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# Supplementary Information to 'Reference-free X-ray fluorescence analysis using well-known polychromatic synchrotron radiation'

André Wählisch<sup>1</sup>, Malte Wansleben<sup>1,2</sup>, Rainer Unterumsberger<sup>1,2</sup>, Yves Kayser<sup>1,3</sup>, and Burkhard Beckhoff<sup>1</sup>

<sup>1</sup>Physikalisch-Technische Bundesanstalt, 10587 Berlin, Germany
<sup>2</sup>Present address: Helmut Fischer GmbH, Institut für Elektronik und Messtechnik, 12489 Berlin, Germany
<sup>3</sup>Present address: MPI für Chemische Energiekonversion, 45470 Mülheim an der Ruhr, Germany

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#### A. Purity of absorber

To verify the purity of the absorber material (Si), SRXRF measurements were conducted on individual parts of the absorber stack consisting of three wafer parts. A resulting spectrum is shown in figure A1. The spectrum is dominated by the Si K lines, as is expected. While minor signals from the sample holder (steel) are visible in the form of XRF radiation of Cr, Fe, and Ni, no signals of contaminations were detected. The information depth for Si is in the order of about 20 µm, lighter elements generally have less information depth and heavier elements generally more. Nevertheless, the information about the purity from this SRXRF analysis can be considered representative of the whole absorber material because of the very high homogeneity of the wafers. The photon energy of the monochromatic excitation radiation ( $E_0 = 9.7 \text{ keV}$ ) was enough to excite K radiation for elements up to and including Zn (Z = 30) and L radiation for elements up to and including Hf (Z = 72).



Figure A1: SRXRF spectrum of Si absorber based on monochromatic excitation ( $E_0 = 9.7 \text{ keV}$ ). Some stray light from the sample holder can be seen (Cr, Fe, Ni). The oxygen signal, which is below the limit of detection, is indicated for ease of reference.

### B. Lateral homogeneity of samples

The lateral homogeneity of both foils was analysed by means of laboratory-based  $\mu$ XRF. The results of the  $\mu$ XRF experiments were achieved with a commercial  $\mu$ XRF device (tube voltage 50 kV and current 1 mA) and are shown in figure A2. Here, both foils were placed on top of each other to reduce measurement time. The dwell time for each position was 25 s, while the step width in both lateral directions was about 30 µm, and the beam width was about 15 µm. Differences in the lateral homogeneity with this µm-resolution is in the range of a few percent over the whole measured area. All measurements presented in the main text were conducted in the centre of the samples.



Figure A2: Normalized  $\mu$ XRF maps for the determination of the lateral homogeneity of titanium and copper foils. Recorded with a commercial  $\mu$ XRF device.

## C. Contributions to the uncertainty budget

Contributions to the uncertainty budget of the titanium quantification based on (undispersed) polychromatic SR. These numbers were used to produce figure 6 of the main text.

Table A1: This table lists the relative standard uncertaint	ies of individual parameters involved in determining the mass thick-
ness based on equation 2 of the manuscript.	

Parameter	Rel. standard uncertainty / $10^{-2}$	Comments
effective solid angle of detection $\frac{\Omega}{4\pi}$	6	distance of detector to sample
incident photon flux after aperture $\Phi_0^{\text{Schwinger}}$	1	see [1] & aperture diameter
fluorescence intensity $\Phi_i$	1	deconvolution & counting statistics
thickness Be window $d_{\rm Be}$	10	estimated
density Be window $\rho_{\rm Be}$	0.6	estimated
mass attenuation coefficient Be window $\mu_{\text{Be},E}$	3	estimated
thickness Si absorber $d_{\rm Si}$	3	digital calliper
density Si absorber $\rho_{\rm Be}$	0.5	estimated
mass attenuation coefficient Si absorber $\mu_{\text{Si},E}$	3	estimated
fluorescence yield of Ti K	4	see [2]
transition probability of Ti K $\alpha_1$ , K $\alpha_2$	3	estimated based on $[3, 4]$
mass attenuation coefficient of Ti $\mu_{\text{Ti},E}$	3	unpublished PTB values
photoionization coefficient of Ti $\tau_{\text{Ti},E}$	5	estimated based on [5]
angle of incidence and angle of detection $\theta_{\rm in}$ , $\theta_{\rm out}$	negligible	motor resolution and alignment
SDD efficiency $\varepsilon_{\text{Ti-K}\alpha}$	negligible	efficiency is known, see [6]
absorber composition	negligible	confirmed by SRXRF

#### References

- R. Thornagel, R. Klein and G. Ulm. 'The electron storage ring BESSY II as a primary source standard from the visible to the X-ray'. In: *Metrologia* 38.5 (2001), pp. 385–389.
- [2] M. Kolbe and P. Hönicke. 'Fundamental parameters of Zr and Ti for a reliable quantitative X-ray fluorescence analysis'. In: X-Ray Spectrom. 44(4) (2015), pp. 217– 220.
- [3] G. Zschornack. Handbook of X-Ray Data. Springer, 2007.
- [4] V. W. Slivinsky and P. J. Ebert. 'Measurement of Relative K-Radiative Decay Rates'. In: Proceedings of the International Conference on Inner Shell Ionization Phenomena and Future Applications. Ed. by R. W. Fink, S. T. Manson, J. M. Palms and P. V. Rao. Vol. 1. 1972.
- [5] M. O. Krause, C. W. J. Nestor, C. J. J. Sparks and E. Ricci. 'X-ray fluorescence cross sections for K and L x rays of the elements'. In: *Technical Report ORNL-5399* (1978).
- [6] F. Scholze and M. Procop. 'Measurement of detection efficiency and response functions for an Si(Li) x-ray spectrometer in the range 0.1-5 keV'. In: X-Ray Spectrom. 30.2 (2001), pp. 69–76.