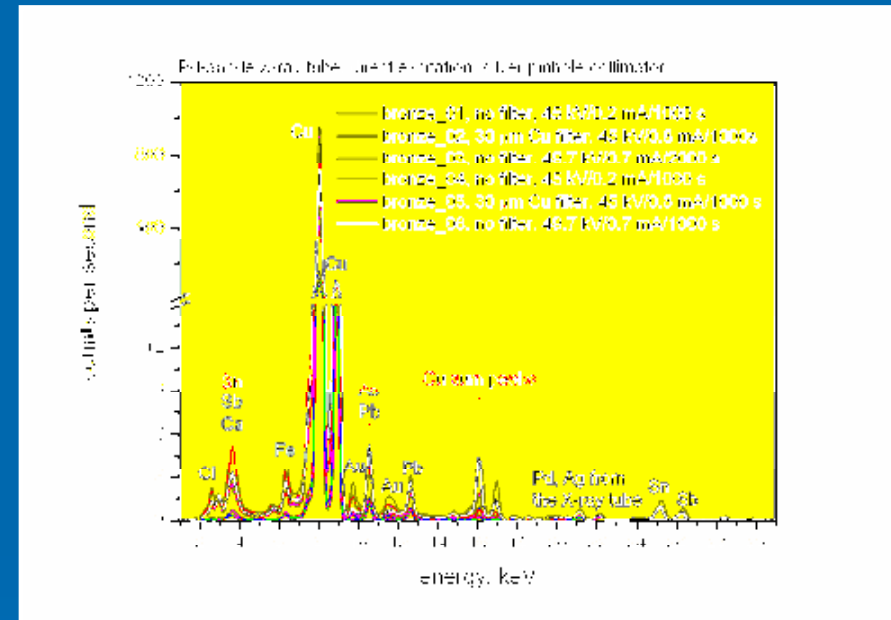
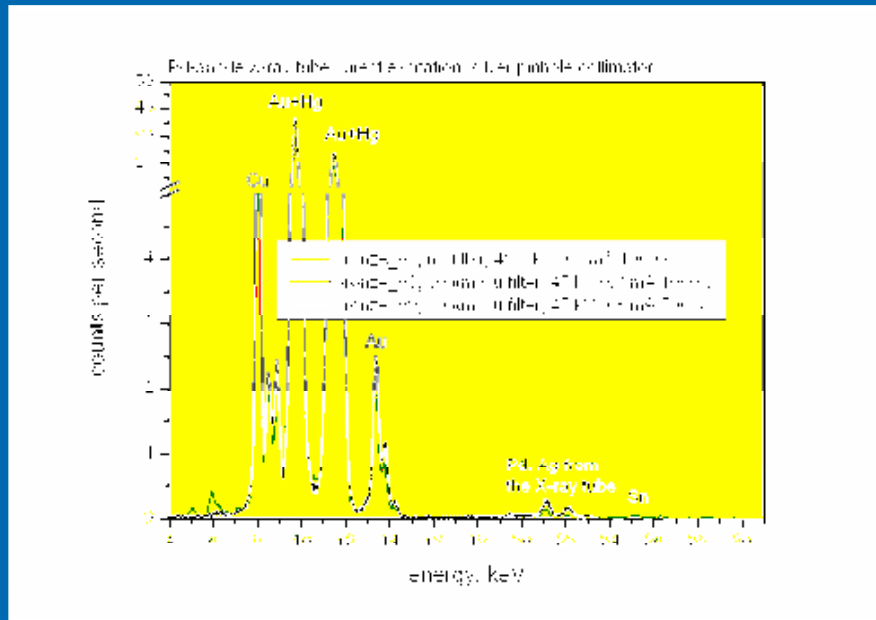
EXAMPLES OF APPLICATIONS

(Analysis of alloys – bronze tondo)



“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.

