# Quantitative spectrochemical Analysis of $Na_3AlF_6$, $ZrSiO_4$ and InSb with the Analytical Electron Microscope (TEM & SEM)

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## Quantitative spectrochemical Analysis of $Na_3AlF_6$, $ZrSiO_4$ and InSb with the Analytical Electron Microscope (TEM & SEM)

Eine Reihe zertifizierter natürlicher Mineralien und synthetisierter Zwei- und Mehrelementverbindungen, Kryolith ($Na_3AlF_6$), Zirkon ($ZrSiO_4$) und Indiumantimonid (InSb) [1] - teilweise in oxidischer Form vorliegend - wurde nach standardfreier Methodik mittels energiedispersiver Röntt-

1 Reference Standards for TEM, registered Stand. No. 5998, Science Services München

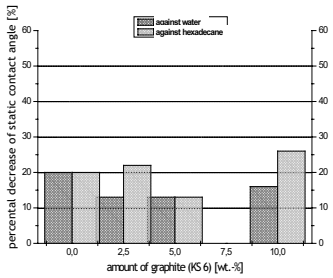


Fig. 10: Influence of the amount of graphite (KS 6) on wear resistance determined by decrease of static contact angles against water and hexadecane after 1000 cycles taber abrader test respectively – coating material: PMDA/ BAPPS with 10 wt.-% Fluorolink D and 40 wt.-% SiC – substrate material: stainless steel (1.4301) – coating technique: spray-coating – curing conditions: 2 h at 200°C

genspektrometrie (EdXS) sowohl im TEM als auch ergänzend bzw. vergleichend im SEM chemisch analysiert. Zur quantitativen Auswertung der Röntgenspektren wurden für die Analytik im TEM ein Dünnschichtmodell und für die Analytik im SEM die für dicke Proben übliche ZAF-Korrektur genutzt. Die analytischen Befunde werden bewertet, und es wird unter dem Aspekt der praxisbezogenen Anwendung auf die mit der TEM-Dünnschichtanalytik verbundenen Probleme hingewiesen.

**Introduction and methodical background**

X-ray spectrometric investigations of certified powder materials using TEM and SEM attached with EDXS are concerned with questions about the reliability of microanalytical results in connection with the morphologic structural information of electron microscopical imaging. The results are of importance with respect to the knowledge of structure property relations and take influence on conceptions and design of relevant problems and objetives in materials science.

Compared with the ZAF correction (Z – atomic number, A – absorption, F – fluorescence) in the SEM the analytical thin film model applied in the TEM generally yields wider distributed, i.e. less reliable results; thus, - if suitable for the problem and materials - SEM/EDXS should be prefered or additionally applied. This fact is associated with the morphological structures of the powder-like materials. They are prepared as TEM specimens and therefore deposited onto holey carbon films at Cu grids. A typical example demonstrating the morphological properties of the materials is given in Figure. 1: It was taken in the SEM by the secondary electron signal and the image shows widespread powder particles of irregular habitus having diameters up to 20 µm, average sizes are some µm. From this reason the applicability of the thin film approximation in the analytical TEM is affected, and the estimation of an absorption correction may be necessary.

In terms of analytical investigations in the TEM the properties of specimens (habit, size and shape of particle aggregations) and the micro-geometry (roughness, porosity, shadowing effects by adjacent phase constituents) of the X-ray excited specimen ranges can modify the generated X-radiation in such a way that lower energetic photons may suffer a relatively stronger absorpti-

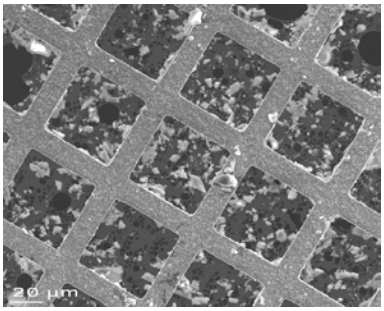


Fig. 1: Cryolyte ($Na_3AlF_6$), prepared at holey C film on Cu grid, SEM, 20 keV, SE

on on their way to the detector than higher energetic ones. Besides the influences of the geometrical parameters the chemical composition – on the one hand the presence of light elements together with heavier ones (esp. oxides) or otherwise only small Z differences of the material – plays an important role for the certainty of the quantitative analytical results. Finally, the available software package determines the quality of handling and evaluation of the original spectral data. From the co-operation of the discussed influences one can conclude: A general valid specification of the accuracy of the quantification preferably should be replaced by introduction of an error budget which is associated with the special analytic problem, i.e. the parameter of influence as discussed before.

