ONLINE WEBINAR

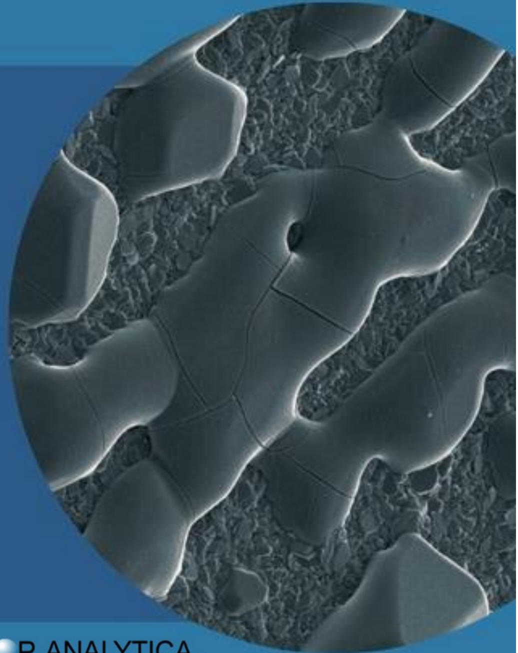
QUANTITATIVE EDS ANALYSIS

X-ray analysis with SEM/EDS is the most widely used analytical tool for microanalysis. Its strength lies in the fast identification of all elements (Z≥Be) on a micrometer scale. The measured spectra can be quantified with high accuracy, but this requires certain actions from the user.

This webinar will focus on the factors affecting the accuracy and precision of EDS analysis:

- Definition of accuracy and precision
- Analysis with or without standards
- Matrix corrections (ZAF vs. $\varphi(\rho z)$)
- Selecting the measurement parameters
- Sample preparation

Secure your spot today!



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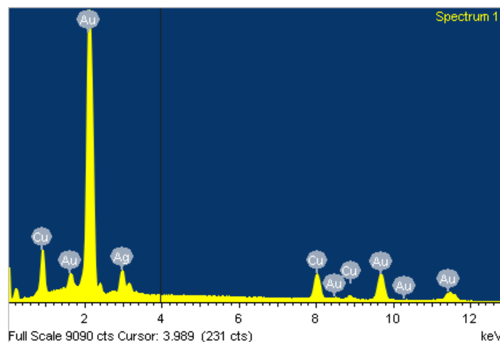
Motivation

Personal reason: Is the wedding ring 18 Ct gold or was I cheated 35 years ago?

24 Ct = 100 % gold
18 Ct = 75 % gold
14 Ct = 58.3 % gold



Spectrum	Wt % Cu	Wt % Ag	Wt % Au
Spectrum 1	15.5	9.2	75.2

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E E (?) 750 M8

Inspection stamp goldsmith Au 75.0 wt-% Production year (1989)

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Material specification: Superheater materials in combustion boilers. These boiler units may have several kilometers of steel tubes. The material selection should be optimized against price and corrosion resistance.

In a published scientific article, a piece of stainless steel was used as a test material and the composition was measured by SEM/EDS:

	Cr	Fe	Mn	Mo	Ni	Si
Measured (wt%)	19.19	70.21	2.02	0.32	7.72	0.47
L304 Spesification	17.5-19.5		< 2.0		8.0-10.5	<1.0

The measured Ni concentration is too low by 3.5 %

- Should the steel producer to be reclaimed?
- Is the measurement accurate? Measured values are given with 2 decimals
- Steels are not homogeneous and SEM/EDS is not the best method for bulk analysis

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Mineral identification: The analyzed material contains iron and oxygen. In the table the amount of Fe is given for the common Fe-O –minerals (wt-%). For reliable identification better than 1 % (relative) accuracy is needed.

Wustite	Magnetite	Hematite
FeO	Fe3O4	Fe2O3
77.23	72.36	69.94

Accurate microanalysis results are utilized in geology in several ways. For example Mg/Fe-ratios are used in garnet-biotite thermobarometry to reveal the metamorposis temperature, where these minerals were formed.