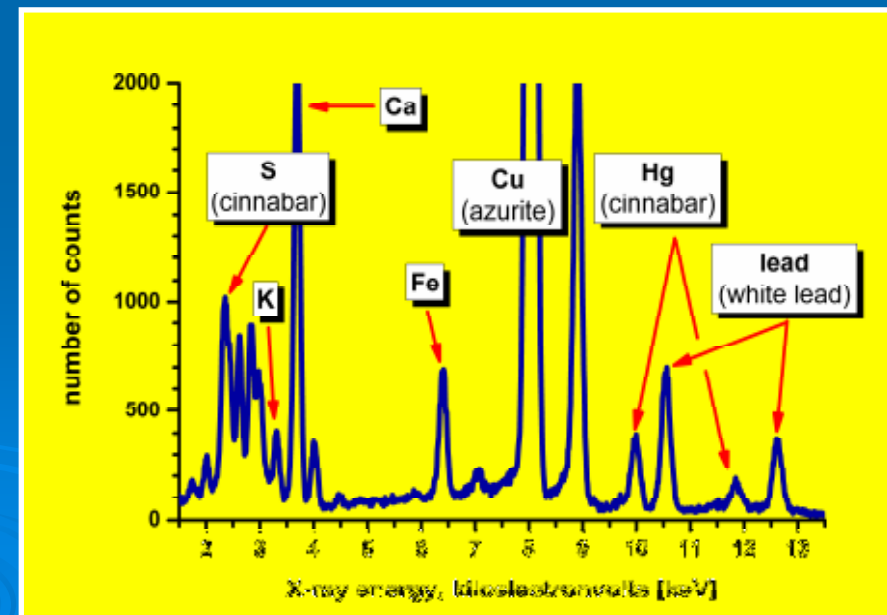
Bronze tondo



Left: X-ray spectra acquired at the “chest of the Child” and the area “between Madonna and the Child”; right: X-ray spectra acquired at the “forehead and knee of the Child”

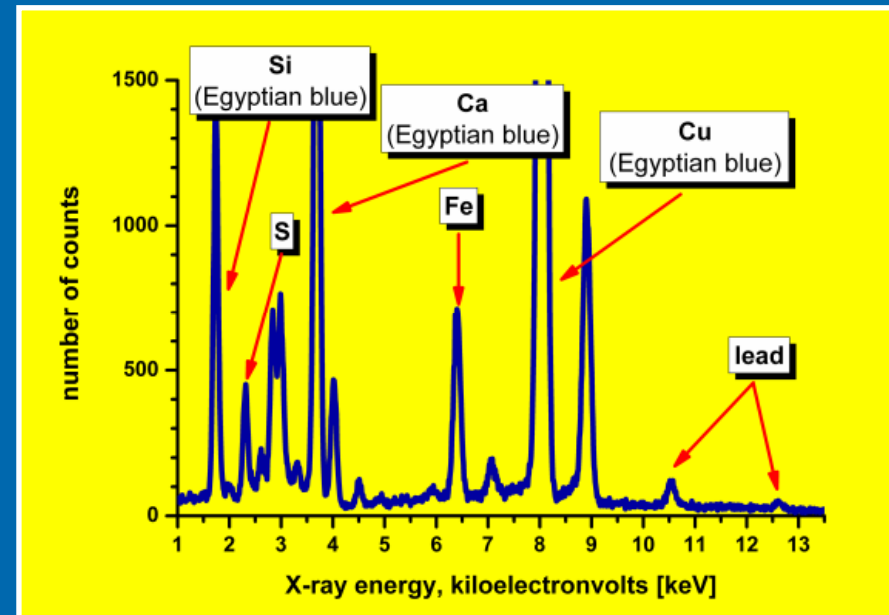
EXAMPLES OF APPLICATIONS

(Oriental saddle)



