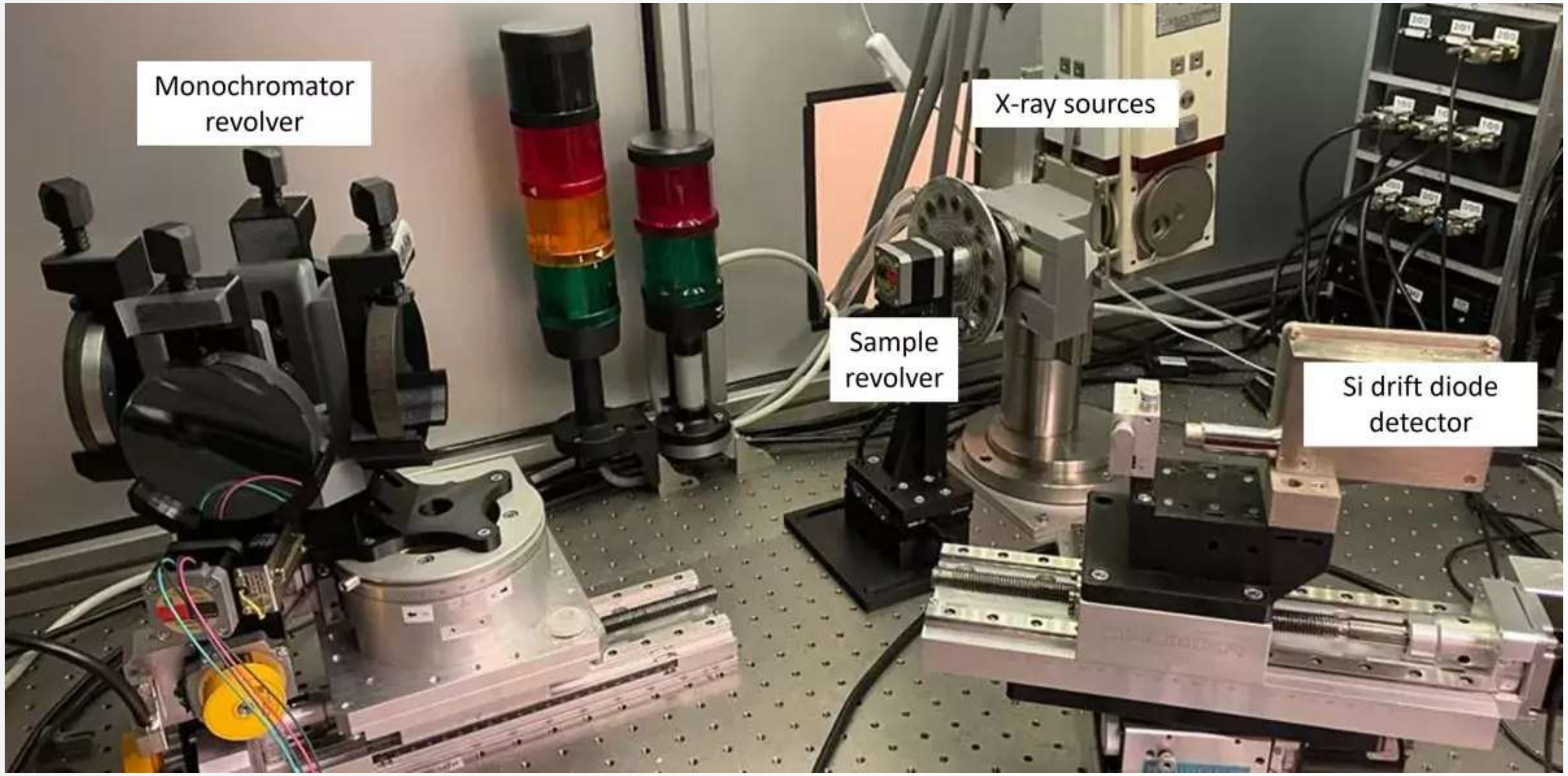
# VERSATILE AUXILIARY EQUIPMENT, SAMPLE ENVIRONMENTS, AND RECENT RESULTS FROM HEL


Antti-Jussi Kallio, René Bes, Simo Huotari
X-ray laboratory, University of Helsinki

