Microfluorescence X dans le MEB : principe, apports, comparaison avec l'EDS

(Micro-X-ray fluorescence combined with SEM/EDX)

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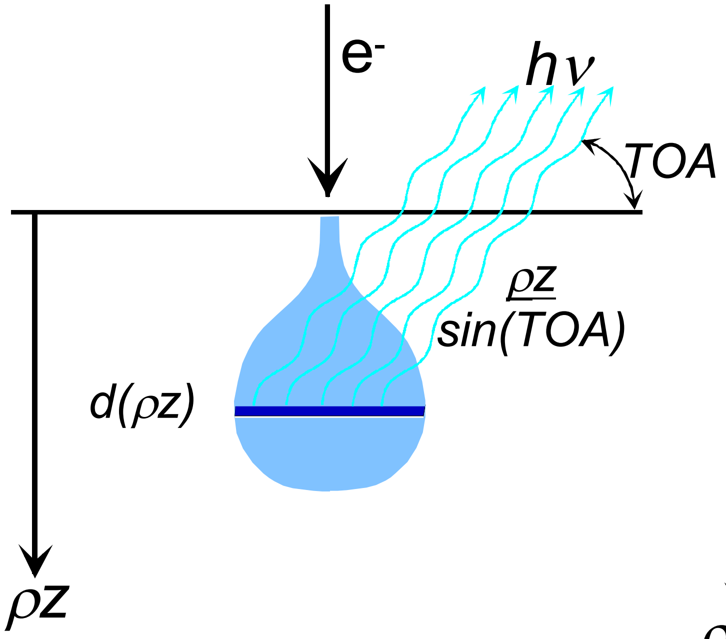
Outline

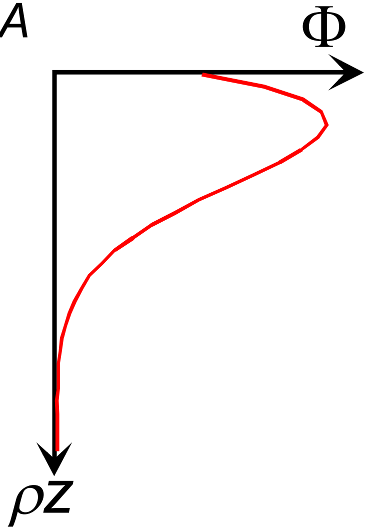
- X-ray spectroscopy - physical background
- Experimental equipment and software for µ-XRF with SEM/EDX
- Examples of application
- Summary and Outlook

X-ray spectroscopic methods

Method	Excitation	Abbr.
Electron probe microanalysis	keV-Electrons	**EPMA** (WD-EPMA), **EDS**, EDX, ED-EPMA
X-ray fluorescence analysis	X-ray Photons	**XRF** (WD-XRF, ED-XRF)
Proton induced X-ray emission	MeV-Protons	**PIXE**

EPMA: analysed specimen volume





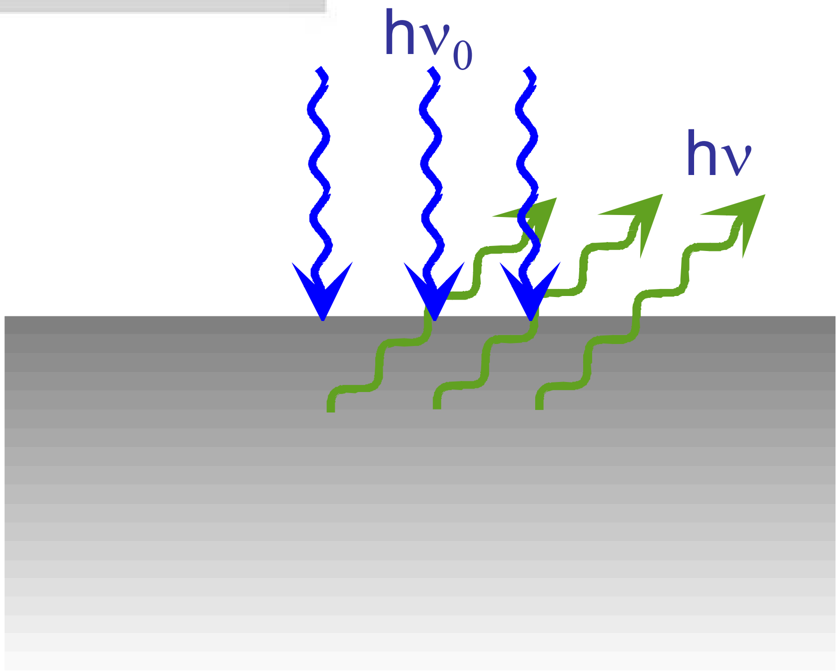
Stopping of primary electrons determines size of analysed specimen volume !

Dmr. ~ 1 µm

Spectrum = characteristic radiation + bremsstrahlung

Bremsstrahlung sets the detection limit!

XFA: analysed specimen volume



Absorption of **emitted** X-radiation determines size of analysed specimen volume !

depth: 10 ... 100 µm

Detection of buried objects

Spectrum = characteristic radiation (+ scattered radiation)

Low background is the reason for low detection limits (down to 10 ppm level)

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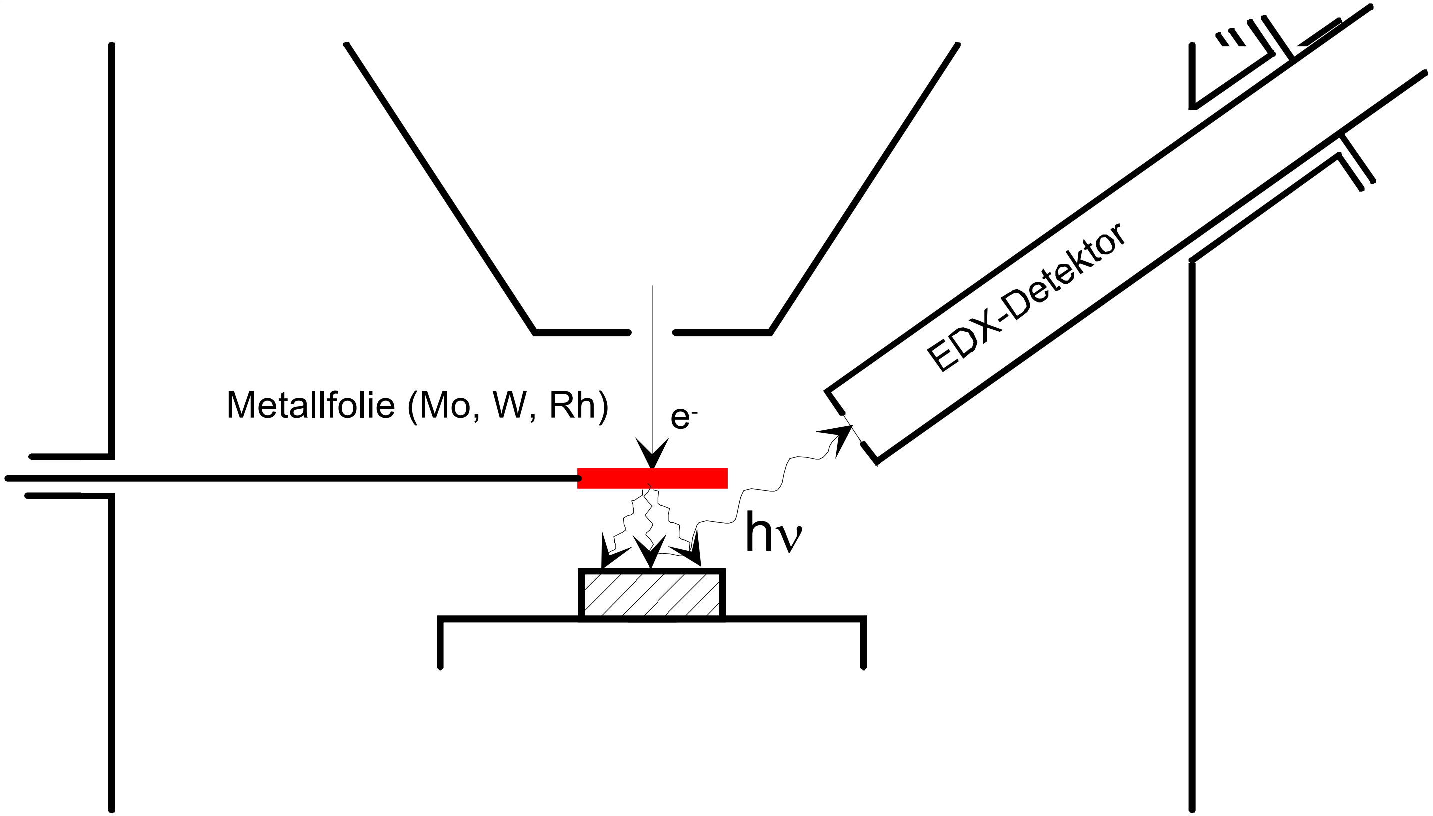
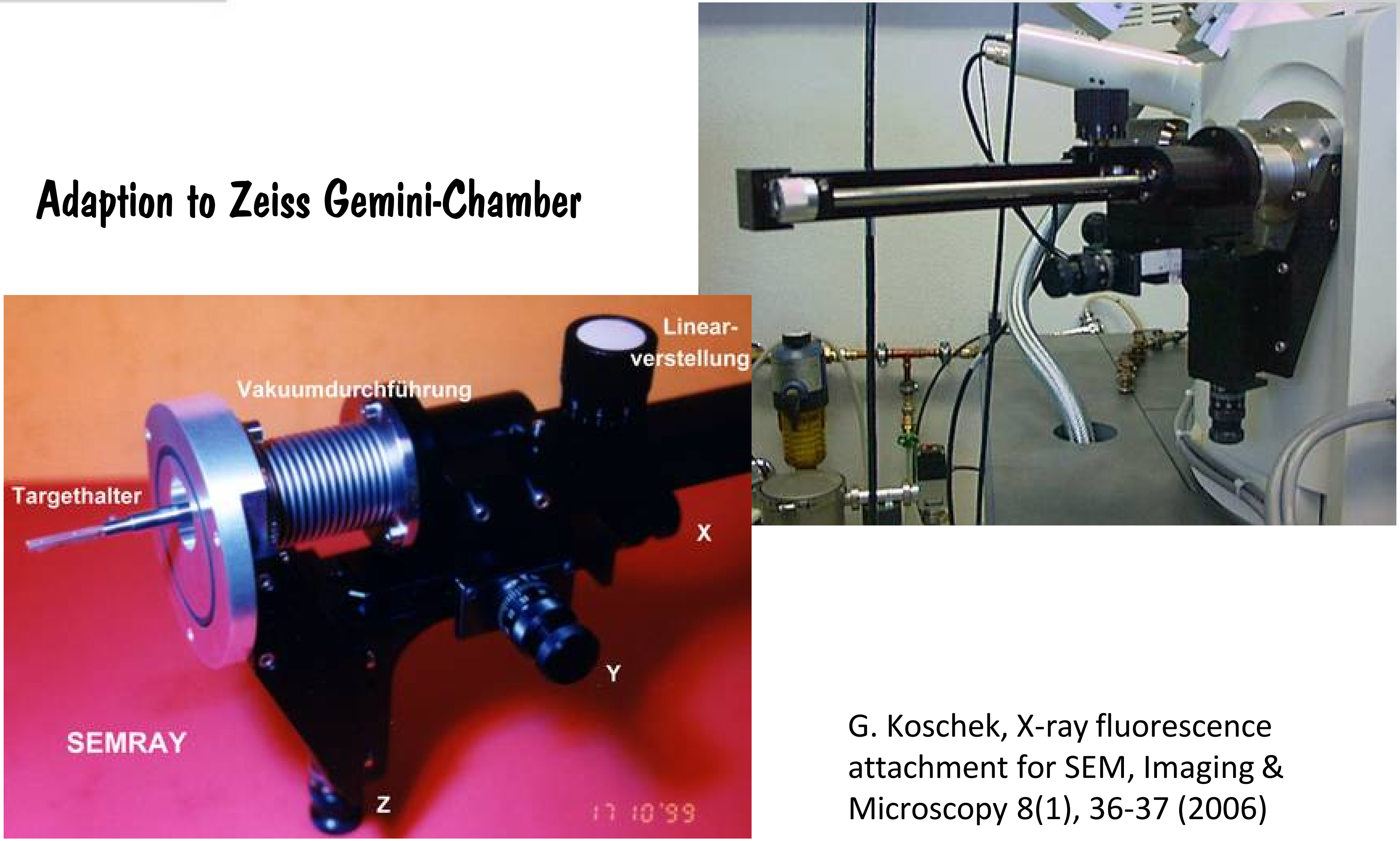
ED-XRF with SEM since EDS has become commercially available !



