Reference samples for µ-XRF and TXRF analysis

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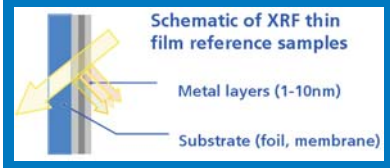
Introduction

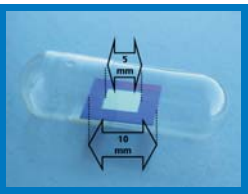


Applications:
- Quality control in XRF setups: alignment, optimization, calibration, minimum detection limits
- Confocal setups: depth resolution, detector capillary calibration

Advantages:
- Absorption free standard – no matrix correction needed
- Very low substrate background signal, transmission possible
- Wide range of suitable elements for simultaneous detection
- Selection of non-overlapping X-ray fluorescence lines
- Signal strength easily adjustable by layer thickness, comparable peak intensity for all elements
- High degree of lateral uniformity and homogeneity by PVD

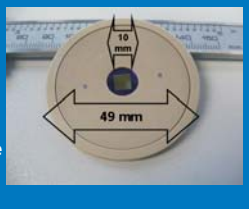
Fabrication

Multielement samples were fabricated by PVD methods such as Ion Beam Sputtering (IBS), Pulsed Laser Deposition (PLD) and Magnetron Sputtering (MSD).



Silicon nitride membrane

Ultrathin silicon nitride membranes were used as low background substrates. Temperature stable PEEK holders were used for easier and safer handling.



PEEK sample holder

Characterization

Various complementary physical and chemical techniques were applied to specify and characterize the reference samples. The element content was quantified with inductively coupled plasma optical emission spectrometry (ICP-OES), atomic absorption spectrometry (AAS) and X-ray techniques such as µ-XRF mappings or grazing incidence XRF.

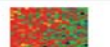
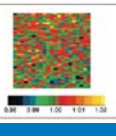
Radiation energy:
- 9.5 ..10 .. 25 .. 26 .. 28 keV synchrotron
- 20.2 keV (Rh Kα) X-ray tube

Radiation sources:
- PTB beamline, BESSY, Berlin, Germany
- ANKA FLUO-Beamline, KIT, Karlsruhe, Germany
- Beamline L, HASYLAB at DESY, Hamburg, Germany
- µ-XRF Eagle III, Los Alamos National Laboratory, USA

Homogeneity

The lateral homogeneity of the material deposition on the XRF samples was characterized by µ-XRF mapping scans at the ANKA FLUO beamline

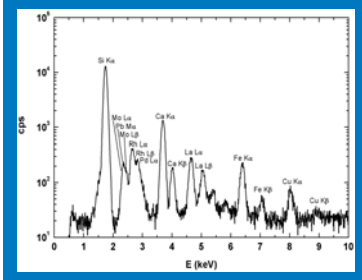
Scanning areas:
0.3x0.3 mm² up to 15x15 mm²
Probe/Beam size:
µm² range up to mm² range
Elements scanned:
Si, Ca, La, Fe, Cu, Pb, Mo, Pd
Homogeneity:
The mass deposition deviation was less than 1% within the entire scanned area.

	Large area map SF1	µ beam "mapping" SF1
Energy	26 keV	26 keV
Area	15 x 15 mm²	1.4 x 1.4 mm²
Beam size	0.8 x 0.4 mm²	2.3 x 6 µm²
Step size	0.8 x 0.4 mm²	2.3 x 6 µm²
Cu Kα		
La Lα		

Mass depositions and energy spectrum

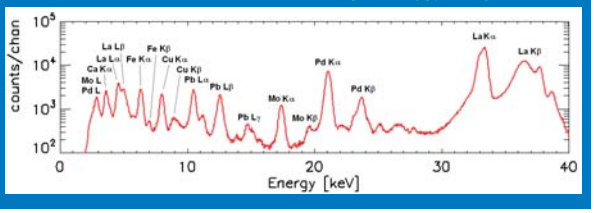
Mass depositions on the sample are in the range from 2 ng/mm² to 20 ng/mm². These amounts were selected to achieve comparable peak heights for all elements. The deposition values listed here with characteristic emission line energies are average values measured by AAS, ICP-OES and µ-XRF.

Element	Mass (ng/mm²)	Emission Lines (eV) Kα	Lα
Pb	7.61±0.96	85335	10541
La	11.01±0.62	33298	4649
Pd	1.8±1.0	21123	2838
Mo	1.32±0.40	17444	2293
Cu	2.84±0.35	8040	930
Fe	5.04±0.87	6401	747
Ca	19.31±1.10	3691	341
Si	Substrate	1740	



Sum spectrum of reference sample RF4 measured at a laboratory µ-focus X-ray tube (Eagle III, Rh Kα, 20.2 keV) at Los Alamos National Laboratory.

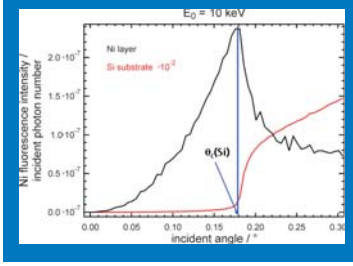
Sum spectrum of sample RF4 measured at 40 keV at HASYLAB beamline L.



TXRF reference samples

Special requirements for TXRF reference samples:
- very low deposition (sub-monolayer) of ~ 10^{13}, 10^{12}, 10^{11}, 10^{10} atoms/cm²
- very good lateral homogeneity: layer rather than droplet „crater"

Challenges:
- scale down the deposition to a homogeneous but not continuous „layer"
- confirm the homogeneity / layer structure
- quantify the amount of deposited material without reference samples



Angle scan of a TXRF Ni reference sample at PTB/BESSY confirms the layer structure.

Fundamental parameters calculations give a mass deposition of ~1.8·10^{14} at/cm² of Ni (~20% of a monolayer).

Further scaling down of the deposition is possible.

Results

- Successful production of multi-element and sub-monolayer reference samples.
- High degree of homogeneity and reproducibility.
- Low X-ray absorption.
- Large spectral range without line overlapping, emission lines have similar peak intensities.
- Use of membrane substrates in order to withstand high radiation doses, permit transmission and reduce substrate background signal.