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X-Ray Emission Techniques for Forensic Applications

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PORTABLE PORTABLE XRF SPECTROMETERS FOR IN-SITU MEASUREMENTSMETHODOLOGY AND APPLICATIONS

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PORTABLE XRF SPECTROMETERS FOR IN-SITU MEASUREMENTS- METHODOLOGY AND APPLICATIONS

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CONTENTS

INTRODUCTION

- 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

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) 88	1.07 0.04
^{241}Am	433	59.5	0.36

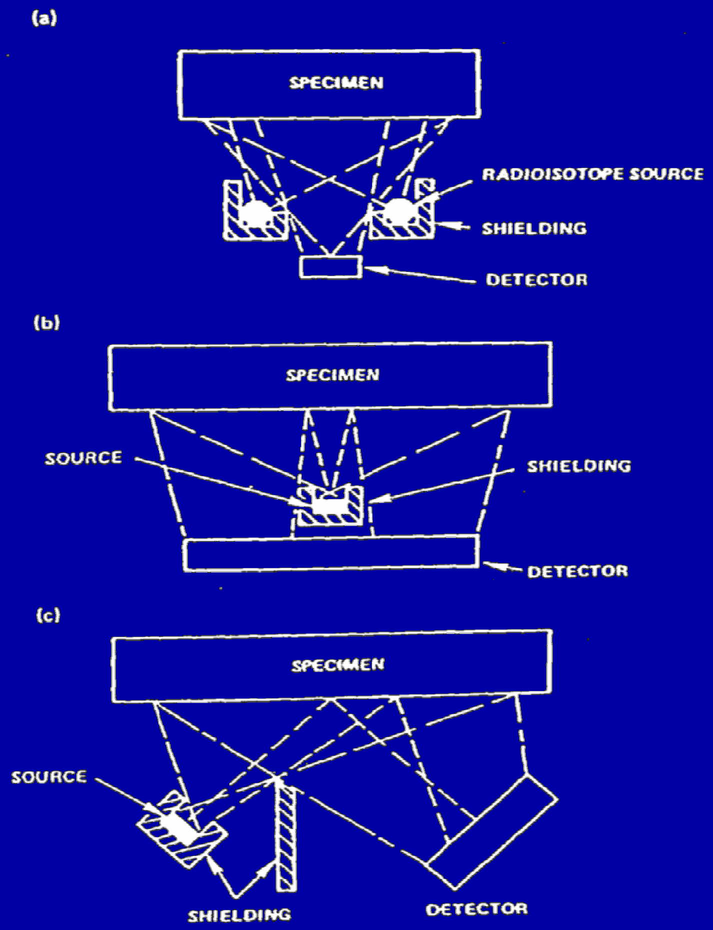
DESIGN CRITERIA
Excitation geometries

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

a) annular source

b) central source

c) side source

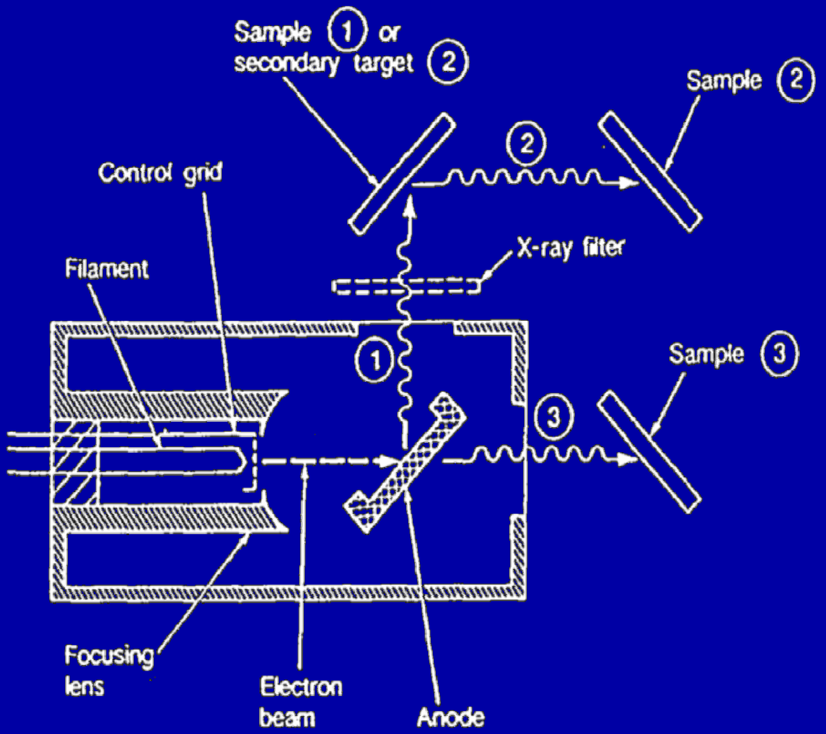


DESIGN CRITERIA
Excitation sources

Typical excitation geometries

for an X-ray tube:

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



DESIGN CRITERIA
Detectors

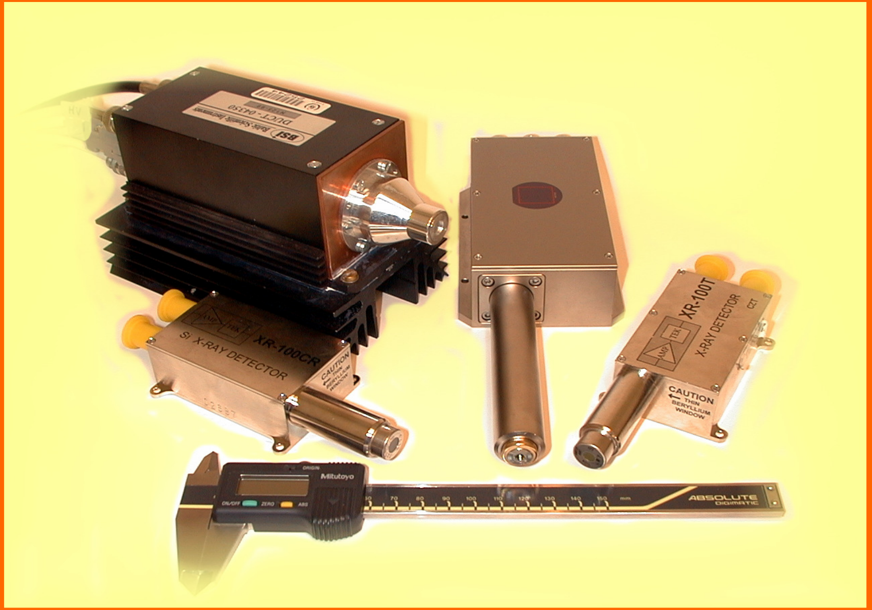
Selection of detectors - parameters to be taken into account:

- **question to be answered (single or multi X-ray lines)**
- **energy of X-rays to be detected**
- **required energy resolution**
- **required efficiency**
- **portability**
- **costs, not only of the detector but also of the related electronics and of the eventual cooling system**