**Experimental and Discussion of Results**

The software packages of standardless procedures for quantitative electron probe microanalysis apply the so-called *first principles calculations*. These account for all physical aspects of X-ray excitation and propagation in the material as well as the detection of X-ray photons by means of characteristic parameters of the spectrometer system.

The analytical measurements were carried-out with equipments and under working conditions as follows:

- TEM: CM200 FEG (Philips), ED X-ray spectrometer using thin materials quantification software (EDAX Genesis); time of analysis = 300 s (life time), primary energy = 200 keV.
- SEM: JSM-700F (JEOL), spectrometer with ZAF software package (EDAX Genesis); time of analysis = 300 s, primary energy = 20 keV.

The spectra accumulated in the SEM only show slight fluctuations. Thus, the acquisition of 3 to 5 spectra was sufficient to estimate reliable averages. Significant stronger local variations appear in the TEM. Therefore, up to 20 spectra were taken to recognizing and exclude partially strong deviations of the spectral structures caused by imponderable micro-geometrical influences on the X-ray excitation and propagation.

Into the thin film approach[2] to quantitative electron probe microanalysis a theoretical model for the calculation of ionization cross sections[3] was included. Generally, the model is very suitable; however, in presence

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of low-energetic spectral lines (esp. oxides) the thin film approximation often reveals very imperfect data. The results could be improved in a lot of cases by means of an empirical determined absorption correction (i.e. estimation of the thickness of analyzed ranges). Furthermore, a suitable method for analyses of oxides is given with the option *Oxygen by difference* which is offered in the set-up for quantification; this option excludes Oxygen from direct evaluation, and it is determined by normalization to 100%.

Selected results of quantification of identical specimens analyzed as well in the TEM as in the SEM are summarized in Tables 1 to 3.

Table 1 shows the data of a low Z material: Na Al Fluoride, which is a specimen prepared from natural mineralic powder (Cryolite). Using TEM/EDXS the application of an absorption correction results in good agreement with the data of SEM investigation; here, the minority constituents are not taken into account.

Results of the quantification of Zircon (nat. mineral, stoichiometric $ZrO_2$ + $SiO_2$) are shown in Table 2. The elemental concentrations from analysis in the SEM fit the mineral data as certified very well. This also is the case for the results of thin film analysis in the TEM if the *Oxygen by difference* option was applied. If the elements are quantified independently and additionally, an empirical absorption correction was introduced the light elements, Oxygen and Silicon, exhibit systematic differences with opposite signs. But, the results remain within acceptable limits of confidence. Finally, if stoichiometric oxides are suggested the resulting concentrations are in very good agreement with the certified data.

Due to the high primary voltage in the TEM the K-radiation of Zr ($EK_\alpha \approx 15.7$ keV) – not overlapped by neighboured spectral lines - can be used in the quantification procedure. This is not possible by working with the SEM; here, the lower energetic L series must be evaluated. Consequently, peak extraction (within the series) is required which may appear as a source of uncertainties of the quantification procedures. Such a case is demonstrated with the data in Table 3: The binary compound InSb ($Z_{In}$ = 49, $Z_{Sb}$ = 51) was analyzed in the SEM by means of L radiation and in the TEM using both, L and K radiations. In the SEM the results are in good agreement with the certification. This is also the case for TEM/EDXS if the high energetic K lines

| | Major Constit. | | | Minor Constit. | | |
|---|---|---|---|---|---|---|
| Spectr. Line | F K | Na K | Al K | Si K | Cl K | Ca K |
| Certif. Comp. | 54,3 | 32,85 | 12,85 | --- | --- | --- |
| **Weight % by Element, SEM** | | | | | | |
| Mean Value | 55,8±1,9 | 31,6±1,6 | 12,6±0,5 | --- | --- | --- |
| **Weight % by Element, Absorption t = 250 nm, TEM** | | | | | | |
| Mean Value | 55,0±5,7 | 28,6±3,4 | 15,8±4,6 | 0,4±0,4 | 0,1±0,1 | 0,1±0,1 |