Drawback: low X-ray power – 0.3 mW @ 30 kV and 10 nA

SEMRAY

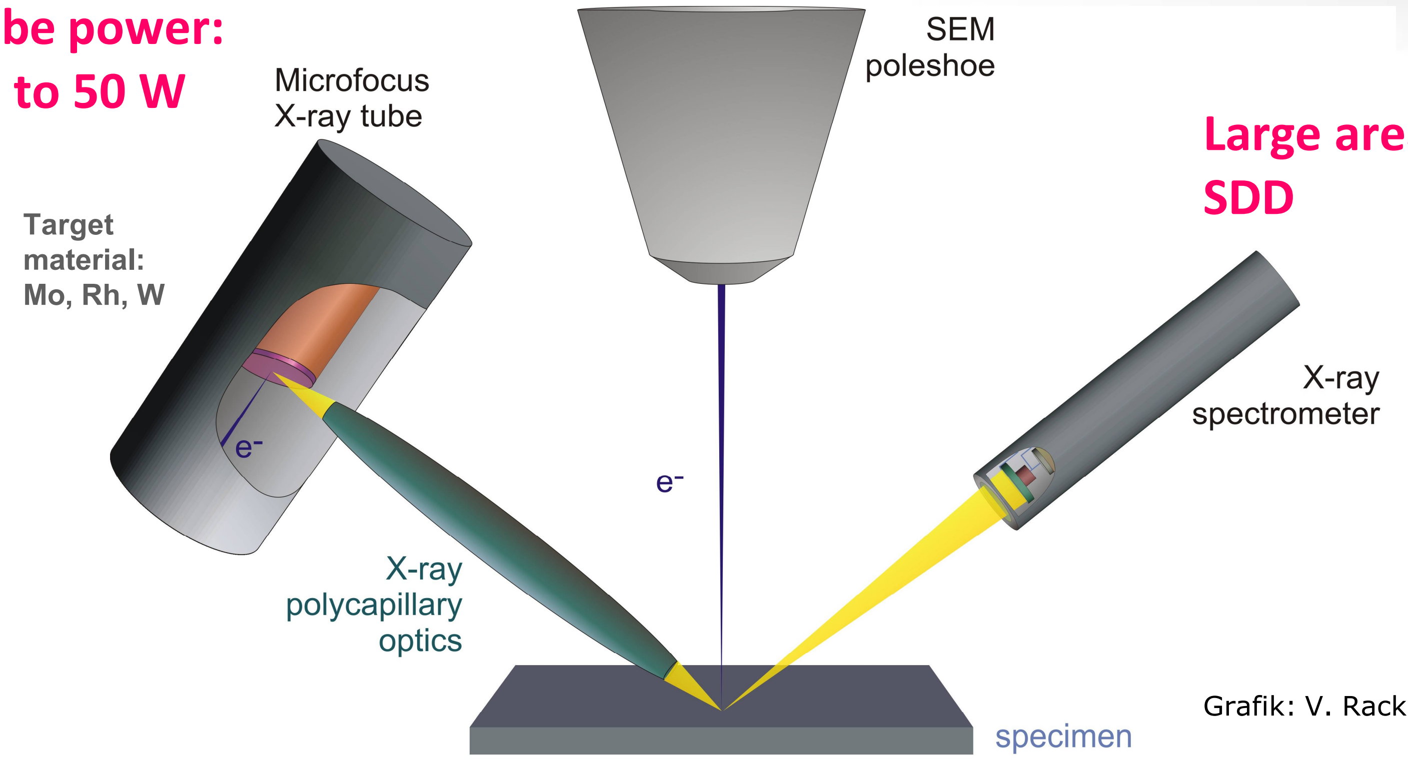
Adaption to Zeiss Gemini-Chamber



G. Koschek, X-ray fluorescence attachment for SEM, Imaging & Microscopy 8(1), 36-37 (2006)

Modern µ-XRF with SEM/EDX - principle

Tube power:
30 to 50 W



Large area SDD

Grafik: V. Rackwitz, BAM

Combination of electron microscopy, electron beam micro-analysis and X-ray fluorescence analysis

