IFG Institute for Scientific Instruments

µ-XRF and EPMA
An interesting combination for SEM's?

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- **Motivation**
- **Capillary optics for X-Ray beam shaping**
- **µ-XRF in a SEM**
- **Benefits and applications (sensitivity, distribution analysis, coating thickness determination, sample stability)**
- **Standardless quantification for XRF**
- **Combination of quantification for EPMA and µ-XRF**

IFG

Motivation

Most technical materials are inhomogeneous

=> for a complete characterisation position sensitive analytical methods are necessary

Methods for elemental analysis with good spatial resolution are known

⇒ EPMA, but limited sensitivity

New X-Ray optics allow the concentration of X-Rays to small spots

⇒ Also X-Ray fluorescence can be used for position sensitive elemental analysis

Main features for the both methods

Method	Spotsize [µm]	Element range	LOD [µg/g]	Analysed Volume [µm³]
EPMA	few	C – U	1000	50 – 100
µ-XRF	down to 20	Na – U	down to 20	20.000 – 100.000

Concentration of excitation radiation by capillary optics

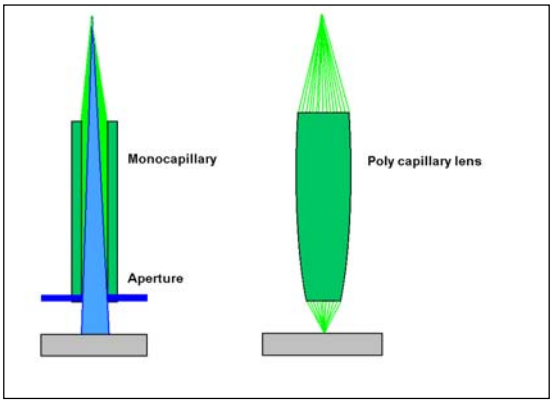
Propagation in glass capillaries due to multiple external total reflection.

In that way it is possible to shape the beam i.e. make a convergent or also a parallel beam.

So it will be possible to concentrate the excitation radiation to a small sample area.

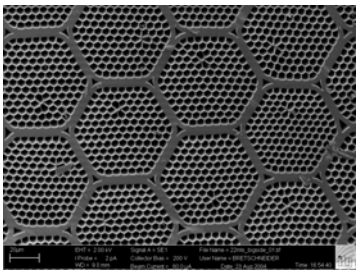
The spot size can be adapted to the special task by different optics

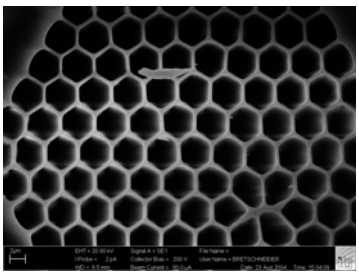
Intensity gain in the range of up to 5000 is possible.



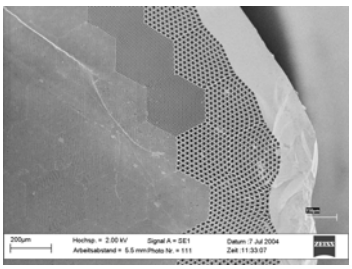
Optics	Input ∅	Transmission	Brilliance
Collimator	1 mm	100 %	1
Mono cap	300 µm	≈ 80 %	≈ 10
Poly cap	3 mm	≈ 5 – 10 %	≈ 5000

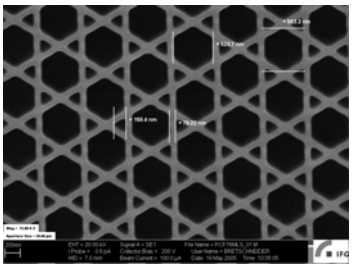
Multiple level structure of lenses





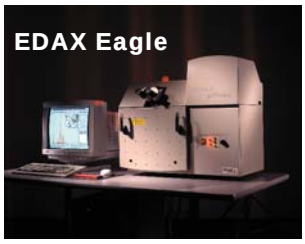
Combined structure for lenses





Poly-capillary optics are used already in several µ-XRF instruments

EDAX Eagle



Röntec ArtTax

JEOL Yuki

Veeco MDX

Shimadzu EDX 1200

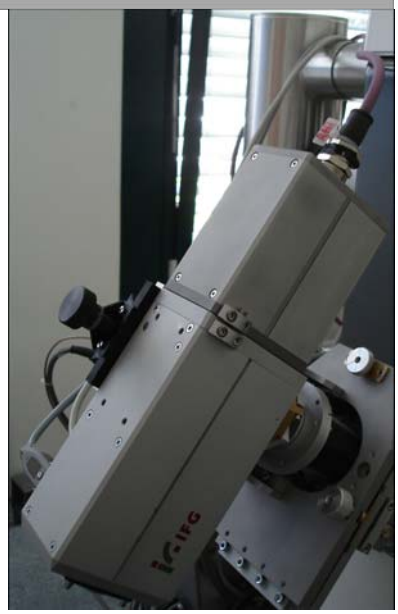
Motivation for the combination of µ-XRF with EPMA

The availability of X-Ray optics opens the possibility for µ-XRF also in SEM

Then it is possible to combine electron excitation with X-Ray excitation using the same EDS-detector for measuring fluorescence of both excitation

Benefits:

- **Higher sensitivity for trace analysis**
- **Enhanced information depth**
- **Easy sample preparation (no electrical conductivity needed)**
- **Low sample stress by low heating due to absorbed radiation**
- **Combination of quantification results of EPMA and XRF due to different sensitivities in dependence of atomic number**



Instrument scheme

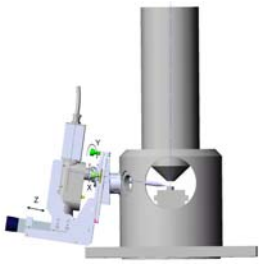
The installation is possible for every SEM.