# OUTLINE

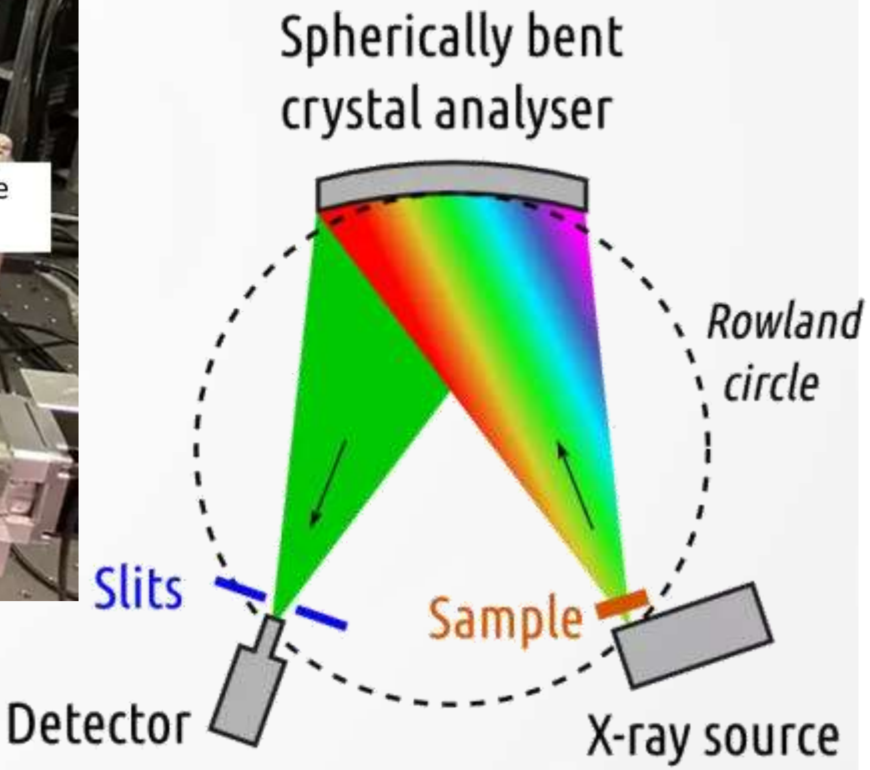
1. User statistics and recent publications
2. Auxiliary equipment (Laue, optical test bench etc.)
3. Increasing the energy range
4. Simultaneous measurement of $I_0$
5. New *operando* sample environment designs

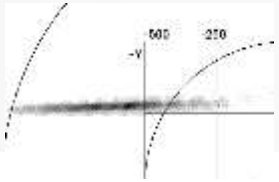
# Hel-XAS instrument: Johann type with spherically bent crystals R=0.5 – 1.0 m




1.5 kW water-cooled diffraction x-ray tube (0.4 mm source size)

100 W Micro-X-ray water-cooled fine line focus tube (<100 micron source size)



Micro X-ray tube with line focus

# Helsinki Center for X-ray Spectroscopy beamlines

| Beamline | Techniques | Application field | Photon energies | Status |
|---|---|---|---|---|
| Hel-XAS 1.5 kW and 100 W x-ray tubes | X-ray absorption spectroscopy (XANES & EXAFS) in transmission and fluorescence mode (+ imaging possibilities) | *in-situ* catalysis / environmental science / Generic material studies | 5-25 keV | Open for users |
| Sampo 50 W | X-ray absorption spectrocopy (XANES & EXAFS) in transmission mode (fluorescence mode under development) | Radioactive samples | 5-20 keV | Open for users |
| Revontuli 50 W | X-ray absorption spectrocopy (XANES & EXAFS) in transmission and fluorescence mode<br>X-ray emission spectroscopy (XES) | Generic material science | 5-23 keV | Open for users |
| HotXAS | X-ray absorption spectrocopy (XANES & EXAFS) in transmission mode | Spent nuclear fuel dissolution products and minor actinide compounds such as MOX fuels | 5-23 keV | Under construction |

# OUTLINE

1. User statistics and recent publications
2. Auxiliary equipment (Laue, optical test bench etc.)
3. Extending the energy range
4. Simultaneous measurement of $I_0$
5. New *operando* sample environment designs

# User statistics

- Helsinki Center for X-ray Spectroscopy (tinyurl.com/c4xshelsinki) is open for users to propose experiments. Proposal form can be found from the web page
- 14 external proposals in 2023: besides universities from Finland, also from France, Netherlands, Switzerland, Denmark, Sweden, and Italy.
- To fulfill a proposal, roughly one week of beamtime is normally needed on average
- Industry would still be more welcome, maybe more advertisement of R&D possibilities are needed?

