

EDS User School

Quantification of EDS spectra

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Spectral Solutions AB



Overview

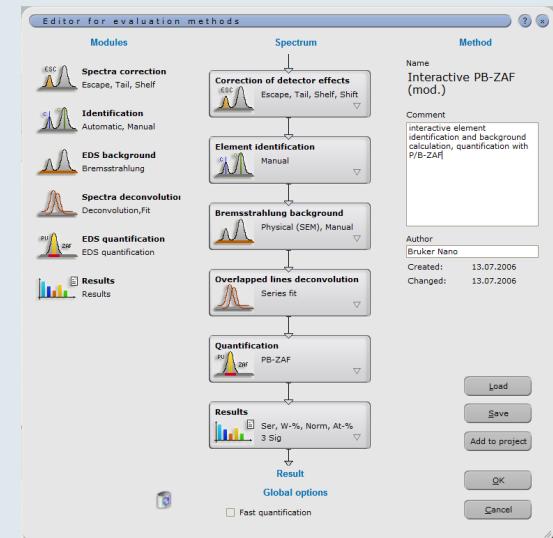
I.) Quantification step by step (= review „method editor“):

- 1.) Identification
- 2.) Background fit
- 3.) Deconvolution models (Bayes vs. FIT)
- 4.) Quantification (standardless vs. standard-based)

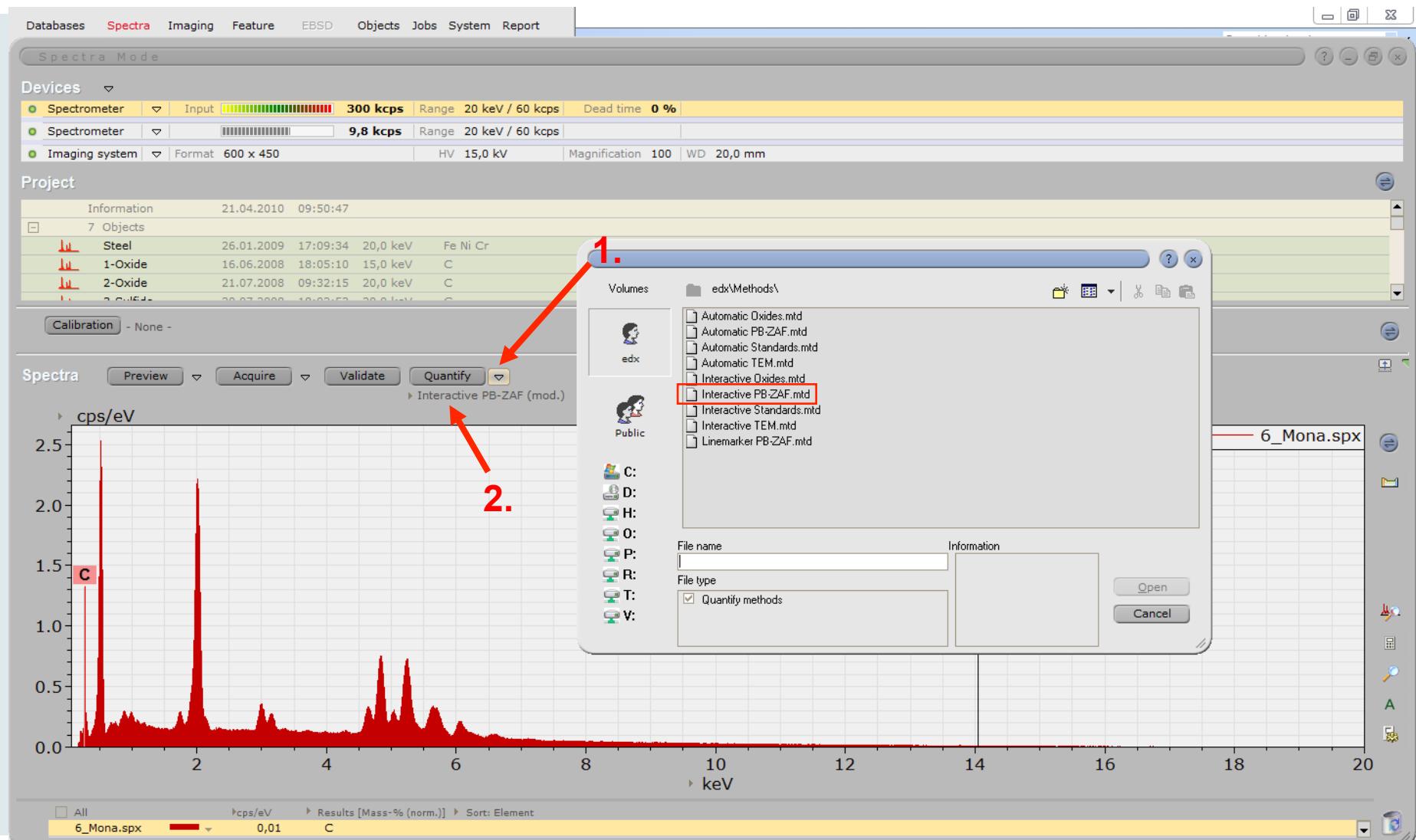
II.) Correction methods:

- ZAF
- PhiRhoZ

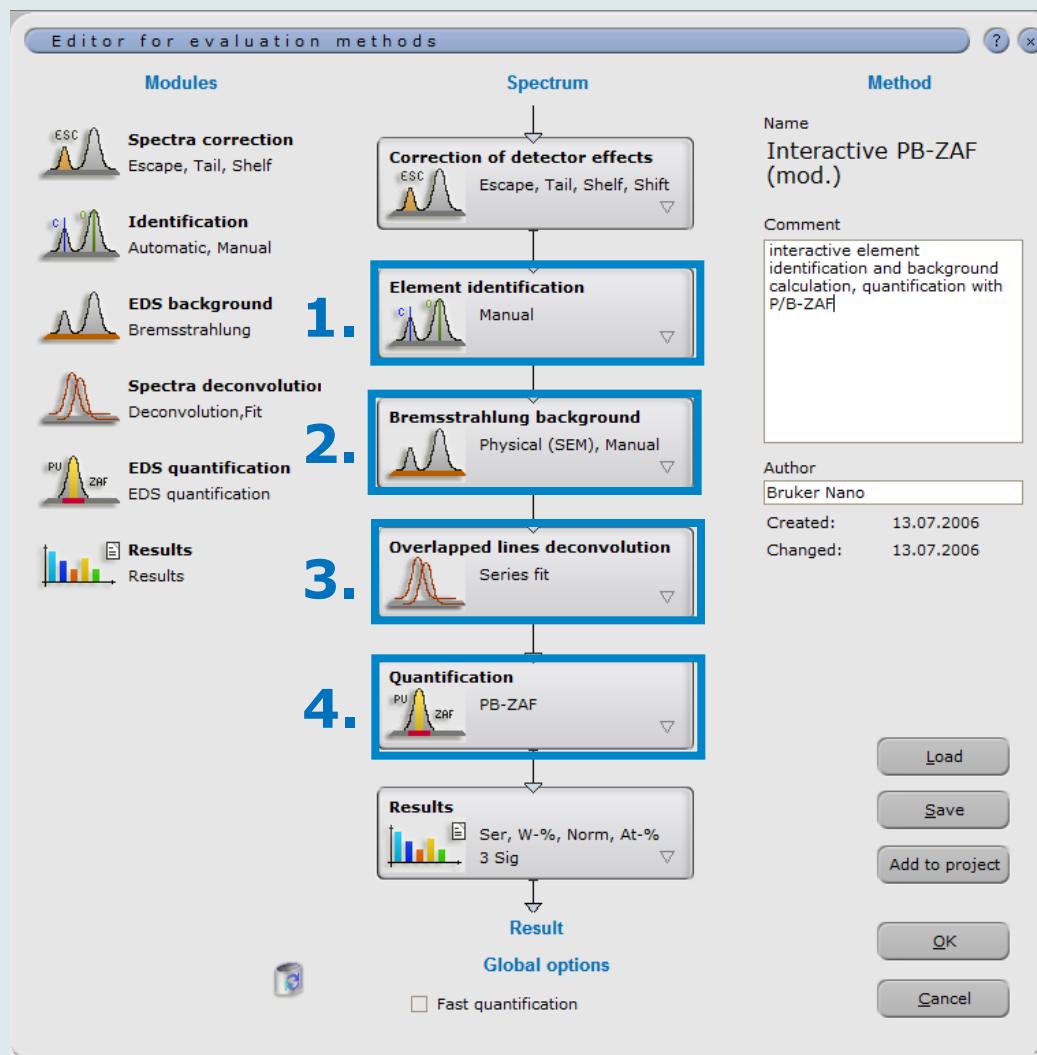
III.) Solid samples – rough surfaces



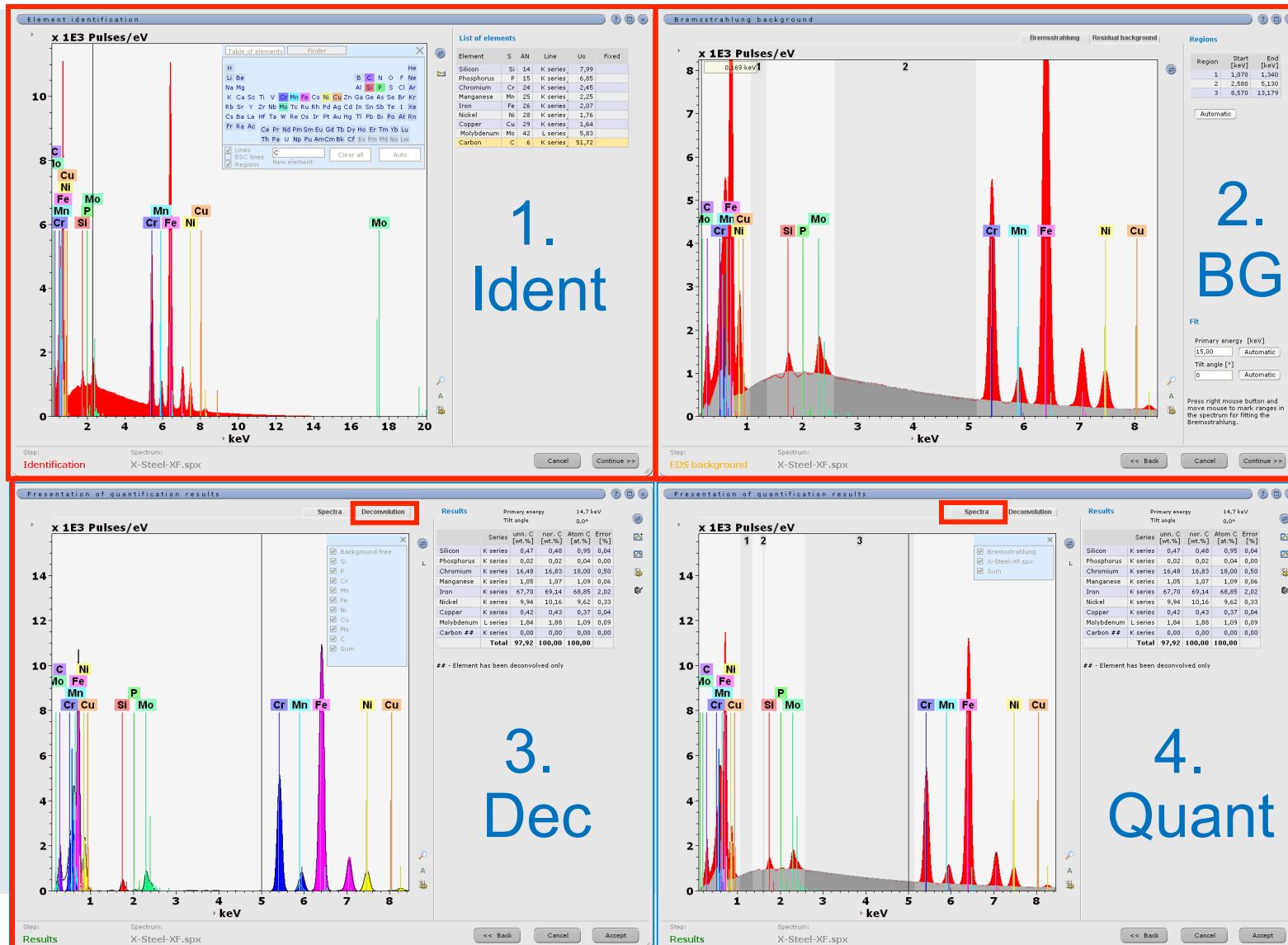
I.) Quantification – step by step:



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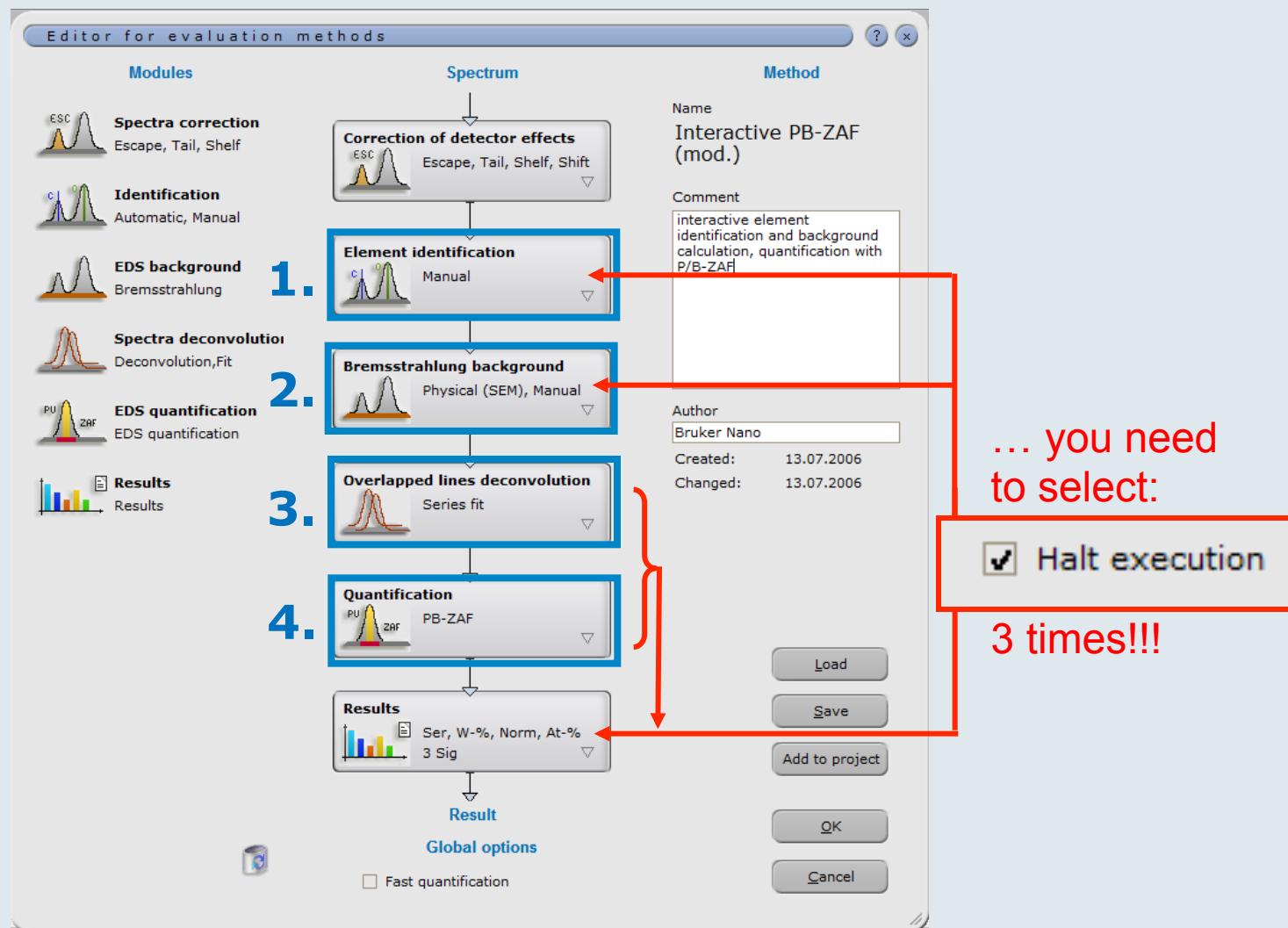
I.) Quantification – step by step:



If you want
all 3 windows
to pop up ...

Bruker Nano

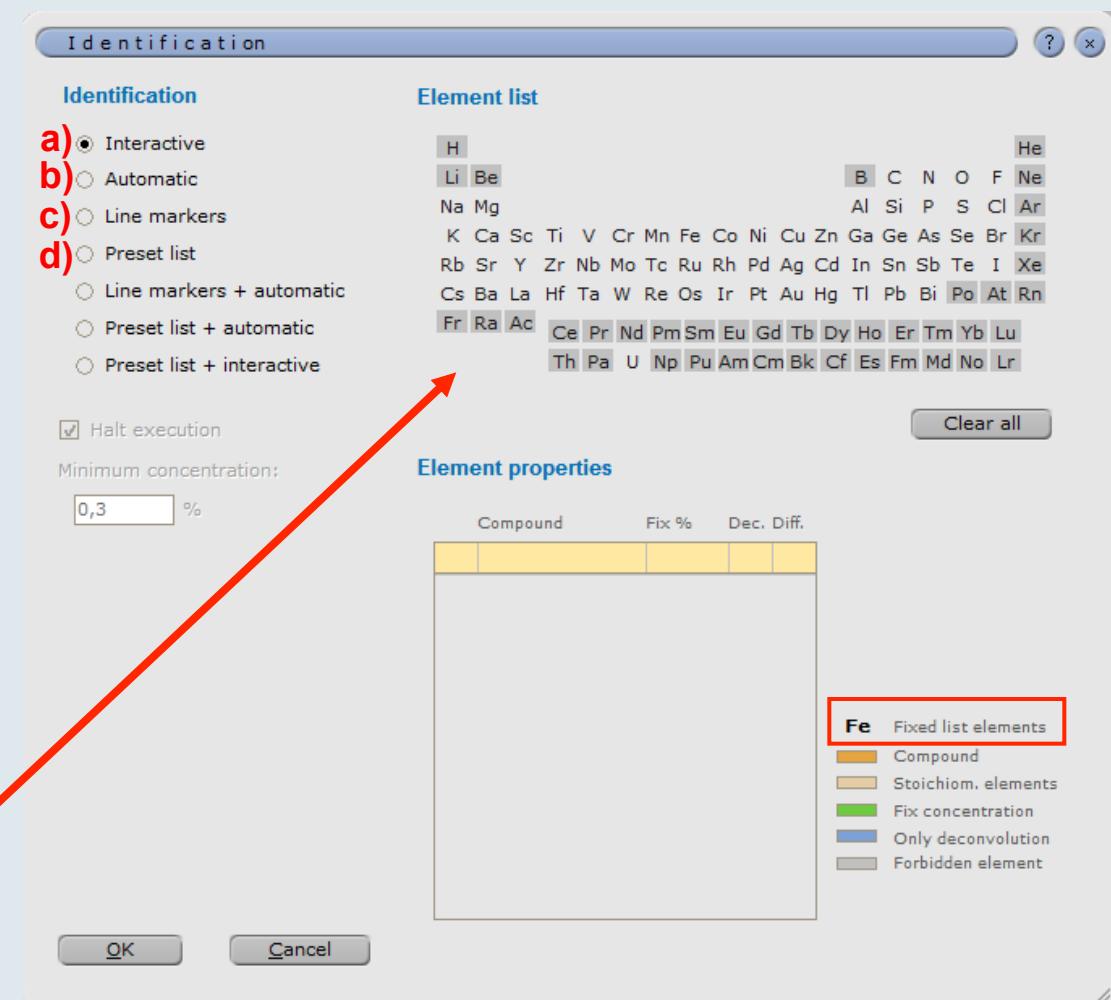
I.) Quantification – step by step:



I.) Quantification of EDS spectra:

1. Identification

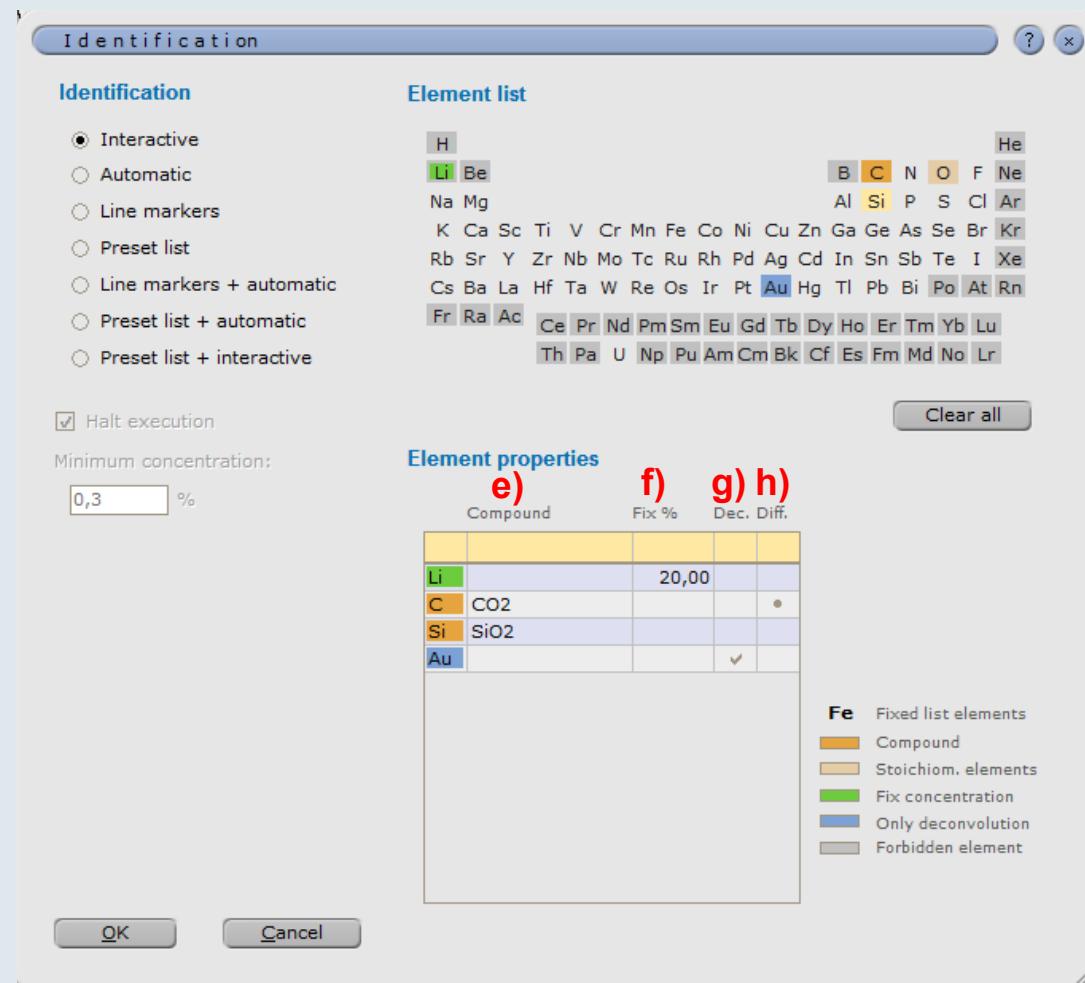
- a) you want to identify the elements („Ident“ window pops up)
- b) elements are identified via Auto-ID („Ident“ window does not pop up)
- c) you want the software to use the line markers that you have already set (via periodic table  while (or after) the spectrum was acquired)
- d) you want to pre-select specific elements – click on those elements in the periodic table until they are bold = fixed list elements



I.) Quantification of EDS spectra:

1. Identification

- e) you want to quantify one or more elements as oxides [enter compound(s) in this column and press „enter“]
- f) you know the concentration of a certain element (in wt%)
- g) you want to include a certain element for deconvolution, but not for quantification (e.g., Au or C coating)
- h) you want to quantify an element (or compound) by difference to 100 wt%



Overview

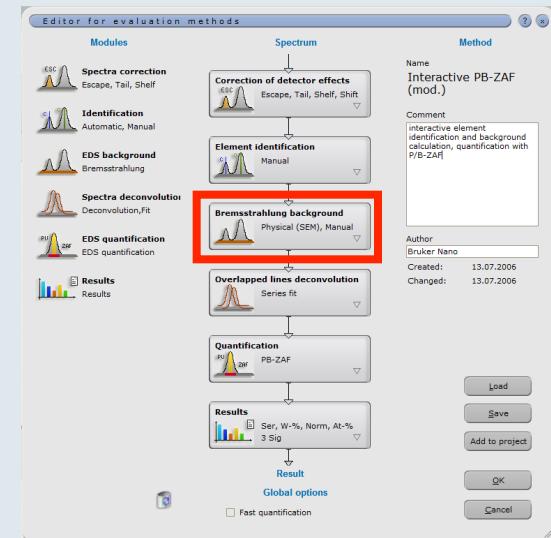
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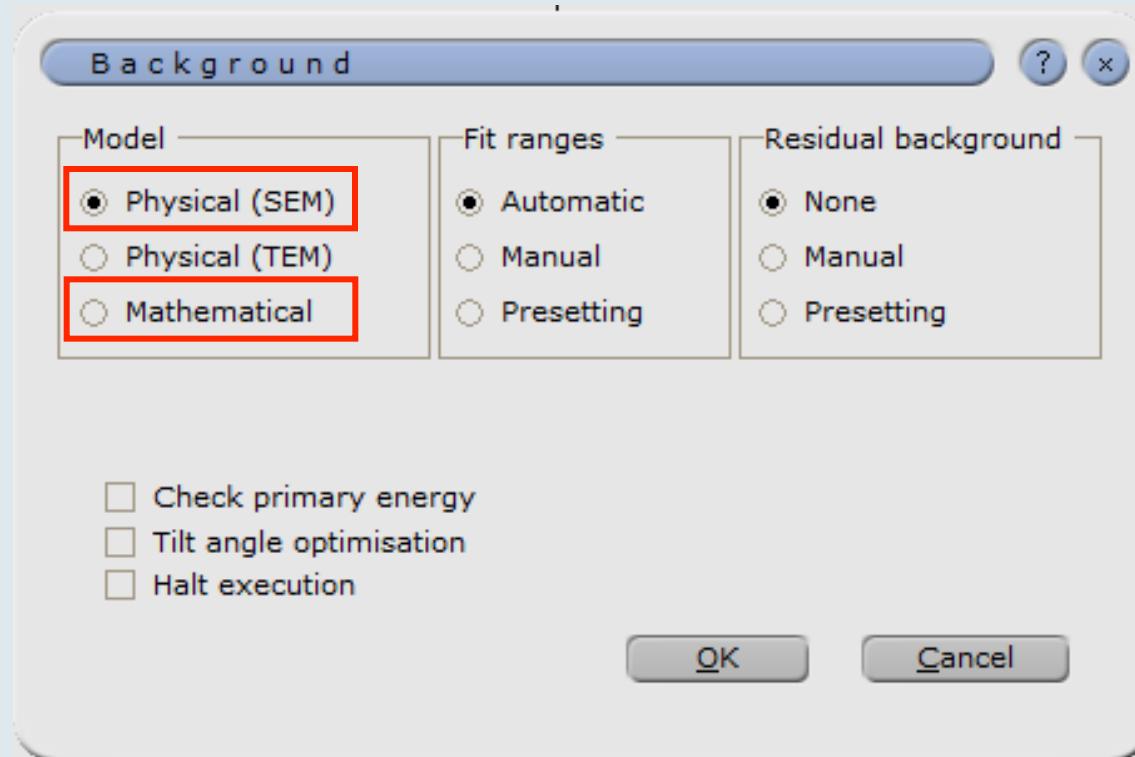
- ZAF
- PhiRhoZ

III.) Solid samples – rough surfaces



I. Quantification of EDS spectra:

2. Background fit



Overview

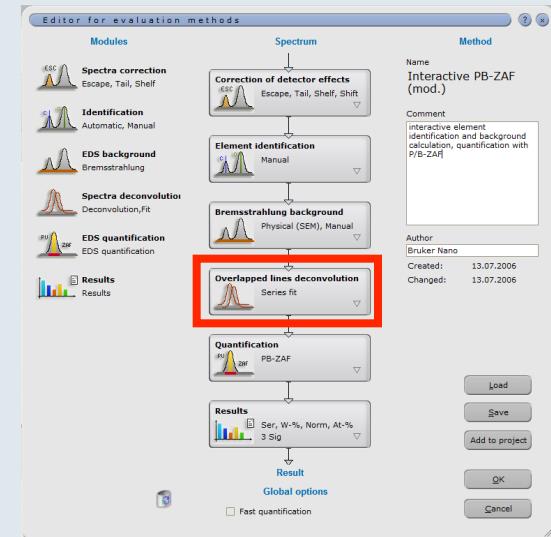
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- P/B ZAF
- PhiRhoZ

III.) Solid samples – rough surfaces

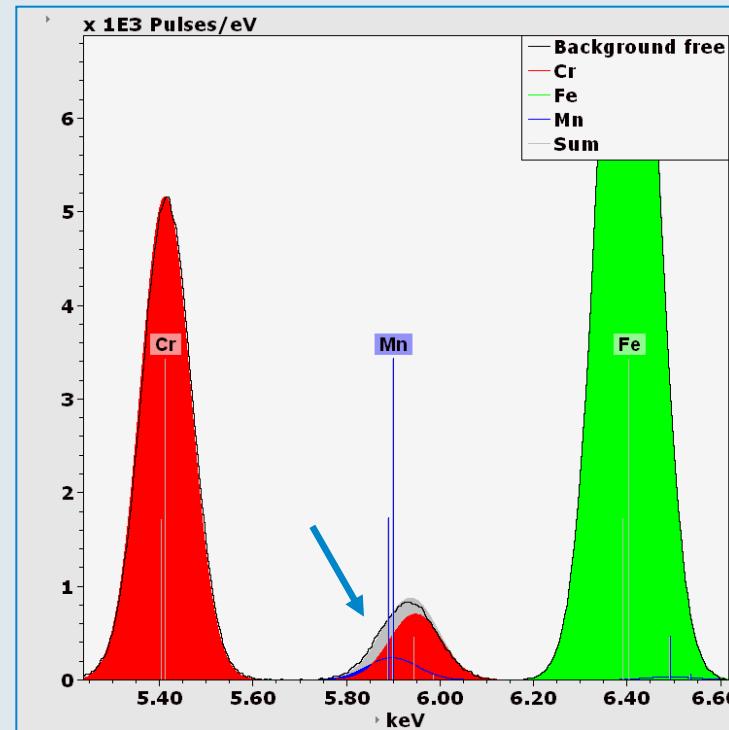
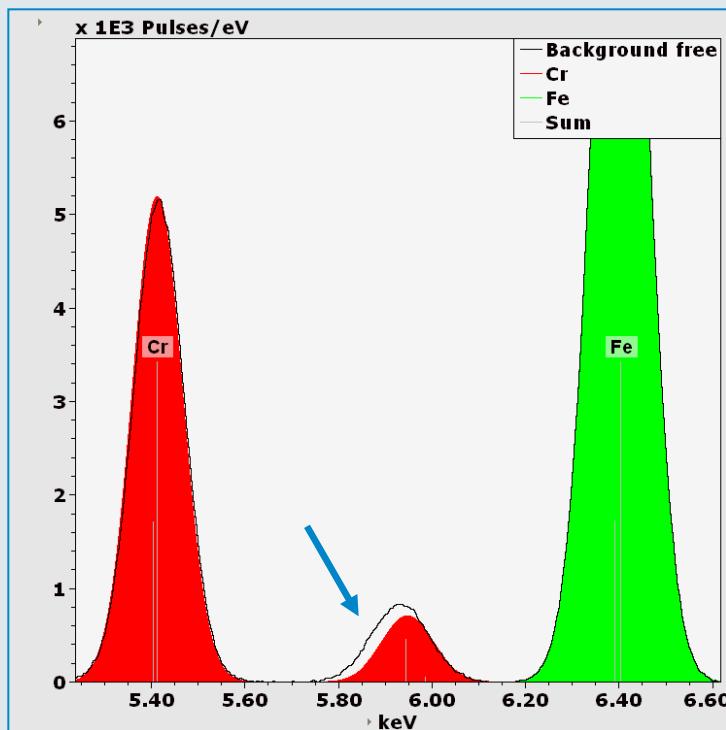


I. Quantification of EDS spectra:

3. Deconvolution

What does deconvolution mean?

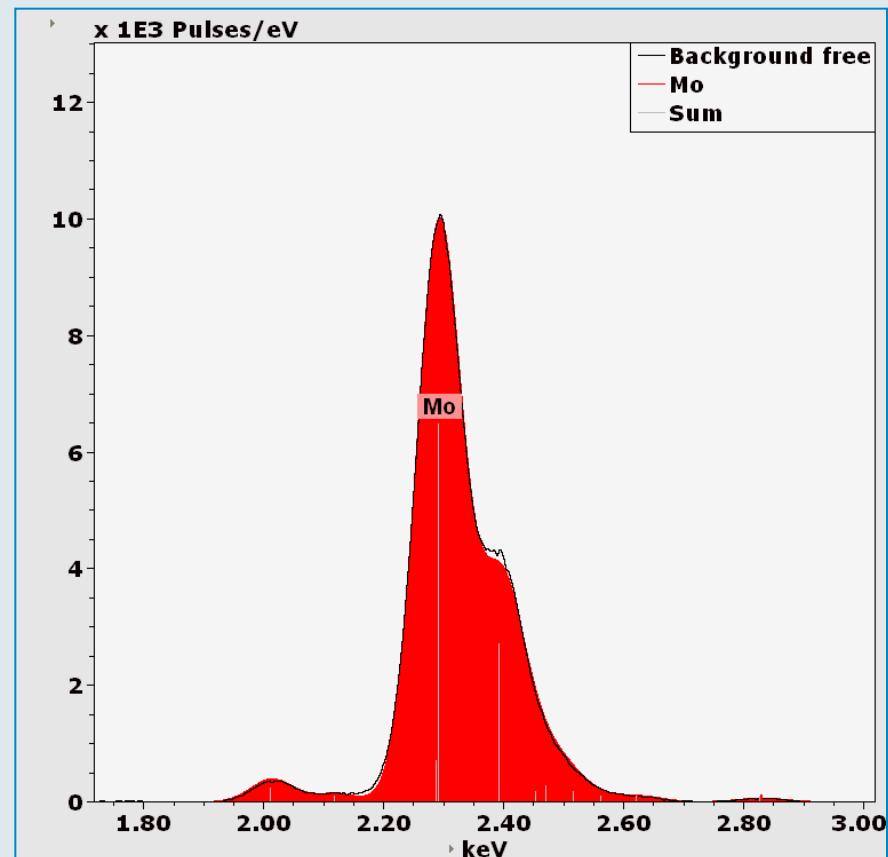
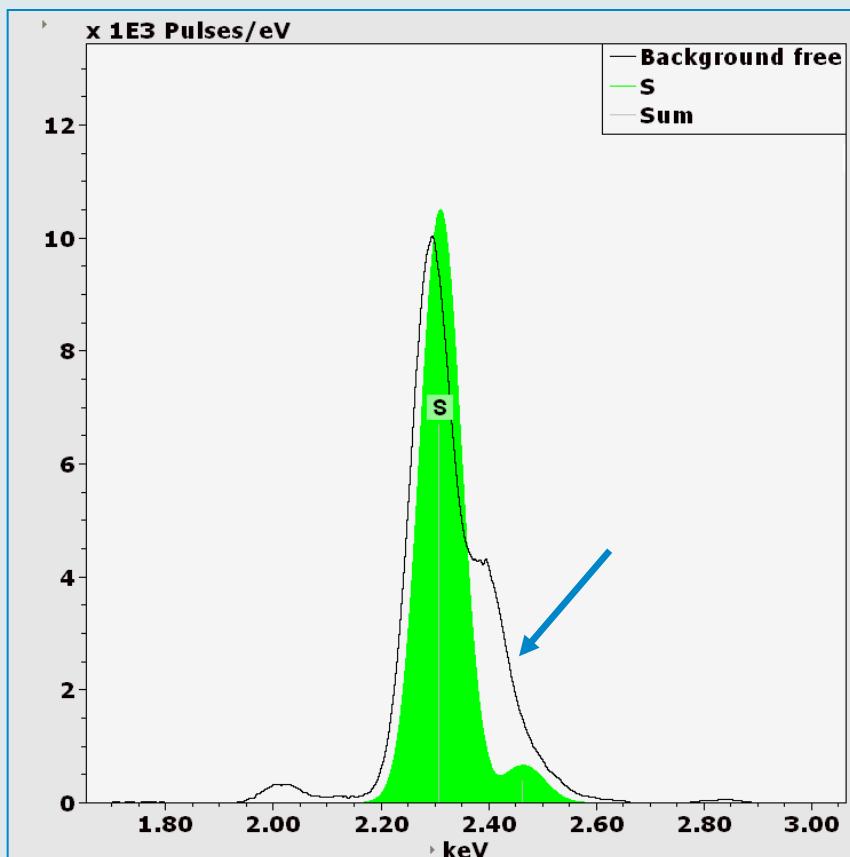
- the background-corrected peak intensities (=net intensities) are attributed to the selected elements according to a mathematical model
- an „experimental“ spectrum (colored+gray) is calculated and can be compared to the acquired spectrum (black line)



I. Quantification of EDS spectra:

3. Deconvolution

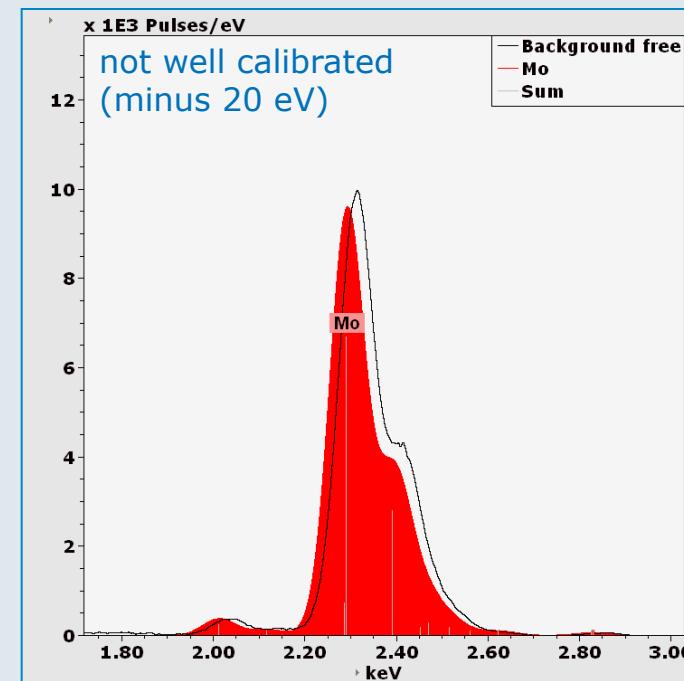
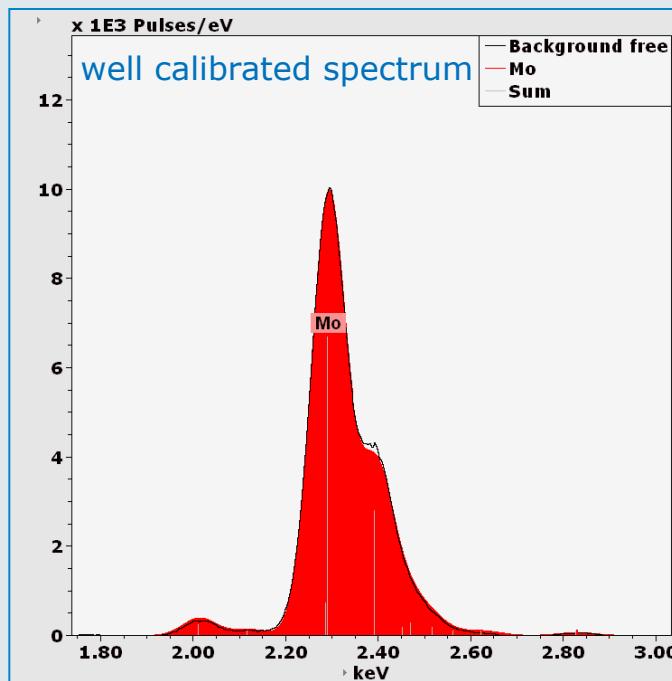
→ looking at the deconvolution result helps you to recognize whether you have overlooked an element or identified an element wrongly:



I. Quantification of EDS spectra:

3. Deconvolution

→ the deconvolution result (Series deconvolution and Series Fit) show whether your energy-channel calibration is ok or not:

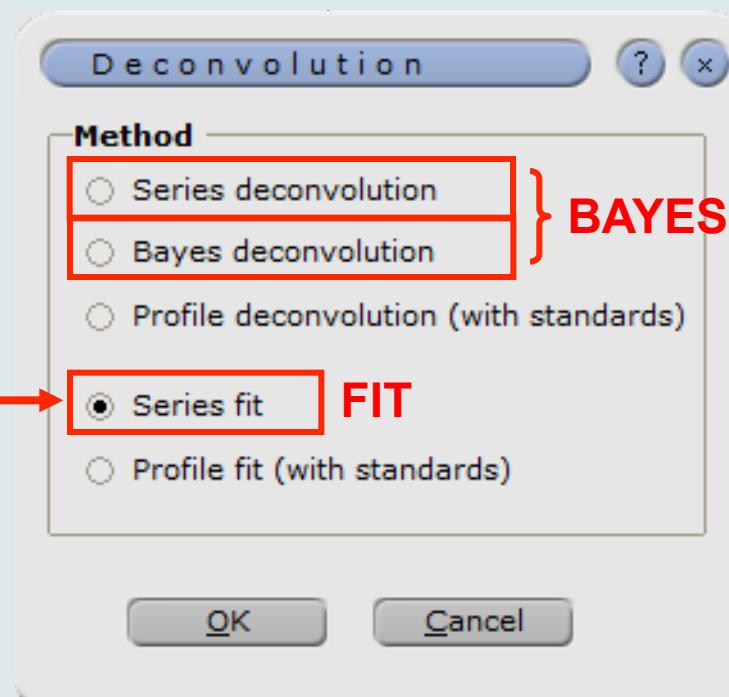


Attention! If Bayes deconvolution is used, you won't see if your spectrum is well calibrated!

I. Quantification of EDS spectra:

3. Deconvolution

→ Deconvolution models (BAYES vs. FIT):



I. Quantification of EDS spectra:

3. Deconvolution

Advantages & disadvantages of the different models:

→ **Bayes Deconvolution** (= single Bayes):

- + if relationships between line intensities within a series change due to binding effects (= differ from theoretical values), e.g., intensities of Ti-LI and Ti-La for TiC and TiO_2
- if energy channel calibration is bad, you won't notice

→ **Series Deconvolution** (= Series Bayes):

- + stable, if you have many peaks overlapping
- + less sensitive regarding energy channel calibration than Series Fit

→ **Series Fit Deconvolution:**

- sensitive regarding energy channel calibration, but if calibration is ok then:
- + stable, if you have many peaks overlapping
- + works better than Series Bayes for noisy spectra (e.g., noisy = acquisition time was too short)
- + compensates better, if a certain element was forgotten / not identified

Overview

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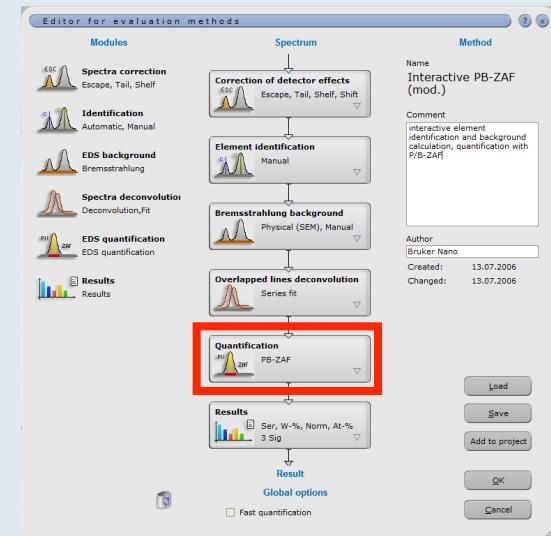
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II.) Correction methods:

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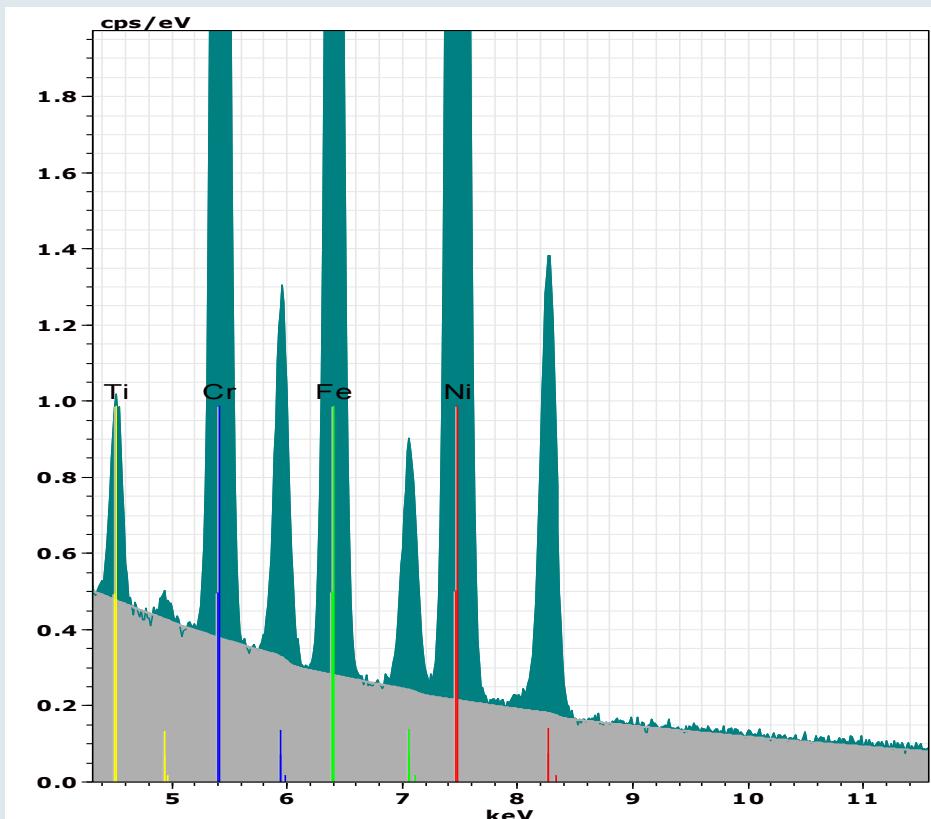
III.) Solid samples – rough surfaces



I. Quantification of EDS spectra:

4. Quantification

How do we derive the chemical composition of a sample (elemental abundances in wt% or atom%) from the EDS spectrum?



Two Options:

- standardless (fast)
- standard-based
(time-consuming, but better results)

Correction methods:

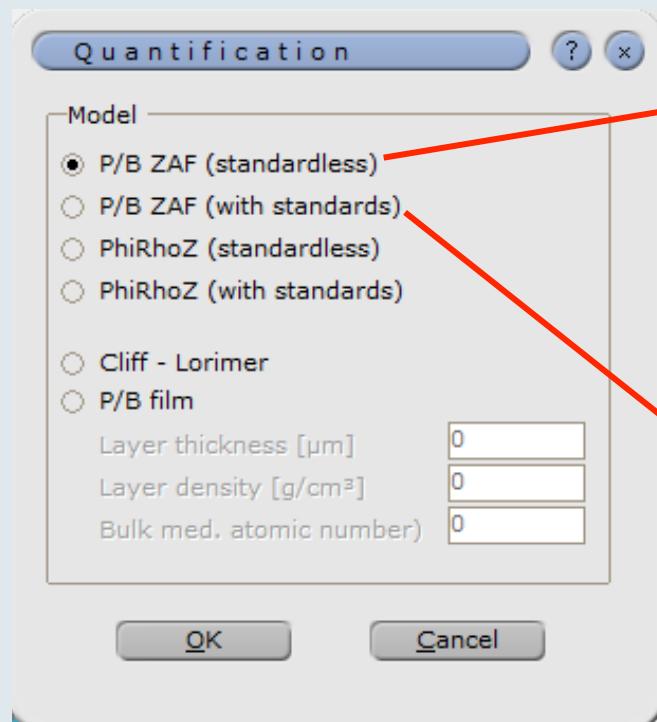
- P/B-ZAF
- PhiRhoZ
- Cliff-Lorimer (TEM)

I. Quantification of EDS spectra:

4. Quantification

standardless P/B-ZAF:

$$\left(\frac{P}{B} \right)_i = \frac{N_i^{char}}{N_i^{br}} \propto C_i \frac{(k_Z k_A k_F)_{i,char}}{(k_Z k_A)_{i,br}}$$



standard-based ZAF:

$$\frac{C_i^S}{C_i^{Std}} \propto \frac{N_i^S}{N_i^{Std}} \frac{(k_Z k_A k_F)_{i,S}}{(k_Z k_A k_F)_{i,Std}}$$

I. Quantification of EDS spectra:

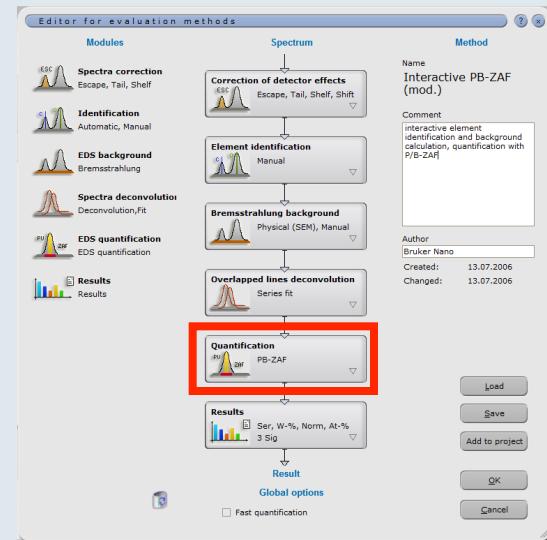
4. Quantification

	Standard-based	Standardless
+	<ul style="list-style-type: none"> ■ Determination of absolute element concentrations normalized to standard ■ Influence of matrix corrections similar if standard similar to sample ■ Small statistical error for net counts of intense lines ■ Some inaccurately known atomic data cancel out 	<ul style="list-style-type: none"> ■ No standard needed ■ Peak and BG spectrum acquired at the same time ■ Spectrum evaluation can be checked step by step ■ Errors due to TOA, detector, surface roughness cancel out ■ Evaluation of rough samples
-	<ul style="list-style-type: none"> ■ More time-consuming, as you need at least two measurements ■ Only accurate for homogeneous and polished samples ■ you need to carefully monitor beam current, microscope and EDS detector settings (use same parameters for sample and standard) 	<ul style="list-style-type: none"> ■ Larger statistical error, especially for low background ■ Accurate determination of background necessary

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II.) Correction methods:

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III.) Solid samples – rough surfaces

II. ZAF correction

Z: atomic number

differences in deceleration of the primary electrons

A: absorption

absorption of primary emitted characteristic x- rays

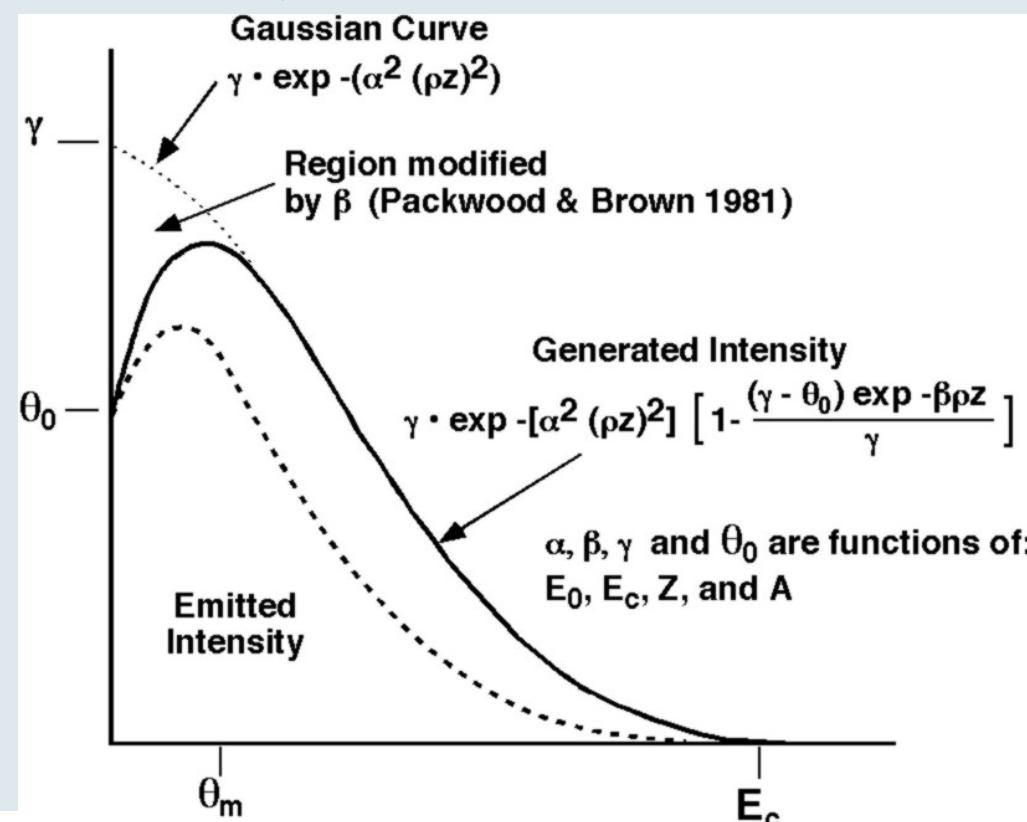
F: (secondary) fluorescence

generation of secondary x- ray fluorescence by
characteristic radiation

II. PhiRhoZ correction

Unlike ZAF, which is conceived as a matrix correction procedure, the ϕ_{pz} method is a general model for the calculation of X-ray intensities.

The emitted and generated intensity can be calculated from a modified Gaussian expression.



II. PhiRhoZ correction

One of the most difficult situations is the measurement of light elements.

The ZAF method breaks down at low Z , due primarily to:

- Uncertainties in absorption coefficients at low Z .
- Uncertainty in J (mean ionization potential) at low Z .
- J can vary with chemical bonding, e.g. $J=109$ for atomic Al, $J=149$ for metal.

$\phi\rho_z$ improves the expressions for Z effects and does a better determination of absorption effects.

→ Thus it is a better correction method for light element analysis.

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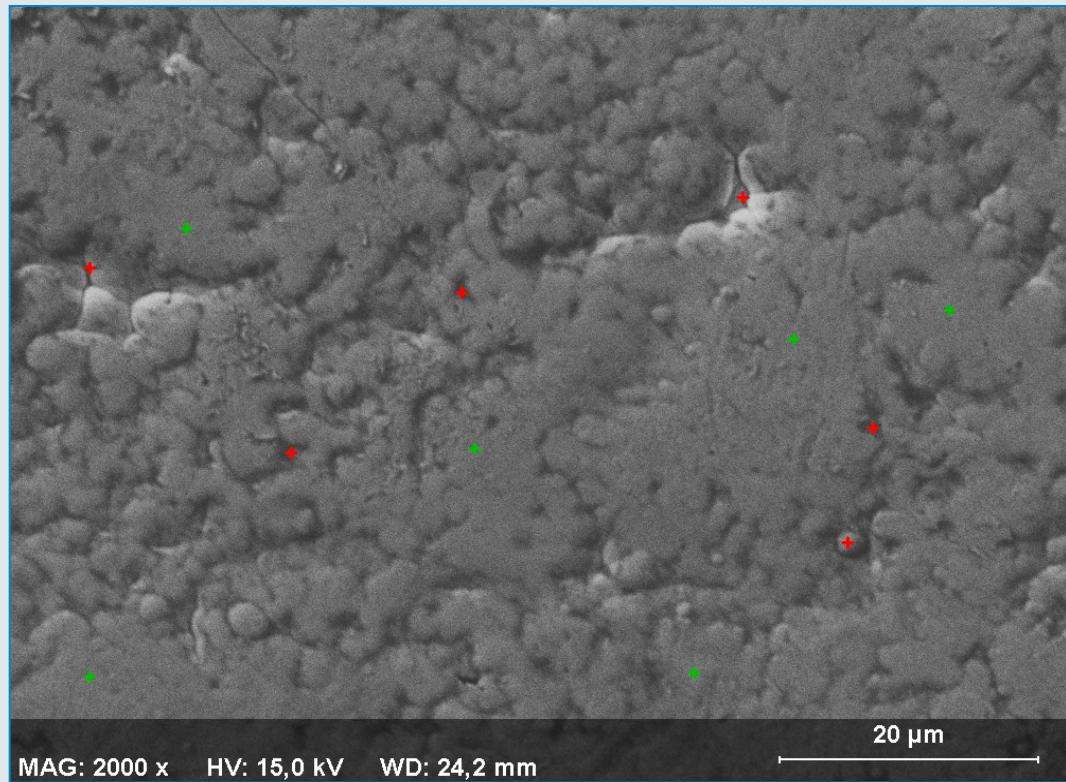
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III.) Solid samples – rough surfaces

III.) Solid samples: rough surfaces

→ galvanically produced Ni-P layer: 12 analysis points

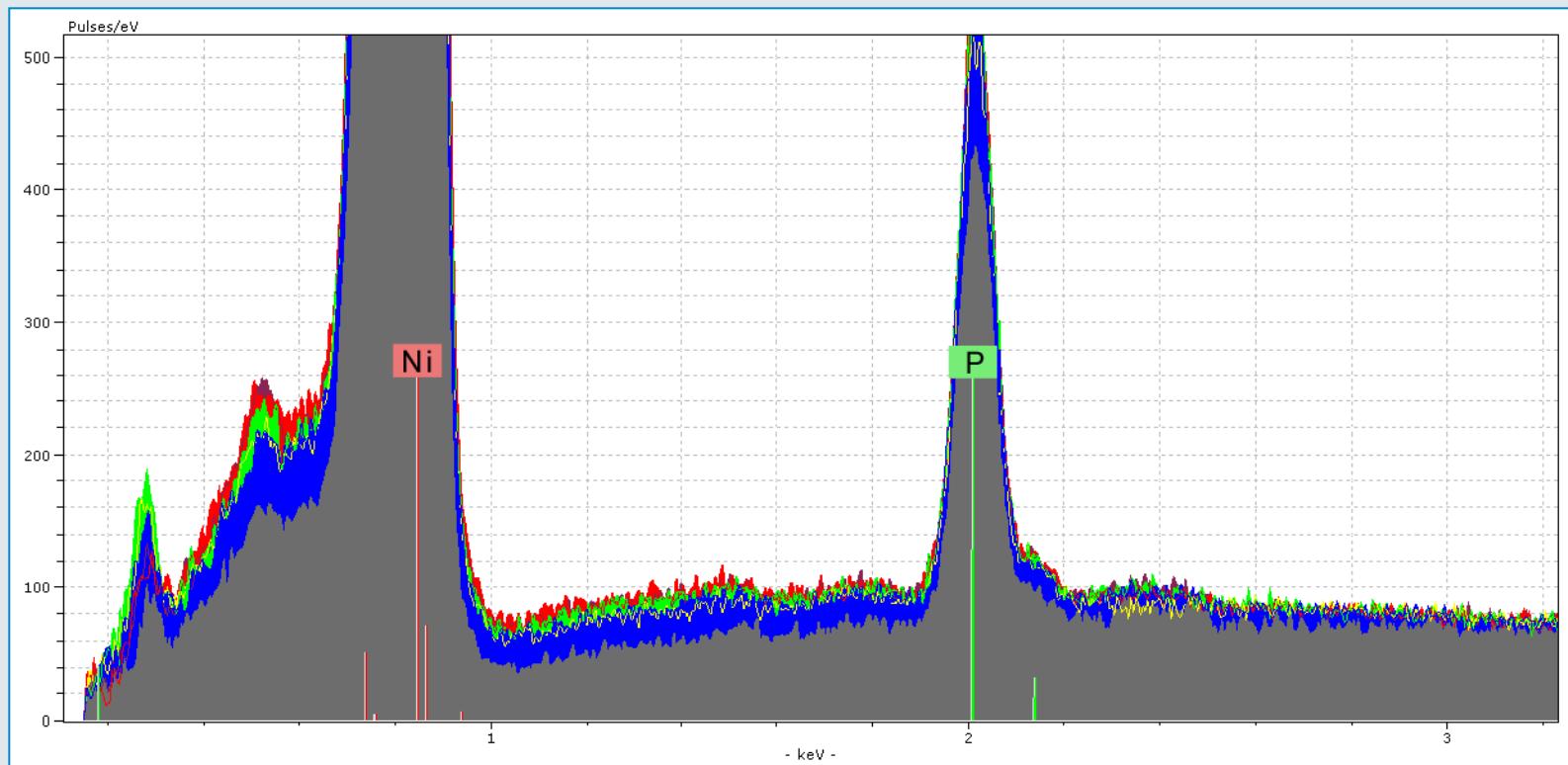


 points #1-6 on smooth surfaces

 points #7-12 on rough surfaces

III.) Solid samples: rough surfaces

spectra of points #7-12 (rough surfaces)



III.) Solid samples: rough surfaces

→ PhiRhoZ analysis with standards:

Points on smooth surface			Points on rough surface		
#	Ni(%)	P(%)	#	Ni(%)	P(%)
1	95,28	4,72	7	95,01	4,99
2	95,29	4,71	8	94,72	5,28
3	95,26	4,74	9	95,32	4,68
4	95,38	4,62	10	94,64	5,36
5	95,29	4,71	11	94,64	5,36
6	95,25	4,75	12	96,06	3,94
MW	95,29	4,71	MW	95,06	4,94
s	± 0,05	± 0,05	s	± 0,55	± 0,55

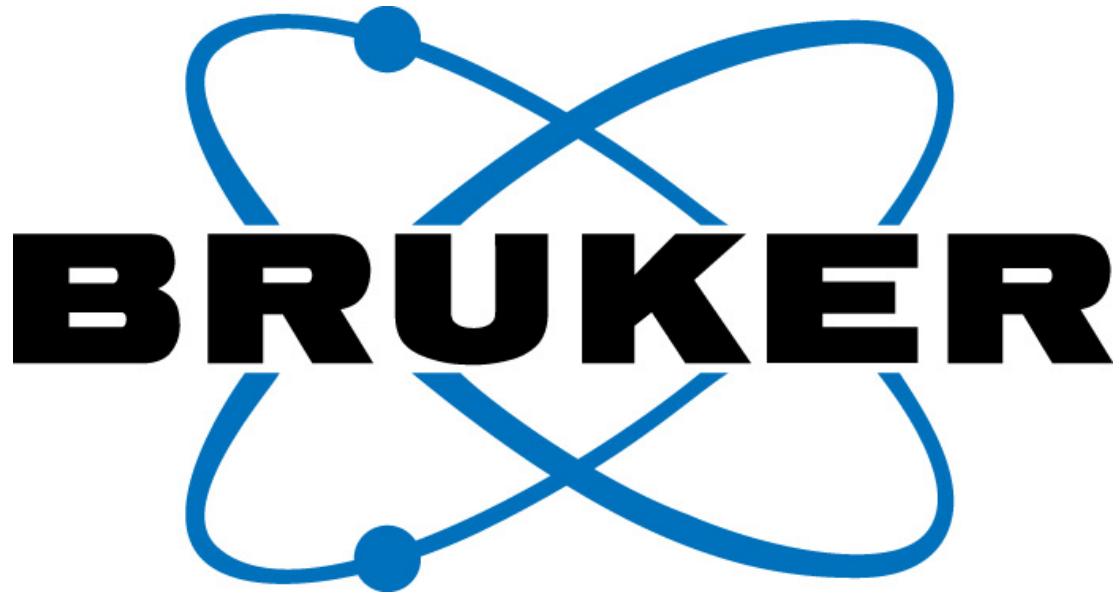
Given value: 4,72 % P

III.) Solid samples: rough surfaces

→ P/B-ZAF analysis with standards:

Points on smooth surface			Points on rough surface		
#	Ni(%)	P(%)	#	Ni(%)	P(%)
1	95,27	4,73	7	95,32	4,68
2	95,29	4,71	8	95,31	4,69
3	95,33	4,67	9	95,31	4,69
4	95,31	4,69	10	95,30	4,70
5	95,28	4,72	11	95,21	4,79
6	95,30	4,70	12	95,35	4,65
MW	95,30	4,70	MW	95,30	4,70
s	± 0,02	± 0,02	s	± 0,05	± 0,05

Given value: 4,72 % P



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