

STANDARDLESS ELECTRON PROBE MICROANALYSIS

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Abstract: A genuine standardless full quantitative software for the evaluation of energy dispersive X-ray spectra (EPMA) is presented here. P/B-ratios are used for quantification. The analysis of rough surfaces and particles causes no problems if the bremsstrahlung energy distribution is included in the evaluation. P/B results determined absolute and standardless are used to calculate the content of light elements. They serve as internal standards (hybride method). The spectrum so becomes a fingerprint of analysed specimen and the evaluation is not or only little influenced by the equipment used.

Zusammenfassung (German Abstract): Auf Basis der lokalen P/U-Verhältnisse wird eine echte standardfreie Software zur Auswertung energiedispersiv gemessener Röntgenspektren (ESMA) vorgestellt. Analysen rauer Oberflächen und von Partikeln sind durch Auswertung der energetischen Verteilung der Bremsstrahlung problemlos möglich. Die Bestimmung der Konzentrationen leichter Elemente erfolgt mit einer Hybridmethode, bei der absolut bestimmte standardfreie P/U-Ergebnisse als innerer Standard genutzt werden.

Introduction:

The requirements facing modern electron probe microanalysis are marked by the necessity of examining a range of very different materials, fragments, the types of dust, powders, and environmental samples of all kinds analytically. The specimens are often in their natural state (no embedding and polishing), and often standards of adequate composition and structure are not available. Rough and rugged specimen surfaces and particles defy conventional analysis using standards, as the differences in self-absorption of the characteristic X-rays between specimen and standard cannot be determined. Computing systems that do not require the analysis of standards, but use the same data internally fail as well.

The relation between concentration and net pulse-count is non-linear due to complex interelement effects. The energy dispersive spectrometer determines not only the characteristic radiation of all elements, but also the bremsstrahlung during acquisition. The bremsstrahlung, which was previously only regarded as a background to be corrected and only reducing the detection limits contains valuable analytical information in its energy-dependent distribution. It is now possible – under consideration of the measured bremsstrahlung - to calculate element concentrations, if the acquired spectrum, the primary electron energy and the type of the detector are known. Even the electron energy can be determined from the bremsstrahlung spectrum. The analytical problems described above can only be solved on a routine basis by using such a "genuine" standardless method.

With this X-ray spectrum in EPMA turns into a unique fingerprint of the analyzed specimen volume that is nearly independent of the analytical instrumentation used.

Model system:

Under consideration of the number of ionizations of the respective electron shell, the fluorescence yield (X-ray yield) and the relative emission rate, one obtains the number of primarily produced characteristic X-ray quanta per incident electron. The X-rays attenuated before leaving the sample – or sometimes even amplified through secondary fluorescence excitation - and registered in the detector under a detector-geometry dependent solid angle. The pulse count measured is proportional to the product of electron current and acquisition

time (corresponds to the number of incident electrons). Considering this, as well as the above mentioned issues, leads to the basic equation of quantitative EPMA for the registration of characteristic radiation emitted by thick specimens:

$$N_i^{ch} = \frac{d\Omega}{4\pi} i_0 t \omega_i \varepsilon_i q_i c_i [S R A (1+F_C+F_B)]_i^{ch} \quad (1)$$

$d\Omega/4\pi$ - solid angle covered by the detector, $i_0 t$ - number of incident electrons, ε_i - detector efficiency for X-rays of the characteristic energy of the respective element i , ω_i - fluorescence yield, q_i - relative emission rate, $c_i S_i R_i$ - primarily generated number of vacancies in the respective shell, c_i - concentration of the element i in % mass fraction, S_i - S-factor (number of the primary ionizations of the respective electron shell), R_i - backscattered electron correction, A_i - absorption correction, F_{C_i} - fluorescence caused by high-energy characteristic radiation, F_{B_i} - fluorescence caused by bremsstrahlung

The correction factors are actually complicated equations that also contain the desired concentrations. A direct dissolution of the set of equations (1) to obtain the c_i is generally impossible, so that an iterative solution is required.

The number of bremsstrahlung quanta measured in a given energy interval (e.g. channel width) at a specific energy can be expressed through the following relationship under consideration of an analog correction model to (1) (similar to the characteristic radiation):

$$N_i^{br} = \frac{d\Omega}{4\pi} i_0 t \varepsilon_i [S R A]_i^{br} \quad (2)$$

It is striking that the energy of the considered element does not appear explicitly. This fact is understandable, if one takes into account that the bremsstrahlung generation is not an element-characteristic excitation, but an effect of the matrix as a whole.