Table 1: Cryolite, Na-Al-Fluoride, $Na_3AlF_6$

# A contribution to climate protection - Electrochromic windows fabricated with the sol-gel technology

Sabine Heusing

were analyzed. In difference to this, the evaluation of the L spectra results in a significant systematic error (> 10% relative). It may be explained with uncertainties in the computation of the ionization cross section at the high excitation energy.


## Summary

Comparative chemical analyses carried-out by standardless TEM/EDXS and SEM/EDXS analytical procedures have shown the resulting compositions of $Na_3AlF_6$, $ZrSiO_4$ and InSb agree within acceptable confidence ranges with certified data. The evaluations of selected materials consisting of lower and higher Z components reveal the analytical strategy using the TEM is – related to the SEM - much more sensitive against imponderable parameters of excitation and propagation of X-radiation in the specimen chamber. The micro-morphological structures of the materials can be verified in the SEM more precisely. Therefore, as far as it is possible from properties of the materials and methodical circumstances the analytical SEM should be accompany spectrometric analyses in the TEM. In comparison with SEM/EDXS an advantage of the TEM consists in the possibility to evaluate higher energetic X-radiation (> 20 keV). In this way the determination of the spectral intensities – as an important step of the quantification – becomes more certain because of the presence of energetic separated, non-overlapping spectral lines.


## A contribution to climate protection - Electrochromic windows fabricated with the sol-gel technology

### Electrochromic systems - Introduction

Electrochromic (EC) windows, also called "smart windows", change their optical properties (transmittance or reflection) in a reversible manner when a voltage is applied and a current flows through them [1, 2]. Large EC glazing are of considerable interest for architectural, automotive and aeroplane applications in order to control the solar radiation entrance to save energy costs for air conditioning in summer and for heating in winter (especially for buildings and automotives) and also to add comfort factors like privacy and to avoid glare and fading.

Further applications for EC systems are EC displays and self-dimming rear-view mirrors for

| Weight % by Element, SEM | | | |
|---|---|---|---|
| Spectr. Line | O K | Si K | Zr L |
| Mineral Data | 34,91 | 15,32 | 49,77 |
| Mean Value | 36,43±4,04 | 15,73±0,91 | 47,83±3,13 |
| **Weight % by Element, Oxygen by Difference, TEM** | | | |
| Spectr. Line | O K | Si K | Zr K |
| Mean Value | 34,9(1,0 | 15,2(1,7 | 49,9(2,6 |
| Weight % by Element, Absorption t>200nm, TEM | | | |
| Mean Value | 30,0(7,6 | 19,3(1,7 | 50,8(6,9 |
| Weight % by Oxide, SEM | | | |
| Component, Radiation | SiO2, Si K | ZrO2, Zr L | |
| Mineral Data | 32,78 | 67,22 | |
| Certificate | 33,57 | 65,93 (+1,27 HfO2) | |
| Mean Value | 34,31(0,05 | 65,69(0,05 | |
| Weight % by Oxides, TEM | | | |
| Component, Radiation | SiO2, Si K | ZrO2, Zr K | |
| Mean Value | 32,7(3,8 | 67,3(3,6 | |
| Remark: Hf has not been detected, neither with TEM- nor SEM-EDXS! | | | |

Table 2: Zircon, $ZrSiO_4$

| Weight % by Element, SEM | | |
|---|---|---|
| Spectral Line | InL | SbL |
| Certificate (synth. Compound) | 48,54 | 51,46 |
| Mean Value | 49,87± 0,30 | 50,13± 0,30 |
| **Weight % by Element, TEM** | | |
| Spectral Line | InK | SbK |
| Mean Value | 50,1±0,2 | 49,9(0,2 |
| **Weight % by Element, TEM** | | |
| Spectral Line | InL | SbL |
| Mean Value | 43,6±1,8 | 56,4±1,8 |

Table 3: Indium Antimonide, InSb