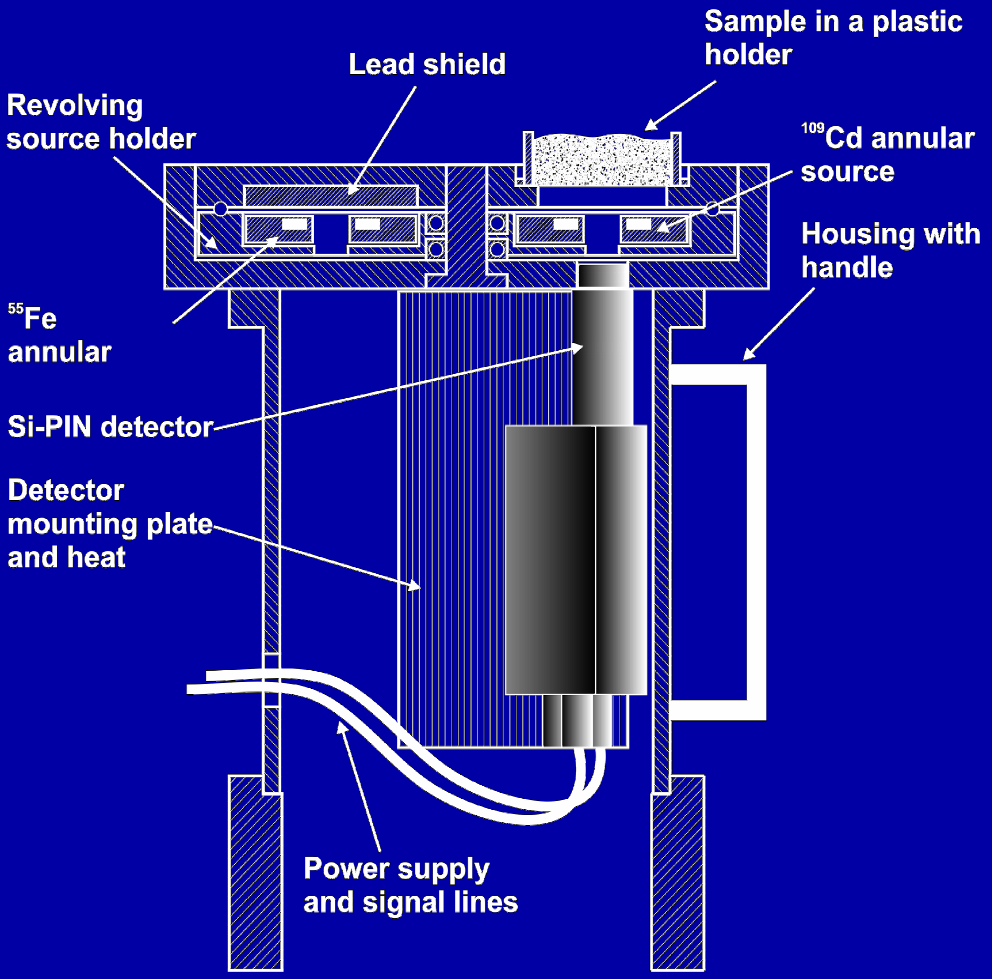
DESIGN CRITERIA
Detectors

- Room temperature and Peltier-cooled semiconductor detectors:

HgI_2 Si-PIN Si-drift CdTe



DESIGN CRITERIA
Development



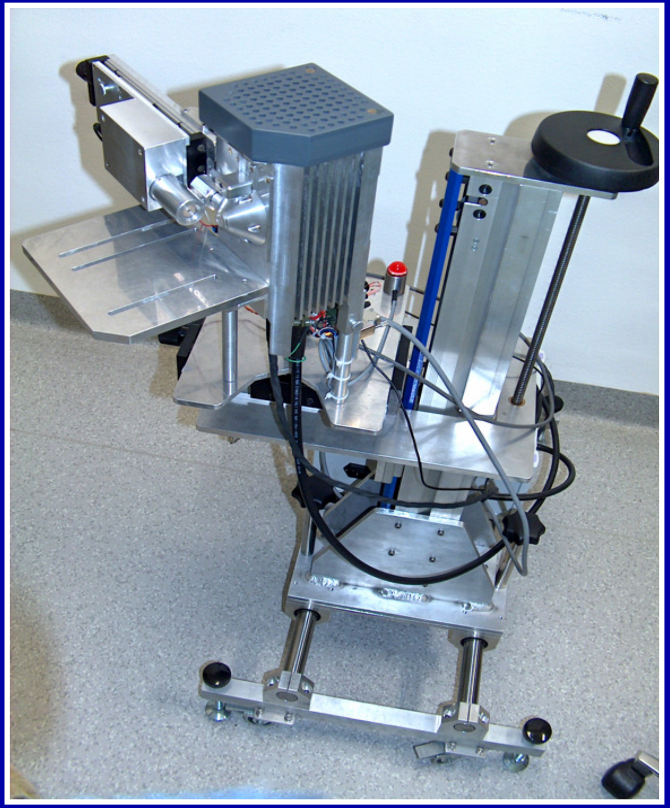
EXAMPLES of FPXRF SYSTEMS

- Portable XRF unit with thermoelectrically cooled Si-PIN detector

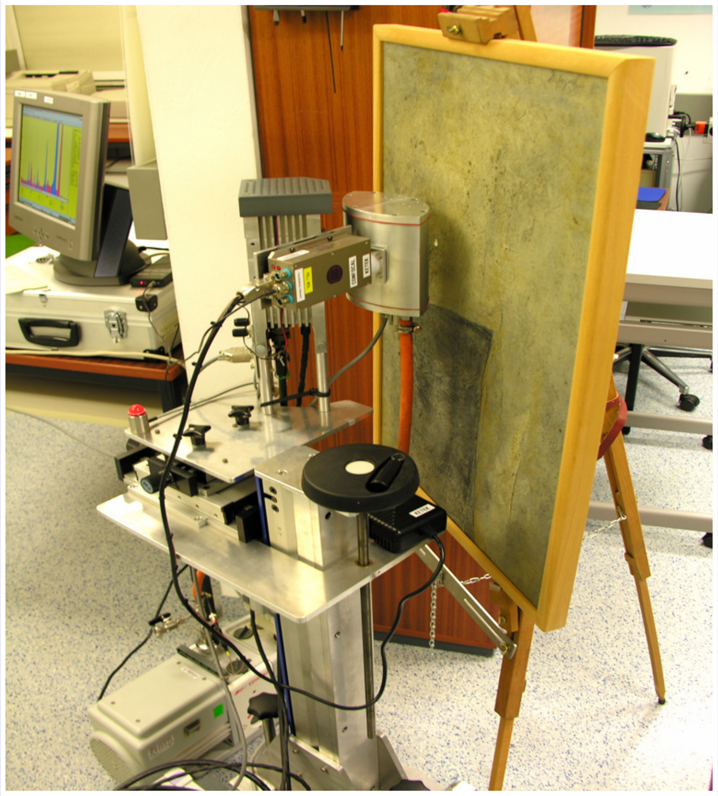
EXAMPLES of FPXRF SYSTEMS

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

EXAMPLES of FPXRF SYSTEMS

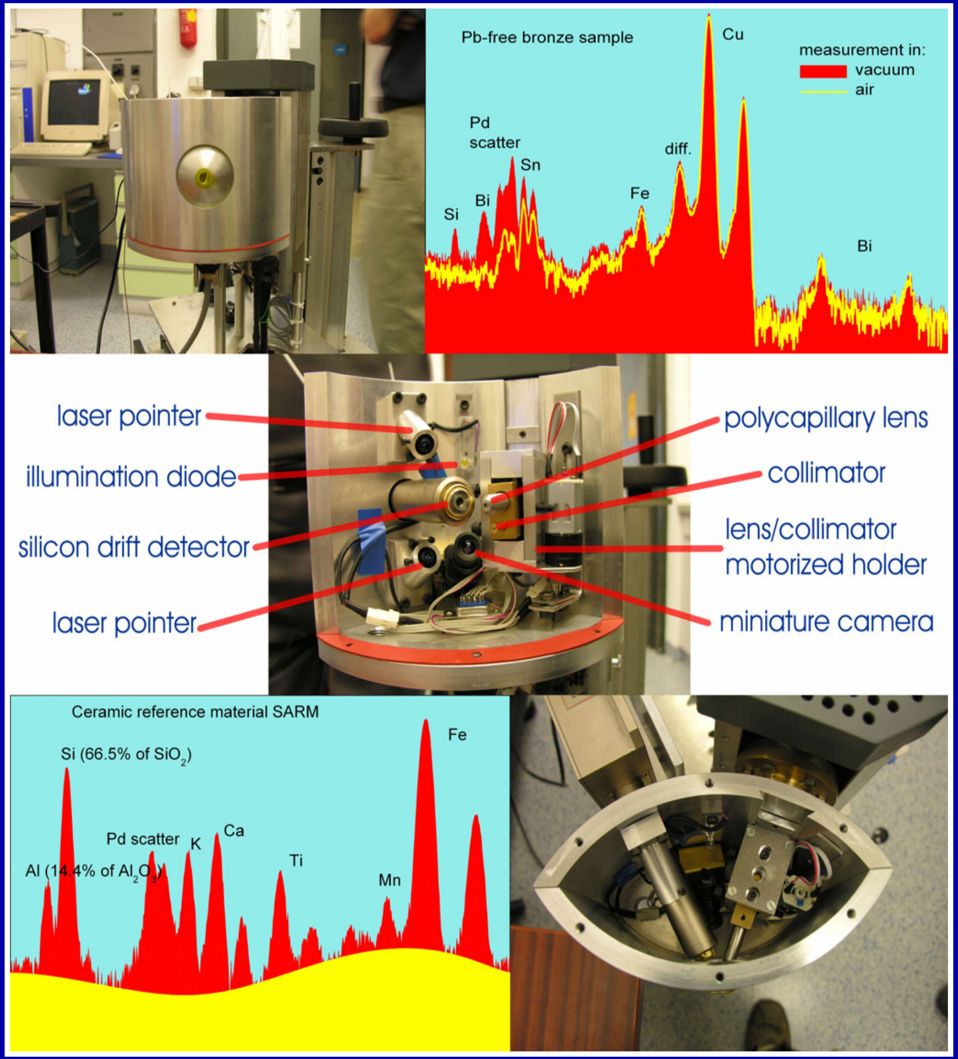


Direct/secondary excitation in air, Si-PIN detector, pinhole collimator



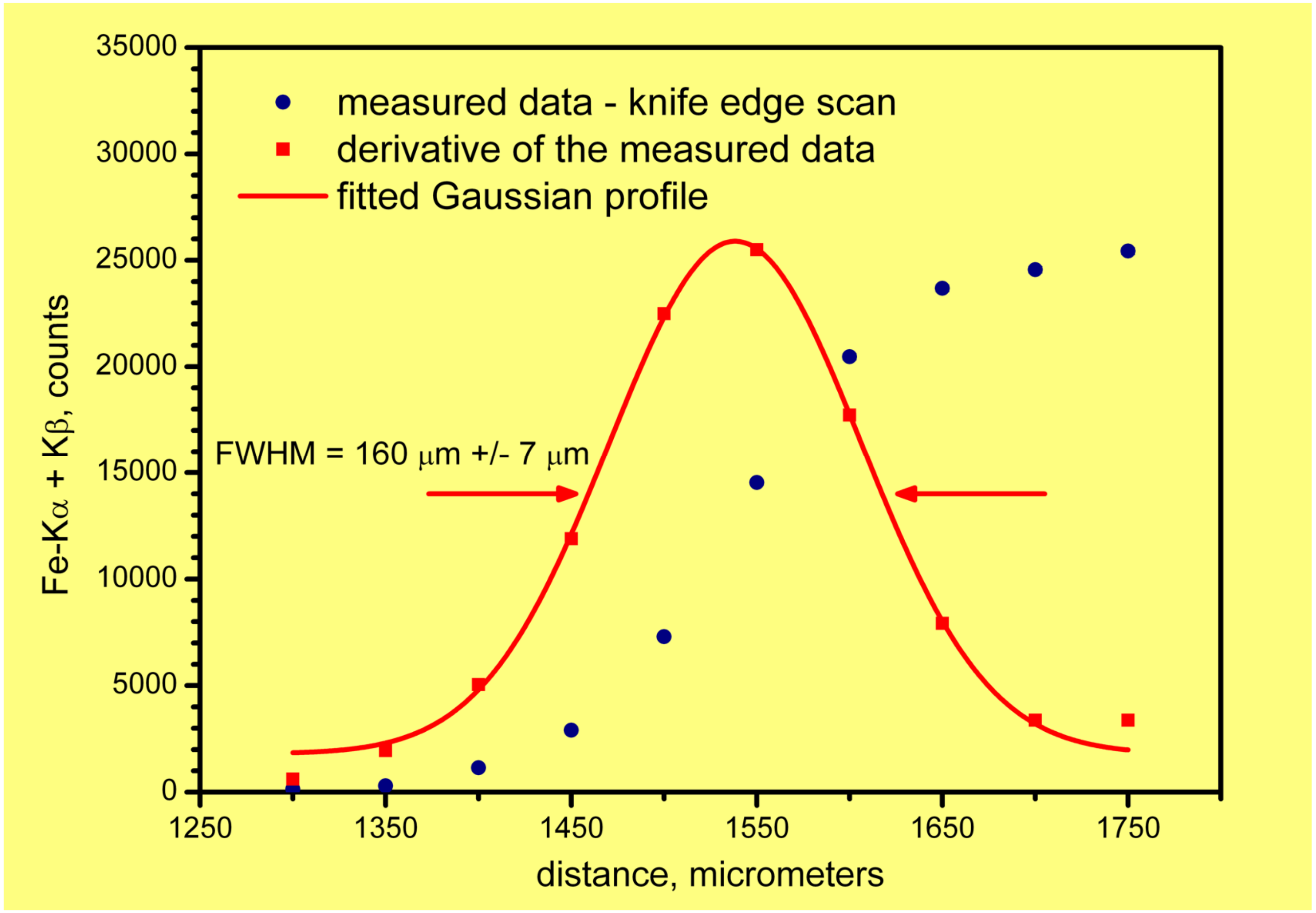
Direct excitation, vacuum attachment, SD detector, polycapillary optics/collimator