When dividing equation (1) by equation (2), one receives the number of the characteristic X-ray quanta with relation to the number of bremsstrahlung X-ray quanta of the same energy, the so-called P/B-ratio. The number of the characteristic radiation quanta can be determined by the sum of all counts in a peak. The bremsstrahlung is measured over a specific interval ΔE . This method was first proposed by WENDT /1/, SMALL /2/ und STATHAM/3/.

$$(P/B)_i = \frac{N_i^{ch}}{N_i^{br}} = c_i \omega_i q_i \frac{[S R A (1+F_C+F_B)]_i^{ch}}{[S R A]_i^{br}} \quad (3)$$

(3) shows quite clear that the P/B ratio is no longer dependent on the arc angle, the detector efficiency and the number of the electrons shot at the target. After the P/B-ratios have been determined for all characteristic lines within the spectrum, all parameters in (3) – except the desired concentration itself – are known or can be calculated, respectively. Checking of the result quality can be done easily by critical assessment of the sum of all element concentrations. Errors in the determination of a single element can only affect results of the other elements through error propagation in case of very high atomic number differences.

Forced normalization blurs subjective and objective errors during element identification and the subsequent quantitative processing and evaluation of spectra.

If one takes the normalization relation into account, equation (3) is redundant. This means, one element can be determined by difference to 100%. This variant is possible, as the P/B-ZAF-correction (PUzaf) uses the bremsstrahlung as additional analytical information. Previously, analysis per difference could only be done with conventional ZAF-correction using element standards.

This model system requires only comparatively moderate efforts to the theoretical description of the excitation and absorption conditions within the sample. The absorption conditions for characteristic radiation and bremsstrahlung of same energy are similar or even identical in the specimen as well as the detector X-ray entrance window. A complex computation of the mass attenuation coefficients is therefore not necessary. The relations of the correction factors differ only slightly from 1, so that a fast and certain convergence of the iterative solution of the equation system ensues.

All element concentrations are determined absolutely, as the normalization equation $\sum c_i = 1$ does not have to be included in the formalism. This permits its use as an "internal standard", e.g. to evaluate the content of light elements, which cannot be determined standardless and quantitative with the P/B-method. Below an energy of around 1 keV the peak to background (bremsstrahlung) ratio (P/B) is no longer useful quantity for direct measurement. The absolutely determined concentration of elements with an atomic number $Z < 11$ are used as "internal standard" to calculate the concentrations of light elements (e.g. C and O). The net counts of the "internal standard" N_{st}^{ch} and the already absolutely determined concentration of the selected element c_{st} are brought into relation with the net counts of the light elements. The consideration of the differences in excitation and the sometimes extremely high absorption is done through a correction calculation (called ZAF):

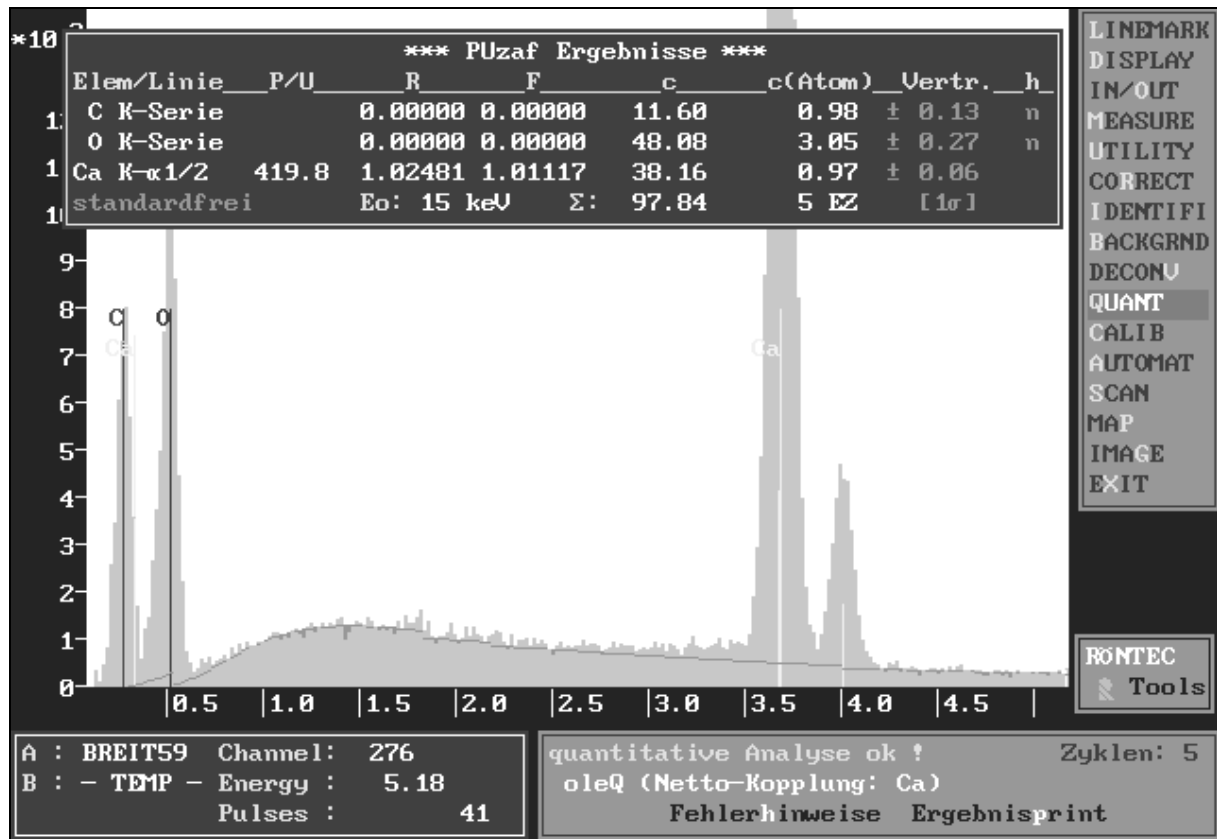
$$c_i = c_{st} \frac{N_i^{ch}}{N_{st}^{ch}} \frac{(ZAF)_{st}^{ch}}{(ZAF)_i^{ch}} \quad i \text{ over all elements with } Z < 11 \quad (4)$$