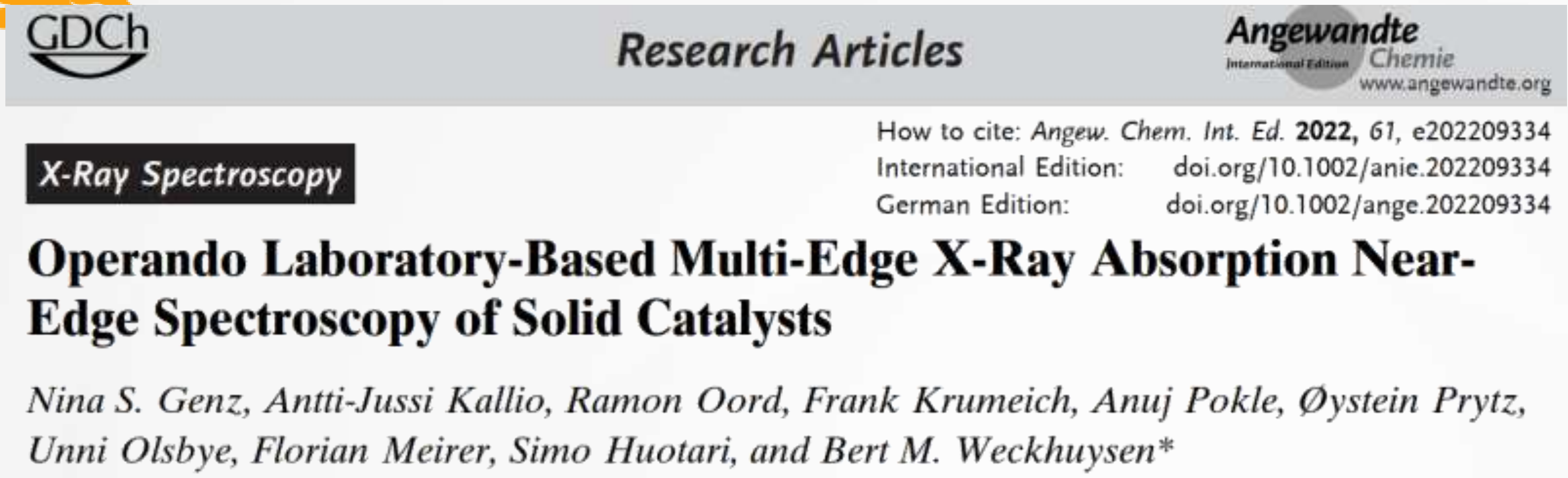
# Overview of recent publications

**Method development:** Ari-Pekka Honkanen and S. Huotari: **Monochromatic computed tomography using laboratory-scale setup: proof-of-concept**, **Scientific Reports** 13, 363 (2023); Salla-Maaria Latva-Äijö et al.: **Inner product regularized multi-energy X-ray tomography for material decomposition**. **Applied Mathematics for Modern Challenges** 2, 1-16 (2024); Morten Johansen, Jannie Kirk Verdelin, Antti-Jussi Kallio, Tommy Ole Kessler, Simo Huotari, and Dorthe Ravnsbaek: **DANOISE: a 3D printable battery cell for laboratory operando X-ray diffraction and absorption spectroscopy**. **Batteries & Supercaps**, e202400033 (2024).

**Inorganic chemistry:** Nicholas P. L. Magnard et al.: **Control of H-Related Defects in gamma-MnO2 in a Hydrothermal Synthesis**, **Inorg. Chem**. 62, 13021 (2023); J. Yim et al.: **Atomic Layer Deposition of Zinc Oxide on Mesoporous Zirconia Using Zinc(II) Acetylacetonate and Air**. **Chemistry of Materials** 35, 7915–7930 (2023); Nina S. Genz, Antti-Jussi Kallio, Florian Meirer, Simo Huotari, Bert Weckhuysen: **Operando Laboratory-based X-ray Absorption Spectroscopy: Guidelines for Newcomers in the Field. Chemistry Methods**, e202300027 (2024); Leticia S. Bezerra et al., **Triple Play of Band Gap, Interband, and Plasmonic Excitations for Enhanced Catalytic Activity in Pd/HxMoO3 Nanoparticles in the Visible Region. ACS Applied Materials & Interfaces** 2024 (article ASAP); Benjin Jin et al.: **Amorphous carbon modulated-quantum dots NiO for efficient oxygen evolution in anion exchange membrane water electrolyzer**, **Applied Catalysis B: Environment and Energy** 358, 124437 (2024)

**Geochemistry**: Changxun Yu et al.: **Manganese cycling and transport in boreal estuaries impacted by acidic Mn-rich drainage. Geochimica et Cosmochimica Acta** 365, 136-157 (2024)