Requirements:

- **Free port on the SEM**
- **Port should be opposite to the EDS-detector, geometry of 90 deg would be optimal**
- **Design has to be optimised for every SEM type and port**

  => the length of the X-Ray optic has to be adapted

Technical specification of the iMOXS



X-Ray excitation :

HV:	max. 50 kV
Tube current:	max. 800 µA
Filament heating	max. 5 A (depends on the tube)

Electronics:

H x B x T:	165 x 376 x 420 mm³
weight:	15.4 kg

X-Ray tube:

Type	Air cooled metal-ceramic tube
Anode material	Rh, W, Mo, Cu (further on request)
Anode spot	50 µm
tube window	0.1 mm Be
Filter wheel	up to 4 filter, on request
Tube housing	with a controlled shutter
Bauartzulassung	according to German RöV

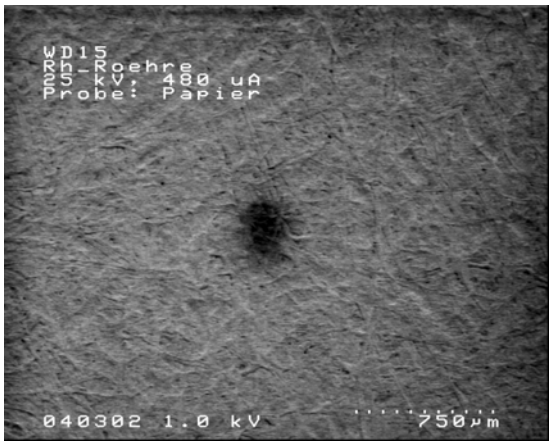
X-Ray optics:

Mono-capillary or Poly-capillary-Lens, adapted to the SEM

Spot size	100 – 300 µm (mono-cap)
	30 - 100 µm (E > 15 keV pol-cap lens)
Optic cover	with tools for alignment

Alignment flange: Alignment flange for adaptation to different SEM-types

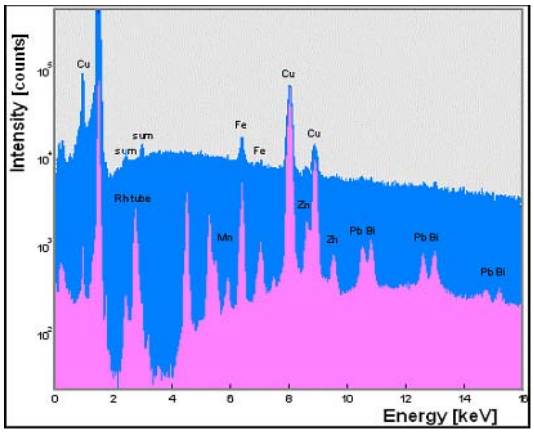
Alignment of iMOXS



An alignment of the X-Ray spot is necessary to the position of the non-deviated electron beam

The X-Ray spot is visible by a contrast caused by charging effects on non-conductive material (paper)

Advantage in analytical performance



Improvement of P/B ratio

Spectra of an Al-alloy (log – scale)

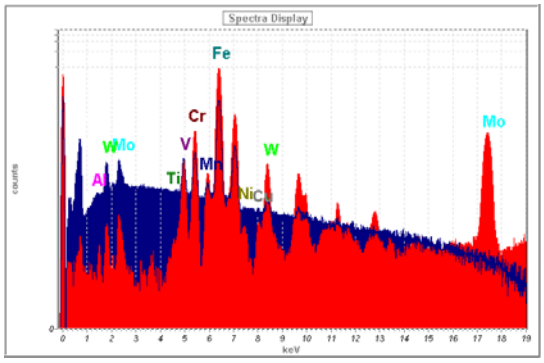
excited by electrons (blue) and by X-Rays (red)

The X-Ray excited spectrum have a significant lower background due to lack of bremsstrahlung in case of X-Ray excitation

Peaks that are overlapped by the back-ground for EPMA can be detected in case of X-Ray excitation (for example Mn, Pb, Bi)

=> Limit of detection are down to 20 ppm, that means sensitivity can be improved by a factor of 20 to 50!

Advantage in analytical performance



Spectra of high alloyed steel (CRM 486)

Excitation by electrons (blue) and X-Ray (red)

⇒ **High intensities for main components (smaller error)**

⇒ **Undoubtely identification of Mo**

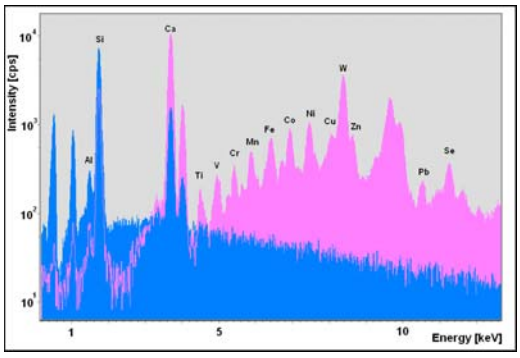
⇒ **Identification of traces like Ni, Cu**

Comparison of typical limits of detection

Measured for different Fe- and Cu-alloys [ppm]

Elem	X-Ray	Electron
Ti	100	1000
Cr	80	800
Mn	50	800
Fe	40	800
Ni	30	900
Cu	20	1000
Zn	20	1000
Mo	200	2000
Sn	300	4000
Pb	200	5000

Advantage in analytical performance



Spectra of the NIST 612 (multiple element glass standard)

excited by electrons (blue) and by X-Rays (red)