EXAMPLES of FPXRF SYSTEMS

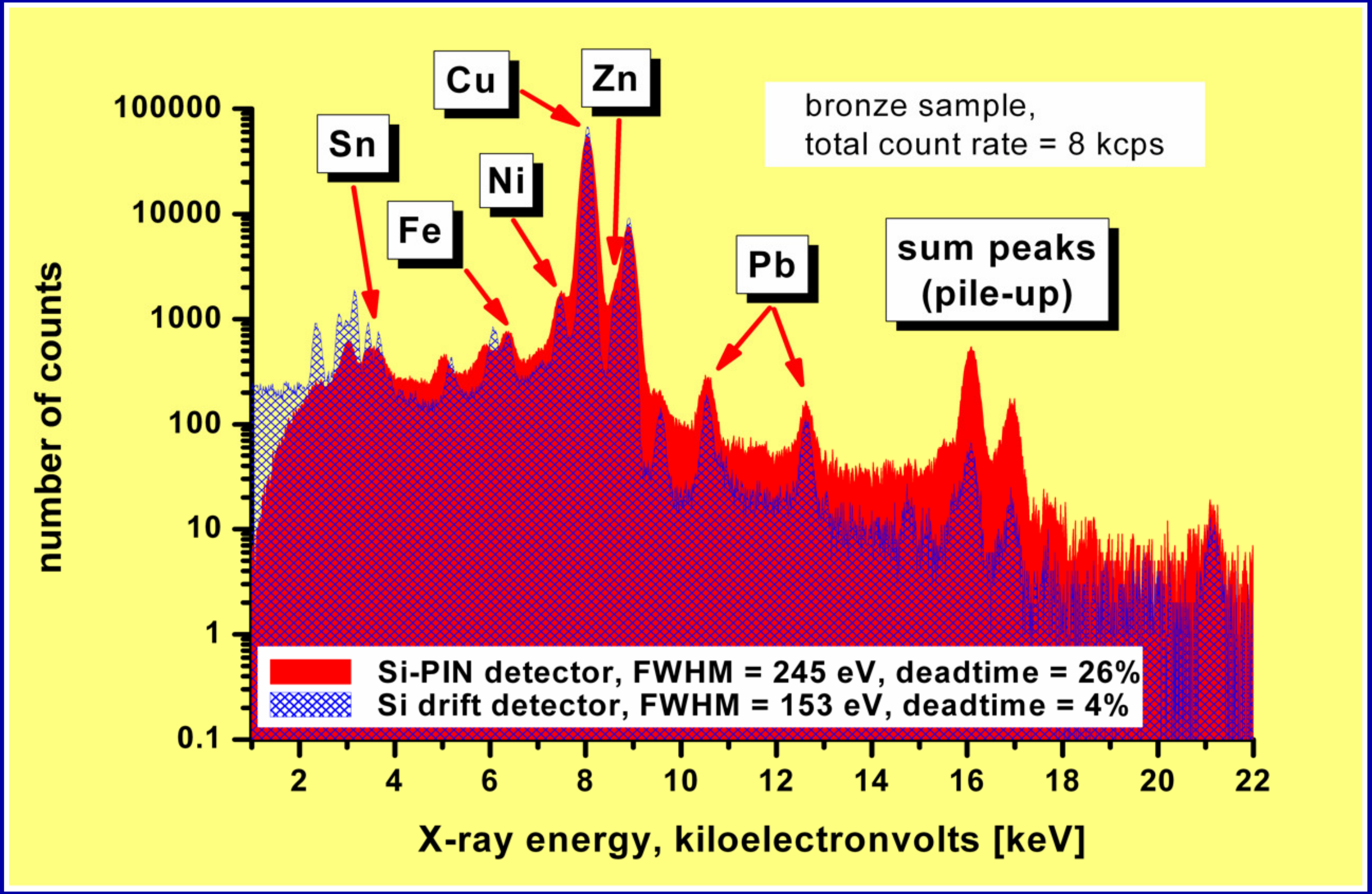


- Pd-anode X-ray tube (50W), direct excitation in vacuum or air
- pollycapillary lens and brass collimator,
- silicon drift detector, thermoelectrically cooled, 10 mm2 active area, 300 micrometers nominal thickness, 140 eV FWHM at 5.9 keV, 1 microsecond shaping,
- 2 laser pointers,
- CMOS camera with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