# Overview of recent publications



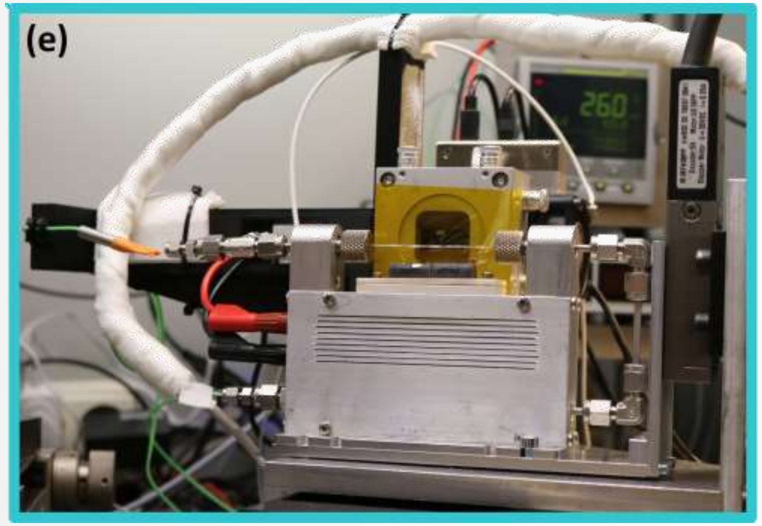
GDCh — Research Articles — Angewandte Chemie International Edition www.angewandte.org

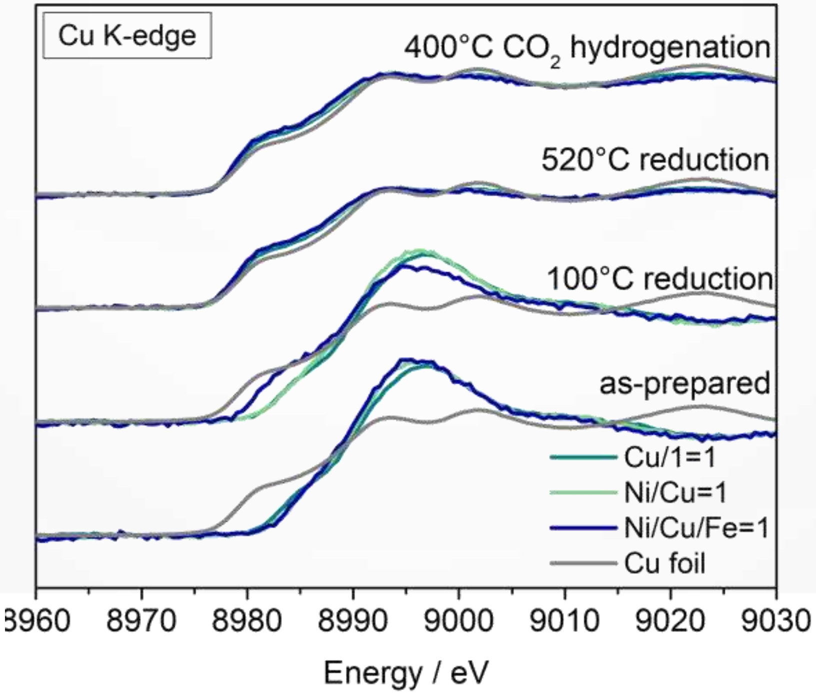
**X-Ray Spectroscopy**

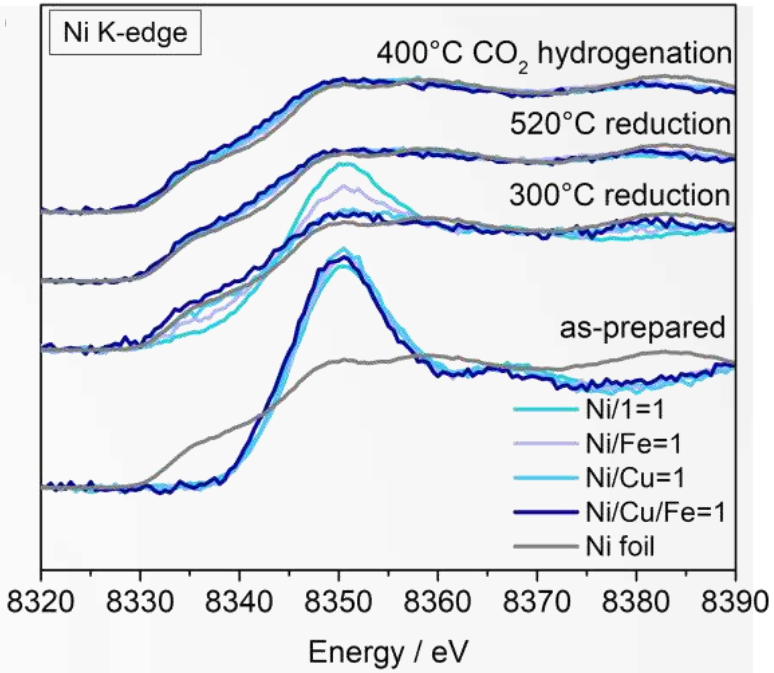
How to cite: *Angew. Chem. Int. Ed.* **2022**, *61*, e202209334
International Edition: doi.org/10.1002/anie.202209334
German Edition: doi.org/10.1002/ange.202209334