Combination of EPMA and µ-XRF

Due to differences in excitation probability

⇒ **Light elements are better excited with electrons**

⇒ **Heavy elements are better excited with X-Rays**

For approx. Z = 20 the measured intensities are comparable for both excitations

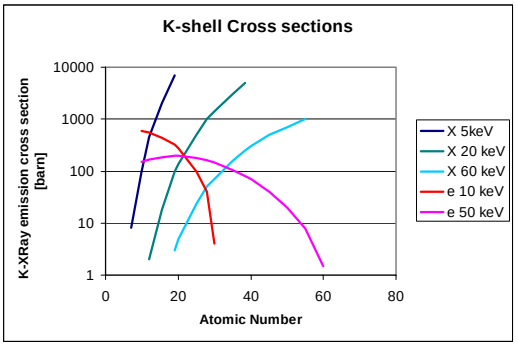
⇒ **A combination of both quantification results should be improve the overall accuracy**

High sensititivty due to effective excitation and lack of spectral becakground

=> Limit of detection in the range of 10 – 30 ppm

Element	LOD
Ti	50
V	40
Cr	30
Mn	30
Fe	25
Ni	25
Cu	25
Zn	20
Pb	30
Rb	15
Sr	15

Advantage in analytical performance



K-Shell cross sections for electron and x-ray excitation for different excitation energies and atomic numbers

Electron excitation has a larger cross section for light elements (up to 1 orders of magnitude)

X-Ray excitation is more efficient for heavy elements

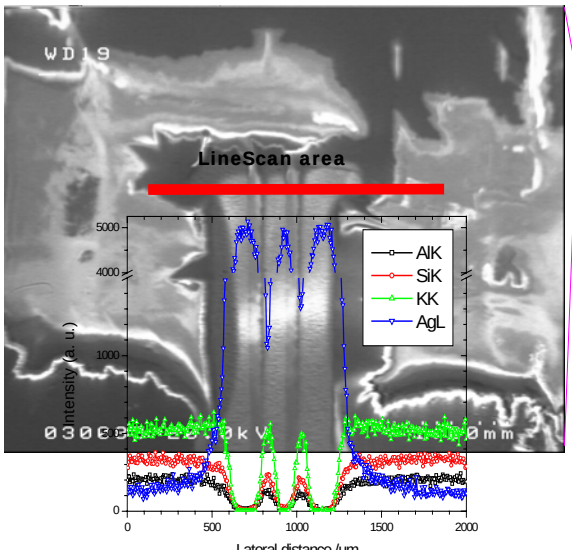
Combination of analytical results of both methods

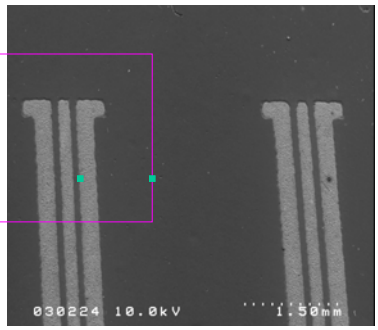
=> improvement of analytical results due to

- two results enhance the confidence
- weighted averaging of results
- reduction of analytical errors
- iterative using of results of both excitations

⇒ **Improvement of accuracy of analytical results**

Application: Multilayer ceramics substrate with Ag-circuit paths (1)





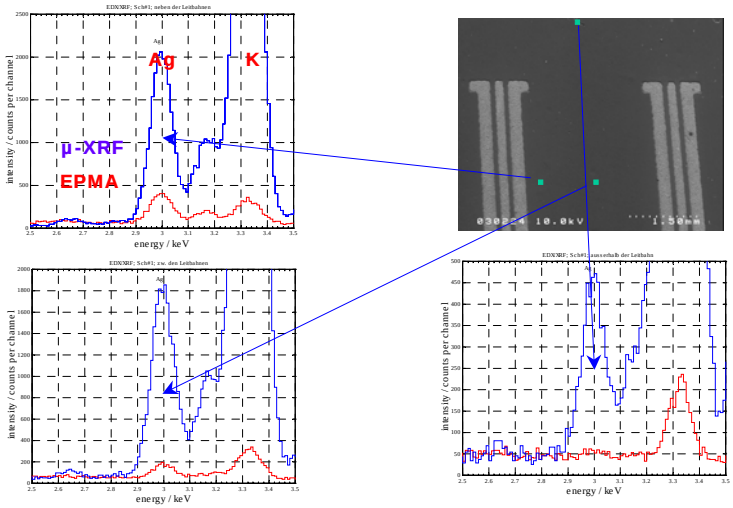
Ag seems to be present only in the tracks with EPMA. But the higher sensitivity of µ-XRF displays Ag also in measuring points away from the track.

The Ag diffuses into other regions and can enhance the conductivity.

Analysis performed by M.Procop

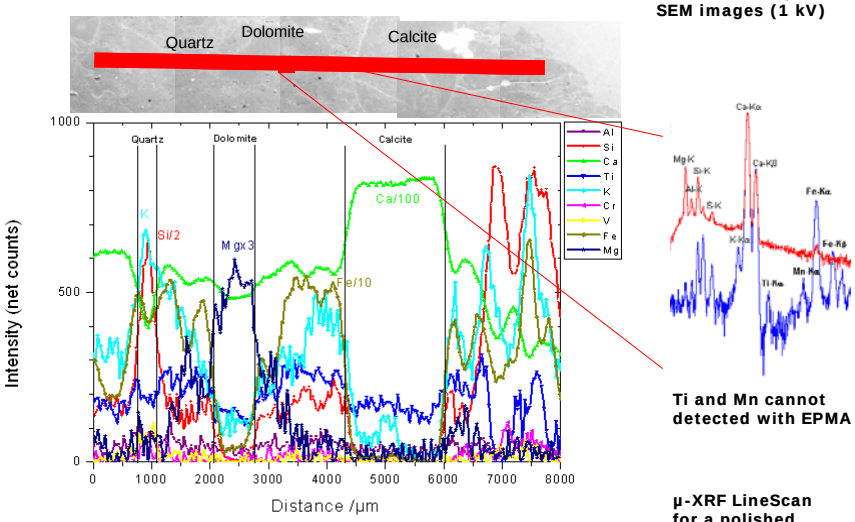
BAM

Application: Multilayer ceramics substrate with Ag-circuit paths (2)