Other example is geochronology, where the age of rock is determined by quantitative analysis of Th, U and Pb in specific minerals like monazite. Very accurate measurement is needed as an 1% (relative) error will give an error of 20-50 million years.

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Terminology

- Qualitative analysis measure the presence or absence of a substance
- Semi-quantitative examinations provide an estimate of how much of the measured substance is present (typically in a non-numerical form)
- Quantitative analysis is the accurate determination of their concentrations. The result is given in a numerical form (with an error estimate)

measurement = (best estimate ± uncertainty) units

$$\text{Relative Error} = \frac{\text{measured value} - \text{expected value}}{\text{expected value}}$$

- Accuracy is the closeness of agreement between a measured value and a true or accepted value. Measurement error is the amount of inaccuracy.
- Precision is a measure of how well a result can be determined (without reference to a theoretical or true value). It is the degree of consistency and agreement among independent measurements of the same quantity; also the reliability or reproducibility of the result.
- The uncertainty estimate associated with a measurement should account for both the accuracy and precision of the measurement.

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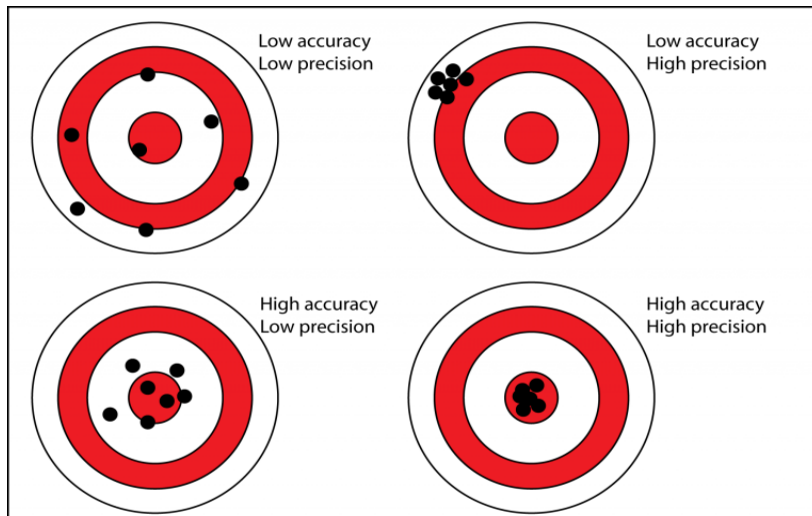

Accuracy = tarkkuus, virheettömyys (oikeellisuus)
Precision = tarkkuus, täsmällisyys (toistettavuus)

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Types of error

Random errors

- counting statistics
- fluctuations in E beam intensity
- sample roughness
- beam damage
- variations in WD
- sample heterogeneity
- drift in energy calibration
- etc

Random errors can be evaluated through statistical analysis and can be reduced by averaging over a large number of measurents

Systematic errors

- errors in matrix corrections
- bad standards
- variations in detector efficiency
- missing elements
- oxidized surface
- background subtraction errors
- peak deconvolution errors
- etc

Systematic errors are reproducible inaccuracies that are consistently in the same direction. They cannot be detected or reduced by increasing the number of observations

