Nanometer & sub-nm layer reference samples for X-ray fluorescence
New results and applications

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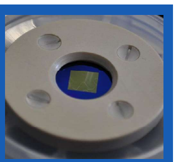
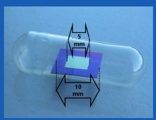
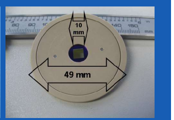
Thin film XRF reference samples

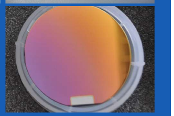


- Absorption free standard: no matrix correction necessary
- Thickness of 200 nm permits transmission measurements
- Background signal from substrate is low
- Mass depositions in the range of ng/mm² (few atomic layers) permit quantification without the need to interpolate from higher values
- Uncertainty ≤ 1 ng/mm² (1 atomic layer)
- Wide selection of non-overlapping XRF lines, exact calibration curve, many points over large energy range
- Signal strength easily adjustable by thickness, similar intensity for all elements
- High degree of uniformity & homogeneity (better than 1% for the full sample area)
- Application for adjustment of confocal µ-XRF is possible
- Wide range of available elements (standard and tailored compilations)

The reference samples are available in different designs: Frame sizes 5×5 mm² or 10×10 mm² with a 200 nm thin usable area of 2×2 mm² or 5×5 mm² in the center. For easier handling these can be glued to a PEEK holder of 3 mm thickness with an outer diameter of 30 mm or 49 mm. Other sizes are available on request. Further, the reference sample elements can be coated onto 2" diameter wafers or square wafer pieces (18×18 mm²).

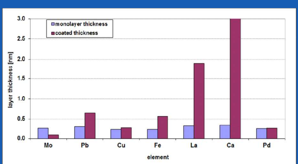






Clockwise from top: XRF reference samples on silicon nitride (Si_3N_4) membrane without holder, with optional PEEK sample holder and on Si wafer.

Mass deposition:
Mass deposition on the samples ranges from ~1 ng/mm² to ~120 ng/mm² for the elements listed in the table for standard mass version C_0 and high mass version C_{10}. The mass deposition values listed here are average values measured by AAS, ICP-OES and XRF. A data sheet with actual values is delivered with each individual reference sample. Despite the very precise measurements these reference samples are no "Certified Reference Materials (CRMs)".

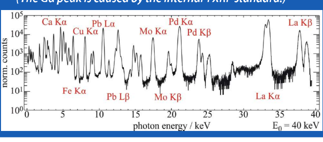


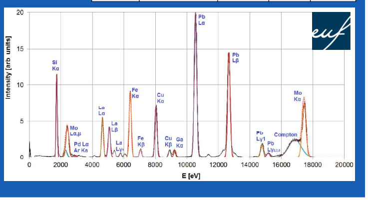
Samples contain 6 elements: Pb, La, Pd, Mo, Cu, and Fe, plus Si and N from the silicon nitride membrane. Further, there may be traces of C, Ar or other contents of ambient air that are not important for most XRF measurements. Different element coatings may be available on request.
** Ca is only included in sample series prior to RF17.*

Element	C_0 / C_{10} (ng/mm²)	Emission lines [eV]		
		Kα	Lα	Mα
Pb	7.6 / 84.9	74162	10541	2346
La	11.7 / 121.4	33298	4649	833
Pd	1.5 / 23.3	21123	2838	
Mo	0.8 / 8.6	17444	2293	
Cu	2.0 / 22.2	8040	930	
Fe	3.9 / 43.9	6401	747	
Si	Substrate	1740		

Energy spectra of thin film XRF reference samples at different labs
- RF7, synchrotron radiation, 40 keV (BAMline, BESSY Berlin)
- RF17, lab TXRF, Mo-K radiation, 50 kV (University of Flensburg)

(The Ga peak is caused by the internal TXRF standard.)



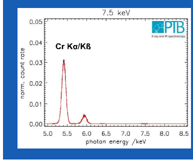


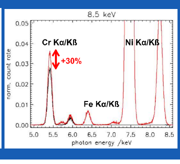
Substrate thickness

Secondary fluorescence occurs if the photon energy of radiation excited in one element in the sample is high enough to excite a different element. This can be very critical if the first element is present in a high concentration, for example as a (bulk) substrate. Example layer systems:

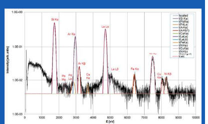
- 250 nm Cr on 10 µm mylar (PET, $C_{10}H_8O_4$, black curve)
- 250 nm Cr on 2 µm Ni (red curve)
- 7.5 keV and 8.5 keV excitation energy

Strong Ni K lines are visible for 8.5 keV and a Fe peak (probably contamination or from the set-up), plus a strong intensity increase of the Cr signal due to secondary excitation.