Application: Line scan on a concrete

Simultaneously SEM images (1 kV)



Ti and Mn cannot detected with EPMA

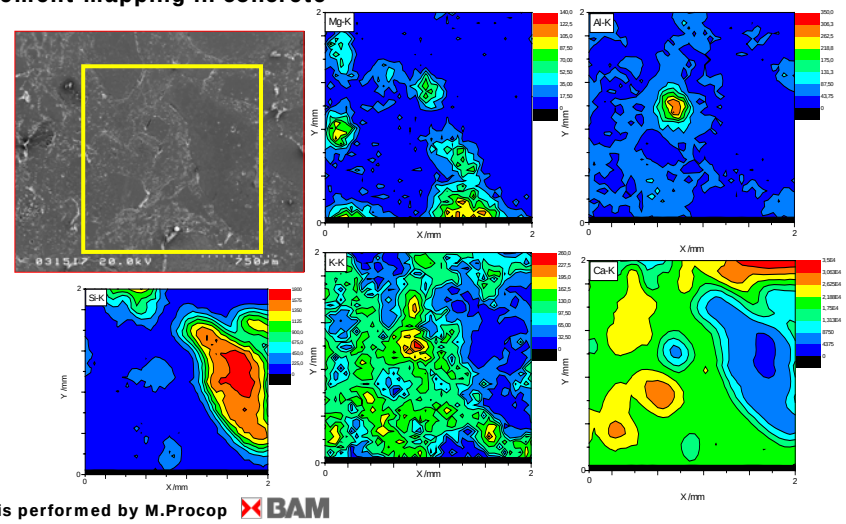
µ-XRF LineScan for a polished concrete specimen

Analysis performed by M.Procop BAM

Distribution analysis:

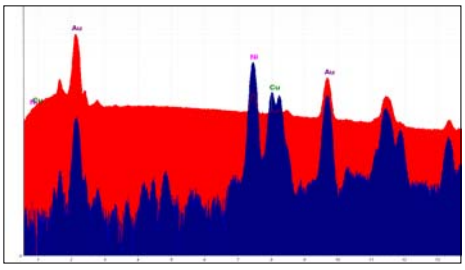
2D element mapping in concrete

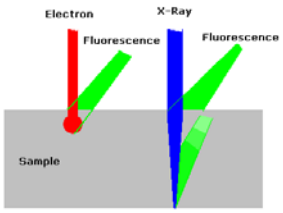
40 x 40 Pixels a 4s, mapping via stage control



Analysis performed by M.Procop BAM

Advantage in analytical performance





Enhancement of information depth

Spectra of a coating system of Au(2.0 µm)-Ni (2.1 µm) on Cu

excited by electrons (blue) and by X-Rays (red)

Cu can observed only with X-Ray excitation due to deeper penetration of X-Rays into the sample

⇒ **More representative sample characterisation for bulk samples**

⇒ **Examination of thicker layers or multiple-layer structures**

⇒ **but high sensitivity also for very thin coatings due to detector with high resolution and using low energetic radiation. Limits of detection in the sub-nm-range can be achieved**

Applications:

Analysis of thin AuPdNi-LAYERS (1)

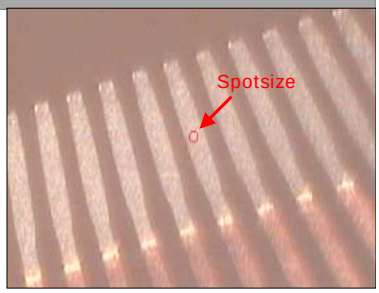
The Problem

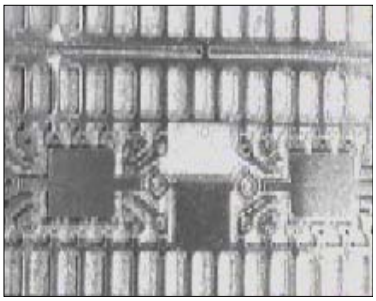
LeadFrames are produced actual from Cu. The contact area only is coated with Ag. Therefore they have to be masked which needs a few additional step in manufacturing procedure. The Ag-thickness is in the range of a few µm and can measured with XRF.

New LeadFrames will be "over all" coated with very thin Au on Pd on a Ni diffusion layer. Typical coating thickness are 10 – 30 nm of Au and 20 – 40 nm Pd. Sometimes the coatings are also without the intermediate Pd layer. These layers are prepared by electro-galvanic or sputtering procedures

For analysis of these thin layers it is necessary to have a very sensitive spectrometer i.e. a detector with high resolution and peak-to-background ratio.

Further it can be necessary to perform these measurements on very small areas. In this case a high intensity on the sample can realised with capillary optics that concentrate the radiation on a small spot.

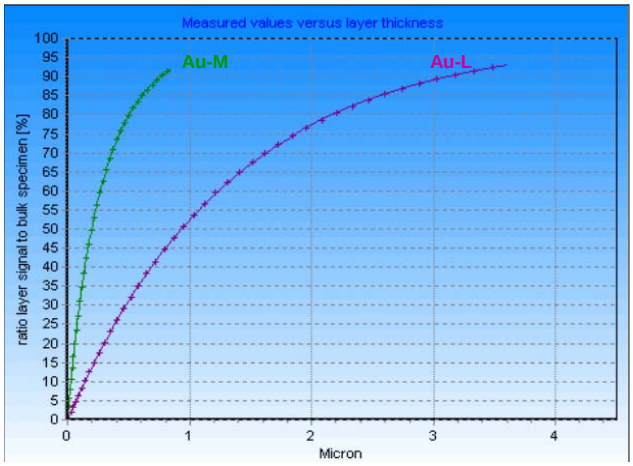




Applications:

Analysis of thin AuPdNi-LAYERS (2)

Self-absorption curves for Au-M and Au-L



Because of the stronger absorption of radiation with lower energies the slope for the M-radiation is higher than for the L-radiation.