The evaluation strategy is varied in accordance with the specimen composition (oleQ, optimized light element quantification). If no suitable element is available for the as an "internal standard", the light elements are determined per difference. The specific fractions are calculated through the net pulse counts under consideration of excitation and absorption:

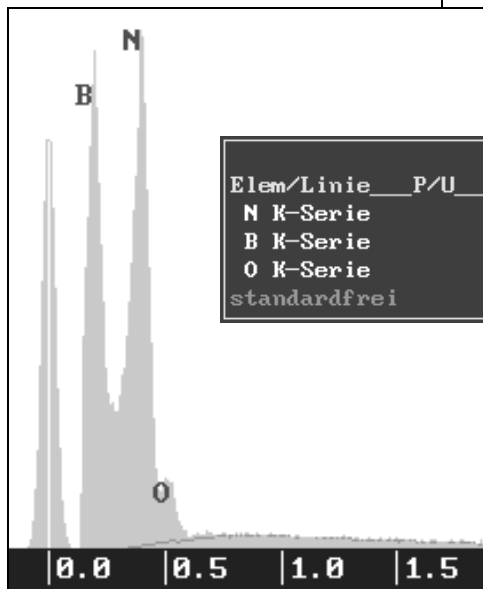
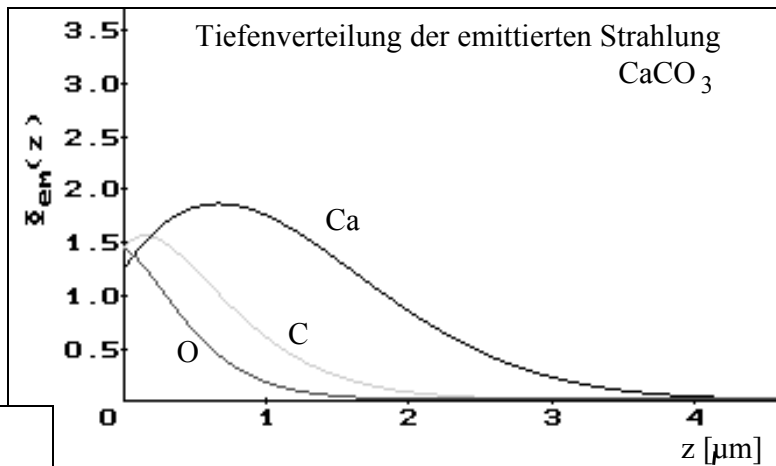
$$c_i = \frac{N_i^{ch}}{i_0 t \omega_i \epsilon_i q_i (ZAF)_i^{ch}} \quad (5)$$

$$\sum c_i = 1 - \sum c_j \quad j \text{ über alle Elemente mit } Z \geq 11$$

Examples for Standardless Spectra Evaluation:



A correct standardless calculation of the element contents of CaCO₃ can be performed in spite of abnormal absorption conditions (O-Kα is attenuated more than the less energetic C-Kα due to the Ca-L absorption edge). The Ca K-radiation was used as "internal standard".