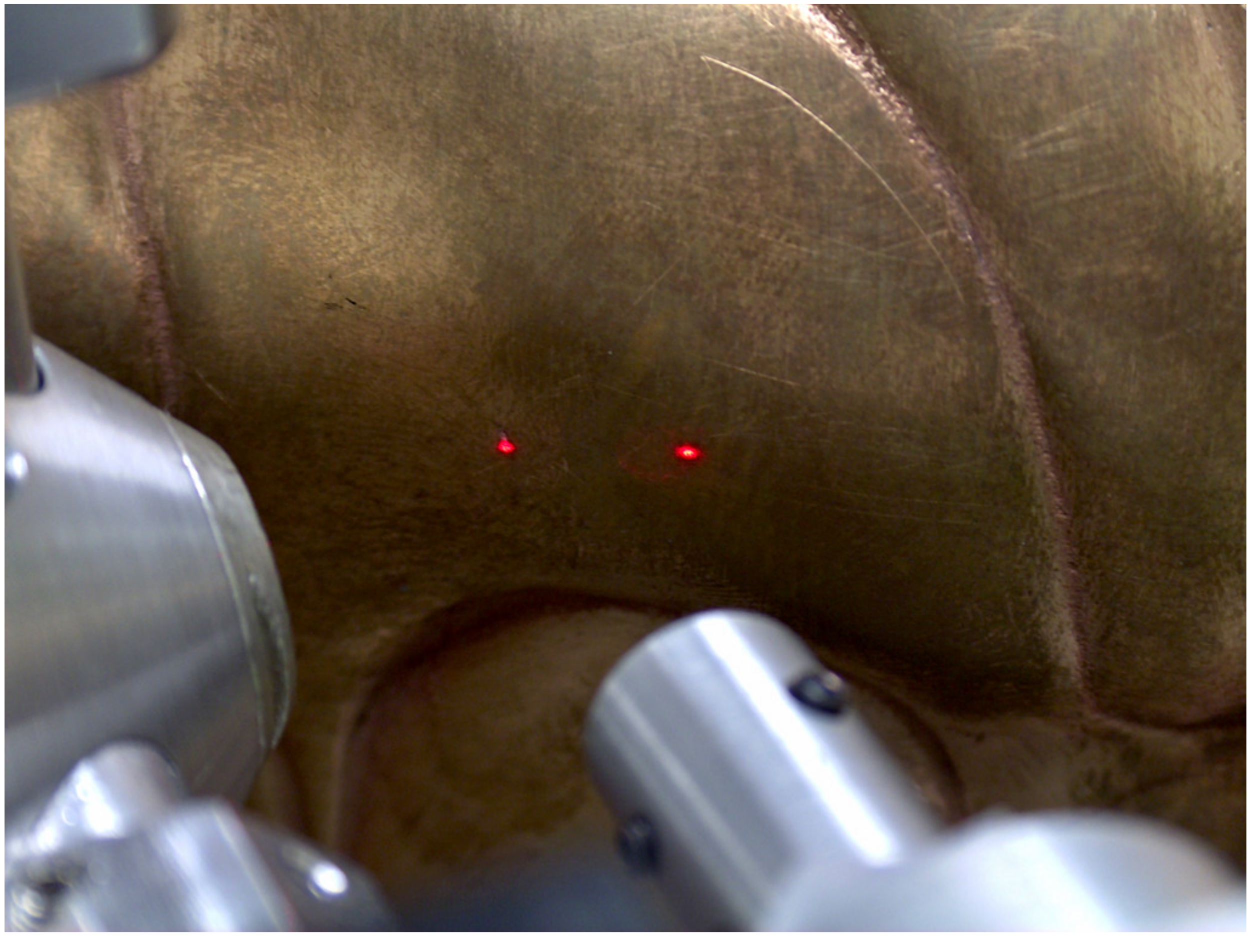
X-ray beam profile, polycapillary



X-ray detector performance

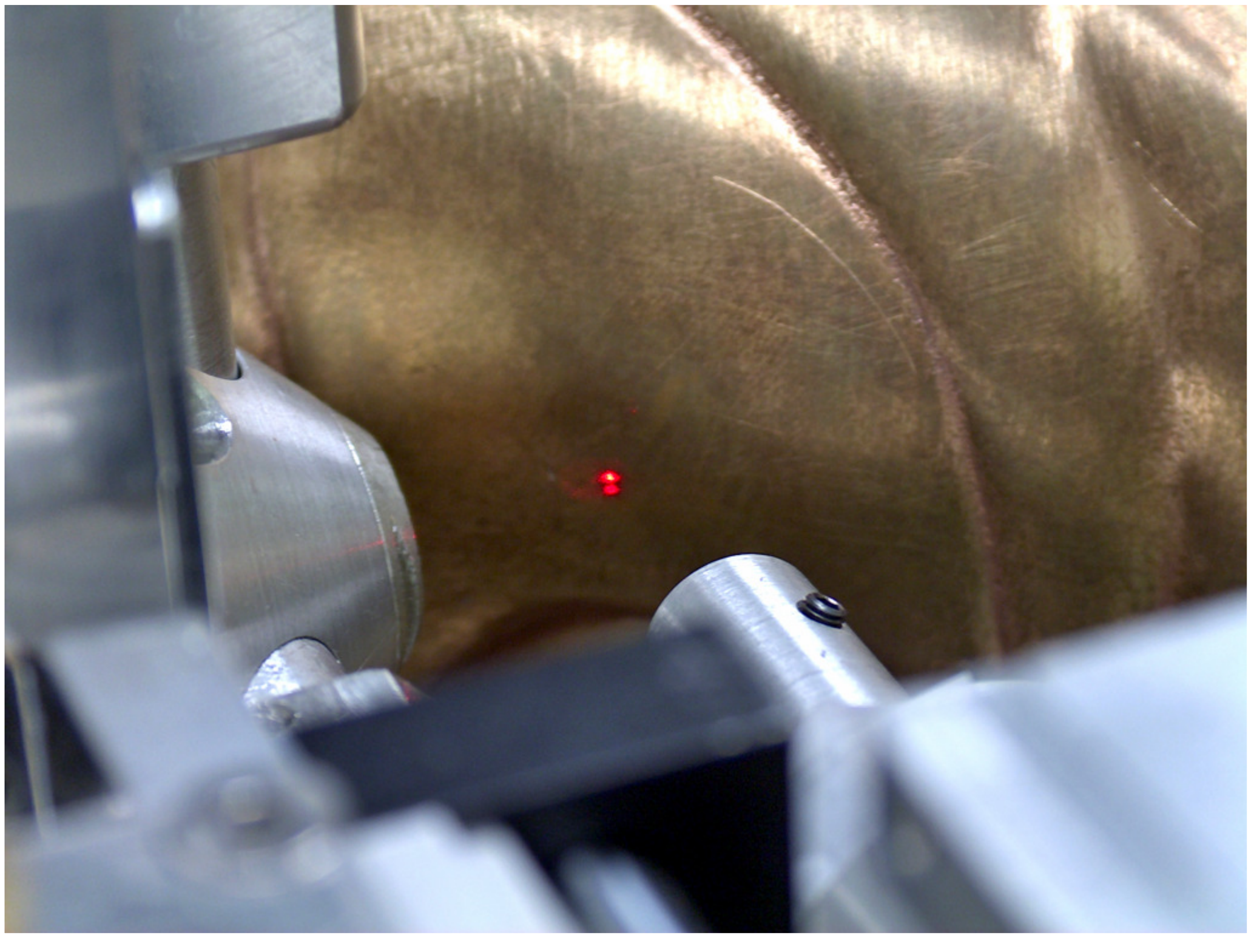


ADJUSTMENTS



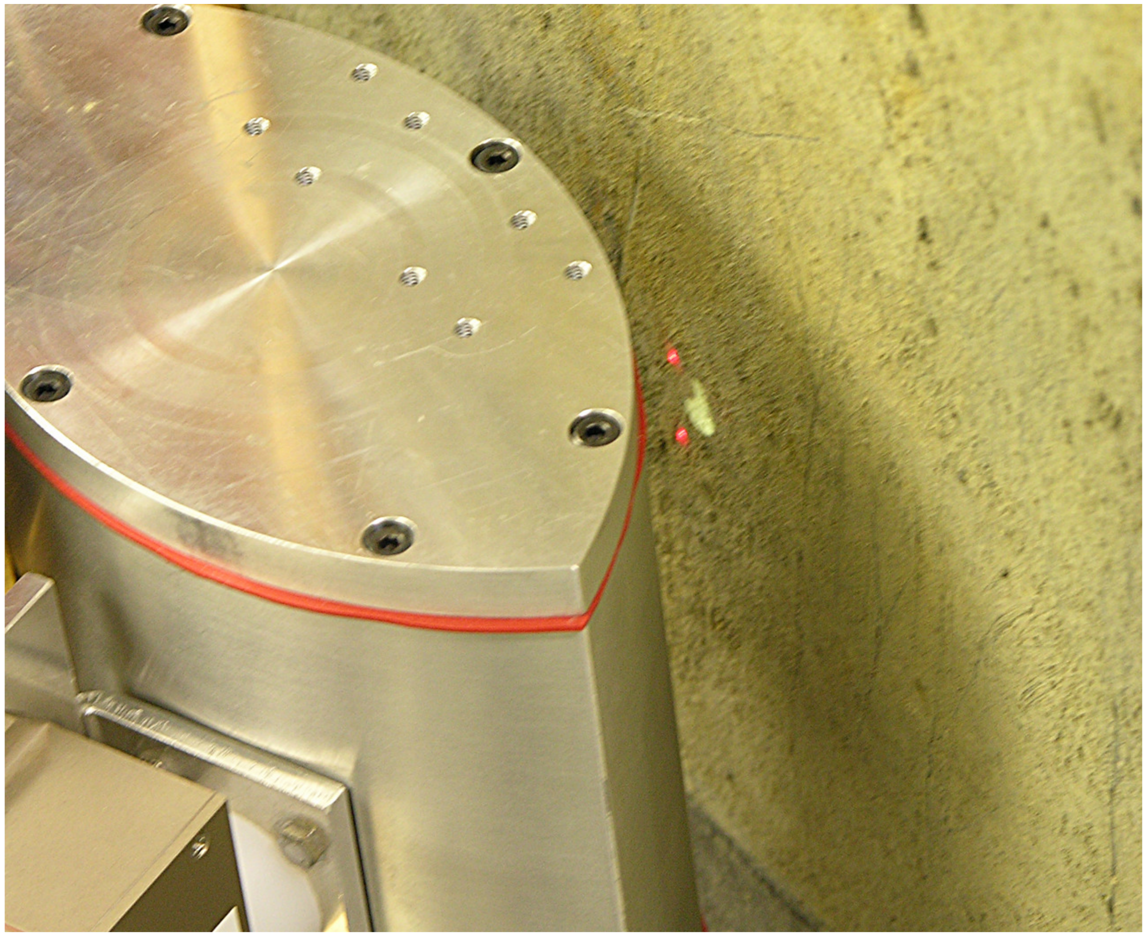
Object not in the optimum measuring position

