

Introduction

To check the general quality of our analytical results, we started an intercomparison between four more or less common non-destructive X-ray based methods (and previously performed atomic absorption spectrometry):

- ▶ low energy particle induced X-ray emission with 2 MeV protons → **LE-PIXE**
- ▶ high energy particle induced X-ray emission with 68 MeV protons → **HE-PIXE**
- ▶ X-ray fluorescence with a portable device → **μ-XRF**
- ▶ synchrotron radiation induced X-ray fluorescence → **SY-XRF**

As test objects we selected **6 Roman coins** with different corrosion layers.



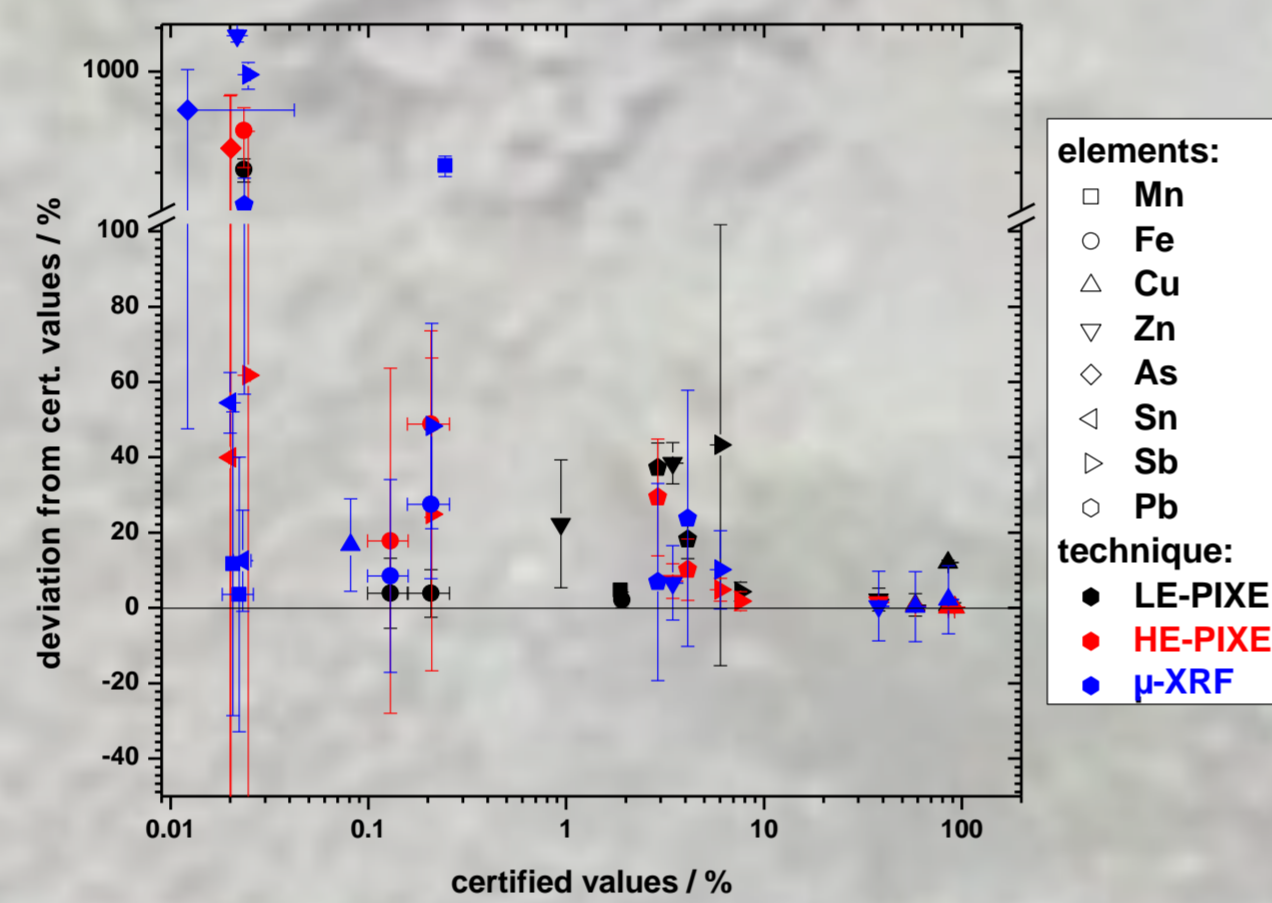
Each coin was analyzed at **3 locations**:

- ▶ originally corroded surface
- ▶ surface with partially removed corrosion layer (by glass fibre brush)
- ▶ surface with fully removed corrosion layer