That means the sensitivity for thin layers is better for the radiation with lower energy .

But than it is necessary to measure in vacuum!

The same is valid for the Pd-K and Pd-L radiation. The upper Au-coating is so thin that the absorption of Pd-L radiation is not to high.

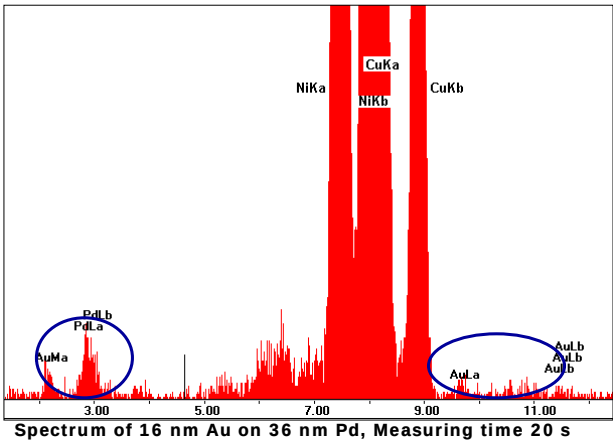
LOD for Au can be 0.1 nm for a measument time of 300 s.

Applications:

Analysis of thin AuPdNi-LAYERS (3)

This very thin layers gives weak signal that can be measured only with a high resolution detector. Another difficulty is caused by the requirement to measure the weak signal on a small sample area – down to 50 µm diameter.

This is possible only with the combination of a highly concentrated X-Ray beam (capillary optic) and a high peak-to-background ratio of the spectrometer (high resolution detector – for example Si(Li)).



Spectrum of 16 nm Au on 36 nm Pd, Measuring time 20 s

⇒ Peak intensities very small !!

⇒ Optimising excitation and measuring conditions

Applications:

Analysis of thin AuPdNi-LAYERS (4)

Repeatability and stability
(all values in nm)

Measurement		Au	Pd	Ni
Series 1 1000 x 30 s	Mean 3 σ	10.96 1.08	53.3 3.6	829 22
Series 2 800 x 30 s	Mean 3 σ	11.02 0.87	53.1 3.2	835 20
Series 3 1300 x 30 s	Mean 3 σ	10.82 0.96	51.9 2.9	820 25
Average	Mean RSD Mean - σ Mean + σ	10.93 ≈ 10 % 10.61 11.25	52.76 ≈ 7 % 51.66 53.86	828 ≈ 3 % 820 836

Conclusion

The stability (long term repeatability) of the instrument is in the range of the statistics.

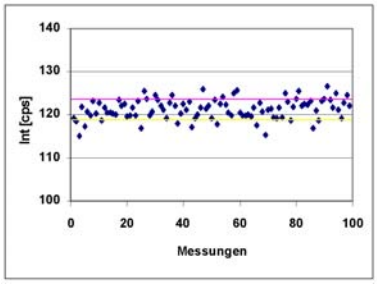
The average values of 3 repeatability measurements (over 3 different days) are within 1 sigma deviation

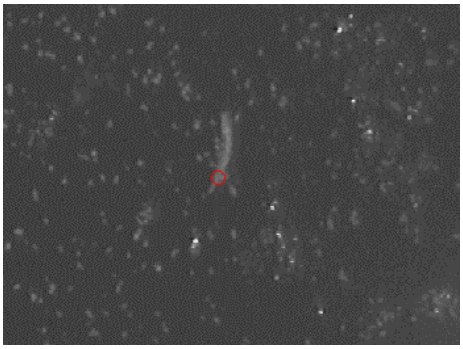
Sample stability

The absorption of radiation in the sample can influence the sample stability.

Prominent examples are salts. In case of electron excitation the sample size can be reduced very fast which can be observed on the SEM.

On the other hand for X-Ray excitation no changes of the sample can be observed. Therefore the intensity of S was measured for a longer period of time.





Crystallites from Ammoniasulfate [NH4)2SO4]

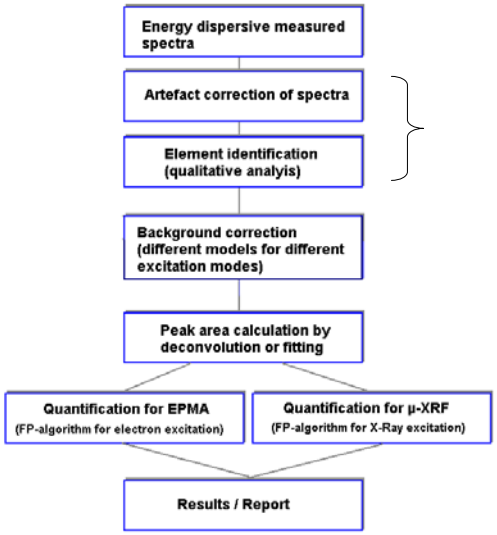
Measurement conditions:

40 kV, 200 µA, 8 W, dead time approx. 55 %, vacuum

Measuring time: 100 x 20 s, repeated

No intensity change of a long period

Quantification model for XRF



⇒ **Measurement with available EDS-detector**

⇒ **can be done both with EDS or iMOXS software package**

⇒ **different models for both excitation necessary**

⇒ **possible again with EDS-software**

⇒ **different models has to be used, iterative combination of results of both excitation needs special software**

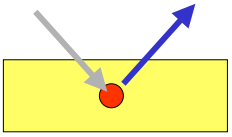
EPMA quantification is perforemd by PUZAF models

Quantification model for XRF (by Tim Elam, EDAX)

$$I_i = G \cdot \int_E \frac{\frac{S-1}{S} \cdot c_i \cdot p_i \cdot \omega_i \cdot \tau_i(E)}{\frac{\mu(E)}{\sin\psi_{inc}} + \frac{\mu(i)}{\sin\psi_{takeoff}}} \cdot I_0(E) \cdot dE$$

Sherman relation

Kramer, Ebel ..