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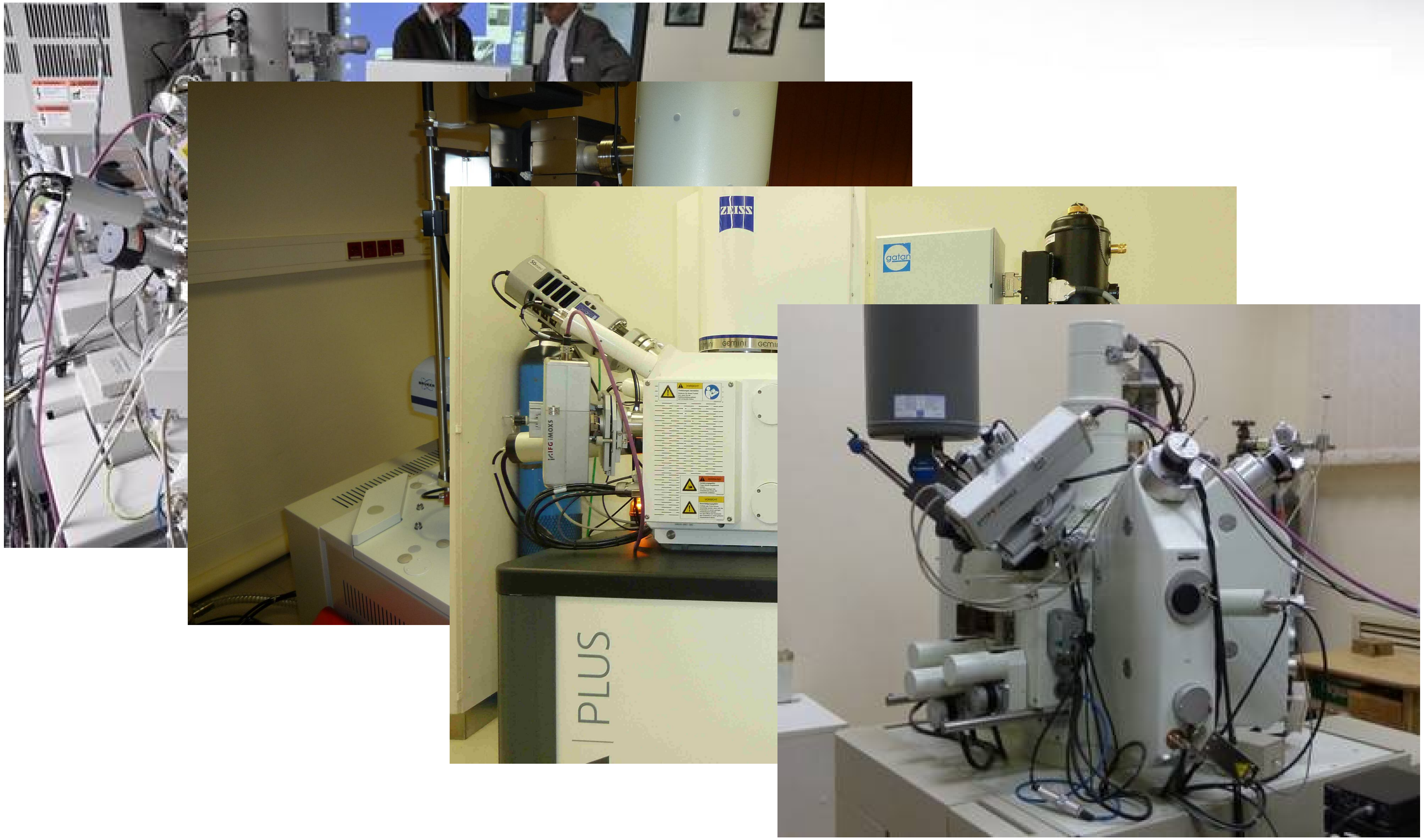
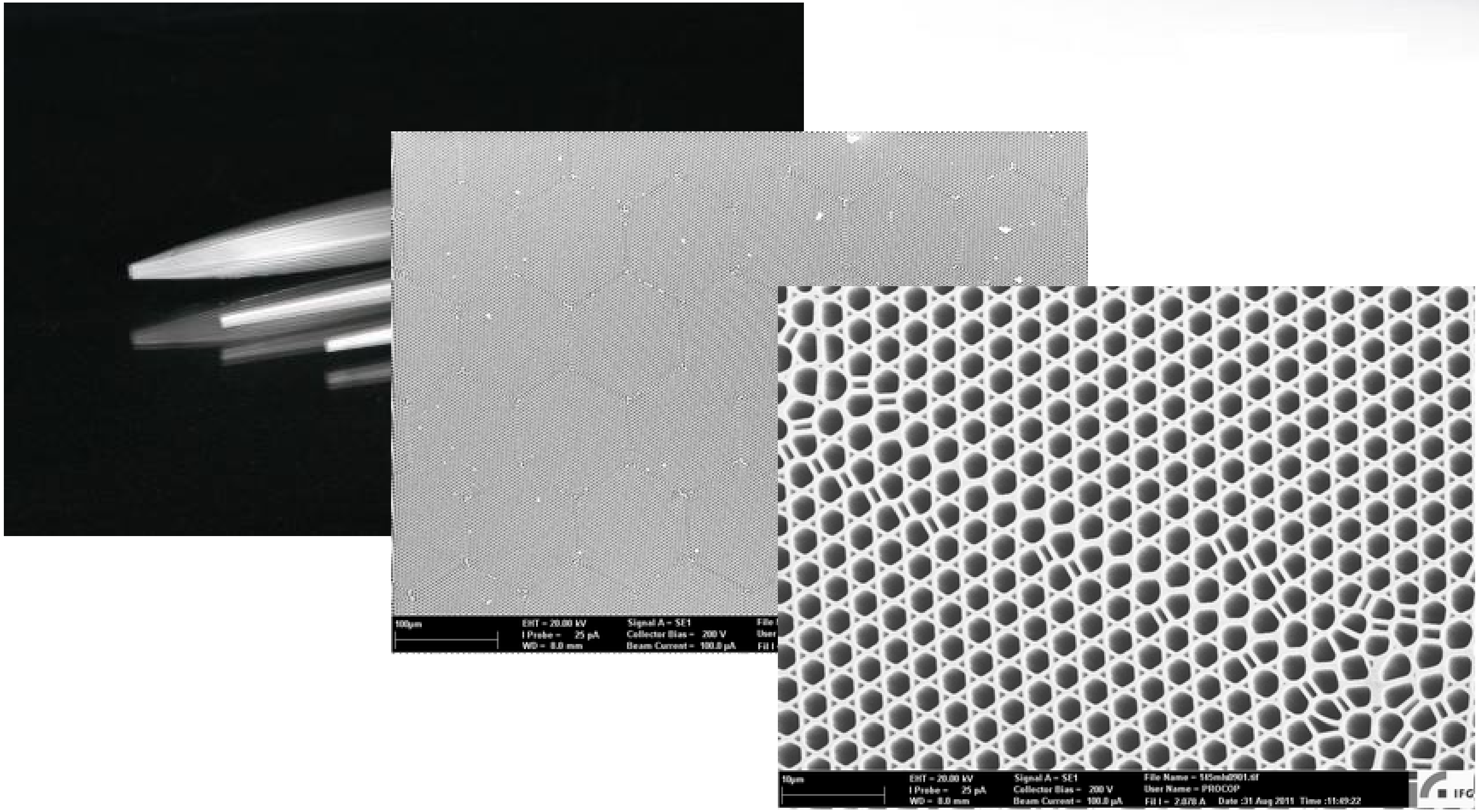
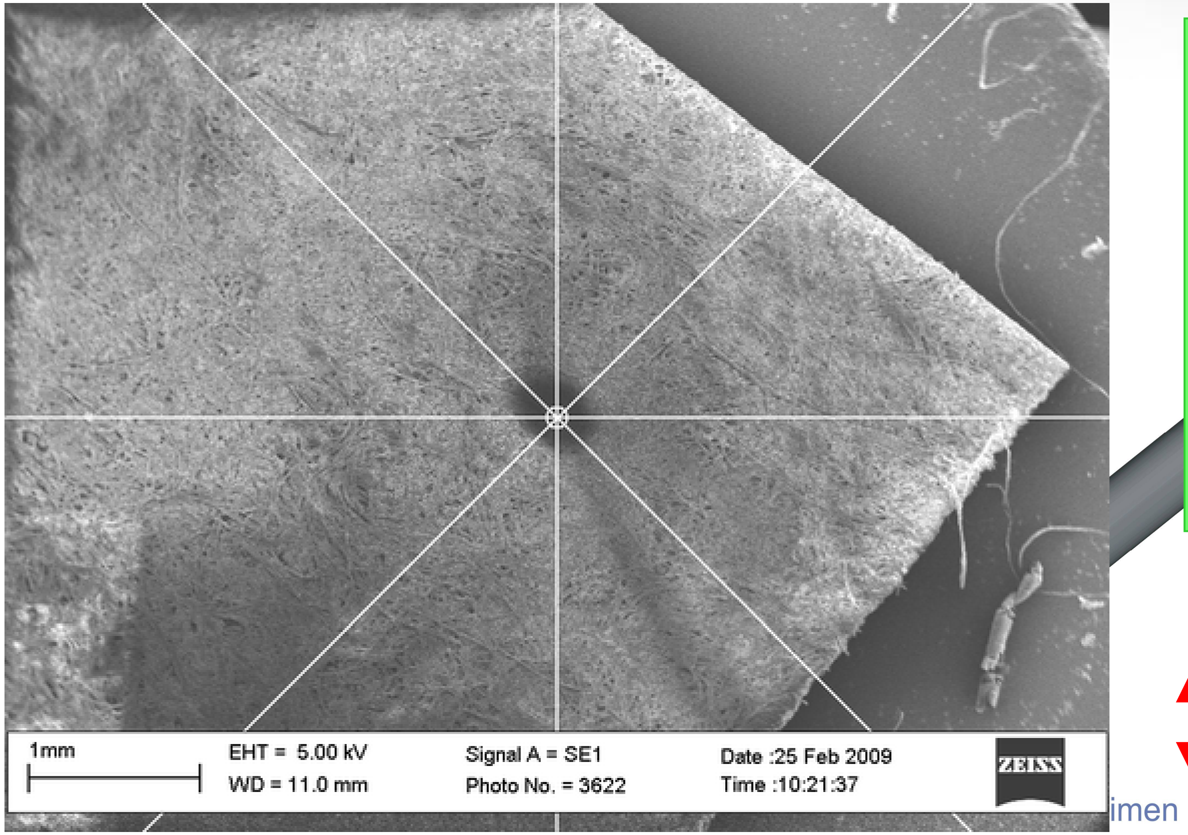
Analytical SEM with EDS, (WDS), EBSD, CL and µ-XRF



IfG – Institute for Scientific Instruments GmbH: Manufacturer for X-ray optics and related instruments



Alignment of micro-focus X-ray source



SEM-Parameters:

HV ≤ 5 kV

I_p ≤ 10 pA

Frame Average

Fast Scan

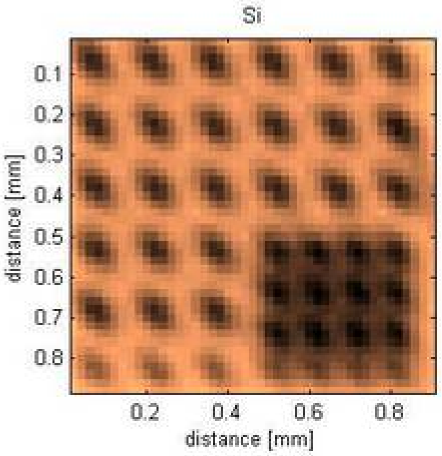
(typ. for LV REM)

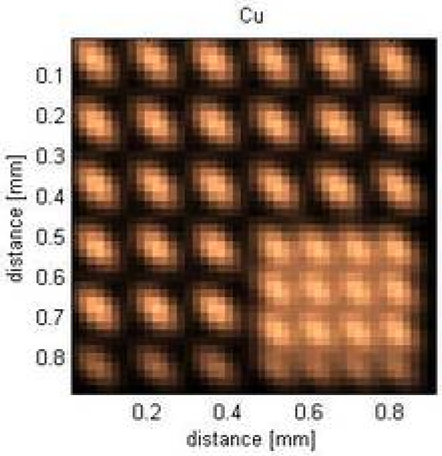
Correct WD is critical to analyse same specimen area

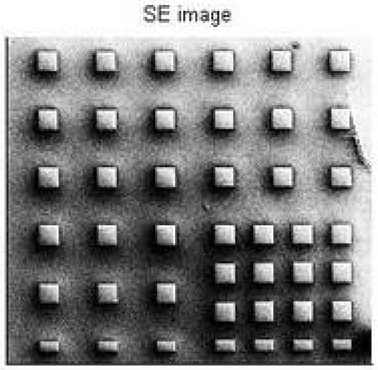
Specimen can be continuously observed at low HV and small beam current

Spatial resolution

(50 µm stripes and squares)