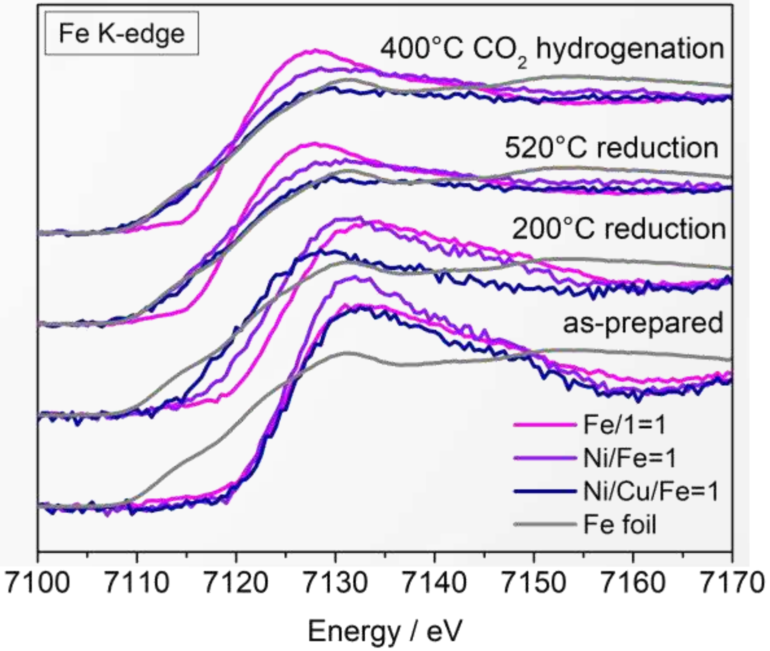
**Operando Laboratory-Based Multi-Edge X-Ray Absorption Near-Edge Spectroscopy of Solid Catalysts**

*Nina S. Genz, Antti-Jussi Kallio, Ramon Oord, Frank Krumeich, Anuj Pokle, Øystein Prytz, Unni Olsbye, Florian Meirer, Simo Huotari, and Bert M. Weckhuysen**