Second order terms are not shown, third order terms are not considered

This integral will be calculated iteratively for different concentrations till calculated and measured intensities are convergent

This procedure offers the possibility

- **to implement single standards to improve the rightness of the analytical result of XRF**
- **to implement concentrations from elements that are quantified with EPMA (light elements).**

Improvement of the rightness in case of presence of light elements by their consideration either for matrix interaction and for normalisation.

With:

G	-	Geometry- and Alignment factor
(S – 1)/S	-	Jump-Ratio
ω	-	Fluorescence yield
τ	-	Photo absorption coefficient
p	-	Transitions probability
μ	-	Mass absorption coefficient
ψ	-	Incident/Take Off angle
I_0(E)	-	Excitation spectrum

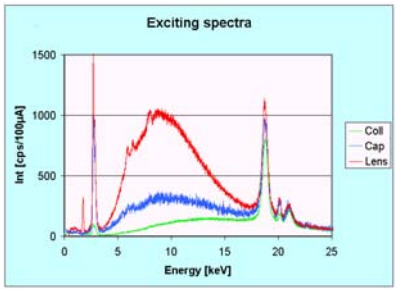
Fundamental-Parameters are known

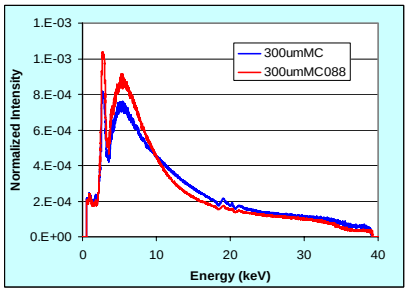
Geometry factor is fitted by normalisation

Excitation spectrum of the tube is influenced by the optic!!

Quantification model for XRF

All parameters are known in the Sherman relation. But it has to be considered that the excitation spectrum from the tube will be influenced by the capillary optic.





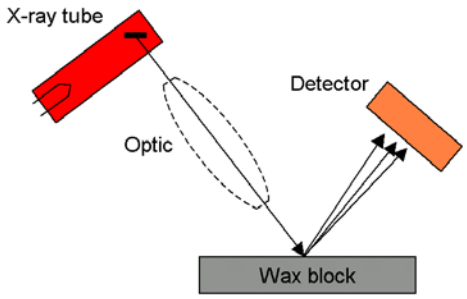
The influence of the optic depends on

- **the type of the optic** (Mono-cap, Poly-cap lens)
- **the optic itself**
- **the alignment of the optic in the instrument**

=> It is necessary to measure the excitation spectrum for every optic in the instrument and in the aligned position

Quantification model for XRF

Measurement of the excitation spectrum



In SEM's the geometry is changing for every instrument.

The scatter spectrum with optic can measured in the SEM but the spectrum without optic would require every time a new adjustment.

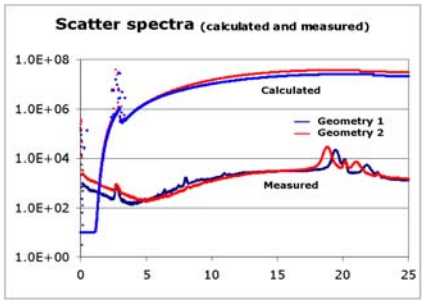
The direct measurement of excitation spectrum is not possible in the instrument (geometrical reason, high intensity)

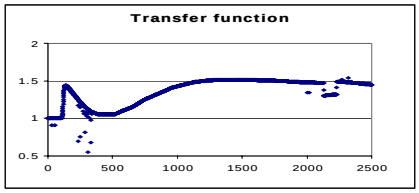
Therefore the following procedure will be used:

- ⇒ **Measurement of the scatter spectrum in the instrument both with and without X-Ray optic**
- ⇒ **Determination of the influence of the scatterer from measurement without optic**
- ⇒ **Determination of the influence of the optic from measurement with optic**
- ⇒ **Calculation of the transmission function of the optic**

Quantification model for XRF

Calculation of scatter spectra





The measurement of the scatter spectrum w/o optic can not be done in the instrument.

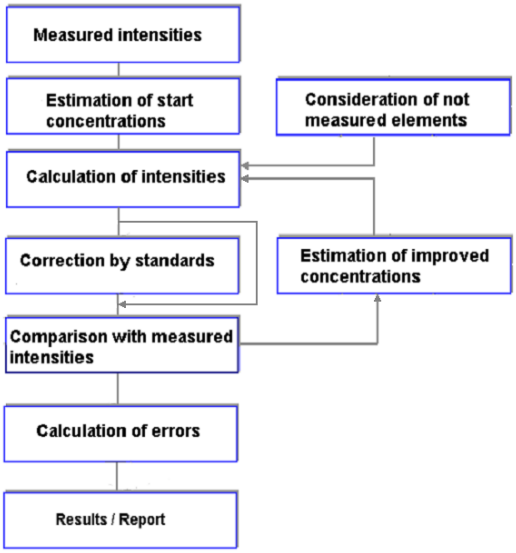
Therefore it is intended to measure the scatter spectrum w/o optic only for one geometry and transfer this to other geometries.

For that reason the scatter spectra can be calculated for different geometries. Between measured and calculated scatter spectra are still some differences caused by detector effects etc.

