

# Achieving 50 nm lateral-resolution quantitative EDX SEM

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**Abstract.** Low Voltage Scanning Electron Microscopy (LV-SEM) has become a very promising approach to perform Energy Dispersive X-ray (EDX) chemical mapping with high-lateral resolution [1]. Using voltages as low as 1.5keV, sub-10nm resolutions can be achieved. In this work, we try to take advantage of the small interaction volume in order to simplify the otherwise more complex SEM quantitative methodology. This way, phenomena such as absorption and fluorescence can be ignored and, effectively treat the quantification as with the Transmission Electron Microscopy (TEM)-based Cliff-Lorimer method. Experimental k-factors have been obtained from a series of standards and used to quantify complex oxide phases in steels.

## 1. Introduction

Scanning Electron Microscopy (SEM) quantitative X-ray microanalysis of bulk samples has been traditionally performed at 20 – 30 keV by integrating X-ray peaks intensities and comparing them to those of relevant standards. The role of the interaction volume at these high voltages is taking into account by correcting for atomic number, absorption and fluorescence (ZAF) effects. In order to simplify the calculation, the ratio of the extracted intensities to that of the standard is related to the ratio of the concentrations by using the ZAF or the  $\phi(\rho z)$  methods [2]. When using voltages below 5keV, the volume where electrons can produce characteristic X-lines will be smaller than 100 nm for most element of interest and, therefore, the ZAF corrections might be neglected, i.e. the SEM sample could be treated as a “thin” sample, and the X-ray quantification could be calculated with the Cliff-Lorimer approach. In this study, we will demonstrate that this is the case for surface oxides in stainless steels. Oxides are traditionally challenging to quantify by Energy Dispersive X-ray (EDX), but the right quantification calibration can make this a very easy-to-use and reliable method.

## 2. Materials and experimental method

We will use commercially available stoichiometric oxides and various metallic alloys which composition was validated by gas chromatography for the calculation of experimental k-factors. Their compositions are shown in Table 1. Then, we will use them to verify that the composition of in-service oxides is the same that was calculated by Transmission Electron Microscopy-Electron Energy Loss Spectroscopy (TEM-EELS) and/or Atom Probe Tomography (APT).

X-Ray spectra were collected with a Zeiss Merlin Field Emission Gun (FEG)-SEM equipped with an Oxford Instruments detector (X-Max 150mm<sup>2</sup>). Acquisitions were made at 1.5, 2, 3 and 5 keV; with an acquisition time of 30 s, the slowest processing time and a dispersion of 5eV/channel.



Peak area integration was performed via background and peak deconvolution, using NIST's DTSA-II software [3]. The k-factors were then calculated for each nominal composition with the Cliff-Lorimer equation [2] using K lines for O and L lines for Fe, Cr and Ni.

**Table 1.** Wt. % composition of standards and reference alloys.

|                                | Wt. %      |             |              |             |                |
|--------------------------------|------------|-------------|--------------|-------------|----------------|
|                                | O          | Fe          | Cr           | Ni          | Other Elements |
| FeO                            | 22.3 ± 0.5 | 77.7 ± 0.5  | -            | -           | -              |
| Fe <sub>2</sub> O <sub>3</sub> | 30.1 ± 0.5 | 69.9 ± 0.5  | -            | -           | -              |
| Fe <sub>3</sub> O <sub>4</sub> | 27.6 ± 0.5 | 72.4 ± 0.5  | -            | -           | -              |
| 304 SS                         | -          | 70.0 ± 0.5  | 18.3 ± 0.5   | 9.2 ± 0.5   | 2.5 ± 0.5      |
| Alloy 600                      | -          | 8.39 ± 0.05 | 16.07 ± 0.05 | 73.8 ± 0.05 | 1.74 ± 0.05    |

### 3. Results and discussion

#### 3.1. Interaction volume at low High Tension (HT)

One of the benefits of working at low HT (< 5kV) is the smaller interaction volume reached at these voltages. The interaction volumes at different HT were simulated for the three standard oxides and reference alloys using Casino software [4]. Figure 1 represents the lateral and depth dimensions from which 95% of the Fe L X-rays were generated for standards and references at each HT. It can be seen that the interaction volume and spatial resolution is dependent on the element composition and below 100 nm in most cases.