Test structures from

FhG-IZM, Berlin

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Instruments

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- X-ray spectroscopy - physical background
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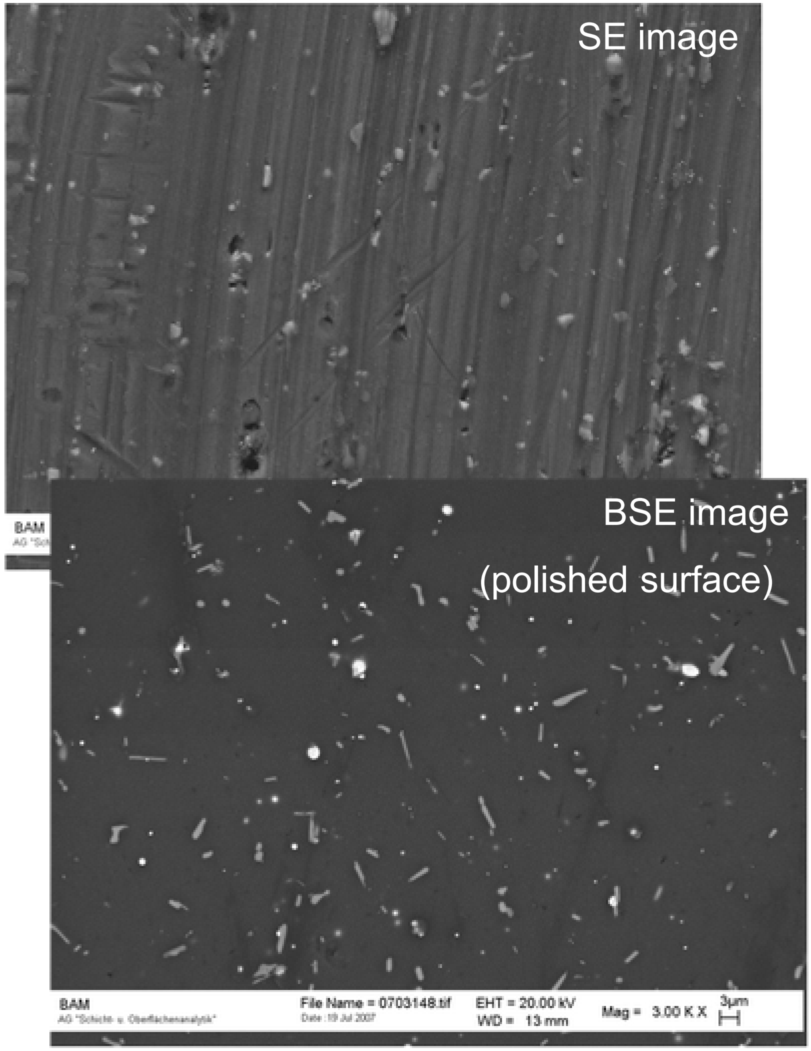
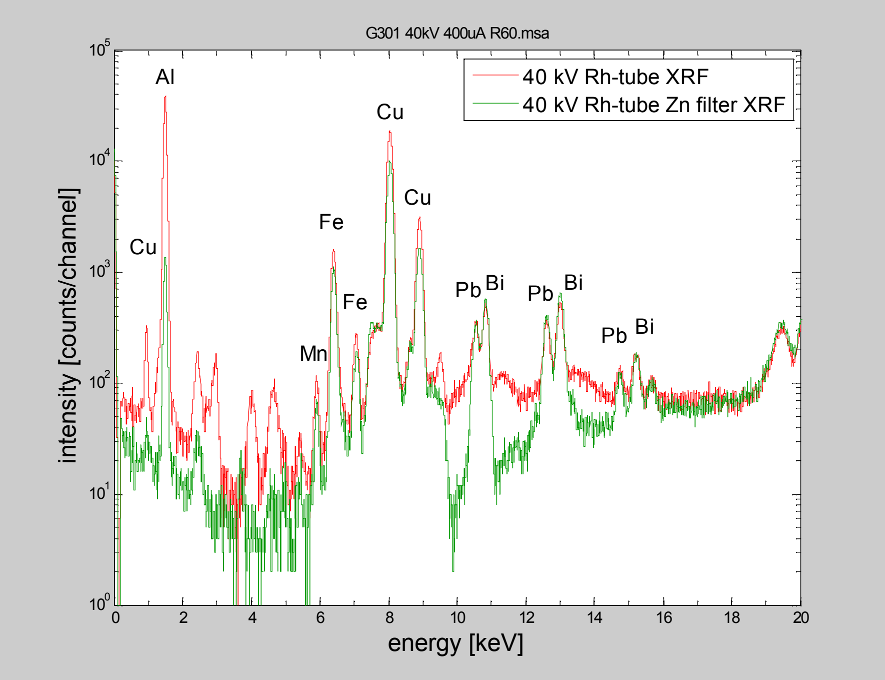
- Examples of application:
  (1) combined EPMA+µ-RFA+SEM investigation
- Summary and Outlook

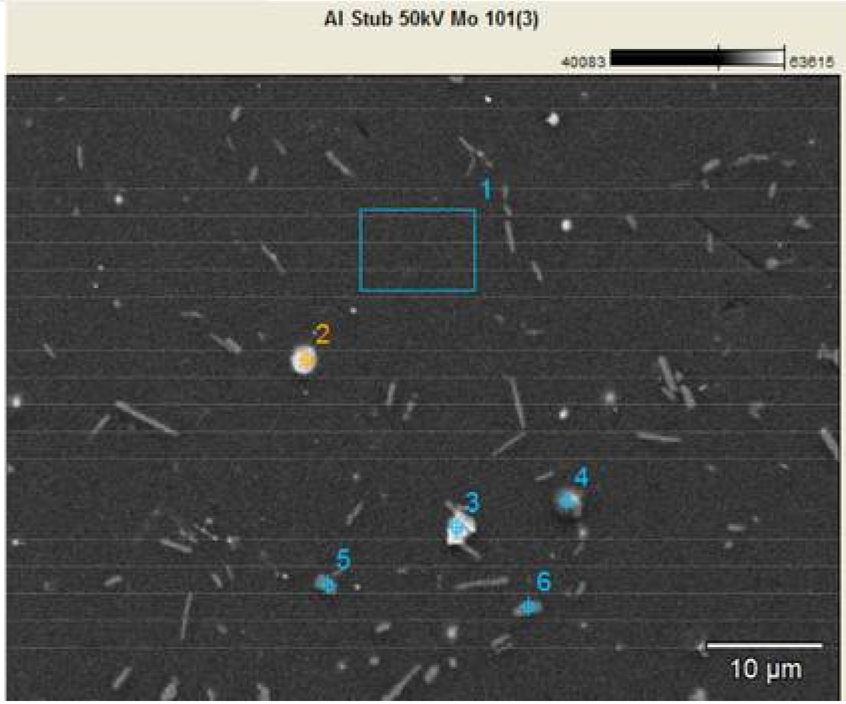
Aluminum forgeable alloy (SEM sample holder Agar G301)

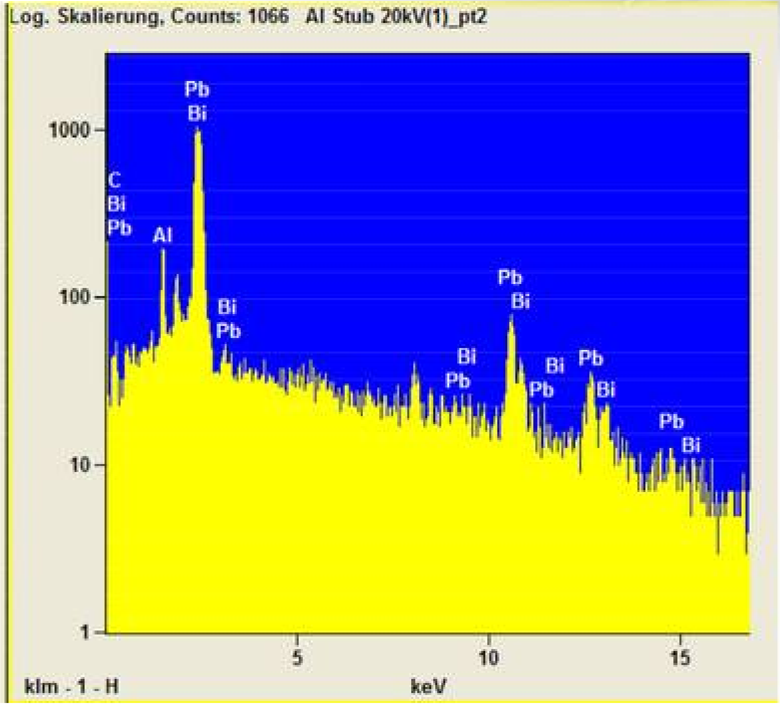




Standardless EPMA (ESPRIT)	
element	wt. %
Al-K	93.5
Cu-K	5.8
Fe-K	0.7
Total	100.00

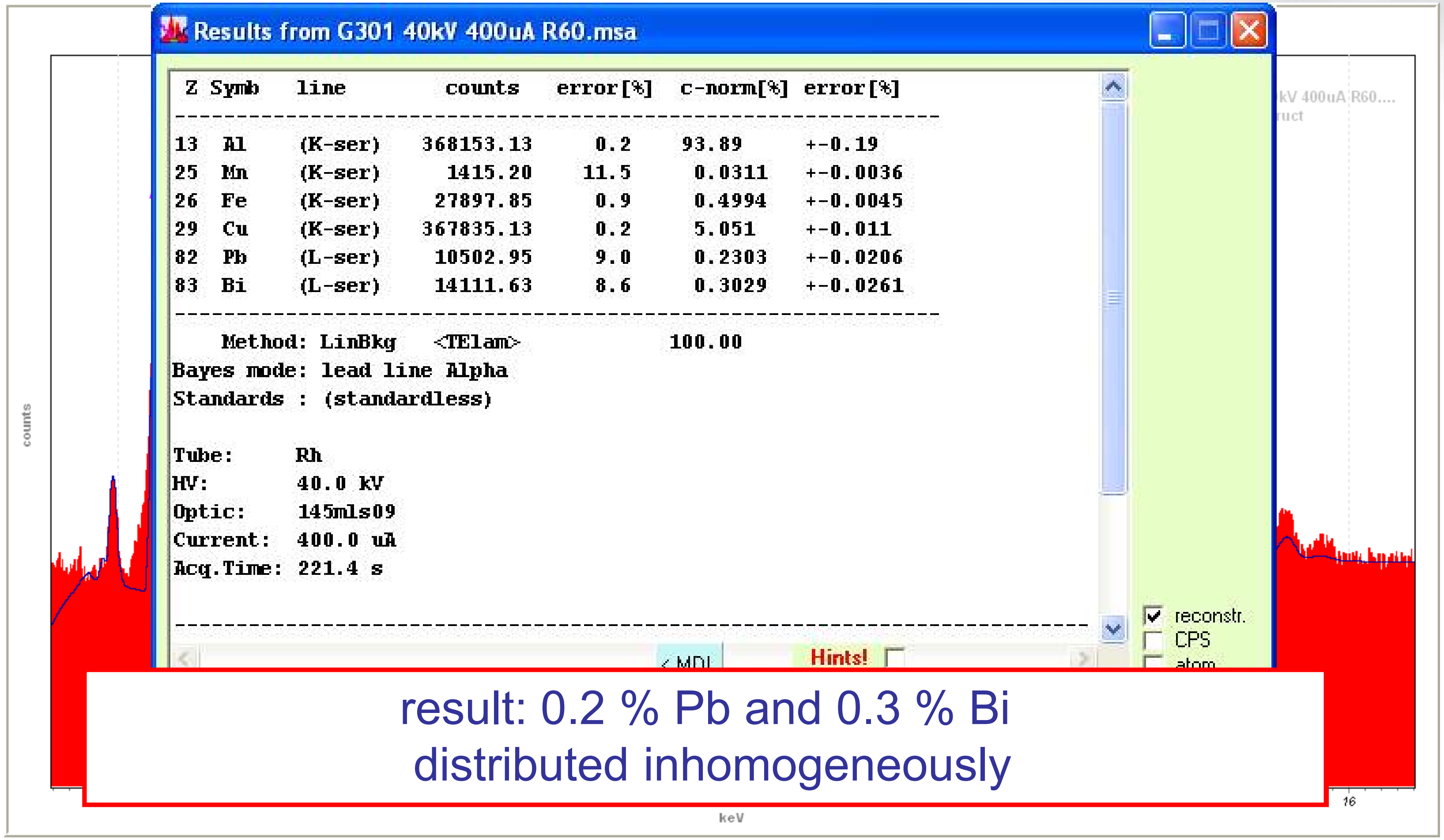
Aluminum forgeable alloy : EPMA





- EPMA identifies bright spots as Pb-Bi precipitates, but
- What about Pb and Bi concentration in the specimen?