ADJUSTMENTS

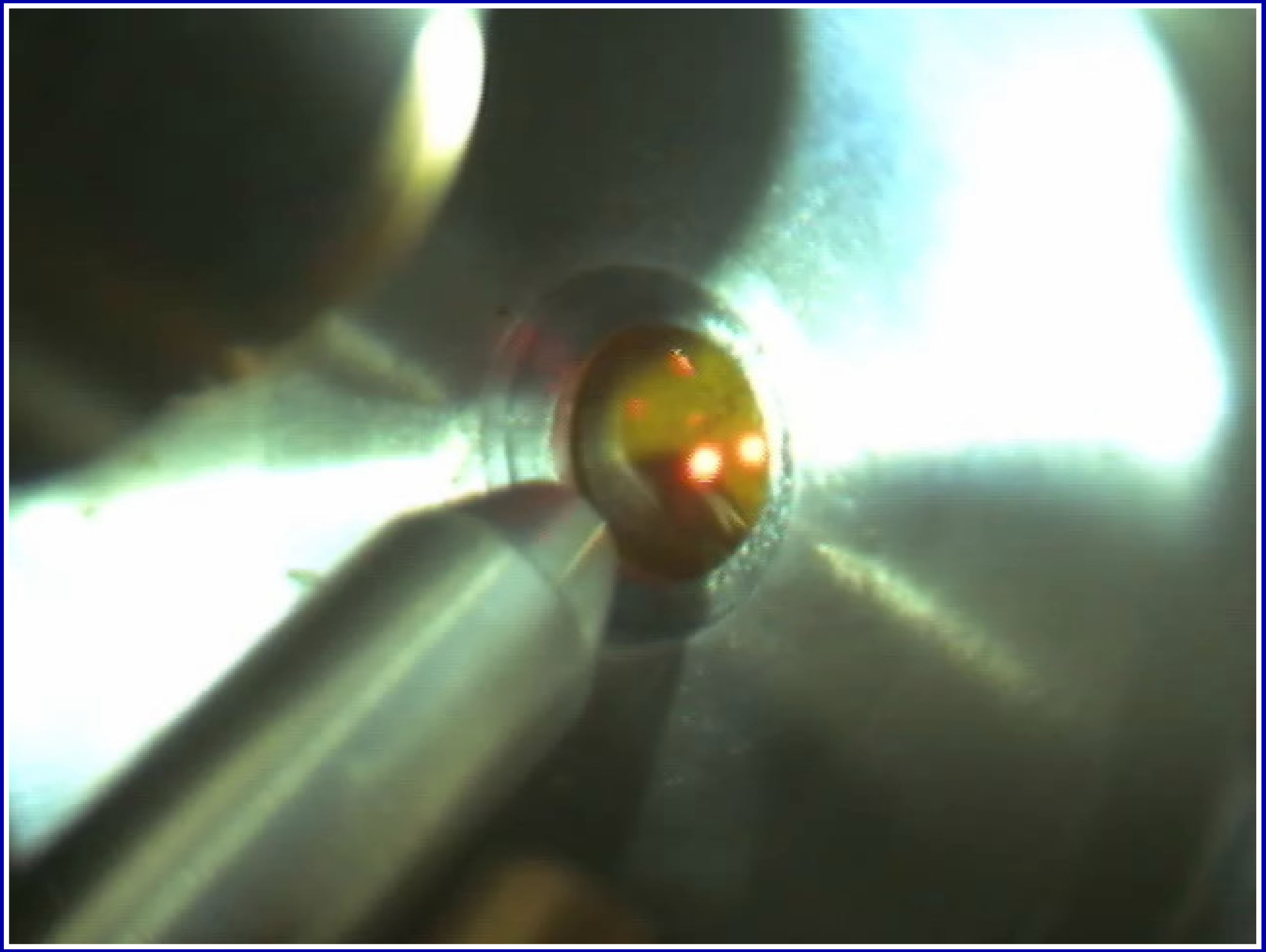


Object in the optimum measuring position

ADJUSTMENTS



ADJUSTMENTS



ANALYTICAL PERFORMANCE

- capable of detecting chemical elements with the atomic number >= 11 (sodium)
- detection limits in the PPM range
- beam spot diameter: 0.1 mm, 1 mm
- local and bulk analysis capability

PARAMETERS OF IN-SITU MEASUREMENTS

- Critical penetration depth (information depth)

  “Sample thickness from which 99% of a fluorescence signal originates”

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

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

PARAMETERS OF IN-SITU 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 MEASUREMENTS

- 50 % of d_{crit} ⇒ 90% of fluorescence signal
- 35 % of d_{crit} ⇒ 80% of fluorescence signal
- 15 % of d_{crit} ⇒ 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 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 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 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 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 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 cm^2 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: grounding 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 that 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

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

$$\Downarrow$$

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

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:

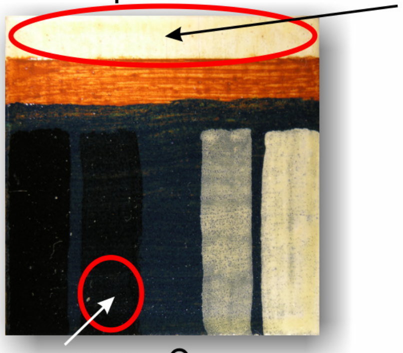
$$I_i = Q_i K_i(E_0) \frac{1 - \exp\left\{ -\left[\sum_j F_j + F_A + F_B \right] \right\}}{\sum_j F_j + F_A + F_B} \left(1 + F_i^{Enh}\right) S_i; \quad F_j = Q_j \left(\frac{\mu_j(E_0)}{\sin \Psi_1} + \frac{\mu_j(E_i)}{\sin \Psi_2} \right)$$

$$F_{A/B} = Q_{A/B} \left(\frac{\mu_{A/B}(E_0)}{\sin \Psi_1} + \frac{\mu_{A/B}(E_i)}{\sin \Psi_2} \right)$$

EXAMPLES OF APPLICATIONS
(Inorganic pigments)

Test pattern A

area no. 1
(chalk)



area no. 2 (chalk,
ochre, azurite, vine black)

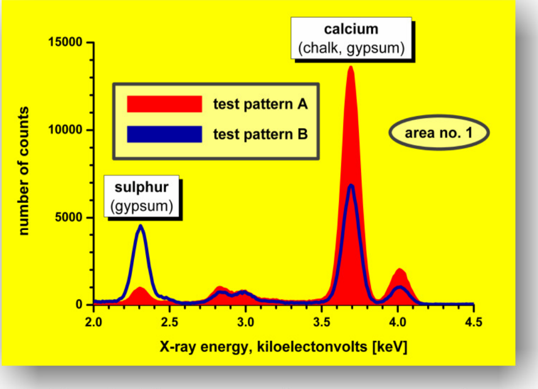
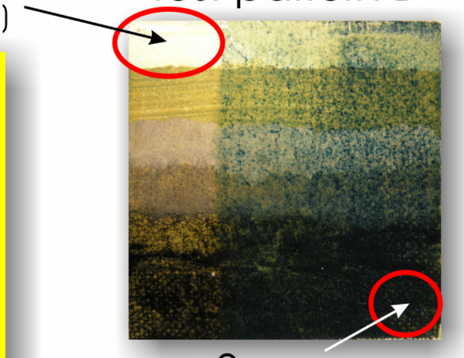


Fig. 1. X-ray spectra, area no. 1

area no. 1
(gypsum)

Test pattern B



area no. 2 (plaster, verdigris,
white lead, umber, smalt, carbon,
ultramarine, azurite)