It is intended to calculate a transfer function from the calculated spectra and use this transfer function to a measured scatter spectrum for one geometry.

$$I_{scatter,Geo1} = \frac{I^{calc}_{scatter,Geo1}}{I^{calc}_{scatter,Geo2}} \cdot I^{Measured}_{scatter,Geo2}$$

Calculation principle for quantification (by Tim Elam, EDAX)



⇒ Measurement with EDS-detector

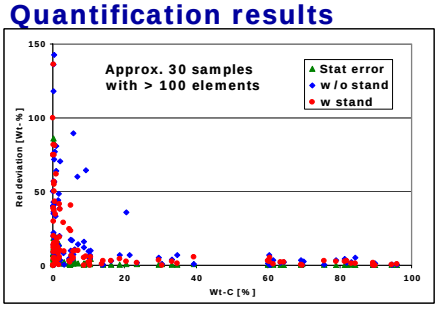
⇒ not measured elements (i.e. light elements) can be considered

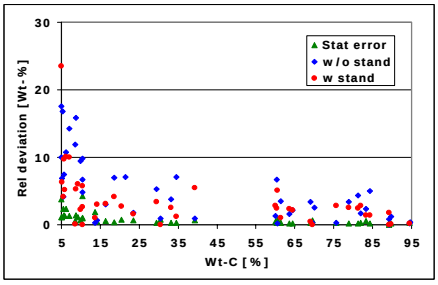
⇒ Correction with standards (if available)

⇒ Test of differences between predicted and measured intensities (for less 0.1 %)

⇒ Combination of statistical error and error due to intensity difference

Quantification results





Different reference samples (steel, Cu-alloys) were analysed both wo / w one standard

Results:

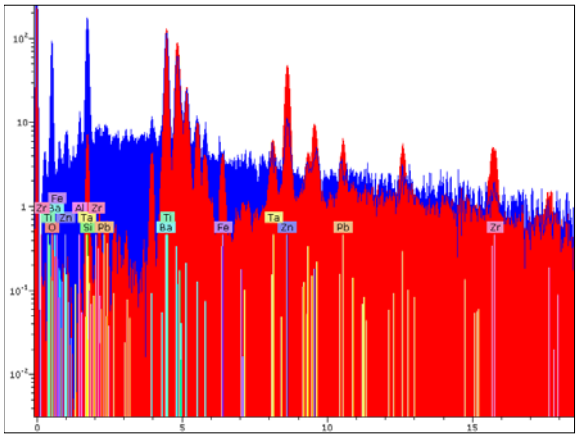
- Consideration of the modification of excitation spectrum seems to work correctly
- Relative deviation from correct result is larger for small concentrations
- Quantification with standards improves the accuracy
- The statistical error is significantly smaller than the deviation

  ⇒ the model, the consideration of the optic influence or fundamental parameters have to be improved

Average relative deviations for major and minor components (C > 5 %)

	Major & Minor C > 5 %	Major C > 30 %
wo stand	8.9 %	2.2 %
w stand	3.2 %	1.9 %
Stat error	0.9 %	0.4 %

Analysis of an oxid – glass



Measurement condition (comparable count rate and intensity)

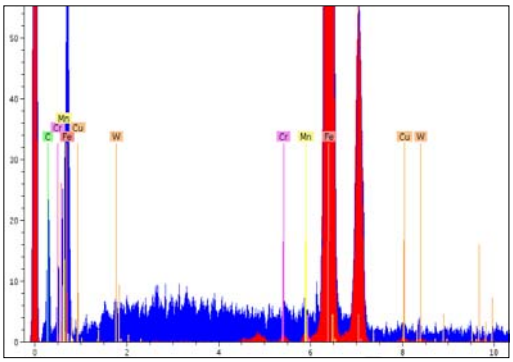
Electron: 20 kV, 2 nA

X-Ray: 40 kV, 350 µA

Analysis of a glass with both modes of excitation

- **light elements are better excited with electrons, traces of heavy elements cannot be detected**
- **heavy elements (especially traces) are better excited with X-Rays, in general L-series of heavy elements can be used, but there is a strong overlapping**
- **sensitivity in the range of Z ≈ 20 is comparable for both excitations**

Analysis of a low alloyed steel (with content of C)



Measurement conditions (comparable count rate and intensity)

Electron: 25 kV, 500 nA

X-Ray: 40 kV, 200 µA

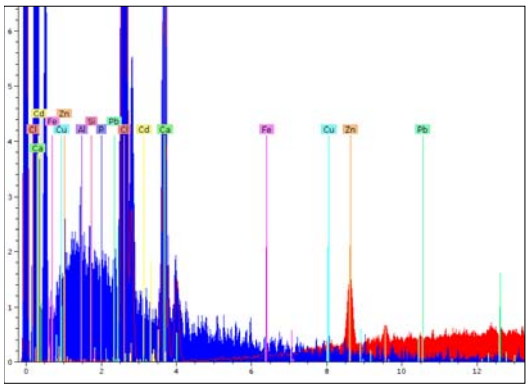
Carbon cannot detected with XRF but with EPMA excitation

Small concentrations of Cr, Mn, Cu and W are covered in EPMA spectrum by the background of bremsstrahlung

⇒ Determination of Carbon with EPMA and using this result for XRF quantification

Elem	Given	EPMA	XRF w/o stand	XRF w stand	EPMA + XRF
C	4.98	4.51	n.d.	n.d.	4.51
Cr	0.15.	n.d.	0.13	0.12	0.11
Mn	0.12	n.d.	0.33	0.21	0.21
Fe	93.49	95.49	96.70	98.30	93.87
Cu	0.28	n.d.	0.37	0.26	0.25
W	0.98	n.d.	2.47	1.11	1.06

Analysis of a plastic sample (PVC)



Measurement condition (comparable count rate and intensity)