Results

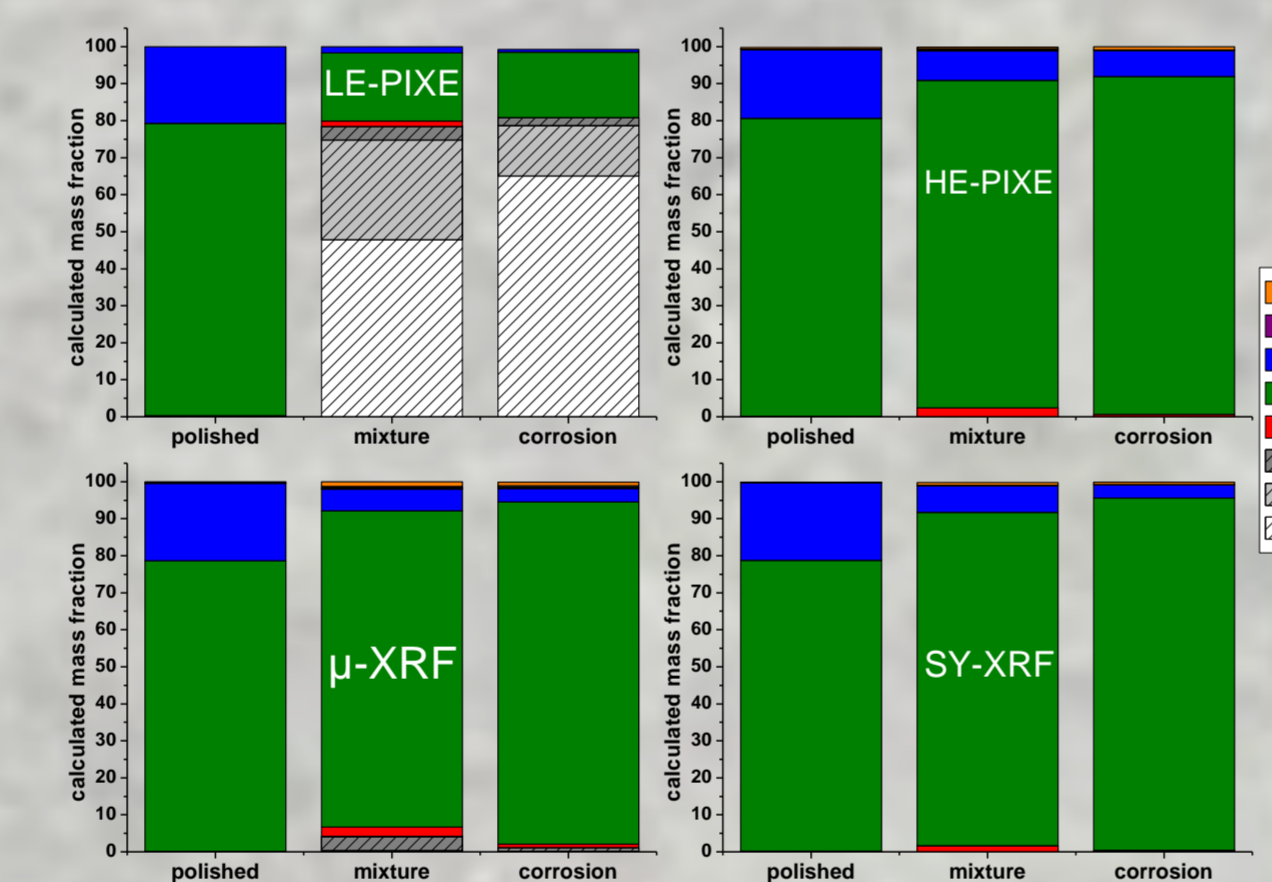
Reference materials

- ▶▶ the lower the concentrations the higher the deviation
- ▶▶ no general trend for method or element (SY-XRF used RMs for quantification, thus, no results)