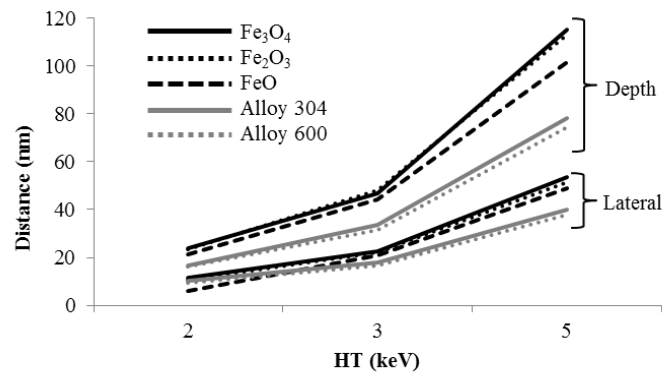


**Figure 1.** Achievable lateral and depth resolutions (95% of the X-ray emitted) for the oxide standards and reference alloys at different HT calculated from the simulations.

#### 3.2. k-factor determination

Experimental k-factors for Fe and O were calculated from oxide standards ( $k_{\text{Fe-O}}$ ) at 5, 3, 2 and 1.5 keV. For Fe, Ni and Cr, k-factors from reference alloys ( $k_{\text{Fe-Ni}}$ ,  $k_{\text{Fe-Cr}}$ ,  $k_{\text{Ni-Cr}}$ ) were calculated at 2 keV since this is the voltage used for the rest of the results presented in this paper (as shown in Table 2).

**Table 2.** Average experimental k-factors calculated from the standards and reference alloys.

| Volt. (kV) | Average k-factor (exp) |                    |                    |                    |
|------------|------------------------|--------------------|--------------------|--------------------|
|            | $k_{\text{O-Fe}}$      | $k_{\text{Fe-Ni}}$ | $k_{\text{Fe-Cr}}$ | $k_{\text{Ni-Cr}}$ |
| 5          | $0.88 \pm 0.03$        |                    |                    |                    |
| 3          | $0.86 \pm 0.01$        |                    |                    |                    |
| 2          | $0.83 \pm 0.06$        | $1.51 \pm 0.04$    | $0.90 \pm 0.04$    | $0.60 \pm 0.02$    |
| 1.5        | $0.74 \pm 0.07$        |                    |                    |                    |

The small relative error is promising for attempting the quantification of oxides and alloys. The lower 1.5kV value might indicate the voltage effect in the generation of Fe L counts.

### 3.3. Validating the simulations

Simulated spectra were generated with NIST-II software from all standards at a voltage range from 2 to 20 keV and k-factors extracted in a similar way. The software simulates the corresponding spectra from a given atomic composition (analytical simulation) modelling the atomic excitation process using a  $\phi(\rho z)$  curve, representing the efficiency of generation of atomic excitation as a function of the depth of penetration into the material.

The average k-factor values at every beam current for experimental and simulated data are represented in Figure 2, where a remarkable agreement is found. Their use would allow a shorter calibration routine.

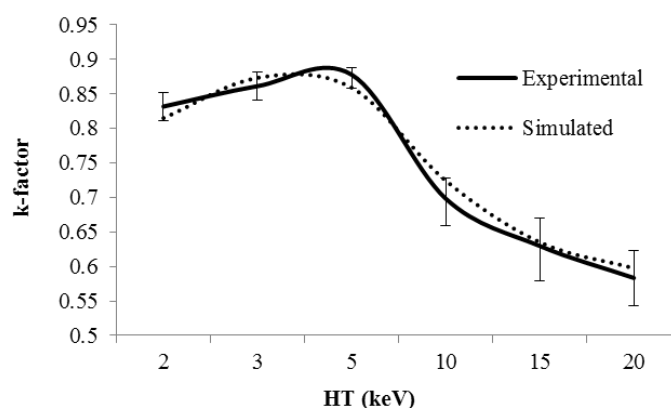


**Figure 2.** Experimental (solid line) and simulated (dotted line) average k-factors represented as a function of the HT.