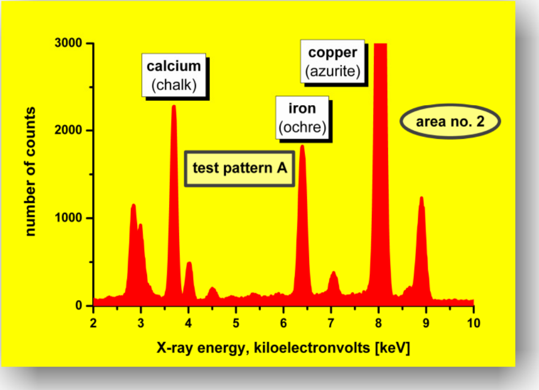


Fig. 2. X-ray spectrum, pattern A, area no. 2

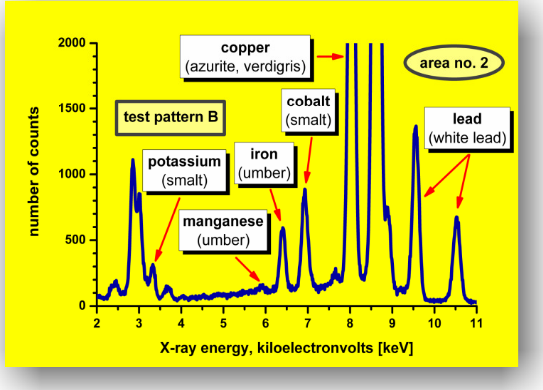


Fig. 3. X-ray spectrum, pattern B, area no. 2

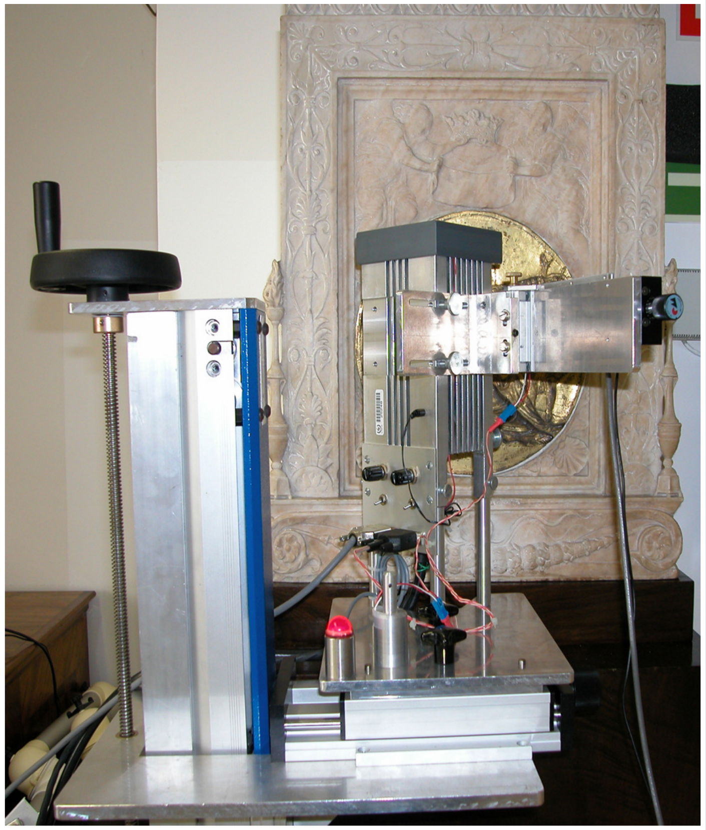
EXAMPLES OF APPLICATIONS

(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)

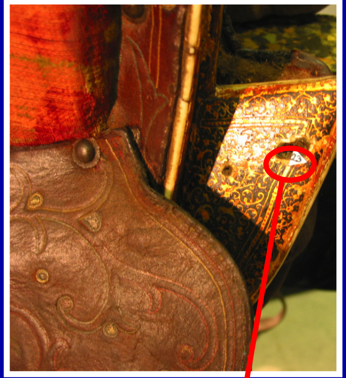
EXAMPLES OF APPLICATIONS

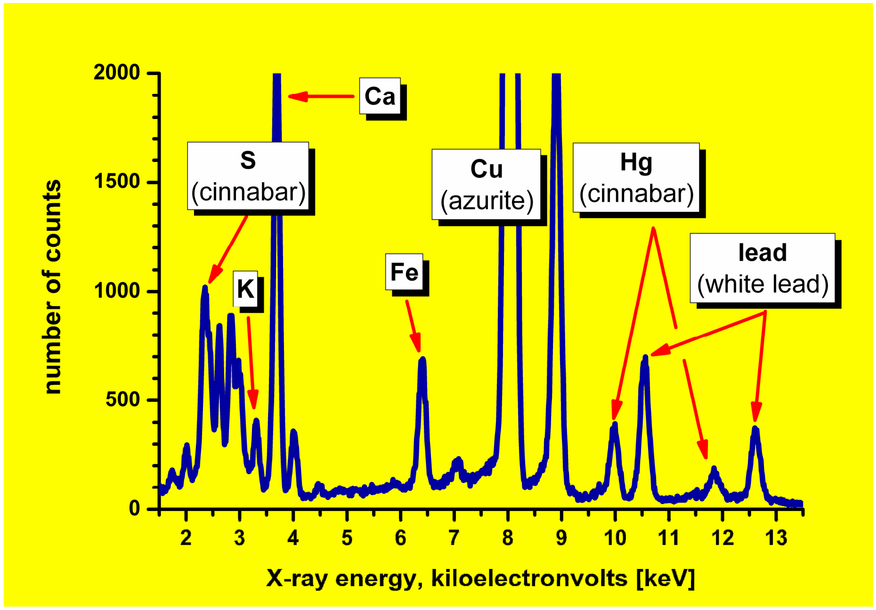
(*Analysis of alloys – bronze tondo)*



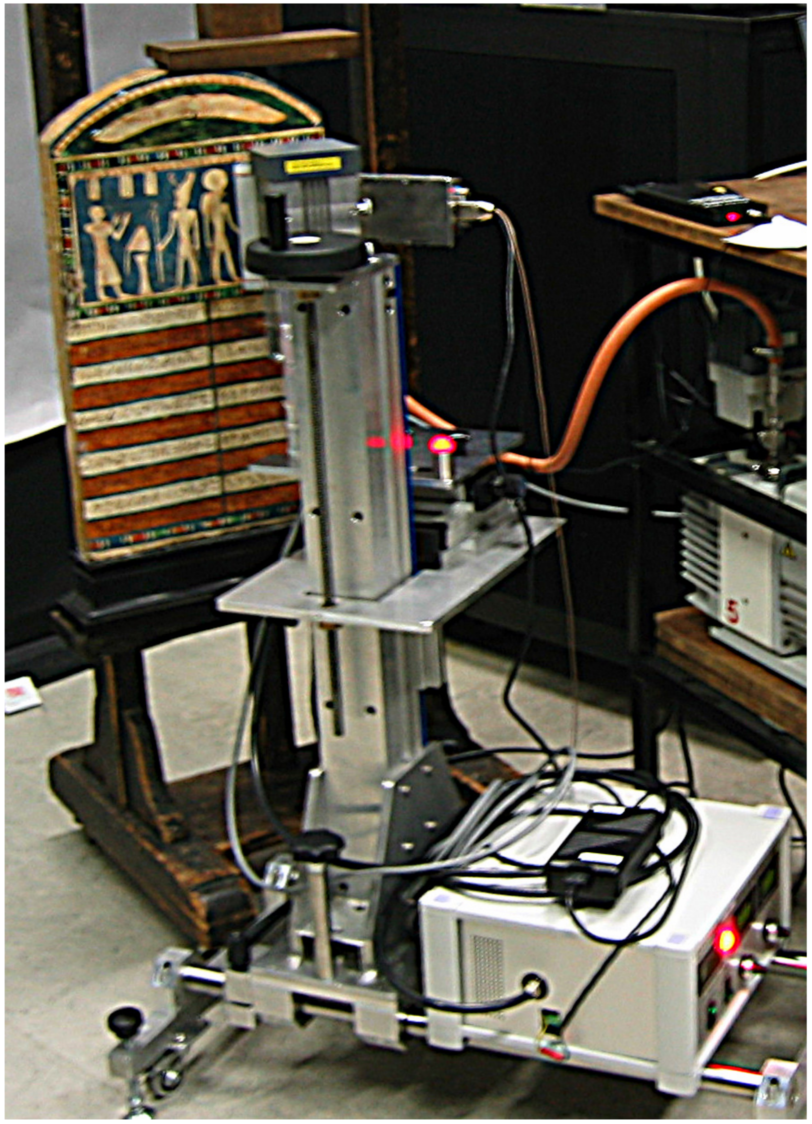
“Virgin and Child” by Donatello (Florence 1386 - 1466) - a bronze tondo from Kunsthistorisches Museum’s (Vienna) collection.
Average composition of the bronze was used for documentation purposes.