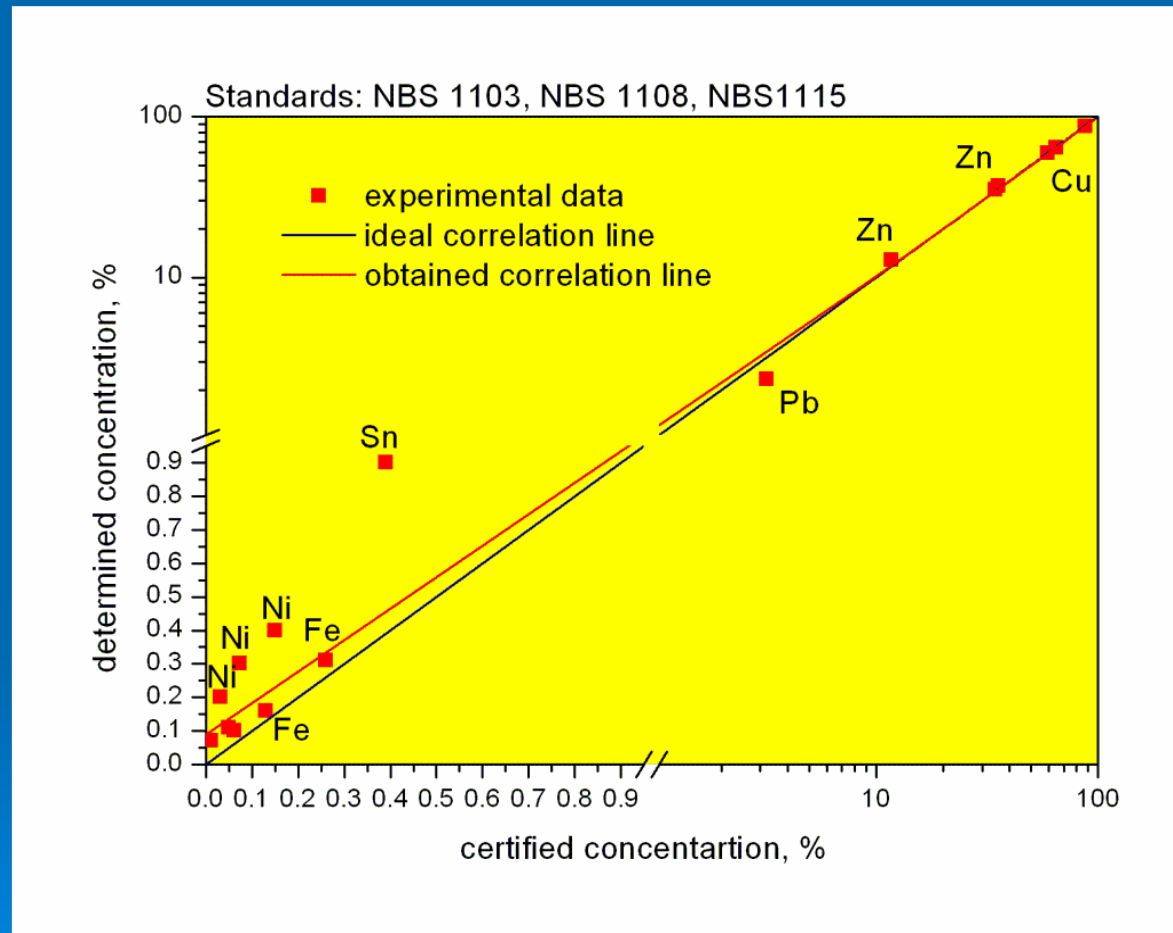
EXAMPLES OF APPLICATIONS

(Wooden stele)



Identification of Egyptian blue ($\text{CaO}\cdot\text{CuO}\cdot 4\text{SiO}$) pigment in a wooden stele from XXVI Dynasty, Thebes (640 B.C.).