### 3.4. Complex oxides quantification

Experimental k-factors were tested on two real oxides of “unknown” composition present in a 304SS alloy which was oxidized under simulated Pressurized Water Reactor (PWR) primary water conditions [5]. Figure 3a shows a cross-sectional area of 304SS alloy where spectrums 304SS\_OX1 (Figure 3b) and 304SS\_OX2 (Figure 3c) were collected from two different oxides next to the surface of the alloy. Both spectra show the C K line peak at 0.28 keV. Since this peak is only due to surface contamination, it has not been taken into account for the quantification. Also, a small Ni L peak at 0.85keV can be observed in the spectrum from region 304SS\_OX1 and has not been taken into account in the final quantification, since it is believed to come from the neighbouring Ni-rich metallic regions surrounding the Cr-rich oxide [5]. EDX spectra from the two “unknown” surface oxides were quantified using the experimental k-factors calculated above, as shown in Table 3.

**Table 3.** Experimental and “expected” composition of the two oxides present in the 304 SS alloy.

|           | Element | At. calculated% | At. expected % |
|-----------|---------|-----------------|----------------|
| 304SS_OX1 | O       | $58 \pm 1$      | $59.0 \pm 0.5$ |
|           | Cr      | $23 \pm 1$      | $21.0 \pm 0.7$ |
|           | Fe      | $19 \pm 1$      | $20.0 \pm 0.7$ |
|           | Element | Wt. calculated% | Wt. expected%  |
| 304SS_OX2 | Fe      | $77 \pm 1$      | $75.0 \pm 0.5$ |
|           | O       | $23 \pm 1$      | $25.0 \pm 0.5$ |