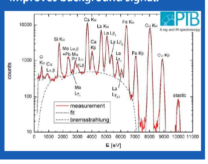




Element	Emission [keV]	Edge [keV]
Cr Kα/Kß	5.41 / 5.95	5.99
Fe Kα/Kß	6.40 / 7.06	7.11
Ni Kα/Kß	7.47 / 8.27	8.33

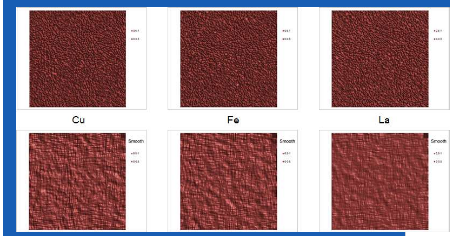


Top: RF3 on 675 µm Si, µ-focus Mo source + ASTIX-f optics (AXO lab)
Bottom: RF8 on 200 nm Si_3N_4, 10 keV (PTB beamline, BESSY Berlin)
► Thin substrate reduces Si signal & improves background signal.



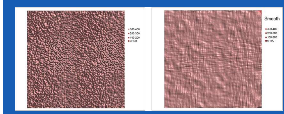
Lateral homogeneity

One multi-element thin film reference sample was scanned with a synchrotron nanobeam (diameter scaleable down to <100 nm) at P04 Variable Polarization XUV Beamline, DESY. The material distribution on the membrane does not show any islands; the lateral homogeneity is very good on a µm scale.



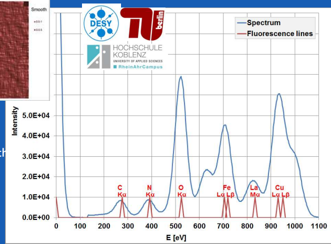
µ-XRF maps of 100×100 µm² areas, step size 1 µm (upper row) and 5 µm binning (lower row) of Cu, Fe and La, each normalized with zero signal.

Graphs based on measurements provided by Lars Lühl, TU Berlin, et al. recorded at P04, DESY, Hamburg.

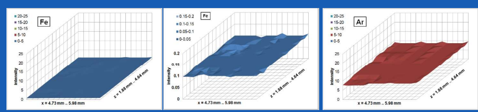


Zero signal of a 100×100 µm² area, step size 1 µm (left) and 5 µm binning (right).

Sum spectrum with fluorescence lines below excitation energy of 1 keV.



Large area mappings with ~40 µm beamsize show also macroscopic homogeneity.
µ-XRF maps recorded at a lab set-up at AXO DRESDEN show absolute intensity and normalized to Ar signal. Deviations are ~%.

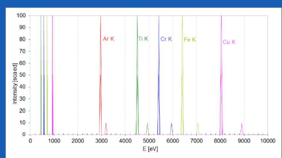


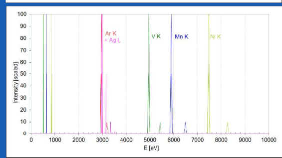
New series of reference samples

The commercially available AXO thin film multi-element XRF reference samples cover a wide energy range with 6-7 different reference elements. However, some energy regions do not feature any fluorescence lines in the present composition. Thus, new element collections should be evaluated and – if there is demand – made available.
If you are a (potential) user of thin film reference samples, please let us know what you need or what you may be interested in so we can consider it in the upcoming new series of reference samples. Right now, two new types, RG and RH, are evaluated.

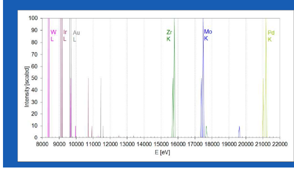
Suggestion RG uses Ti, V, Cr, Mn, Fe, Ni (atomic numbers Z = 22 ... 29) providing more lines in the region between 3 keV (Ar) and 8.0 keV. The L line emission of Ag can be useful, too, although Ag L is very close to the Ar K lines. As Kα and Kβ lines of neighboring elements overlap here, it makes sense to use elements with ΔZ ≥ 2. Suggested compositions are:
RG1:Ti, Cr, Fe, Cu RG2: Ag, V, Mn, Ni

Element	Atomic number	Emission lines [eV]			
		Kα	Kβ	Lα	Lβ
C	6	277			
N	7	392			
O	8	525			
Si	14	1740	1837		
Ar	18	2957	3190		
Ti	22	4510	4933	452	486
V	23	4950	5428	510	546
Cr	24	5412	5947	572	610
Mn	25	5897	6492	637	677
Fe	26	6401	7059	705	747
Ni	28	7474	8266	849	896
Cu	29	8040	8903	928	976
Ag	47	22103	25016	2982	3180





Version RH tries to cover the region between ~10 keV and ~20 keV with Kα,β and Lα,β lines in a better way. Suggestions are: Zr, Mo, Pd (K lines) plus W, Ir, Au (L lines).



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C	6	277				
N	7	392				
O	8	525				
Si	14	1740	1837			
Ar	18	2957	3190			
Zr	40	15746	17704	2044	2152	
Mo	42	17444	19652	2292	2420	
Pd	46	21122	23885	2837	3019	
W	74	58830	67534	8392	9724	1775
Ir	77	64304	73875	9167	10763	1980
Au	79	68135	78325	9704	11500	2123
Pb	82	74162	85335	10541	12675	2342