Method Validation



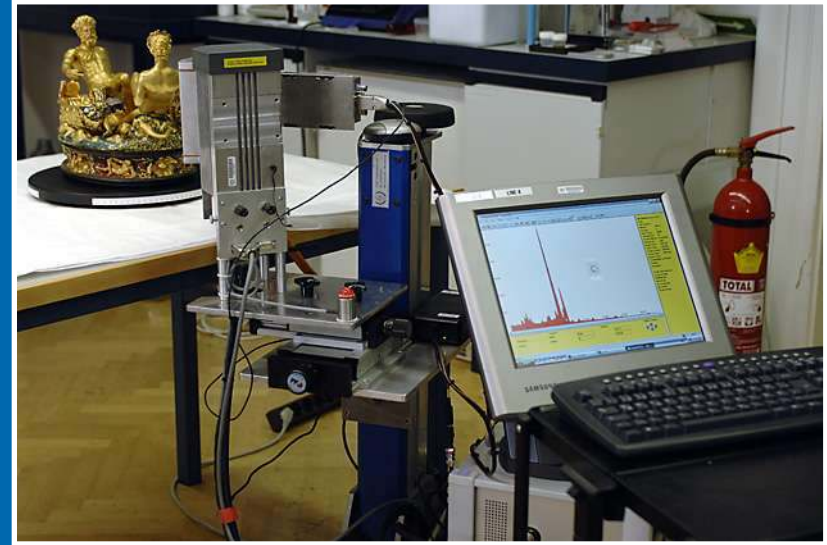
Determined versus certified concentration of elements in bronze standards

Precious goldsmith work



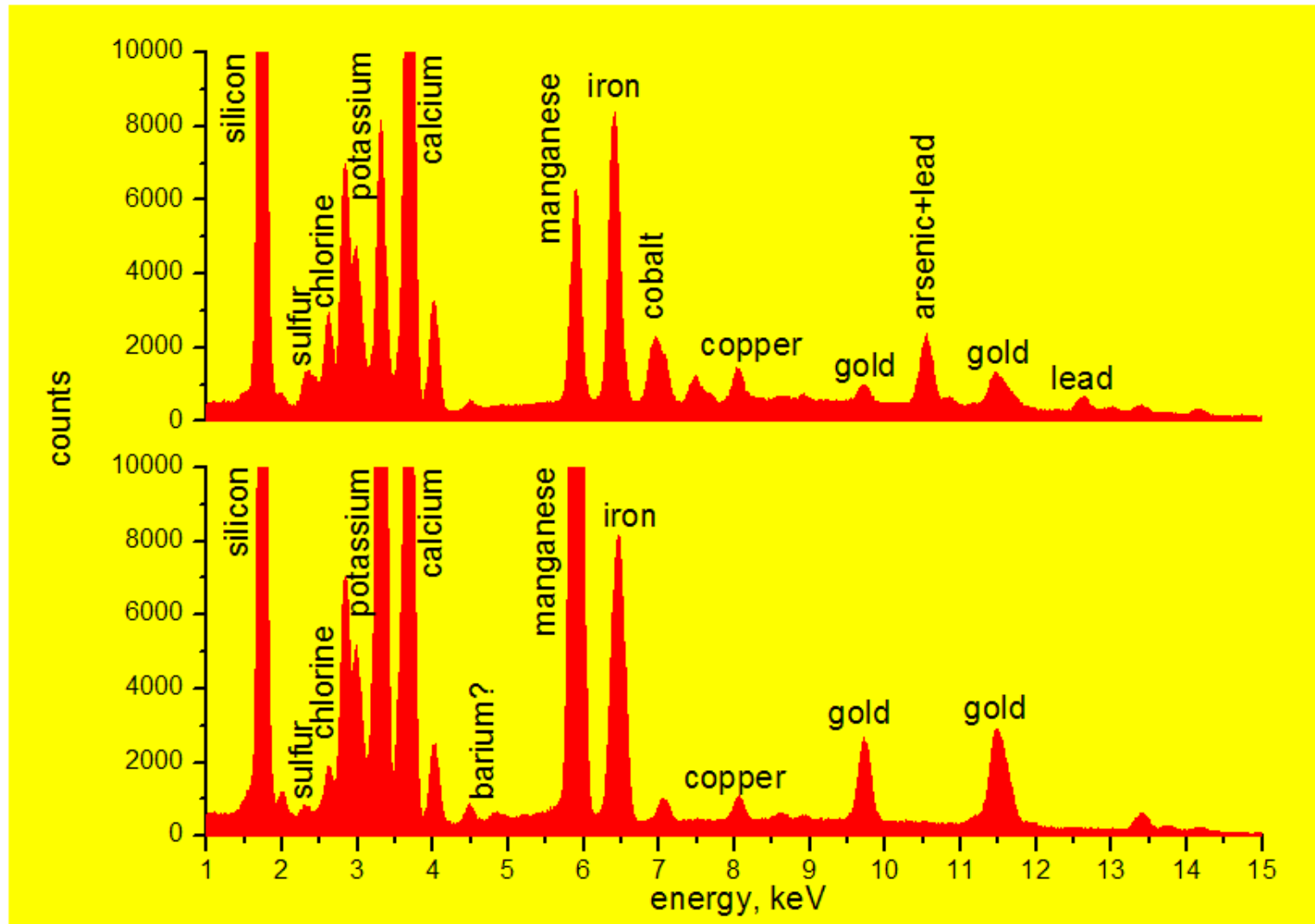
Gold salt cellar, so called *Saliera*, by Benvenuto Cellini (1500-1571). The only work of gold which can be attributed to Cellini with certainty