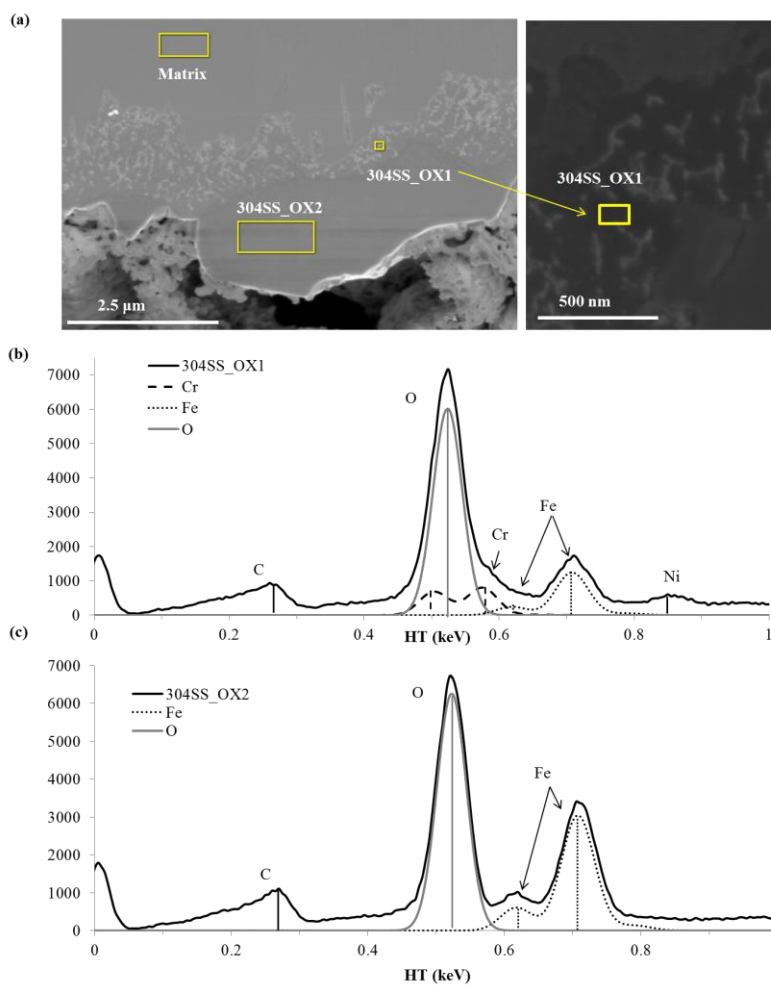


**Figure 3.** (a) Alloy 304SS SEM micrographs showing three areas where X-ray analysis was performed: matrix, oxide named 304SS\_OX1 and oxide named 304SS\_OX2. Experimental X-ray spectra (taken at 2 keV) and elemental deconvolution b) oxide 304SS\_OX1 and c) oxide 304SS\_OX2.

It can be said that the oxide of the spectrum 304SS\_OX1 matches well with a  $(\text{FeCr})_3\text{O}_4$  –type spinel– and spectrum 304SS\_OX2 with  $\text{Fe}_3\text{O}_4$ . In this regard, comparing calculated and nominal composition (also shown in Table 3) it is demonstrated the potential of this approach to quantify surface oxides with high-spatial resolution. It should be noted that oxides from the same samples, with the same morphology and microstructure have been characterized by TEM-EELS and APT in our group obtaining similar compositional results. The low-keV and its corresponding reduced interaction volume, allows the bulk samples to be treated as “thin” samples, in a similar way to TEM samples, which leads to the use of Cliff-Lorimer approach after careful experimental k-factor determination.

### 3.5. Surface contamination effect

Due to the relatively small interaction volume, surface contamination can become a limiting factor for a correct quantification/calibration. This effect will be higher at lower voltages and will result on different peak intensities ratios, i.e. different k-factor. In figure 4 it is represented the k-factor for the FeO as a function of the carbon thickness. It is clear that the k-factor is affected from C thickness thicker than 25 nm.

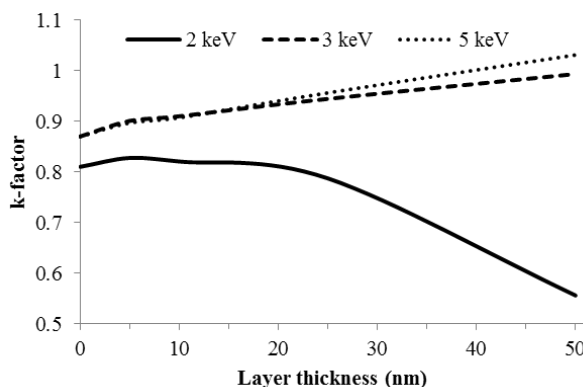


**Figure 4.** Simulated k-factors at 2, 3 and 5 keV represented as a function of C layer thickness.

In base of that, if the k-factor had been determined from a contaminated surface with a 50 nm thick C layer, the composition (wt.%) of the called 304SS\_OX2 would change to 83Fe17O instead of the 77Fe23O.

## 4. Conclusions

The feasibility of using the Cliff-Lorimer approach for the X-rays quantification of SEM samples at low beam currents has been studied and has led to the following conclusions:

- Analytical resolutions smaller than 50 nm can be achieved with SEM-EDX.
- k-factors can be effectively “simulated”, which simplifies the calibration procedure for alternative voltages.
- The small relative error in the experimental k-factors and the good compositional quantification match obtained when applied to “unknown” oxides make it a promising technique for the quantification of oxides and other low Z phases.
- Surface contamination can have an important effect on the k-factor determination (especially at  $HT < 3\text{keV}$ ) and should be minimized when possible.

## 5. References

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