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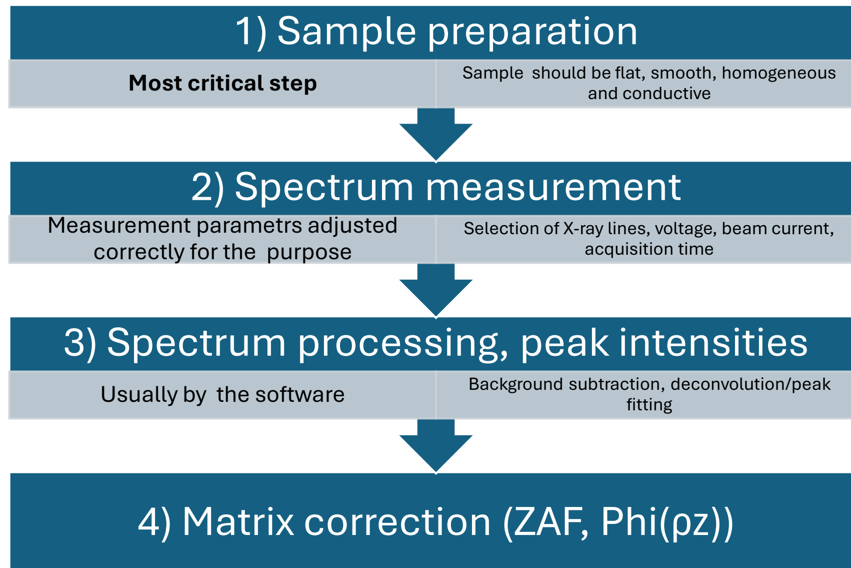

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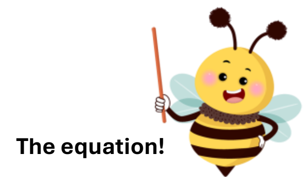
4) Matrix corrections

The X-ray intensity *Ii* emitted by element *i* is written as:

$$I_i = n_{el}\, \varepsilon \frac{\Omega}{4\pi} \frac{N_A}{A_i} c_i\, \omega_{jk}\, (1 + T_{CK})\, R\, (1/S)\, f(\chi)(1 + \sum f_c + f_b)$$



where n_{el} is the number of incident electrons
Ɛ is the intrinsic detector efficiency
Ω /4π is the solid angle of collection
c_i is the weight fraction of element *I*
N_A is Avogadro's number
A_i is the atomic weight of element *i*
ω_{jk} is the partial fluorescence yield
(1 + T_{CK}) is the enhancement factor due to Coster-Kronig transitions
R is the backscattering factor
$f(\chi)$ is the absorption factor with χ = csc(ψ) and ψ being the X-ray take-off angle
1/*S* is the stopping power factor (also called deceleration factor)
f_c and f_b are the characteristic and continuum (Bremsstrahlung) fluorescence factors

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The given equation include parameters Ɛ and Ω, which are specific for the used instrument
Parameters ω_{jk} and $(1+T_{CK})$ are atomic parameters for element i

These parameters are typically not well known, therefore the X-ray intensity is normalized to that emitted from a reference standard that contains the element of interest, which gives

$$k_i = \frac{I_i}{I_i^{std}} \models \frac{c_i}{c_i^{std}} \times \frac{R/S}{(R/S)^{std}} \times \frac{f(\chi)}{f(\chi)^{std}} \frac{(1+\sum f_c + f_b)}{(1+\sum f_c + f_b)^{std}}$$

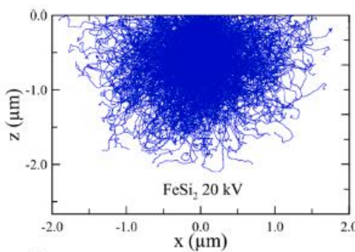
Z-number | Absorption | Fluorescence

$$k_i = \frac{c_i * ZAF_i}{c_i^{std} * ZAF_i^{std}} \qquad c_i = k_i * C_i^{std} * \frac{ZAF_i^{std}}{ZAF_i}$$

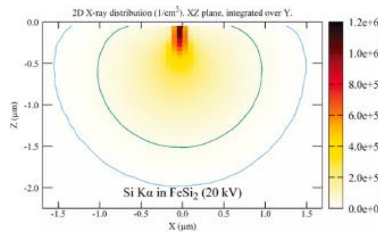
For pure element standards ZAF=1

In some papers ZAF correction is written as $c_i=k_i*ZAF_i*c_i^{std}$, which means that ZAF = 1/ZAF