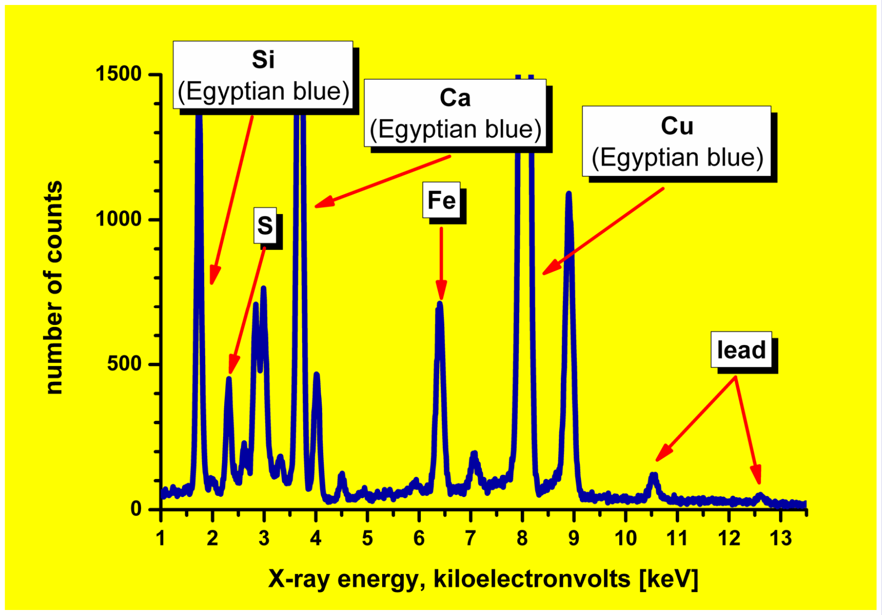
EXAMPLES OF APPLICATIONS
(*Oriental saddle*)





EXAMPLES OF APPLICATIONS
(*Wooden stele)*





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

ANALYSIS of SOIL

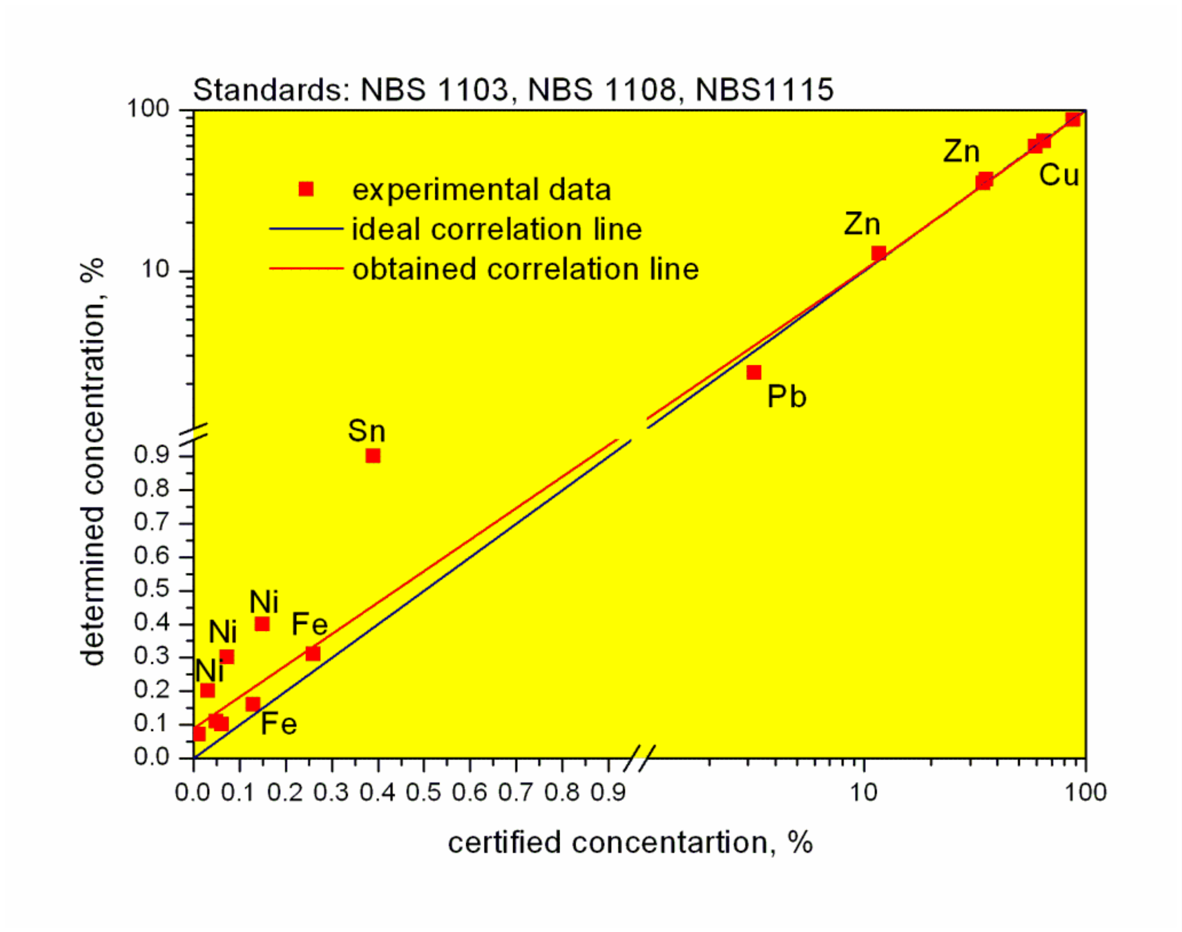
Concentrations of elements in soil obtained from direct in-situ measurements of the soil surface layer and using the powder soil samples after homogenization in the laboratory. The analyses were performed with portable X-ray spectrometer system utilizing the BFP method. The in-situ concentrations were corrected for the moisture contents.

a) - less than the detection limit (DL)

b) – the uncertainties due to counting statistics/range of results

Element	Concentrations of elements determined in two locations, direct in-situ measurements		Concentrations of elements determined in two locations, in-laboratory measurements after processing the soil material	
	Location # 1	Location # 2	Location # 1	Location # 2
	mg/g			
K	< DL a)	< DL	12 ± 2	12 ± 2
Ca	37 ± 5 b)	47 ± 5	65 ± 2	66 ± 3
Fe	16.1 ± 2	15.5 ± 0.5	22 ± 2	19.8 ± 0.2
	µg/g			
Mn	< DL	< DL	400 ± 60	520 ± 40
Zn	54 ± 18	75 ± 30	67 ± 8	68 ± 8
Br	< DL	< DL	4.4 ± 2	4.7 ± 2
Rb	57 ± 10	53 ± 6	84 ± 7	81 ± 3
Sr	72 ± 8	80 ± 10	119 ± 4	129 ± 3
Y	< DL	< DL	23 ± 2	19 ± 3
Zr	80 ± 10	83 ± 6	640 ± 410	490 ± 130
Pb	31 ± 12	44 ± 10	45 ± 5	45 ± 7

Method Validation



Determined versus certified concentration of elements in bronze standards

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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Thank you

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