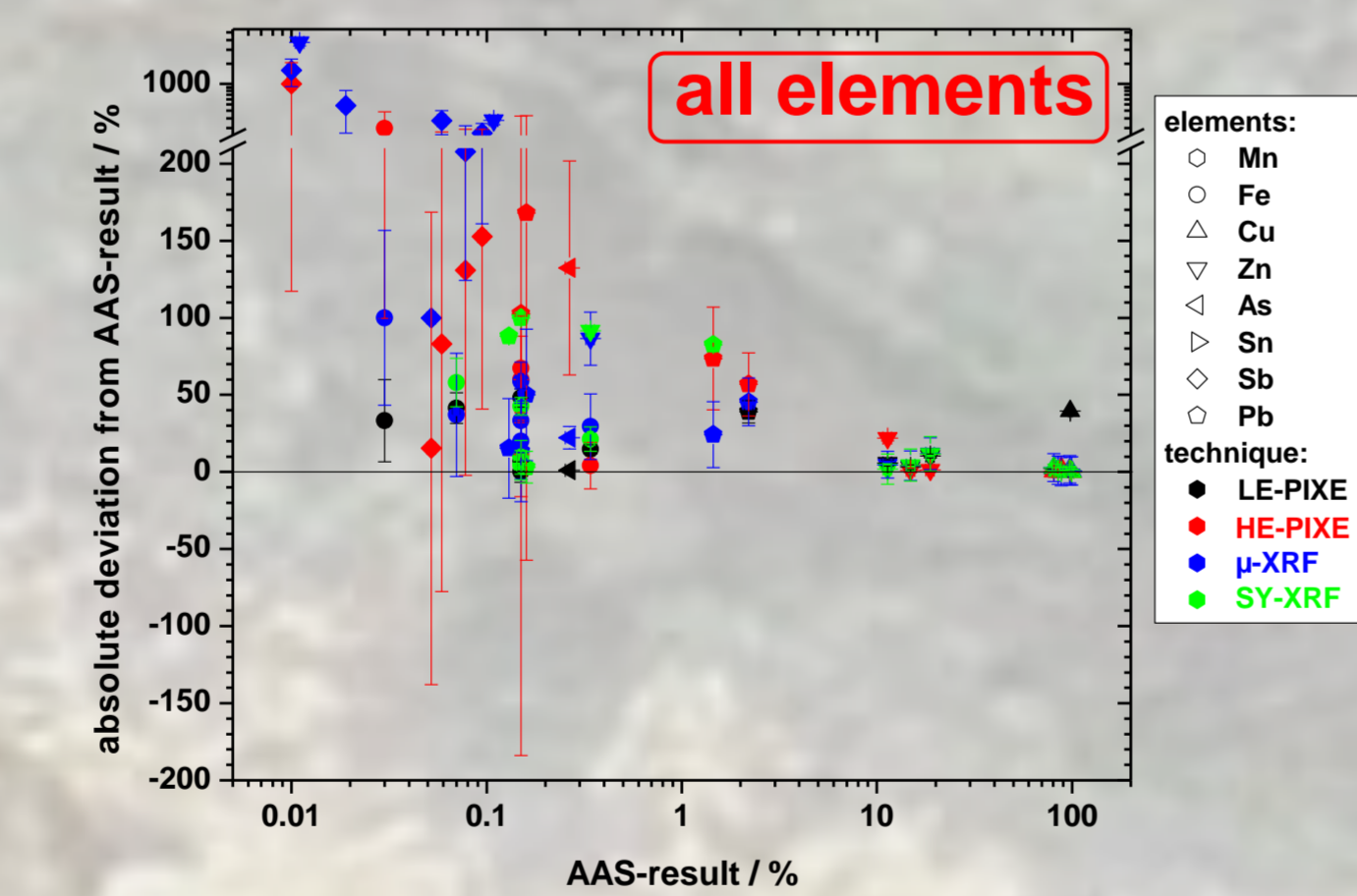
Influence of corrosion layer

- ▶▶ LE-PIXE best-suited for investigation of surface effects like corrosion
- ▶▶ all other methods analyse mixture of different amounts of corrosion layer and bulk
- ▶▶ comparison only for polished areas useful
- ▶▶ Zn depleted in corrosion layer (Zn-compounds more soluble than Cu-compounds)

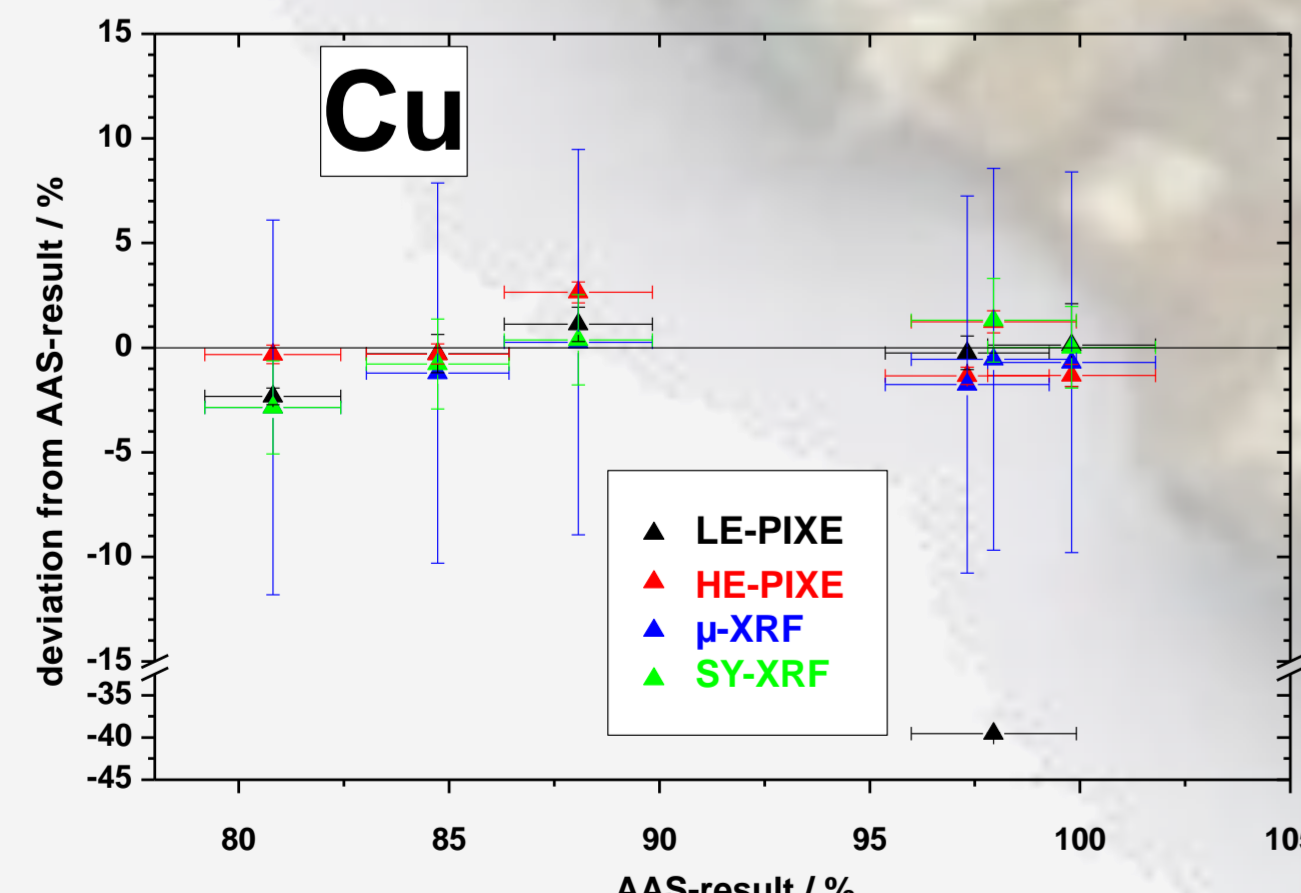


All methods, all coins

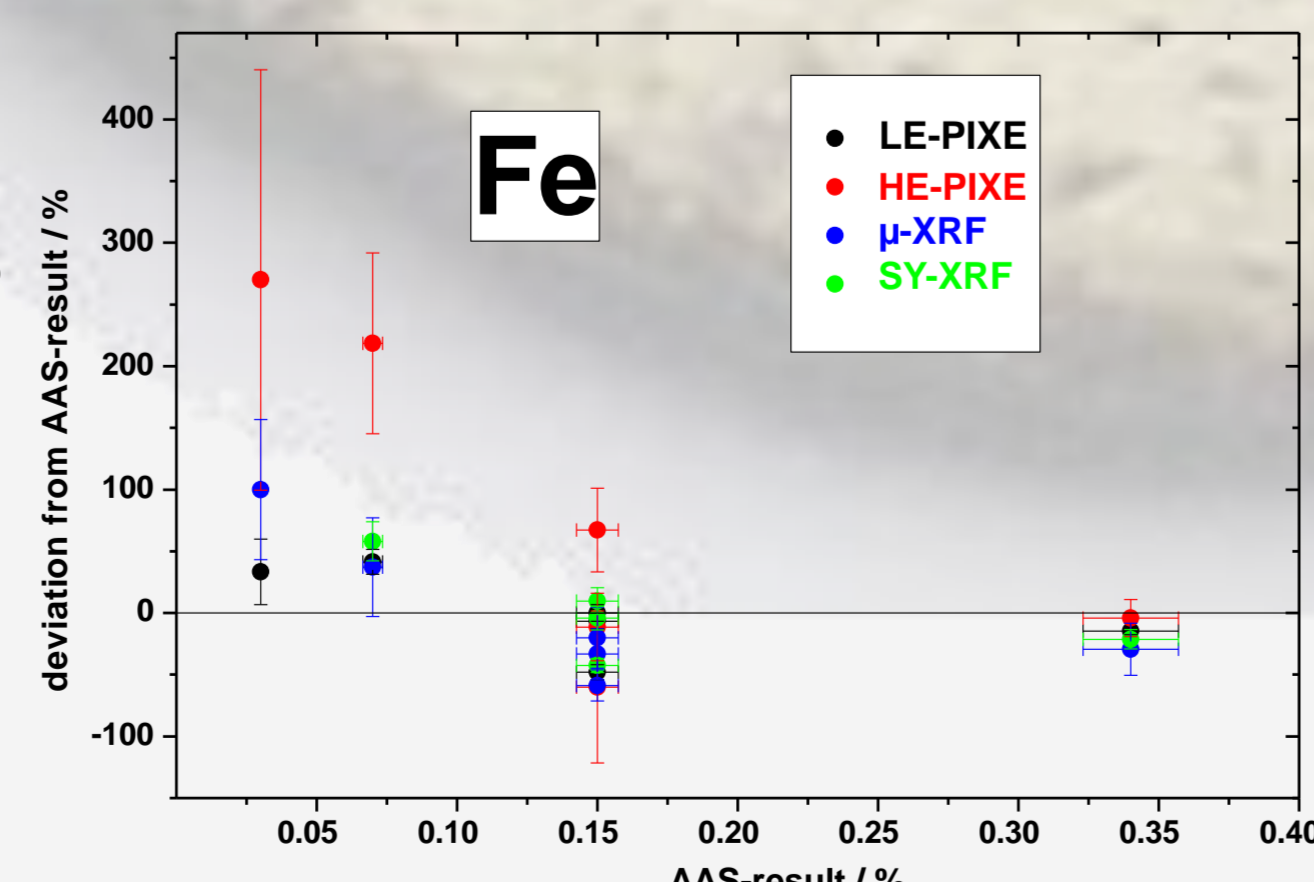
- ▶▶ the lower the concentrations the higher the deviation
- ▶▶ Ni only by SY-XRF
- ▶▶ no Sn by AAS (LOD: 0.25%)



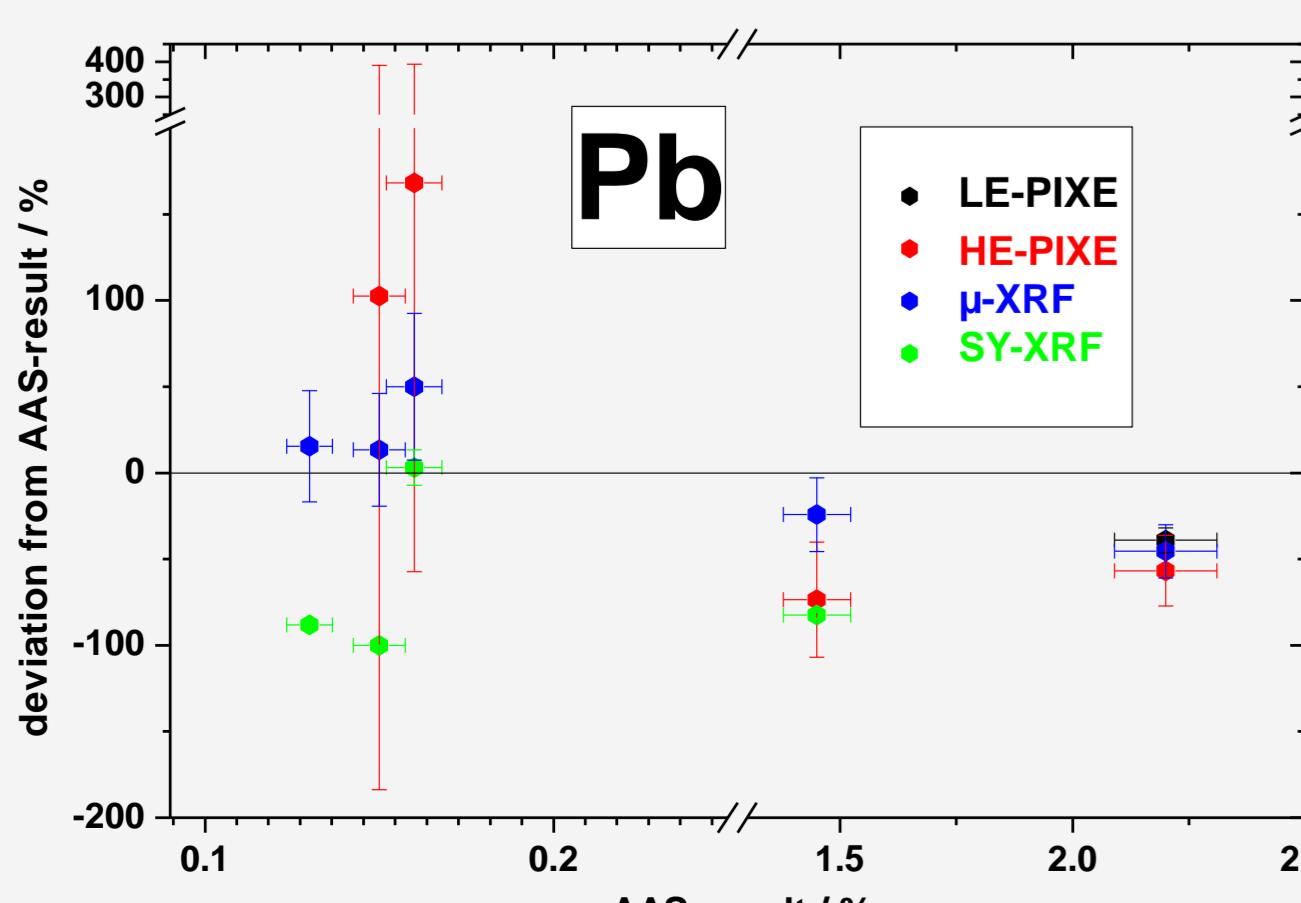
- ▶▶ generally all methods within 3% deviation from Cu-AAS
- ▶▶ 1 Cu-outlier by LE-PIXE (incomplete removal of the patina, which influence mainly surface-sensitive method)



- ▶▶ below 0.1 % Fe all X-ray methods higher than AAS (or AAS overestimates Fe?)
- ▶▶ HE-PIXE overestimates Fe most