Aluminum forgeable alloy: µ-XRF



```
 Z Symb   line          counts   error[%]  c-norm[%] error[%]
------------------------------------------------------------------
13  Al    (K-ser)    368153.13     0.2     93.89     +-0.19
25  Mn    (K-ser)      1415.20    11.5      0.0311   +-0.0036
26  Fe    (K-ser)     27897.85     0.9      0.4994   +-0.0045
29  Cu    (K-ser)    367835.13     0.2      5.051    +-0.011
82  Pb    (L-ser)     10502.95     9.0      0.2303   +-0.0206
83  Bi    (L-ser)     14111.63     8.6      0.3029   +-0.0261
------------------------------------------------------------------
    Method: LinBkg   <TElam>               100.00
Bayes mode: lead line Alpha
Standards : (standardless)

Tube:      Rh
HV:        40.0 kV
Optic:     145mls09
Current:   400.0 uA
Acq.Time:  221.4 s

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result: 0.2 % Pb and 0.3 % Bi
distributed inhomogeneously

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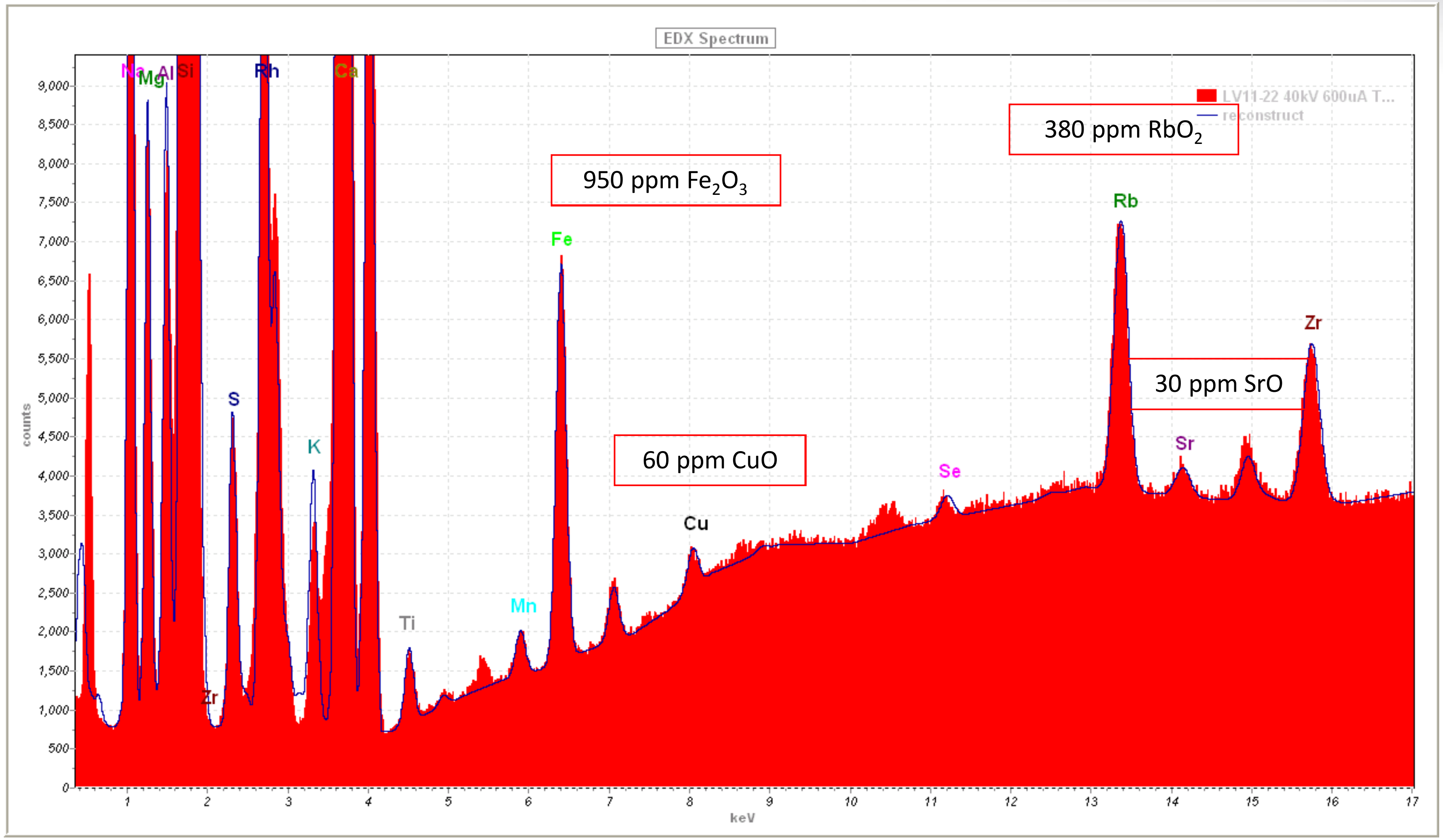
- Examples of application:
  (2) trace elements in glasses, polymers and minerals
- Summary and Outlook

Trace elements in glass
(EDS proficiency test nanoAnalytics 2011)



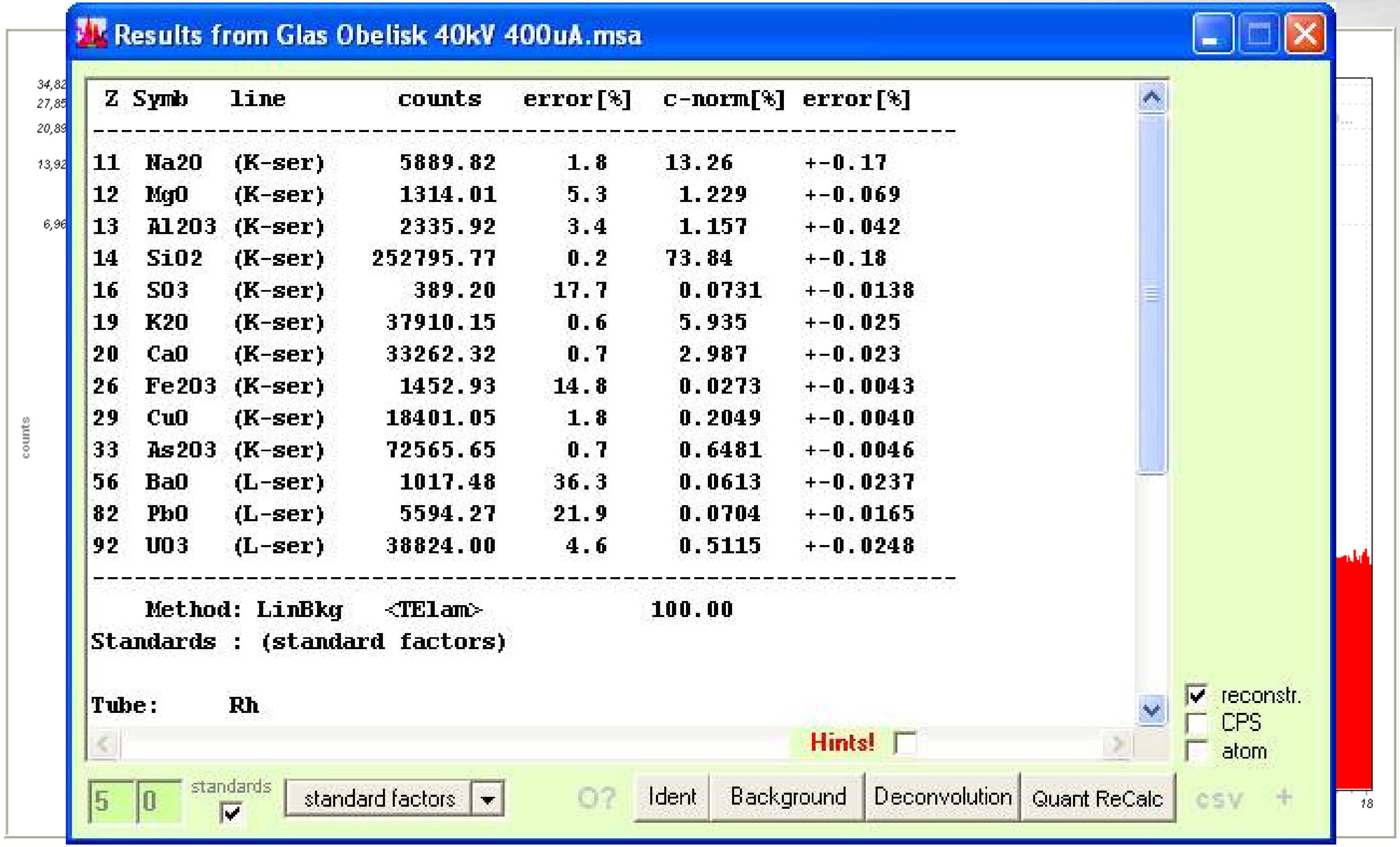
950 ppm Fe_2O_3

380 ppm RbO_2

60 ppm CuO

30 ppm SrO

Decorative glasses

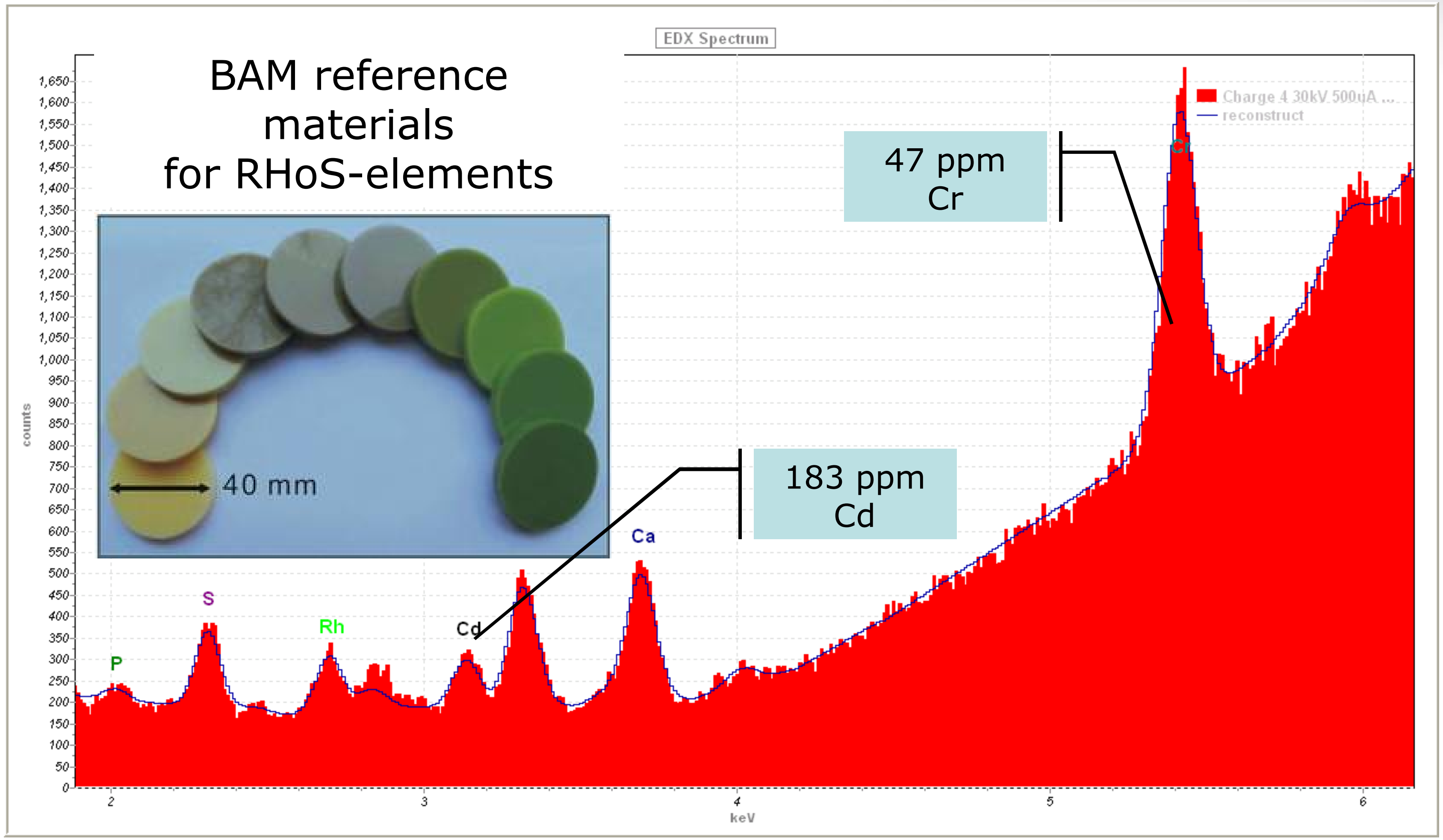


Results from Glas Obelisk 40kV 400uA.msa