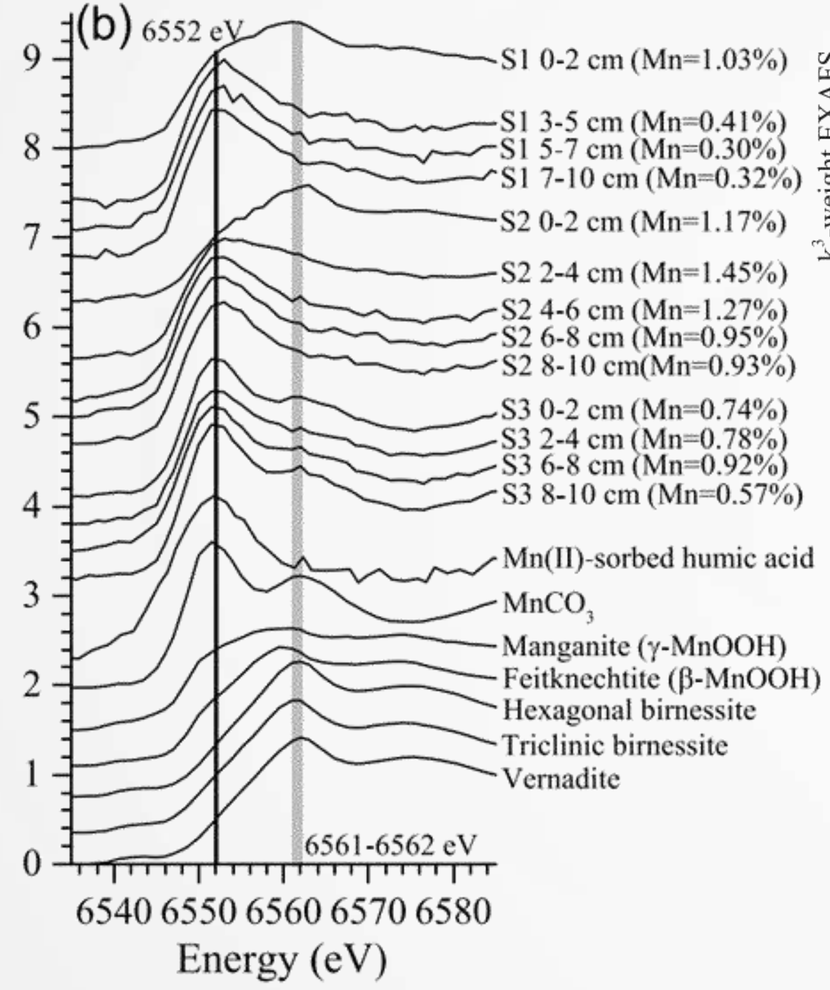


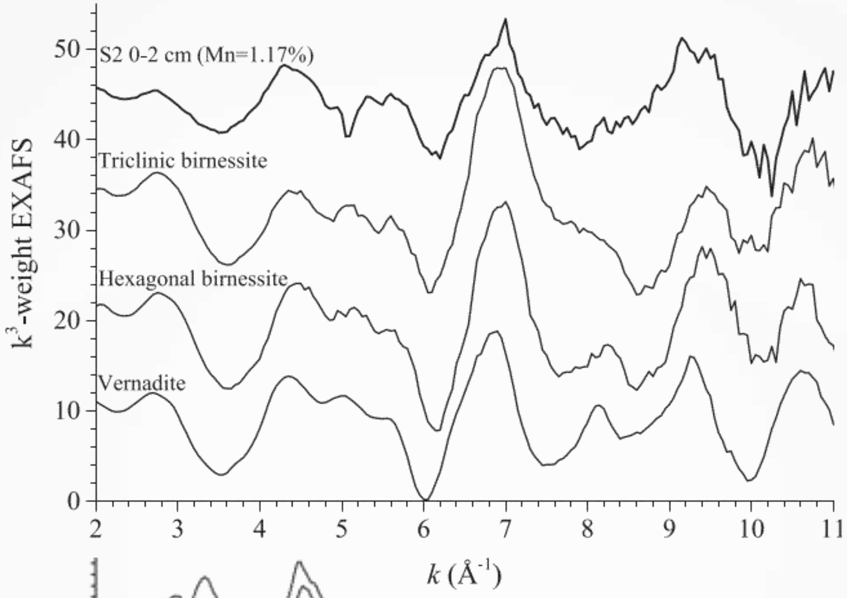



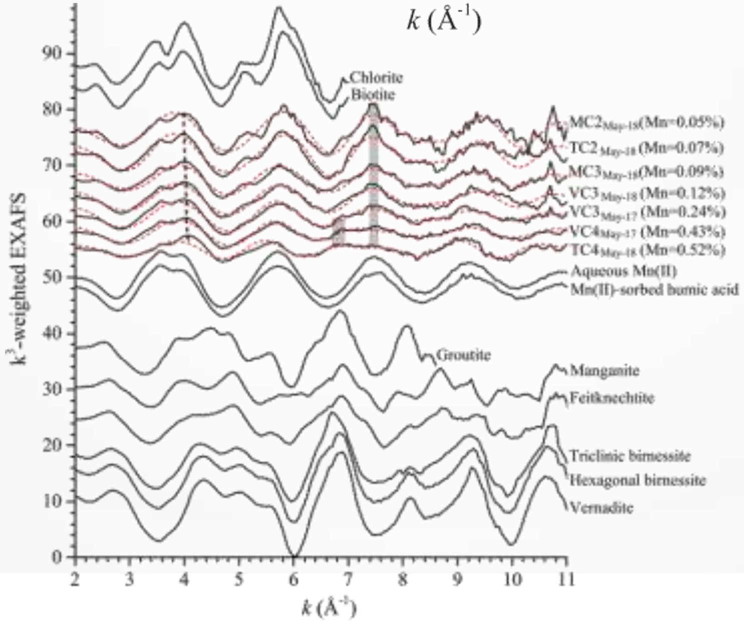



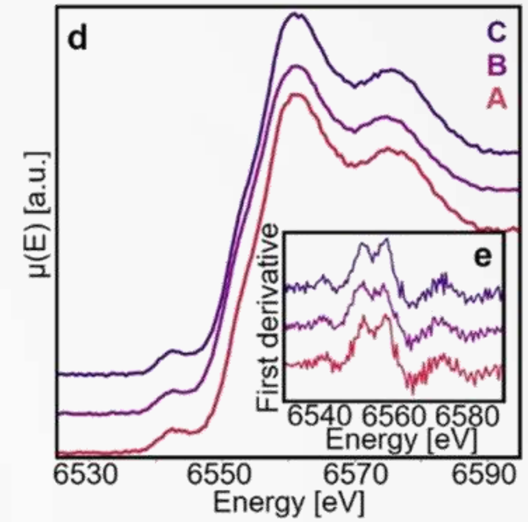



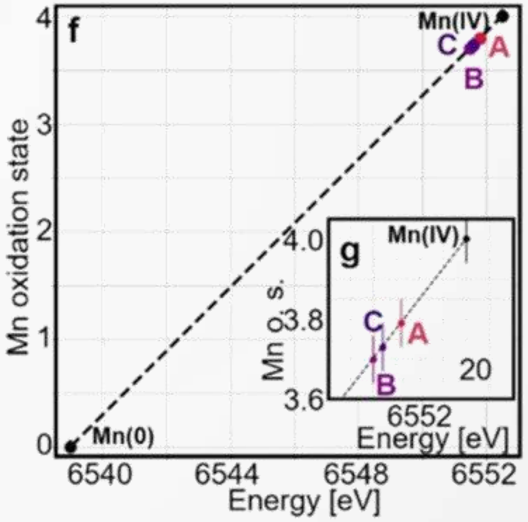
# Overview of recent publications: Mn K edges



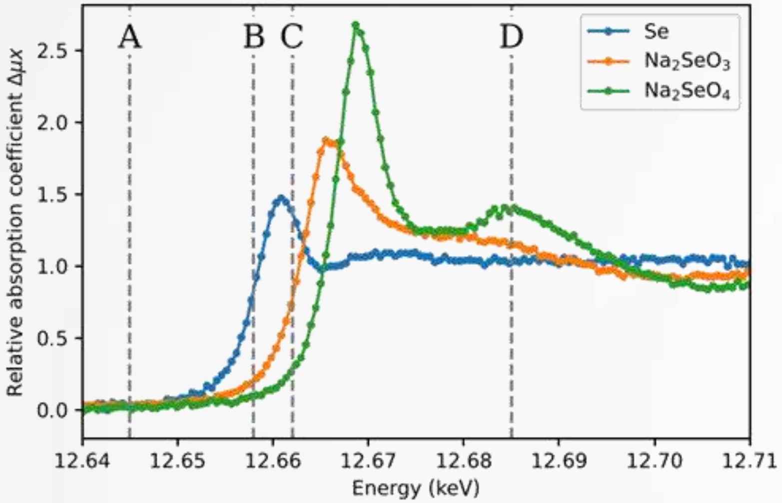



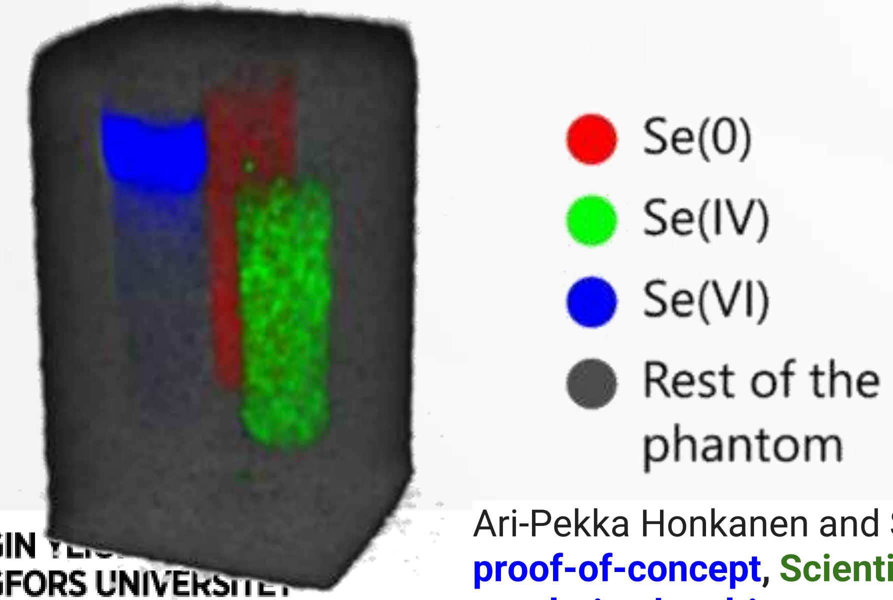



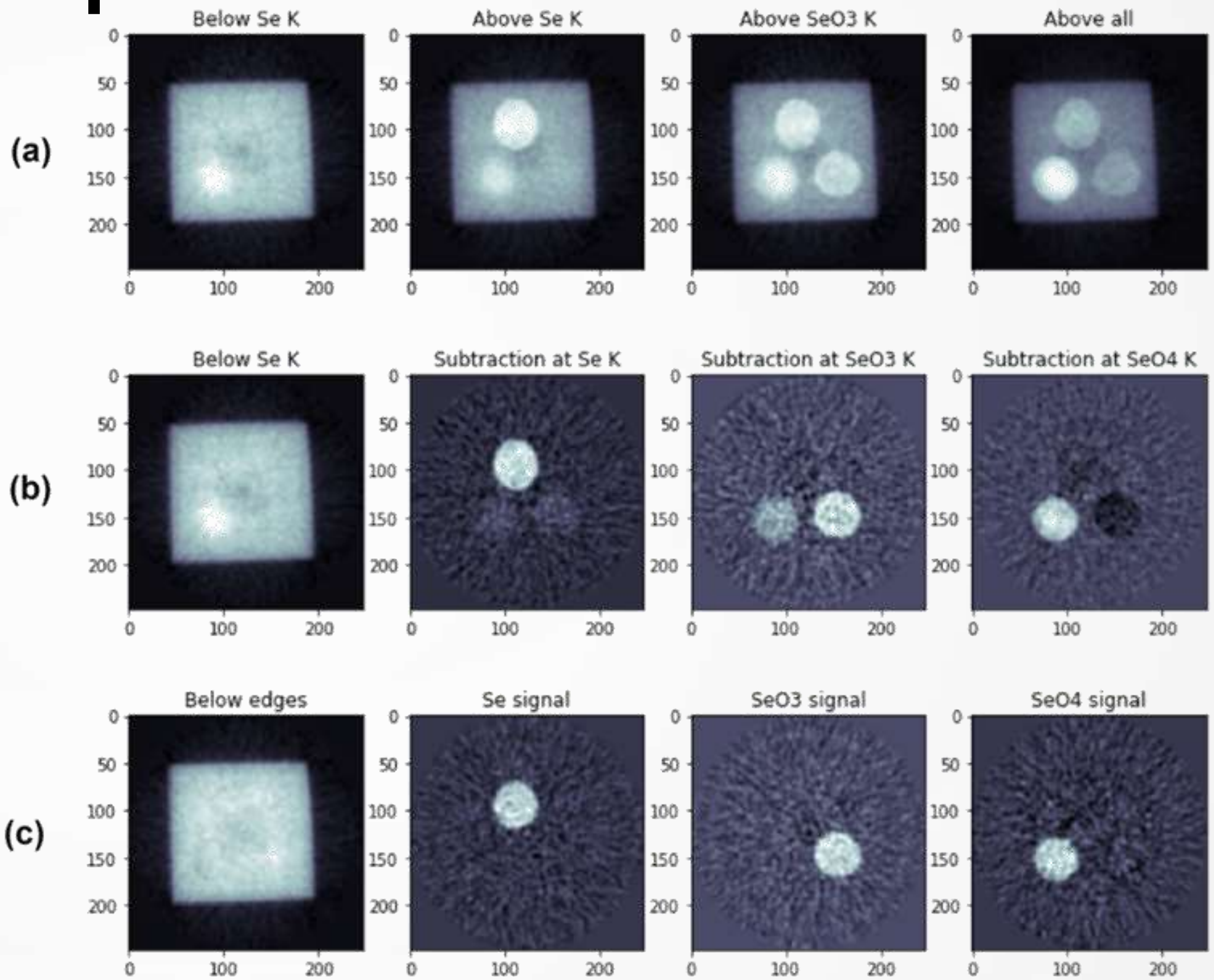

Changxun Yu et al.: **Manganese cycling and transport in boreal estuaries impacted by acidic Mn-rich drainage.** **Geochimica et Cosmochimica Acta** 365, 136-157 (2024)

Nicholas P. L. Magnard et al.: **Control of H-Related Defects in gamma-MnO2 in a Hydrothermal Synthesis**, **Inorg. Chem.** 62, 13021 (2023);

# