Quantitative analysis of corroded coins with four non-destructive X-ray methods

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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.

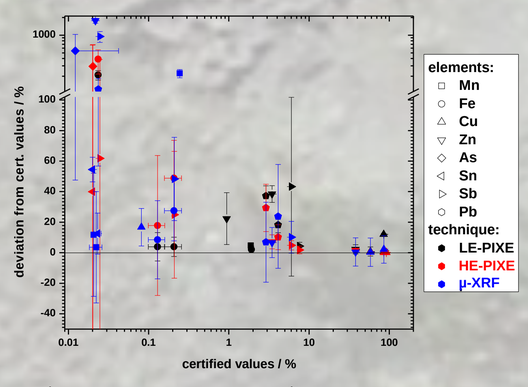
Each coin was analyzed at 3 locations:

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

Results

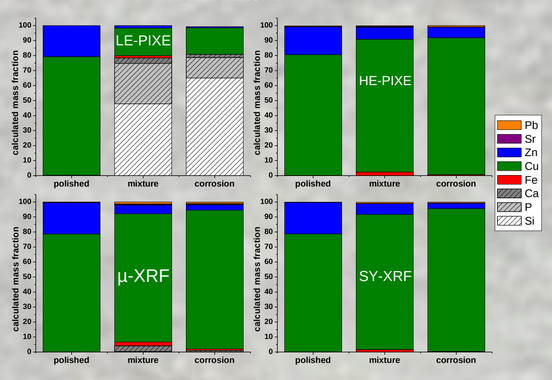
Reference materials

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



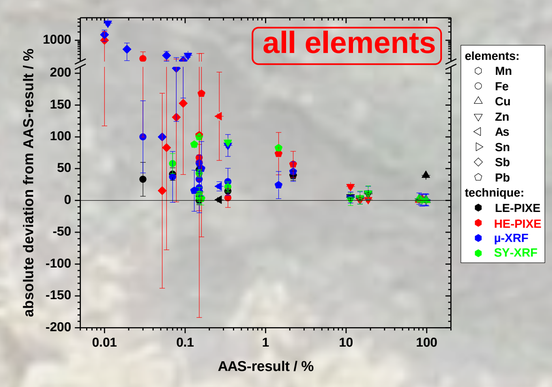
Influence of corrosion layer

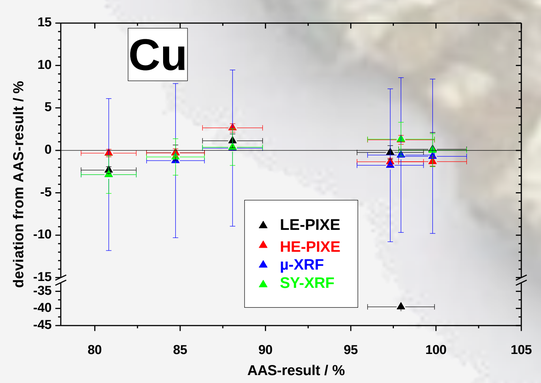
- LE-PIXE best-suited for investigation of surface effects like corrosion
- all other methods analyse mixture of different amounts of corrosion layer and bulk
- comparison only for polished areas useful
- Zn depleted in corrosion layer (Zn-compounds more soluble than Cu-compounds)



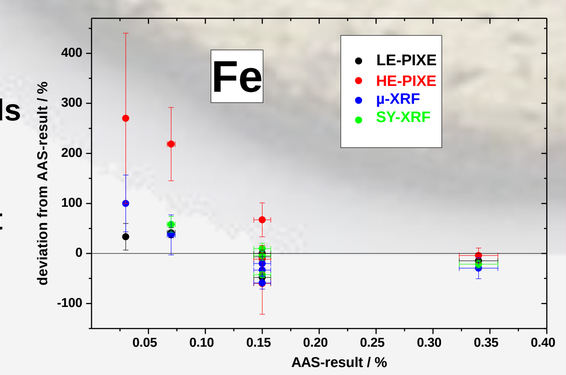
All methods, all coins

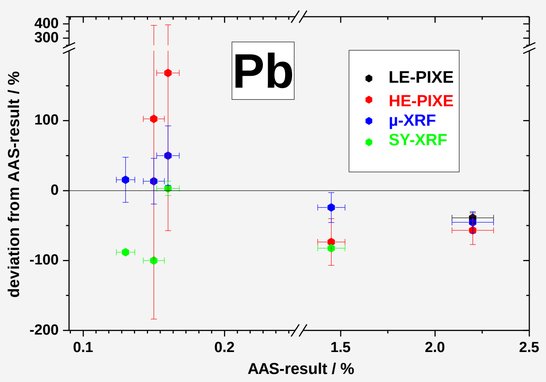
- the lower the concentrations the higher the deviation
- Ni only by SY-XRF
- no Sn by AAS (LOD: 0.25%)





- 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)



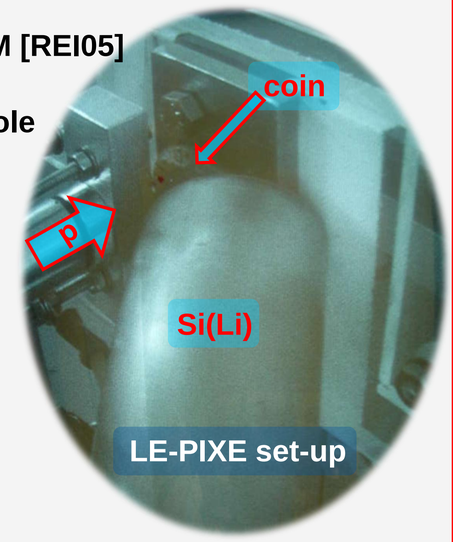


- below 0.1 % Fe all X-ray methods higher than AAS (or AAS overestimates Fe?)
- HE-PIXE overestimates Fe most
- Pb not detected by LE-PIXE (LOD: 500 µg/g)
- Pb (>1.3%) probably overestimated by AAS
- Pb (< 0.2%) up to a factor of 10-25 "different" from AAS

Experimental

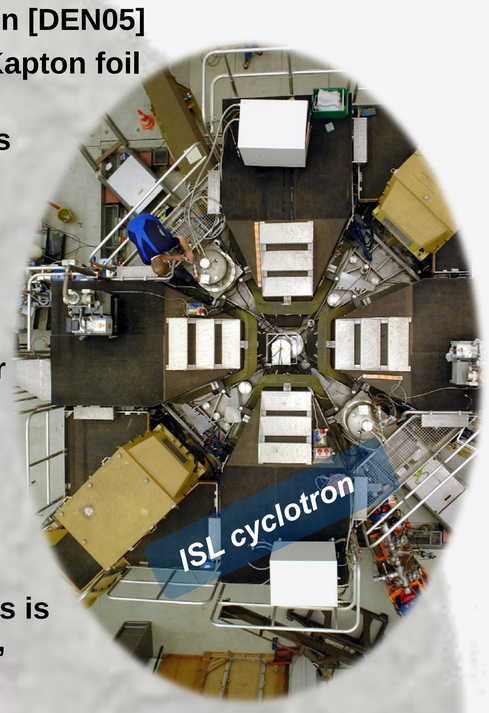
LE-PIXE

- 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 "BAM*line*" @ 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: 10^{12} 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

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References

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