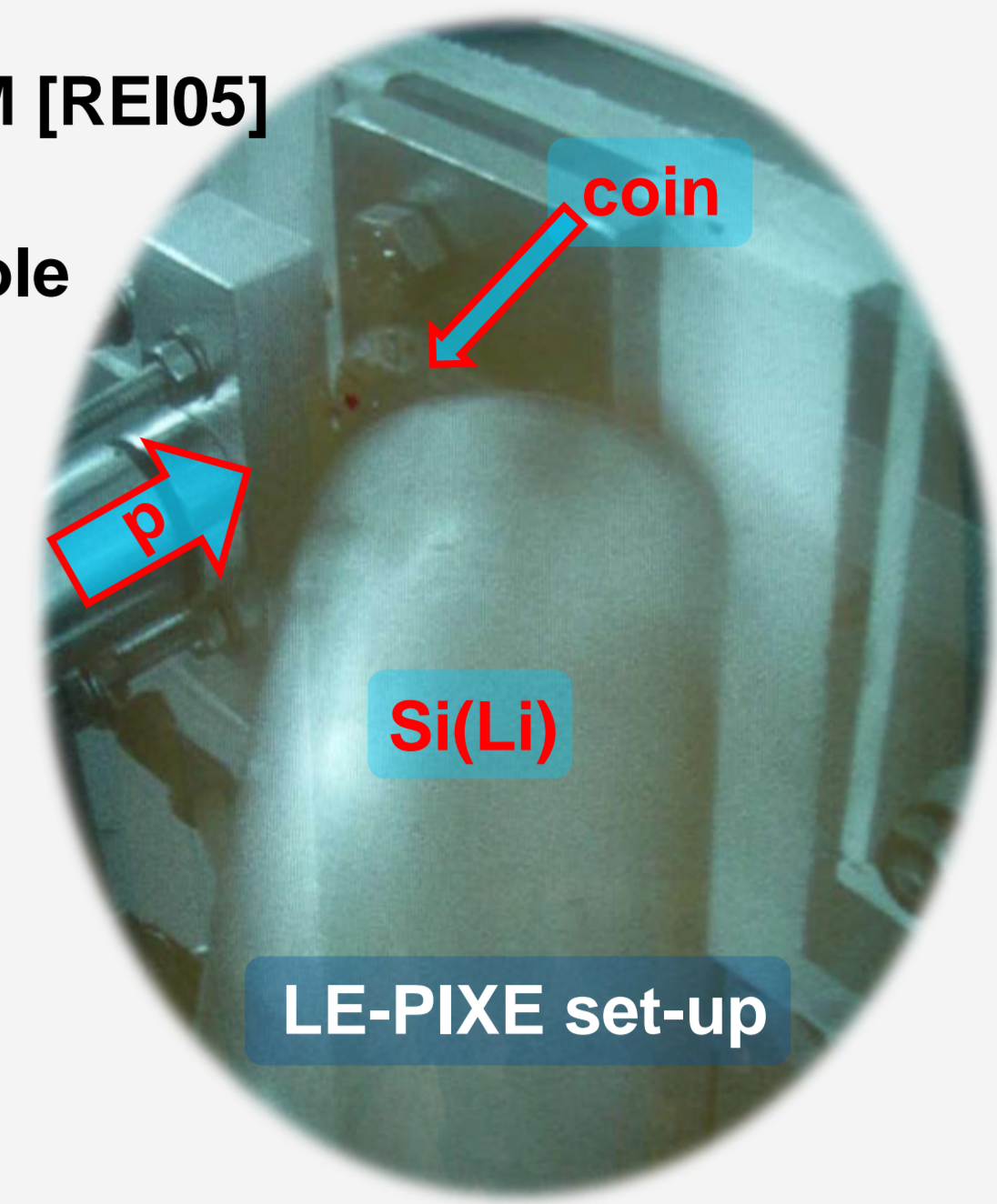
- ▶▶ Pb not detected by LE-PIXE (LOD: 500 μg/g)
- ▶▶ Pb (>1.3%) probably overestimated by AAS
- ▶▶ Pb (< 0.2%) up to a factor of 10-25 "different" from AAS



Experimental

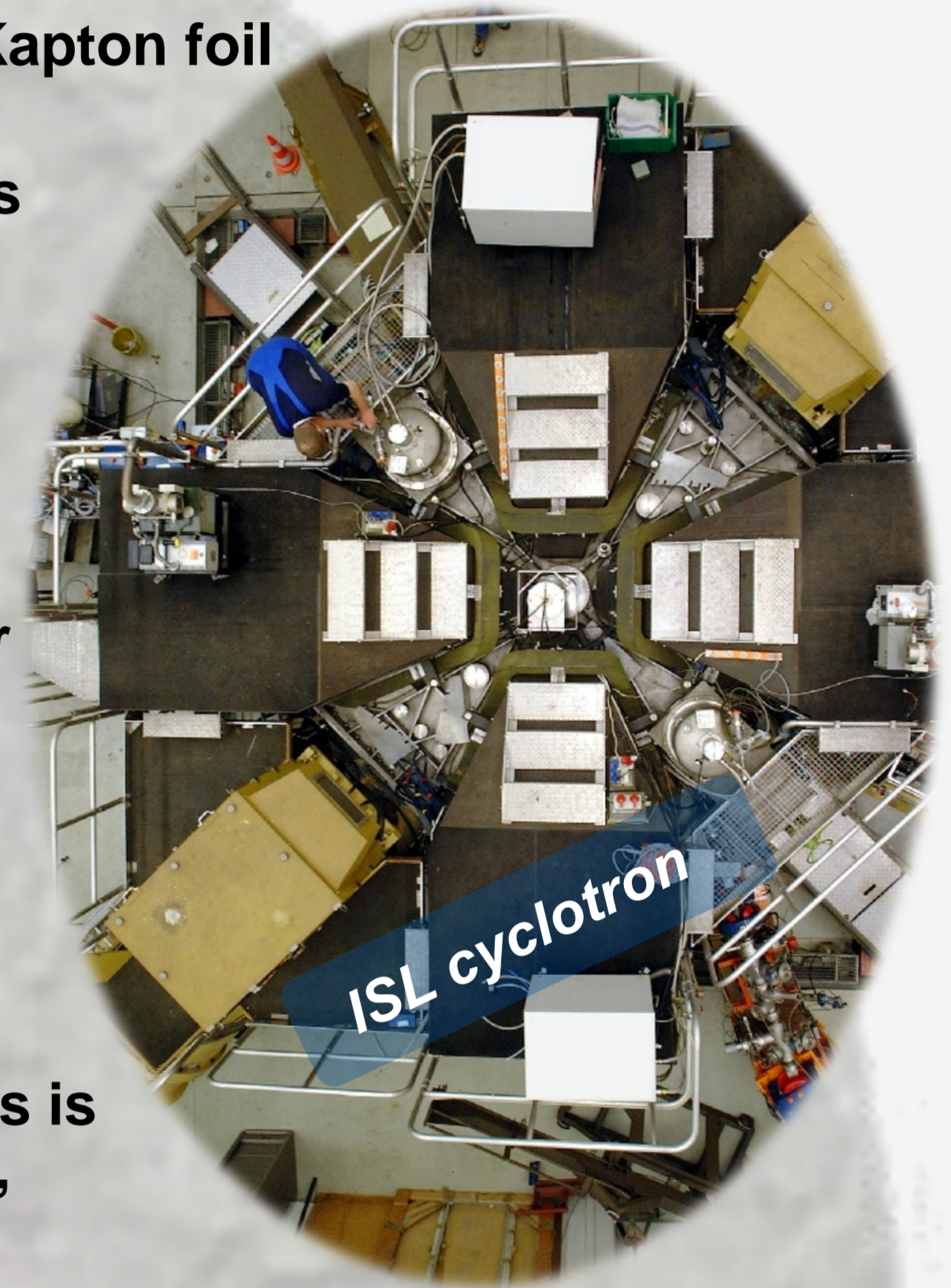
LE-PIXE

- ▶ 30° beamline @ 2 MV tandem accelerator facility BAM [REI05]
- ▶ proton beam (0.5 mm Ø) extracted via a thin (8 μm) polyimide foil into air, focused by magnetic quadrupole doublet followed by carbon aperture (0.7 mm Ø)
- ▶ distance beam to specimen surface: ~ 10 mm
- ▶ distance detector to specimen surface: ~ 30 mm
- ▶ beam current: ~100 pA
- ▶ range of p in Cu: <0.015 mm [ZIE04]
- ▶ information depth Cu-Kα in Cu: ~0.0038 mm [LAG97]
- ▶ 80 mm² Si(Li) detector, resolution of 168 eV @ 5.9 keV in 135° geometry to incident beam
- ▶ measurement time: 180 s
- ▶ GUPIX software package for quantification [CAM00].



HE-PIXE

- ▶ Ionenstrahllabor (ISL), Hahn-Meitner-Institut, Berlin [DEN05]
- ▶ proton beam (1 mm Ø) exits the vacuum via thin Kapton foil (80 μm, E-loss: ~ 200 keV)
- ▶ 68 MeV is used as standard energy as this beam is produced regularly for the eye tumor therapy
- ▶ beam current: ~ 100 pA
- ▶ range of these protons in Cu: ~ 7 mm [ZIE04]
- ▶ information depth Cu-Kα in Cu: ~0.019 mm
- ▶ 2 laser cross-hairs mark beam position on object allowing precise adjustment of the object-detector distance (~55 mm)
- ▶ HPGe detector, resolution of 180 eV @ 5.9 keV in 135° geometry to incident beam
- ▶ measurement time: 200 s
- ▶ GUPIX software for quantification [MAX95, DEN04]
- ▶ excitation probability for K-lines of heavy elements is bigger for HE-p resulting in better detection limits, K- lines suffer less absorption



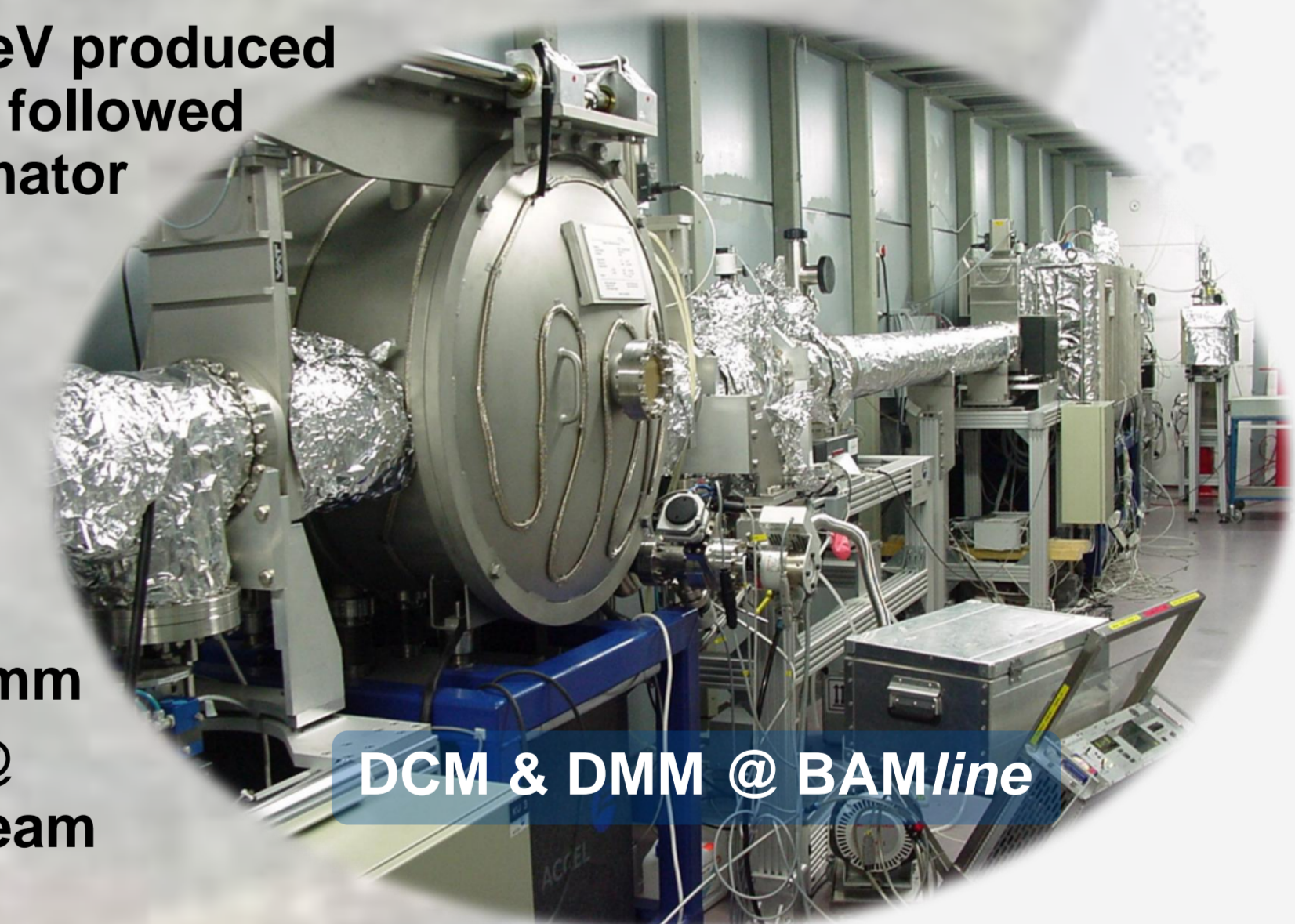
μ-XRF

- ▶ mobile XRF-device with Mo-X-ray tube (30 W) [BRO01]
- ▶ polycapillary → spot size: 70 μm
- ▶ tube current: 600 μA
- ▶ excitation depth in Cu: 0.023 mm
- ▶ information depth Cu-Kα in Cu: 0.022 mm
- ▶ silicon drift detector (SDD), resolution of 170 eV @ 5.9 keV in 40° geometry to incident beam
- ▶ measurement time: 250 s
- ▶ quantification by SPECTRA & fundamental parameter method [ELA02]
- ▶ cheaper than the three stationary methods



SY-XRF

- ▶ hard X-ray beamline "BAMline" @ synchrotron BESSY
- ▶ monochromatic X-ray beam of 32.5 keV produced by 7 Tesla-wavelength shifter [RIE05] followed by Si(111) Double-Crystal-Monochromator (DCM) and W/Si Double-Multilayer-Monochromator (DMM) (here only DMM in use) [GÖR06]
- ▶ crossed slits cut beam to 0.2 mm²
- ▶ beam intensity: 10¹² photons mm⁻² s⁻¹
- ▶ excitation depth in Cu: 0.13 mm
- ▶ information depth Cu-Kα in Cu: 0.03 mm
- ▶ Si(Li) detector, resolution of 130 eV @ 5.9 keV in 45° geometry to incident beam
- ▶ measurement time: 200 s
- ▶ quantification by AXIL and vs. certified reference materials
- ▶ monochromators allow to choose ideal excitation conditions



▶▶▶ **One method is no method ?**
 ▶▶▶ **Correct non-destructive analyses / quantification of corroded objects seems difficult to impossible**
 ▶▶▶ ...

References

[BRO01] H. Bronk et al., *Fresenius J. Anal. Chem.* 371 (2001) 307. [CAM00] J. L. Campbell, et al., *NIMB*, 170 (2000) 193. [DEN04] A. Denker et al., *NIMB* 219-220 (2004) 130. [DEN05] A. Denker et al., *X-Ray Spectrom.* 34 (2005) 376. [ELA02] W.T. Elam et al., *Rad. Phys. Chem.* 63 (2002) 121. [GÖR06] W. Görner et al., *Insight* 48 (2006) 540. [LAG97] G. Lagarde et al., *NIMB* 132 (1997) 521. [MAX95] J.A. Maxwell et al., *NIMB* 95 (1995) 407. [REI05] I. Reiche et al., *X-Ray Spectrom.* 34 (2005) 42. [RIE05] H. Riesemeier et al., *X-Ray Spectrom.* 34 (2005) 160. [ZIE04] J.F. Ziegler, *NIMB*, 219-220 (2004) 1027.

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