Saliera

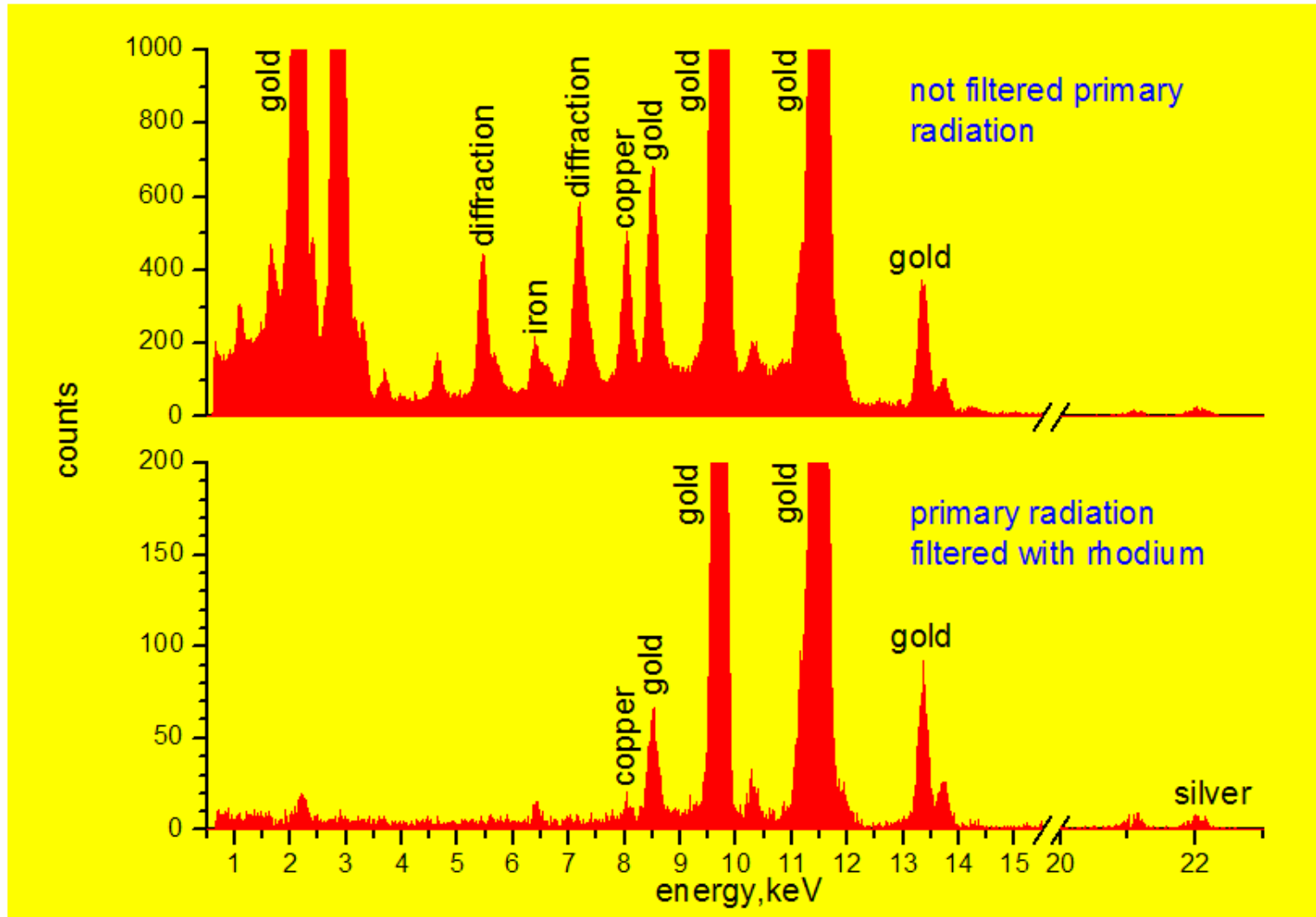


The "Saliera", stolen from the Museum in 2003, was recovered by the Austrian police in 2006. Currently the precious object is undergoing conservation and restoration in the Conservation Workshop of the Collection of Sculpture and Decorative Arts (Kunstkammer) of the KHM. The portable XRF spectrometer provided data on the chemical composition of the various parts of the salt cellar (gold alloy) to support the selection of optimum conservation strategies.

Saliera enamel decorations



Saliera gold alloy analysis



The IAEA Technical Cooperation and Coordinated Research Projects

1. Nuclear Techniques for the Analysis and Preservation of Cultural Heritage.

Rudjer Boskovic Institute (RBI), Department of Experimental Physics, Laboratory for Ion Beam Interactions, Zagreb, Croatia

Croatian Conservation Institute, Hrvatski Restauratorski Zavod; Zagreb, Croatia.

2. Nuclear Techniques for the Protection of Cultural Heritage Artefacts in the Mediterranean Region.

Albania, Bosnia and Herzegovina, Croatia, Cyprus, Greece, Malta, Montenegro, Serbia, Slovenia, The Former Yugoslavia Republik of Macedonia, Turkey.

3. Coordinated Research Project (CRP), Applications of nuclear analytical techniques to investigate the authenticity of art objects.

Brazil, China, Croatia, Cuba, France, Germany, Ghana, Greece, Hungary, Kazakhstan, Lebanon, Malaysia, Mexico, Peru, Poland, Syrian Arab Republic.

4. Use of nuclear analytical techniques and development of databases for the characterization and preservation of national cultural heritage objects (ARCAL)

Argentina, Brazil, Chile, Costa Rica, Cuba, Ecuador, Mexico, Peru

Conclusions

- *In situ* X-ray fluorescence analysis of works of art and objects of cultural heritage provides very valuable information about inorganic composition of the objects in a non-destructive manner
- Analytical performance of the portable energy dispersive XRF spectrometers is very similar to that of a laboratory XRF system.
- *In situ* measurements require max care and good knowledge of XRF analysis to ensure a proper interpretation of the analytical data
- The application of external vacuum chamber (or helium flash) is essential in the analysis of samples with low-Z elements

Acknowledgment

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 - Atominstitut (ATI) – Vienna University of Technology, Vienna, Austria
- **M. Griesser, K. Uhlir** - Kunsthistorisches Museum, Vienna, Austria
- **A. Mendoza** - Conservation and Restoration Cabinet, Havana's Historian Office, Havana, Cuba
- **G. Mank** – Physics Section, Division of Physical and Chemical Sciences, IAEA, Vienna

Thank you

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