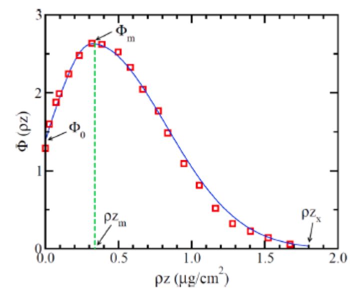
Phi(ρz)-method



Electron trajectories in $FeSi_2$

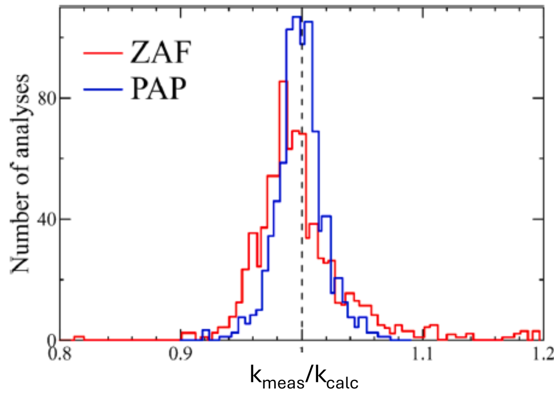


Generation of Si K_α X-rays.
Inner circle 90 % of the total intensity.
Outer circle 99 % of the total intensity.



Generated X-rays as a function of mass thickness (ρz).

Phi(ρz)-method is based on the calculation of the Z-number and absorption correction from the ϕ(ρz)-curve.
Fluorescence correction is the same in ZAF and Phi(ρz) methods



Relative errors measured for 826 binary compounds using pure elements as standards

PAP ϕ(ρz) standard deviation 1.9 %
3 different ZAF methods standard deviation 2.7-4.2 %

ϕ(ρz) methods are better specially in case where absorption correction is large (e.g. analysis of light elements)

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In case with strong absorption the matrix corrections can be large (200-300%). Big corrections decreases the accuracy of the measurents. It is possible to reduce the corrections by optimizing measurement parameters or by using standards with similar composition as the sample.

In the example orhtoclase mineral is analyzed by using either pure elements as standards or using oxides (Al_2O_3, SiO_2 and $KAlSi_3O_8$) as standards.

The corrections are with elemental standards from 18 % up to 42 %. When oxides are used the corrections are less than 8%.

material	K	Al	Si
KAlSi3O8	1.18		
Al2O3		1.36	
SiO2			1.27
KAlSi3O8 pure elements	1.18	1.42	1.39
KAlSi3O8 oxides	1	0.96	0.92

The use of standards with composition close to unknown samples will increase the number of standards and these standards should be with a well known composition.

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Standards vs standardless analysis

The quantitative X-ray microanalysis is based on the measurement of k-ratio

The easiest way to do this is to measure the intensities under same analytical conditions from the unknown sample and the standard

The EDS manufacturers are strongly marketing standardless analyses, where no measurement is done from the standard. There are several ways how standardless analysis can be done:

(i) first principles (uses physical and instrumental parameters)
(ii) peak-to-background (dividing the peak intensity by background intensity cancels the instrumental parameters)
(iii) remote standards (X-ray intensities are measured at factory and stored in the memory)

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(i) first principles
The X-ray intensities are calculated using the equation for a given sample composition and analytical conditions. This requires knowledge of not only fundamental quantities but also instrumental parameters such as the spectrometer efficiency and solid angle of collection. The method is very susceptible to inaccuracies in the physical parameters and models.

(ii) peak-to-background
Allthough several parameters such as the electron current, solid angle and detector efficiency are eliminated, it however requires different models to calculate the matrix correction for the bremsstrahlung emission than those normally used for the matrix correction of the characteristic X-ray emission. Further it suffers from the imprecision of the background intensity (high random error due to its low intensity).

(iii) remote (or virtual) standards
Not a real standardless analysis (for the user it seems to be standardless as the user don’t need to measure the standards). Typically the remote standards are measured with a certain voltage (for other voltages the intensities are corrected from the first principles). The beam calibration can be done by using pure element standard. As the detector efficiency may change due to contamination of the detector window may influence the results especially for low energies. In some systems the remote standards can be replaced with own standards which will improve the accuracy.