```
 Z Symb   line         counts   error[%]  c-norm[%] error[%]
-------------------------------------------------------------
11  Na2O  (K-ser)     5889.82      1.8     13.26     +-0.17
12  MgO   (K-ser)     1314.01      5.3      1.229    +-0.069
13  Al2O3 (K-ser)     2335.92      3.4      1.157    +-0.042
14  SiO2  (K-ser)   252795.77      0.2     73.84     +-0.18
16  SO3   (K-ser)      389.20     17.7      0.0731   +-0.0138
19  K2O   (K-ser)    37910.15      0.6      5.935    +-0.025
20  CaO   (K-ser)    33262.32      0.7      2.987    +-0.023
26  Fe2O3 (K-ser)     1452.93     14.8      0.0273   +-0.0043
29  CuO   (K-ser)    18401.05      1.8      0.2049   +-0.0040
33  As2O3 (K-ser)    72565.65      0.7      0.6481   +-0.0046
56  BaO   (L-ser)     1017.48     36.3      0.0613   +-0.0237
82  PbO   (L-ser)     5594.27     21.9      0.0704   +-0.0165
92  UO3   (L-ser)    38824.00      4.6      0.5115   +-0.0248
-------------------------------------------------------------
    Method: LinBkg   <TElam>           100.00
Standards : (standard factors)

Tube:      Rh
```

Trace elements in polymers: (Cr and Cd in Acrylonitrile butadiene styrene (ABS))



BAM reference materials for RHoS-elements

40 mm

47 ppm Cr

183 ppm Cd

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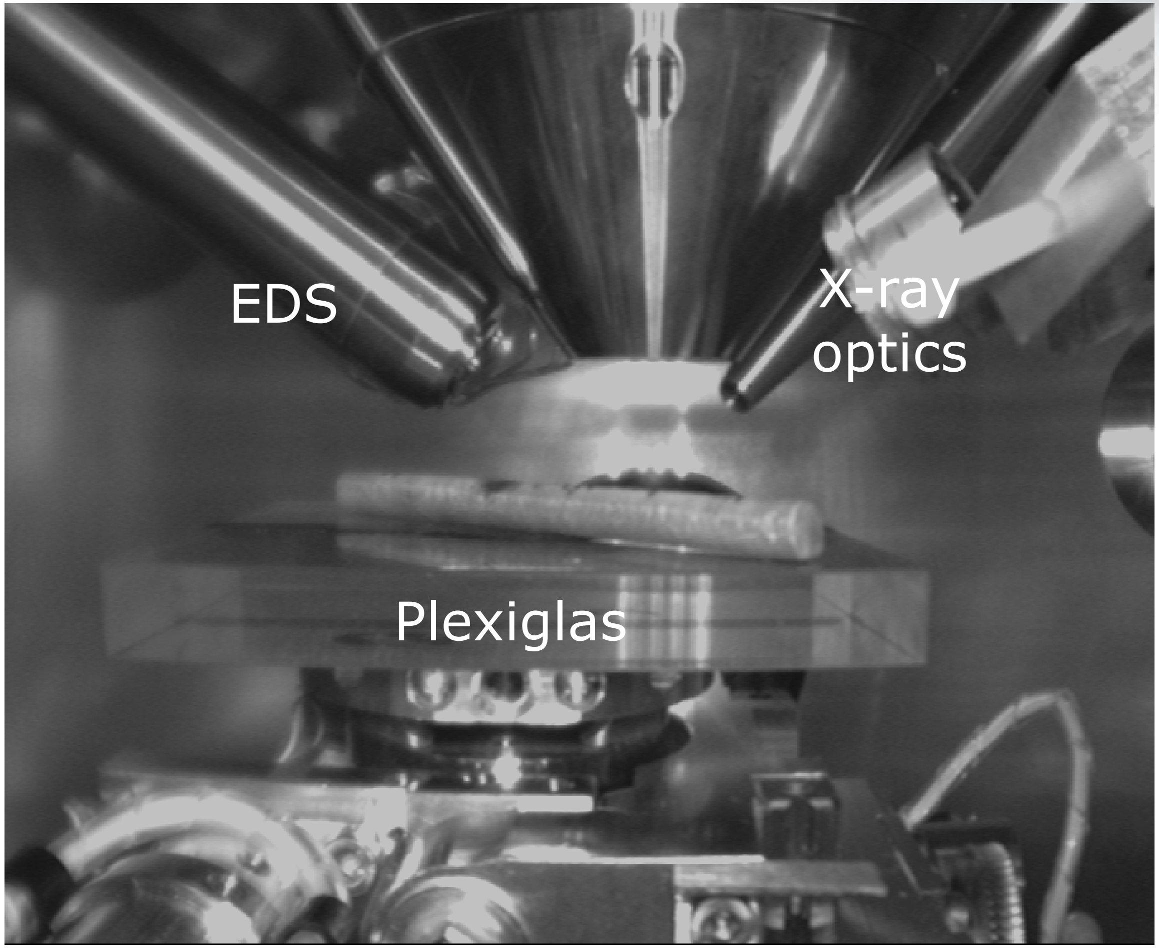
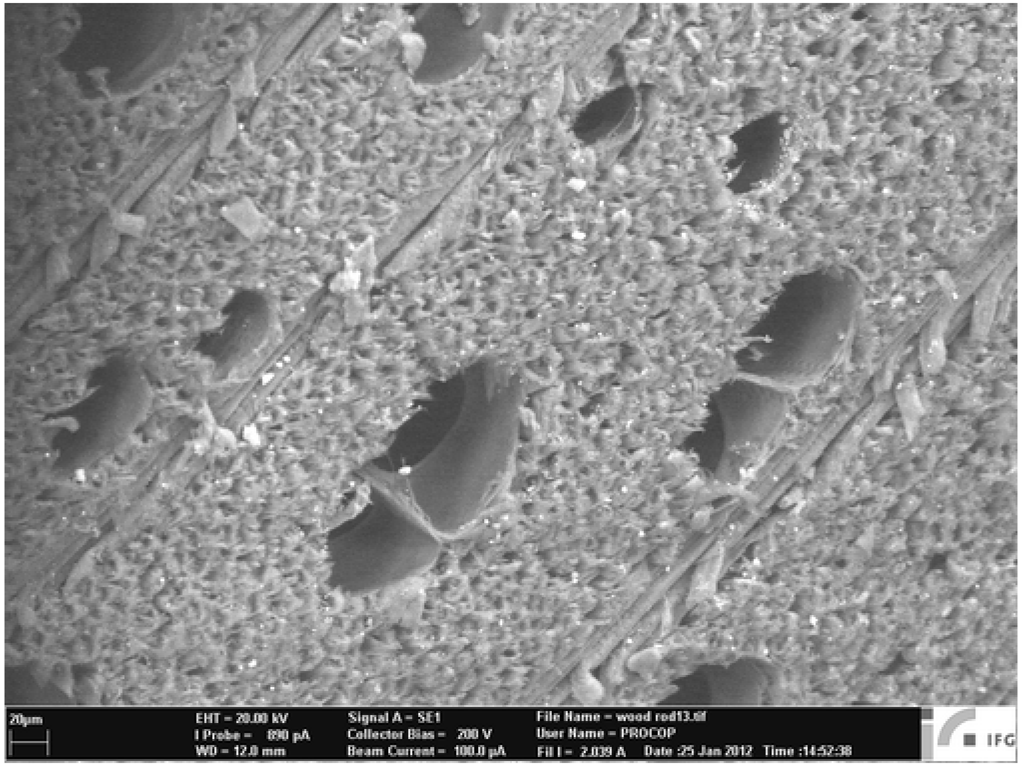
Maple wood



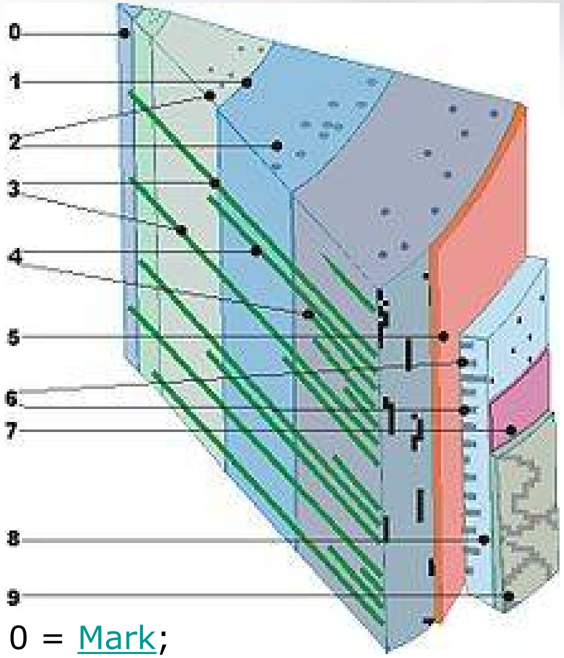
Maple rod, perpendicular to annual growth rings, in Zeiss EVO 40

Maple wood - SEM



SEM-image in VP-mode

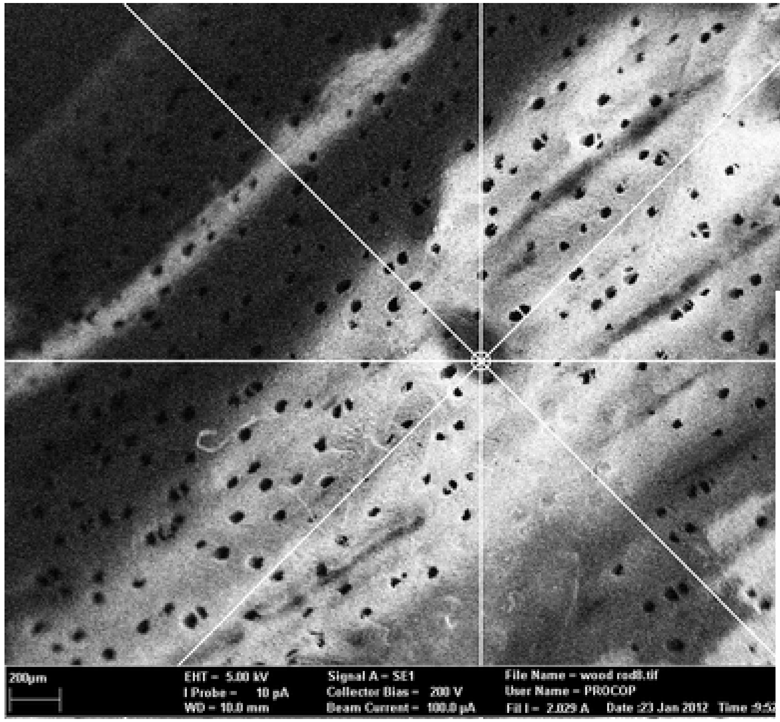
Probe: Dr Rose, INRA Nancy



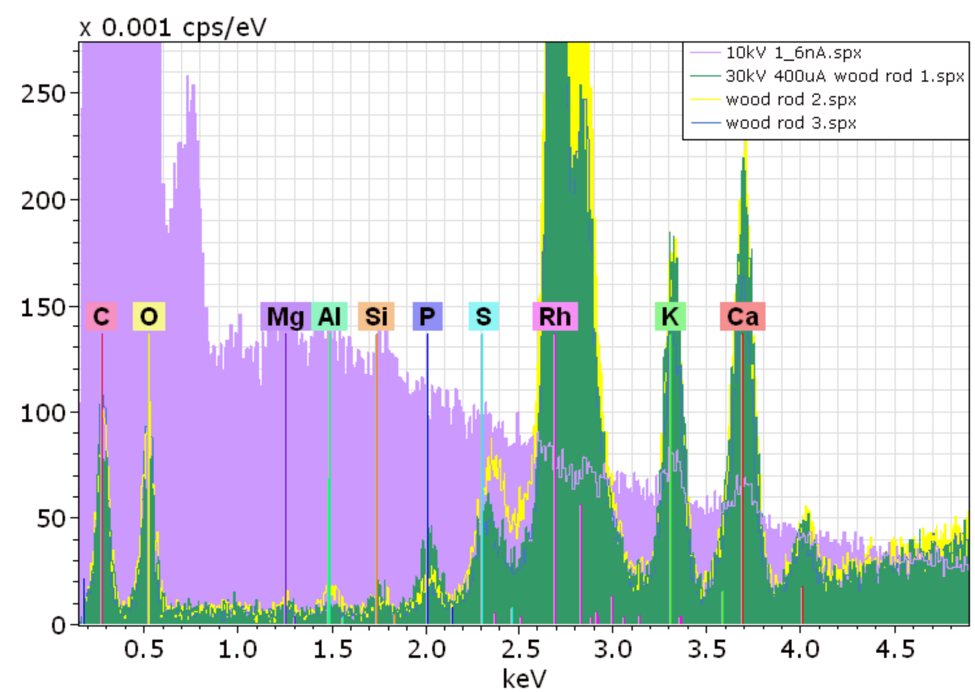
0 = Mark;
1 Jahresringgrenze;
2 Harzkanäle;
3 Primäre Holzstrahlen;
4 Sekundäre Holzstrahlen;
5 Kambium;
6 Holzstrahlen des Bastes;
7 Korkkambium; 8 Bast;
9 Borke

(Quelle: Wikepedia)

Maple wood - µ-XRF

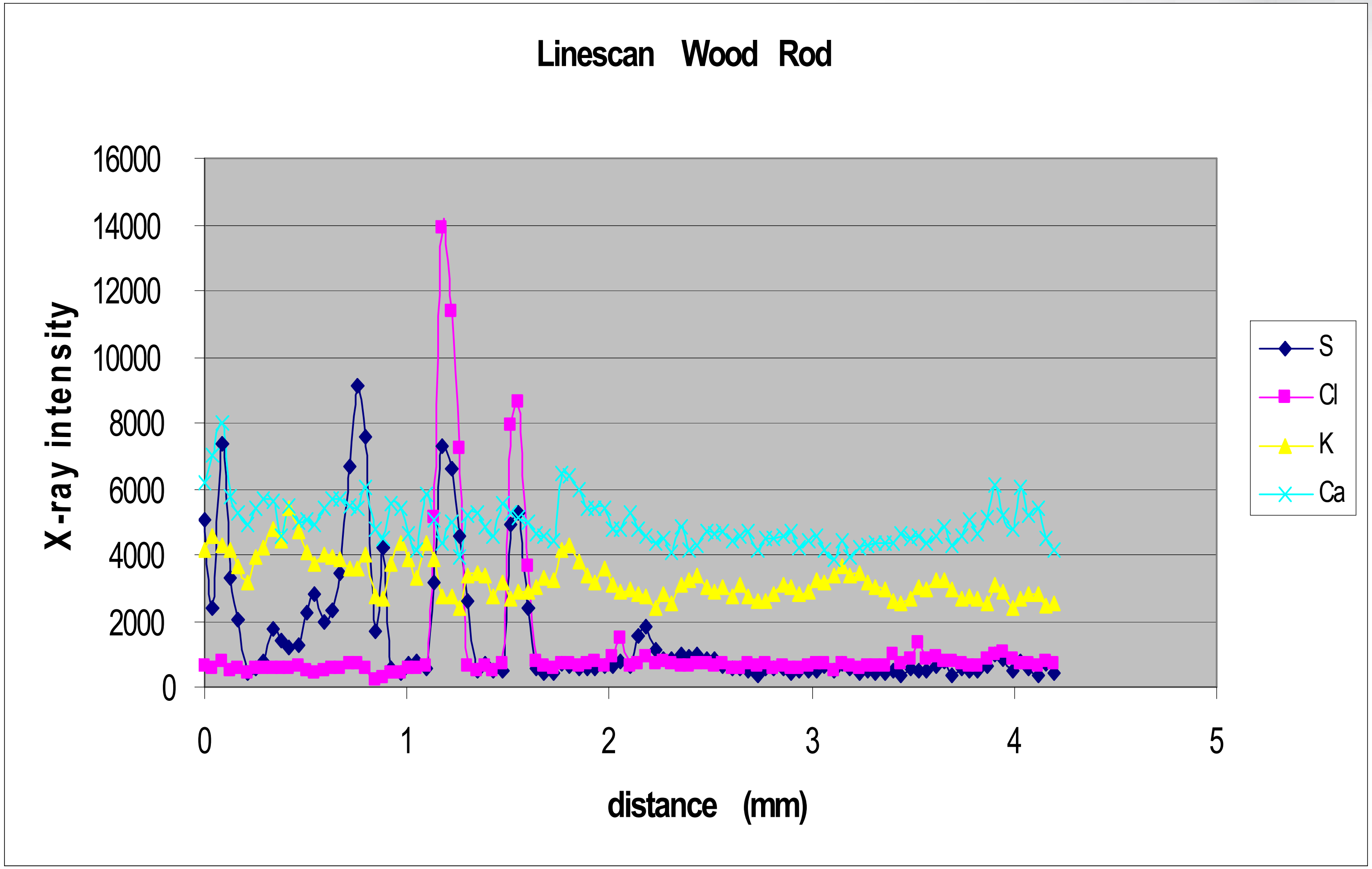


SE-image in HV-mode when X-ray source is turned on

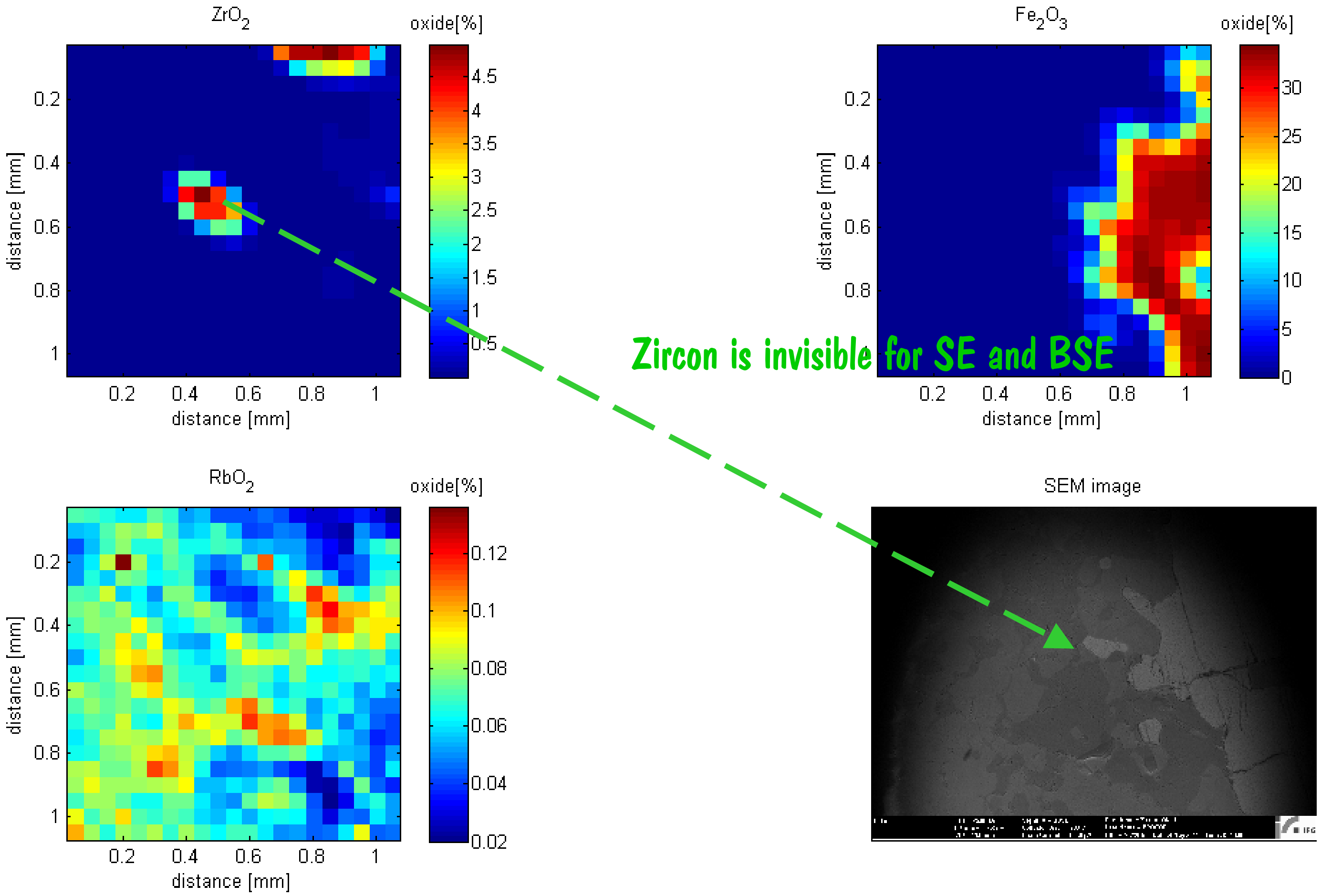


ED-ESMA and ED-XRF
(about same count rates and
measurement times)

Maple wood
Line scan perpendicular to annual growth rings

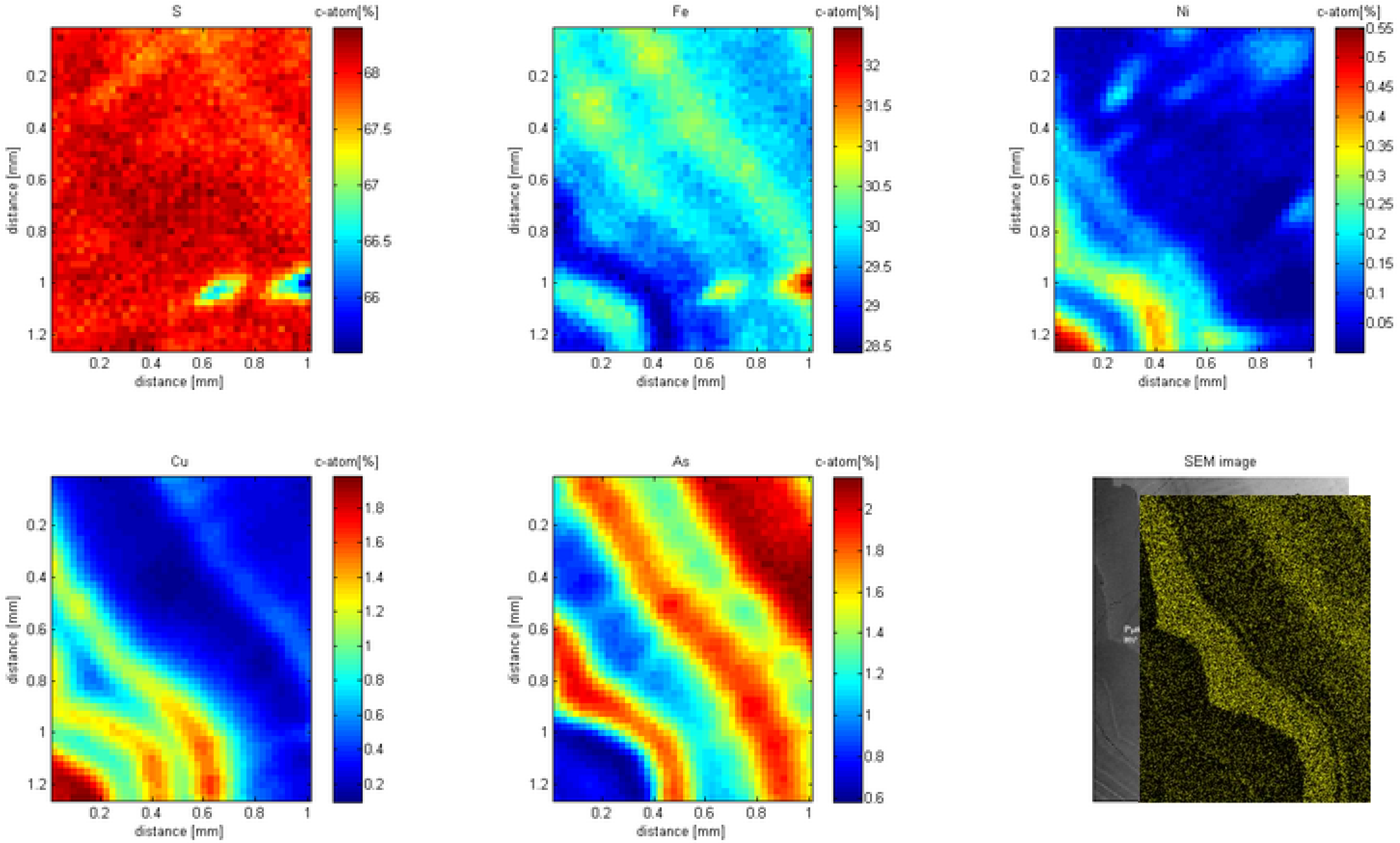


Analysis of rocks: detection of Rb-enrichment near zircon



Zircon is invisible for SE and BSE

Segregation in pyrite (FeS_2) rock (benefits from large area SDDs)



Sample: Dr Berthold, Uni Tübingen

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- X-ray spectroscopy - physical background
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- Examples of application:
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Excellences and weaknesses of µ-XRF

- Excellences
  - Excellent detection sensitivity for elements with Z > 18 due to the very low spectrum background
  - Extension of the spectrum range up to 40 keV @ 50 kV tube high voltage
  - Information depth up to several 10 µm enables spectroscopy of buried objects and layers
  - Small influence of specimen surface morphology (no backscattering)

- Weaknesses
  - Spatial resolution > 10 µm with stand-alone instruments
  - Very low detection sensitivity with stand-alone instruments for elements with Z < 11 (self absorption in the tube target and window)

Benefits of SEM/EDS + µ-XRF

- improved detection limit for Z >18 elements
- analysis of identical specimen positions in the SEM with EPMA for high spatial resolution and XRFA for trace elements
- detection of buried layers and thin film analysis
- extended spectral range up to 40 keV
- investigation of insulating materials without conductive coating

Outlook

- Further improvement of X-ray optics
  - Transmission
  - Focus diameter, but: the smaller the focus the smaller the focal distance (corresponding the WD) and the smaller the depth of the focus
- Improvement of small power micro-focus X-ray tubes (power, windows)
- Improvement of standardless quantification
  - More exact calculation of the tube spectrum
  - More exact measurement of transmission
- Exploitation of large area SDDs to drive detection limit in the 10 ppm range und to increase speed of mapping
- Integration of µ-XRF in the EDS software package

Literature for interested parties

- I. Pozsgai: X-ray Microfluorescence Analysis Inside and Outside of the Electron Microscope, X-ray spectrom. 20, 215-223 (1991) – Review of older work
- B. J. Cross, K. J. Witherspoon: Integrated Electron and X-Ray Induced Microbeam XRF in the SEM, Microscopy Today, 12, 20-23 (2004)
- A. Bjeoumikhov et al.: A new microfocus x-ray source, iMOXS, for highly sensitive analysis in scanning electron microscopes, X-ray spectrom. 34, 493-497 (2005)
- M. Haschke et al.: Micro-XRF excitation in a SEM, X-ray spectrom. 36, 254-259 (2007)
- M. Procop, V.-D. Hodoroaba: X-ray fluorescence as an additional analytical method for a scanning electron microscope: Microchim. Acta 161, 413-419 (2008) – Proc. EMAS workshop in Antwerp
- M. Procop: A Microfocus X-Ray Source for Improved EDS and XRF Analysis in the SEM, Microscopy and Analysis 25, 11-13 (2011)