Towards single atom sensitivity in the analytical TEM

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Quantitative EDXS

concentration of element A (wt%)

$$I_A^{spec} = \underbrace{\boxed{c_A}\frac{N\rho t}{A_A}}_{\text{number of atoms}} \underbrace{(Q\omega a)_A}_{\text{X-ray emission}} \underbrace{D_e}_{\text{electron beam}} \underbrace{\left(\frac{\Omega}{4\pi}\varepsilon_A\right)}_{\text{detection efficiency}} \int_0^{t^*} \underbrace{\varphi(\rho t)}_{\text{depth distribution}} \underbrace{e^{-\frac{\mu}{\rho}\Big]^A_{spec}\rho t\ \csc\alpha}}_{\text{absorption in the specimen}} \underbrace{(1+\delta_A)}_{\text{fluorescence}} d(\rho t)$$

$$D_e = \frac{I_p \tau}{e}$$

$$\varepsilon_A = \exp\underbrace{\left[-\frac{\mu}{\rho}\Big]^A_{window}(\rho t)_{window}\right.}_{\text{absorption by detector window}} \underbrace{-\frac{\mu}{\rho}\Big]^A_{dead}(\rho t)_{dead}}_{\text{absorption by detector dead layer}} \underbrace{\left.-\frac{\mu}{\rho}\Big]^A_{cont}(\rho t)_{cont}\right]}_{\text{absorption by contact layer}} \underbrace{\left\{1-\exp\left[-\frac{\mu}{\rho}\Big]^A_{active}(\rho t)_{active}\right]\right\}}_{\text{detection efficiency in detector crystal}}$$

I_A: intensity of element A's X-ray line
I^*_A: count rate of X-ray line
c: weight fraction
N: Avogadro's number
ρ: density
t: film thickness
A: atomic weight
Q: ionization cross section
ω: fluorescence yield
a: relative transition probability
D_e: electron dose
e: elementary charge
Ω: detector solid angle
ε: absorption in the detector
φ(ρt): X-ray depth distribution
$\mu/\rho]^A_x$: mass absorption coefficient
α: take-off angle
δ: fluorescence factor
csc(α) = cosecant of α = 1/sin(α)
I_p: beam current
τ: acquisition time
n_A: number of atoms of element A
A_{ill}: illuminated area (beam diameter)

EDXS signal per atom

Consider the situation, where only one atom generates the EDXS signal: Absorption and fluorescence are negligible; in addition the signal depends on the illuminated area (beam size). Some results about single atom detection have already been published [1, 2].

$$I_A^* = \frac{n_A}{\mathbf{A_{ill}}}(Q\omega a)_A \frac{\mathbf{I_p}}{e}\left(\frac{\mathbf{\Omega}}{4\pi}\boldsymbol{\varepsilon}_\mathbf{A}\right)$$

In order to get a high count rate I^*_A, some parameters can be optimized:

- **I_p** and **A_{ill}**: C_S probe corrected microscope + high brightness gun
- **Ω** and **ε_A**: big detector area, close distance to sample, windowless design

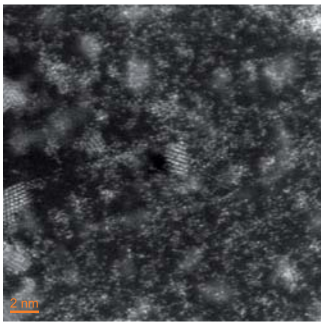
The ASTEM (Austrian Scanning Transmission Electron Microscope) is nicely suited for high efficiency counting of X-rays:

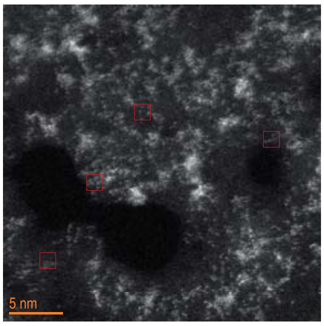
- Titan^3 G2 60-300
- high brightness gun (X-FEG)
- C_S probe corrector
- high sensitivity Super-X EDX system
- ultrafast scanning (EDXS+EELS @ 1ksps)
- full remote control (?)

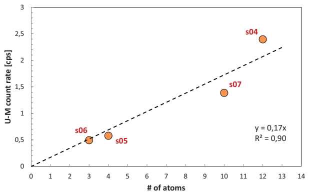
specs:	0.07 nm	spatial resolution **&**
	0.50 nA	beam current **&**
	0.18 eV	energy resolution

EDXS of Uranium

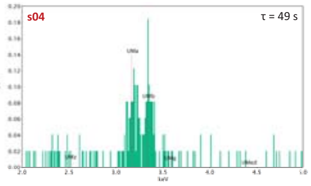
Uranyl acetate was applied onto a 2 nm C film supported by a holey polymer film. Most of the organic components evaporated during heat treatment. Finally, big (polycrystalline) and small (monocrystalline) U oxide crystals formed as well as single U atoms [3]. As the U atoms tend to speed around, windows of (1.5 nm)^2 were used to capture the EDX signals.

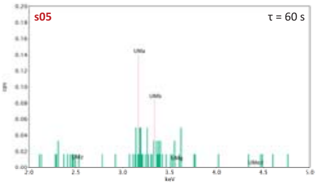


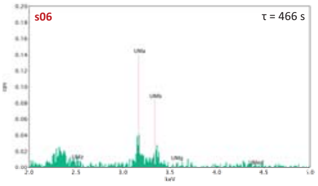


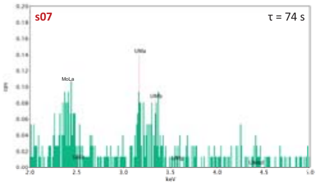


From the estimated/counted number of U atoms (~12, ~4, ~3, ~10) and the count rate determined from the spectra a count rate per U atom was linearly fitted: 0.17 cps/atom.

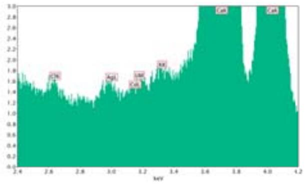






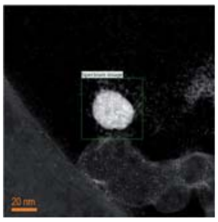


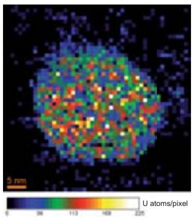
A glass standard (SRM611 from NIST) was measured (see Poster by Stefanie Fladischer). Here, the intensity of the U-M line was determined and combined with the number of U atoms in the illuminated volume (52.000) to yield an estimate for the count rate per U atom: 1.7 cps/atom.



When the count rate per atom is computed using the above formula, the experimentally determined cps can be compared. The agreement is quite good (orders of magnitude alright). For the calculation cross-section values from [4] and [5] were taken.

	SRM611	U acetate	
I_p	850	200	pA
beam diameter	336,8	1,7	nm
number of atoms	52000	1	
I_A^* (calc)	1,25	0,22	cps
I_A^* (exp)	1,7	0,17	cps





Using the procedures described above a rate of 0.67 cps/U atom was calculated, which was then used to determine the number of U atoms in the extracted U map. Assuming UO_2 and a cylindrical shape of the particle a thickness of 4.5 nm could be estimated just by counting U atoms.

References

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[2] K. Suenaga et al., Nat Photonics **6** (2012) 545
[3] Y. Zhu et al., Nat Materials **8** (2009) 808
[4] P. Rez, X-Ray Spectrom **13** (1984) 55
[5] D. Bote et al., Atom Data Nucl Data **95** (2009) 871

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