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How accurate is standardless analysis?

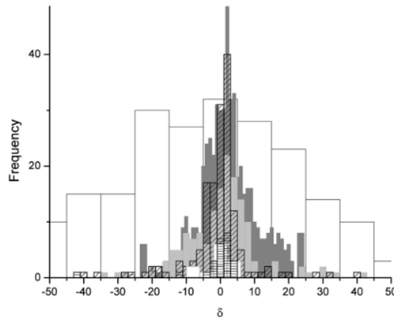

Fig. 2. Histograms of the differences of concentrations relative to the nominal values for standardless quantification methods applied to bulk samples. White and wide bars: DTSA [6], dark gray bars: Wernisch [18], light gray bars: GENESIS [24], diagonal line bars: POEMA [24], white and narrow bars: Horny et al. [23], horizontal line bars: Heckel and Jugelt [16].

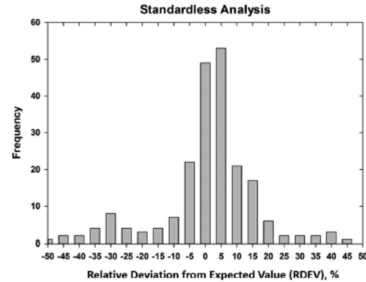

Fig. 14. RDEV histogram constructed with results of a vendor standardless analysis procedure applied to known materials.

The programs are devoloping all the time, the histograms above are from 2014-2016. Results with new software with remote standards give accuracy better than5 % (which is still 2-3 times higher than results with standards).

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3) Spectrum processing, peak intensities

There are 2 possibilities to measure the X-rays: WDS and EDS

EDS (Energy dispersive spectrometer)
- Semiconductor device
- The whole spectrum is measured at same time
- Poor energy resolution (100-150 eV)
- Low peak/background ratio
- More peak overlaps
- Almost constant detection effiency (for different elements and vs time)
- Easy to operate

WDS (wavelenght dispersive spectrometer)
- Crystals with mechanical movement
- Only one energy at time
- Good energy resolution (4-10 eV)
- High peak/background ratio
- Peak overlaps not so common
- Big variations in detection effiency (both for different elements and vs time)
- More difficult to operate

Special SEMs which are designed to be used with 4-5 WD-spectrometers are called Electron Probe Micro Analyzers (EPMA)

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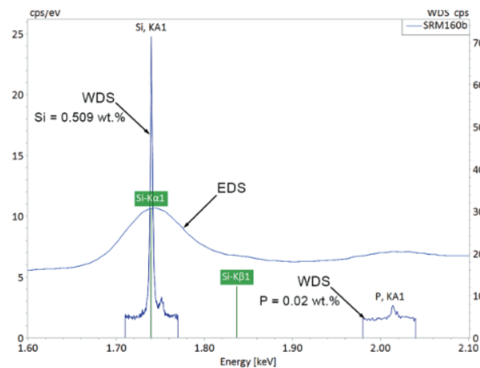

Comparison of EDS spectrum and WDS-spectral scan

The measurement of peak intensity is simple with WDS (single channel count at peak pos - background)
In the case of EDS it is more complicated and the usual way is to integrate the counts over the FWHM of the peak and subtract the background with the same width. Due to the low P/B-ratio a good model for the background is essential.

The biggest difference in quantitative analysis between WDS and EDS is the way how the intensities are calculated

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Extraction of X-ray intensity from an ED spectrum

a) Correction of the energy scale	User calibration
b) Correction of artefact peaks	Software
c) Removal of the background	Software/User
d) Fit of modelled or experimental peak profiles over the X-ray peaks of interest	Software/(user)
e) Extraction of the X-ray intensity from the fitted X-ray peak.	Software