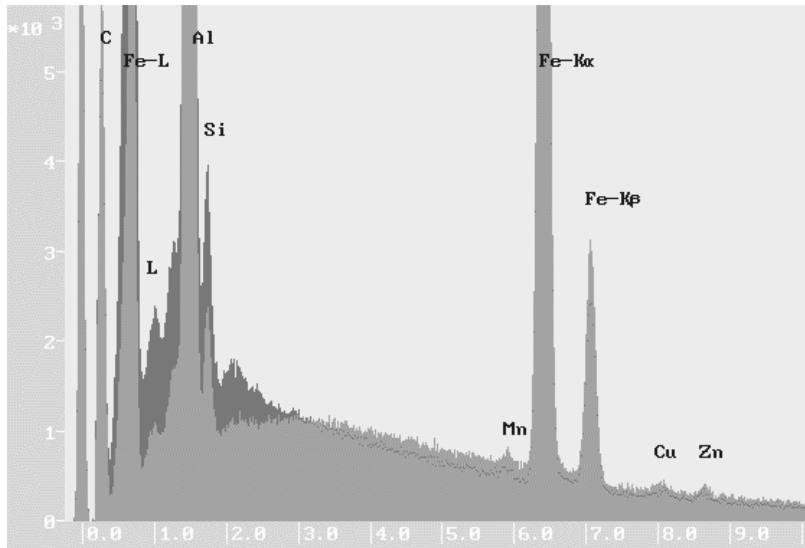


*** PUzaf Ergebnisse ***

Elem/Linie	P/U	R	F	c	c(Atom)	Vertr.	h
N K-Serie		0.00000	0.00000	56.70	1.02 ± 0.15	d	
B K-Serie		0.00000	0.00000	38.64	0.90 ± 0.14	d	
0 K-Serie		0.00000	0.00000	4.66	0.07 ± 0.01	d	
standardfrei		Eo: 5 keV	Σ: 100.00	2 EZ	[1σ]		

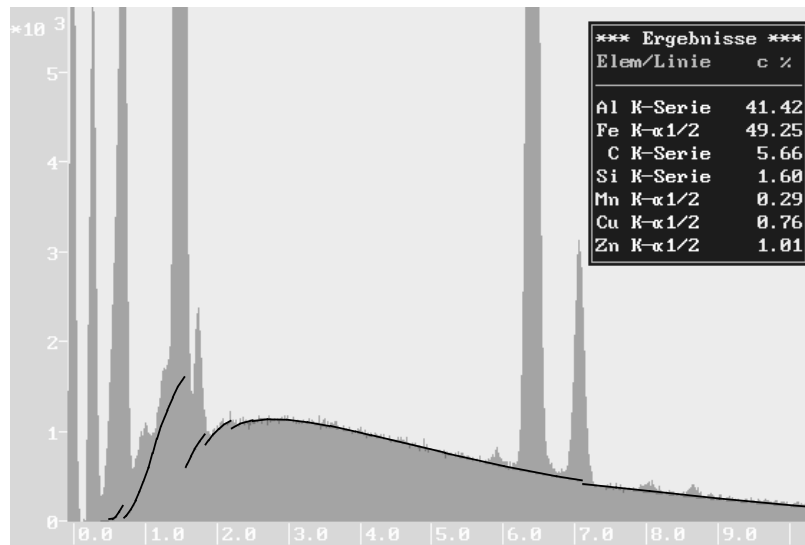
The boron nitrite spectrum was recorded using a primary electron energy of 5 keV. The determination of the element contents of B, N and O took place per difference. As no element could be identified with $Z \geq 11$, the difference is to 100%.

Rough Surfaces:

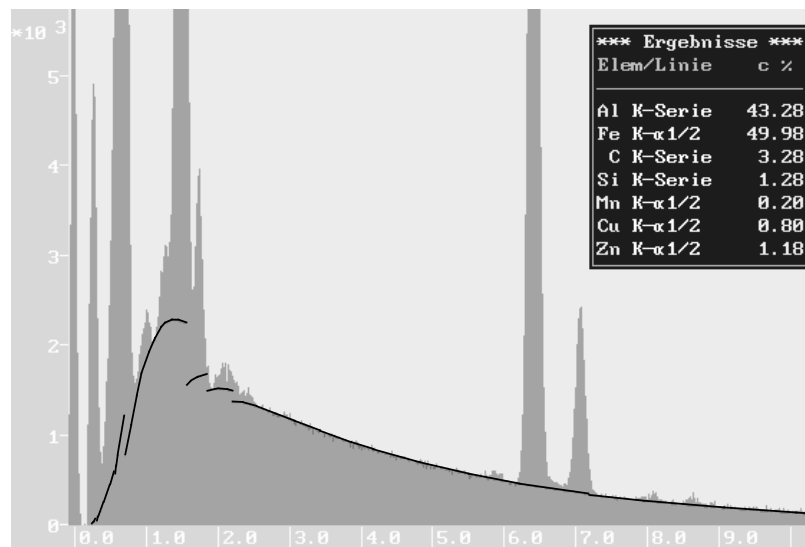


*Spectrum of an inclined surface (approx. 20° tilt angle)
dark: tilted towards the detector
light: tilted away from the detector*

The difference in absorption changes the spectrum dramatically. The net count relation Al/Fe is 4.5 (dark) and 2.3 (light)



The automatic tilt angle optimization has determined an optimum fit of -16° for the bremsstrahlung calculation. Quantitative results are displayed.



The tilt angle optimization for the experimental determination of self-absorption conditions in the specimen resulted in +14°.

Even after simple addition of both spectra, an automatically calculated tilt angle of -2° with an analysis result that is identical within the error limits results.

Prerequisite for a standardless software is - apart from a spectra correction (escape effect /4 /, shelf and tail effect /5/) - a flexible model for the computation of the bremsstrahlung background calculation /6/. After computation of the bremsstrahlung background the determination of the N_i^{ch} is done through simple channel summation or application of an appropriate peak deconvolution /4, 7/. The N_i^{br} are the bremsstrahlung values of a channel of 20 eV width below the characteristic radiation, which are interpolated through use of the fitting regions within the bremsstrahlung spectrum.

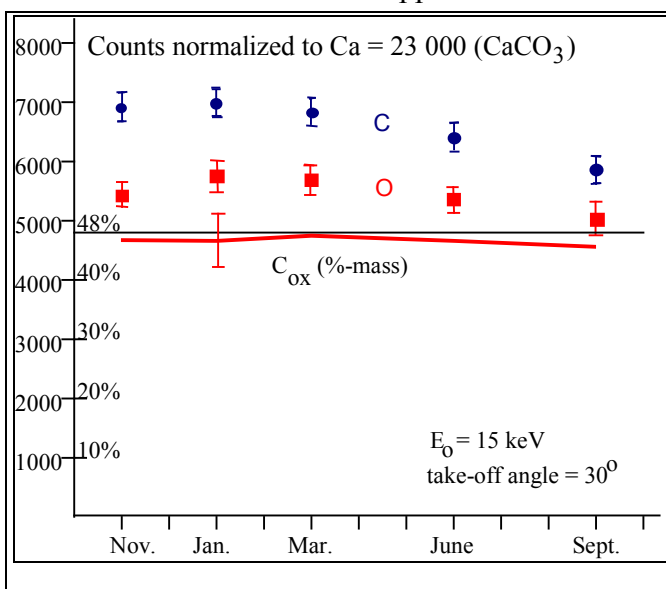
The quality of the bremsstrahlung modelling can be determined by comparison to the acquired spectrum. Deviations in the primary electron energy as well as in absorption are immediately visible. An optimization of the absorption correction during calculation of the bremsstrahlung (optimization of the effective tilt angle) may also take place automatically. The bremsstrahlung spectrum so provides analytical information about absorption, which is included in the Puzaf-correction.

The experimental advantages of an P/B-analysis are:

- little dependence on all experiment parameters
- little dependence on the structure of the specimen and its surface
- high accuracy of the standardless quantitative analysis results (absolute values)

Spectrometer:

Prerequisite for a standardless analysis is the stability of the detector efficiency curve. If this is not the case absorptions occurs, which can no longer be calculated. A UHV-dewar Si(Li)-detector by RÖNTEC was used. The high thermal isolation and the quality of the vacuum in the detection system warrant a stable transmission, as contamination of the window, or even the detector itself does not happen.



The measurements over a period of approximately one year show very high window stability. The increasing drop of C is also due to loss of the specimen's C-coating.

In all cases the standardless quantitative evaluation resulted in $CaCO_3$. Included in the graph is the unnormalized result for oxygen in %-mass-fraction.

- References:**
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 - /7/ EGGERT, F; Transact.12.Intern.Congr.on X-Ray Optics and Microanal., Cracow(1989)71



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