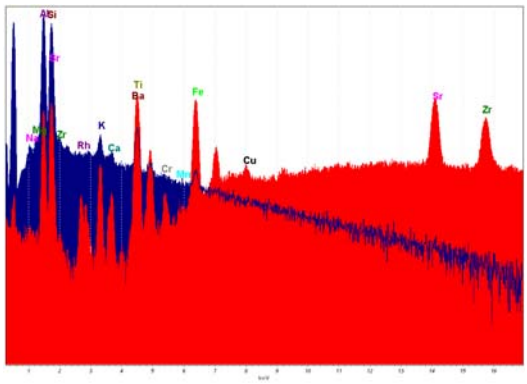
Electron: 20 kV, 2 nA

X-Ray: 40 kV, 350 µA

		iMOXS	EPMA	EPMA +RFA
	Given	Wt-%	Wt-%	Wt-%
C	ns	nd	62.05	62.05
O	ns	nd	17.22	17.22
Cl	ns	67.08	13.21	15.9
Ca	4.5	31.75	4.69	4.69
Fe	ns	0.04	0.57	0.003
Cu	ns	0.11	1.12	0.01
Zn	0.05	0.69	1.14	0.08

Elements that cannot be measured with XRF can determined with EPMA. Their concentrations can be introduced into the XRF-calculation.

Analysis of an oxid – glass K 13



Measurement condition (comparable count rate and intensity)

Electron: 20 kV, 2 nA

X-Ray: 40 kV, 350 µA

Analysis of an oxid – glass K458

Quantification result (Conc are given in Wt-% and error in %)

Elem	Given	EPMA		iMOXS				EPMA + XRF
	Wt-%	Wt-%	stat. error	Wt-%	stat. error	Oxide Wt-%	from oxide Wt.%	Wt-%
O	56.7	55.9		nd			49.16	55.9
Mg	0.088	0.56	7.5	nd				0.56
Al	20.71	21.9	1.4	39.90	1	48.3	25.57	21.47
Si	20.19	19.2	1.5	50.70	0.9	47.4	22.16	20.10
P	0.152	0.50	7.2	0.32	60.1	0.25	0.20	0.095
K	0.42	0.42	4.5	1.40	3.3	0.55	0.46	0.402
Ca	0.095	0.08	17.2	0.29	8.0	0.13	0.09	0.081
Ti	1.11	1.17	3.6	3.79	0.6	1.96	1.18	1.030
Cr		nd		0.06	3.6	0.024	0.02	0.014
Fe	0.320	0.33	7.9	1.31	0.6	0.54	0.38	0.329
Cu		nd		0.03	3.0	0.11	0.09	0.007
Ga		nd		0.03	3.0	0.10	0.07	0.006
Sr	0.153	nd		0.81	0.5	0.261	0.22	0.191
Zr		nd		0.28	0.8	0.104	0.08	0.067
Ba	0.062	nd		1.14	2.5	0.394	0.34	0.309

Oxygen is considered here by the stoichiometric relation to the element

EPMA + RFA:

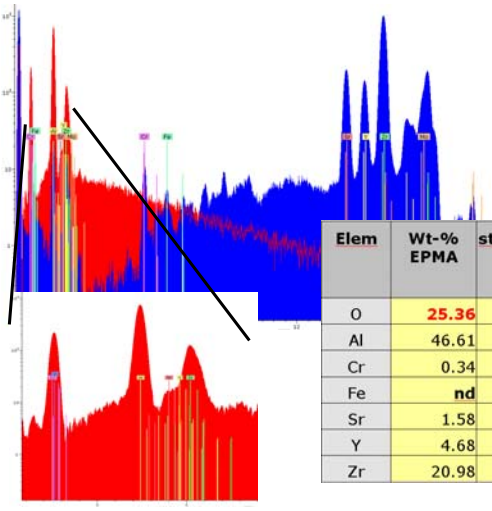
In case of using the analytical result with better statistics and combine the quantification it is possible to improve rightness of the results.

Oxid-ratio:

The stoichiometric relation of oxygen to the elements can be used to calculate the concentration. In this case the oxygen can take into account for the matrix interaction. From the known oxyd ratios the content of oxygen can be calculated.

Analysis of an ceramics

Quantification result (Conc are given in Wt-% and error in %)



The analysis of an ceramic (oxid) can be improved in case of combination of results of EPMA and XRF due to

- the better identification of heavy elements (Sr,Y,Zr)
- the use of results of light elements from EPMA for better matrix interaction

Elem	Wt-% EPMA	stat.error [%]	Wt-% XRF-oxid	stat.error [%]	Transfer to elem Wt-%	Wt-% ESMA+RFA
O	25.36	1.05	nd		30.71	25.36
Al	46.61	0.36	25.46	2.30	13.48	16.16
Cr	0.34	5.14	0.33	2.40	0.23	0.26
Fe	nd		0.11	3.30	0.08	0.09
Sr	1.58	2.92	6.63	0.50	5.61	5.80
Y	4.68	1.66	6.03	0.50	4.75	5.28
Zr	20.98	0.75	61.44	0.20	45.16	47.07

Conclusion and perspectives

- **Excitation with X-Rays concentrated by capillary optics in a Electron Microscope can improve the analytical performance due to higher sensitivity for traces and larger information depth**
- **Further for quantification the combination of results both from EPMA and XRF can enhance the rightness of analysis**
- **A real quantification model is used by an iterative solution of the Sherman relation. The influence of the capillary optic to the excitation spectrum is taken into account by a measurement of the scattering spectrum within the instrument. This procedure is working well and allows a good semi-quantitative analysis**
- **Errors of the Fundamental Parameters, excitation geometry etc. can be corrected if single standards are available. This will improve the accuracy**
- **For samples with a high content of very light elements like C,N,O,F it is possible to use the EPMA results within the Sherman relation. This improves the accuracy of the analytical result**
- **Calculation of scattering spectra would simplify the preparation for quantification. First tests was successful but have to be improved**

=> µ-XRF can be an interesting option for a SEM to improve the analytical performance and expand the range of applications