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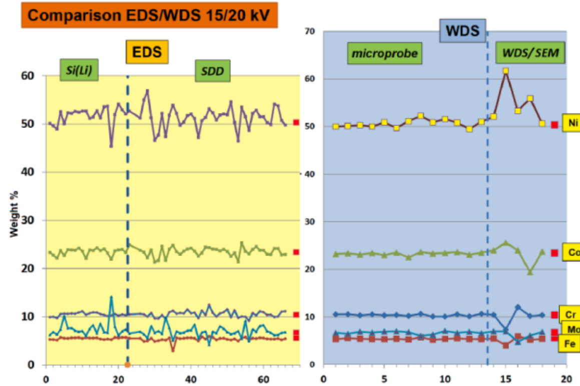
Comparison EDS vs WDS



Metallic melt glass measured in different laboratories with EDS or WDS. The red box marks the certified composition.

Generally the WDS-results are better than EDS. Adding WDS in a SEM doesn't improve the situation

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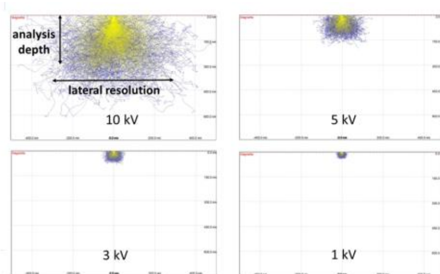
2) Spectrum measurement

Selection of measurement parameters- accelerating voltage E



Monte Carlo calculations for the electron trajectories in magnetite (Fe_3O_4) with different electron energy .

Higher voltage increases the analysis volume

Overvoltage $U = E/E_c$, E_C is ionization energy of the element shell
Best intensity is achieved with U=3-5

Higher voltage causes bigger ZAF-corrections:

E /kV	C ZAF	Fe ZAF
5	1.31	1.03 (La)
10	2.59	1.03 (Ka)
15	4.15	1.02 (Ka)
20	5.44	1.01 (Ka)

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Selection of measurement parameters- beam current and time

- The precision of the measurement depends on variable random errors

- One can measure the precision of the measurement by repeating the measurement in same spot several times and calculate the standard deviation (result is σ_{meas})

- There is always random error from the counting statistics, and its standard devition can be calculated as $\sigma_{count}=1/\sqrt{n}$, where n is number of counts

- Sigma-ratio $\sigma_{meas}/\sigma_{count}$ show if there are other random errors (ratio > 3 indicates significant random errors and their source should be examined)

- In pure metallic samples it is easy to get over 1 million counts at 1 nA and 50 s measurement time. This give a precision of 0.1 % which is good enough. If the concentration drops to 1 %, the precision would be 1% etc.

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Selection of measurement parameters- time constant, count rate and dead time

- Time constant is a parameter which determines how long the detector is processing the incoming X-ray pulse

- When long time constans are used the detector has enough time to process the pulses properly which gives the best energy resolution. Short time constants will worsen the resoltution.

- During the processing the detector is dead (not able to intake new pulses) , this time is called dead time and is given as a percentage

- The dead time will increase when longer time constans are used but also when then count rate increases

- If the aim is to get as much pulses as possible (X-ray mapping) one should use short time constants and the dead time can up to 40-50%

- For accurate quantitative analysis it is better to use low dead times (10-20 %) as there will be more spectral artefacts like pulse pile-up if higher dead times are used.

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1) Ruining the accuracy and precision with bad samples

Sample **must** be:

- Flat
- Homogeneous
- Smooth
- Conductive

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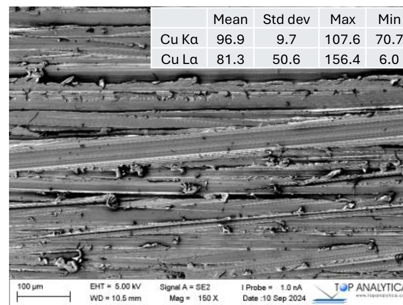
Roughness

Effect of surface roughness

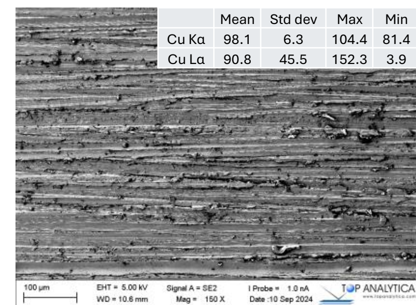
Metallic copper is grinded with different SiC papers.

Both CuKa and CuLa intensities were measured from 16 randomly selected points.



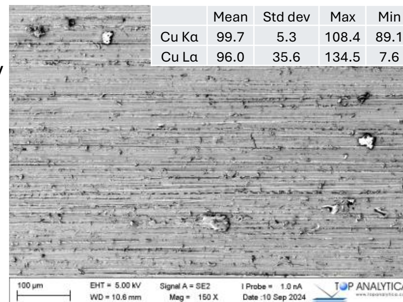
	Mean	Std dev	Max	Min
Cu Kα	96.9	9.7	107.6	70.7
Cu Lα	81.3	50.6	156.4	6.0

SiC paper P120, 125 µm



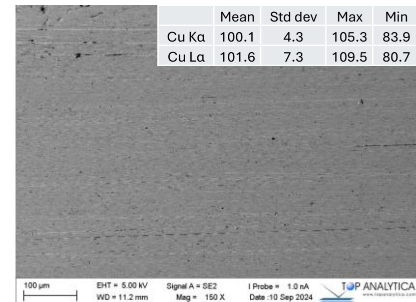
	Mean	Std dev	Max	Min
Cu Kα	98.1	6.3	104.4	81.4
Cu Lα	90.8	45.5	152.3	3.9

SiC paper P220, 68 µm



	Mean	Std dev	Max	Min
Cu Kα	99.7	5.3	108.4	89.1
Cu Lα	96.0	35.6	134.5	7.6

SiC paper P1000, 125 µm



	Mean	Std dev	Max	Min
Cu Kα	100.1	4.3	105.3	83.9
Cu Lα	101.6	7.3	109.5	80.7

SiC paper P4000, 5 µm

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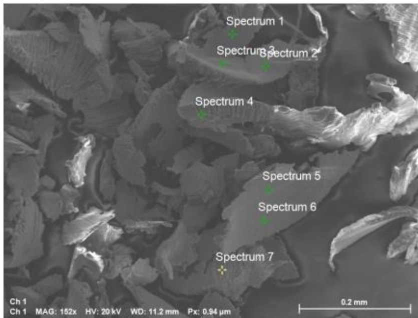
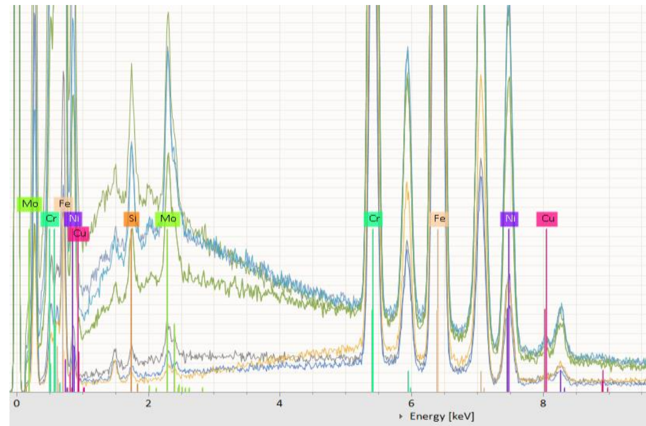
The use of P/B for rough surfaces





316 steel dust

	Si <1	Cr 16-18	Fe	Ni 10-13	Cu	Mo 2.2-2.5
tav ZAF	0.31	18.46	71.22	8.12	0.49	1.41
	0.19	0.94	1.69	1.70	0.08	0.74
Rel dev	63%	5 %	2.4 %	20 %	17 %	74%
ZAF-PB	0.38	17.22	71.62	8.47	0.52	1.79
	0.05	0.39	1.99	1.51	0.14	0.19
	12 %	2.6%	2.8 %	18 %	27 %	11 %

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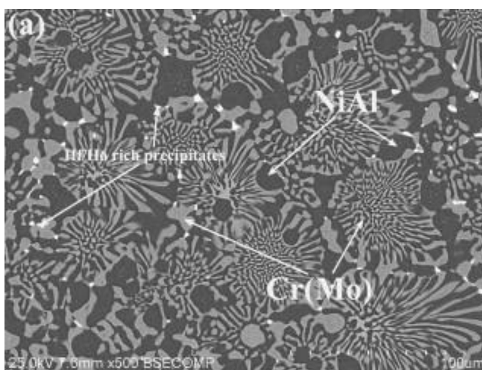
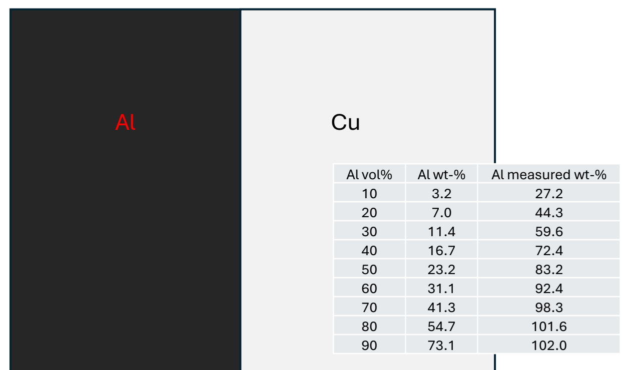
Measuring the average composition of heterogeneous samples





Al vol%	Al wt-%	Al measured wt-%
10	3.2	27.2
20	7.0	44.3
30	11.4	59.6
40	16.7	72.4
50	23.2	83.2
60	31.1	92.4
70	41.3	98.3
80	54.7	101.6
90	73.1	102.0

What is the average composition of this sample?

Test sample: Cu- and Al metal plates on top of each other

Measuring spectrum from a large area will generate huge errors!

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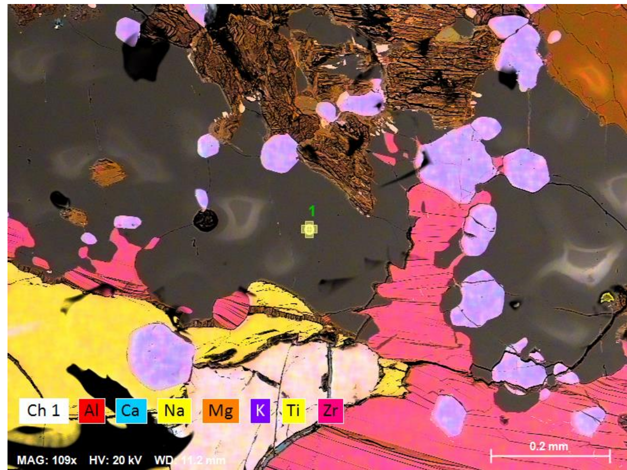
The use of VP-mode will generate spurious X-rays in the vicinity of the analysis point



Spectrum	Oxygen	Magnesium	Aluminium	Silicon	Potassium	Calcium	Titanium	Iron	Zirconium
hv.spx	54.3	0.0	0.1	45.1	0.0	0.0	0.0	0.1	0.0
5pa.spx	51.7	0.1	0.3	47.5	0.0	0.1	0.1	0.3	0.0
11pa.spx	51.2	0.2	0.3	46.6	0.1	0.3	0.3	0.9	0.0
18pa.spx	51.0	0.3	0.4	45.6	0.2	0.6	0.4	1.3	0.2
24pa.spx	50.6	0.5	0.5	43.9	0.3	0.8	0.6	1.9	0.8
30pa.spx	50.2	0.6	0.6	43.1	0.4	1.1	0.7	2.4	1.0

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Conclusion:

EDS-analyses can be done with accuracy and precision better than 1 %

This is possible by using standards and having well prepared samples

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