New Approaches to Determine K Line Ratios of Pure Elements

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For the quantification of X-ray spectra, the knowledge of the atomic fundamental parameters (FP) becomes increasingly important with the tendency to strive for standard-less quantification. Some of these FPs are impossible to assess with laboratory equipment and need to be determined at large facilities like synchrotron radiation sources. Other FPs, however, are seemingly addressable with laboratory equipment and table-top instrumentation. This is especially true for the fluorescence line ratios of pure elements, especially in energy-dispersive spectroscopy, where most of the sub-lines cannot be resolved anyways.

There is a multitude of publications for FPs in general and (K) fluorescence line ratios in particular [1,2,3]. Among these publications the database of Elam [4] stands out for its holistic character and is, hence, often used for FP-based XRF quantification. The values therein are extracted from other papers and missing values are extra- or interpolated based on polynomials.

Given the number of theoretical and experimental publications on the topic it is surprising by how much the database values which are nowadays used differ from each other. For Fe for example the $K\beta/K\alpha$ ratio can be found between 0.135 [2] to 0.143 [4] which accounts for 6 % relative deviation.

So even for common materials like the 3d transition metals the K line intensity ratios, which are only defined by the transition probabilities and absorption effects, show a surprising lack of accuracy where the preparation of pure element samples is simple and the line energies are in a range where the EDS quantum efficiency is well known.

In order to improve the quality of our FP based quantification, different approaches towards assessing the correct values for the line ratios were evaluated. Several X-ray analytical methods and numerical approaches were employed: Straight-forward energy dispersive EPMA and total reflection ED-XRF (TXRF) measurements were carried out, both feature only minimal or negligible self-absorption effects in the detection channel and should, hence, represent the correct line ratio. Complementary, micro-ED-XRF measurements were carried out with different primary beam filters. In this way, the effective depth for the production of X-rays could be varied and the self-absorption leads to XRF spectra with different $K\beta/K\alpha$ line ratios. The line intensities in the different EDS spectra were determined by peak fitting with different background models. These intensities in turn were used as input parameters for a fit which employed an FP-based full forward spectrum modelling and used the atomic line ratio as fit parameter.

As an example, acquired EDS spectra of iron were examined. It was found that $K\beta/K\alpha$ ratios derived from absorption-free TXRF spectra are well in line with the results obtained from absorption corrected micro-XRF measurements of bulk samples with and without filters, fig. 1.

The correct $K\beta/K\alpha$ ratio is important for 3d transition metals as the $K\beta$ line shows a large overlap with the $K\alpha$ line of the successive element. An overestimated $K\beta$ line therefore reduces the detection limit of

a smaller overlapping Kα. E.g. the detection limit of traces of V in Ti alloys is significantly improved with the new data of this work, fig. 2.

References:

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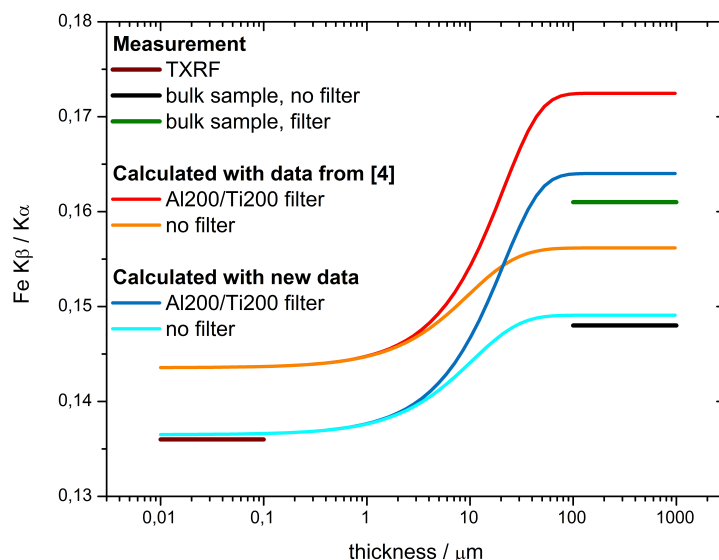[5] B. Möser, Cryst. Res. Technol. **20** (1985), p. 1503

Figure 1. Measured Fe Kβ/Kα line intensity ratios compared to forward calculated ratios based on reference database value [4] and this work.

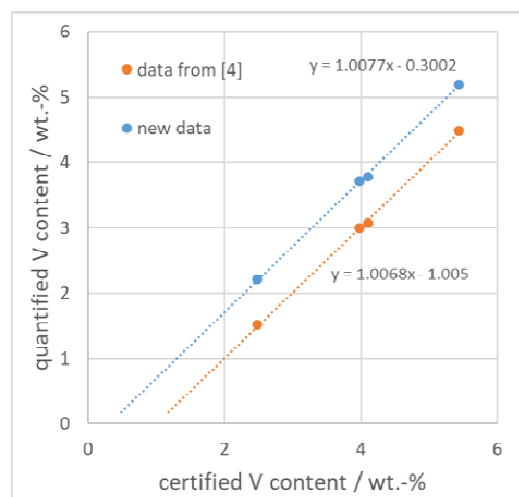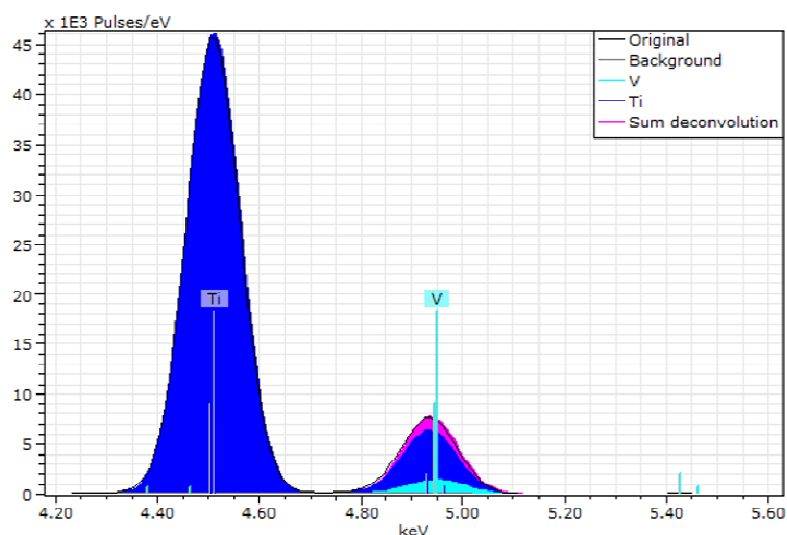**Figure 2.** Fitted Ti and V peaks (left) and how the Ti Kβ/Kα ratio affects the quantification of V in Ti V alloys (right).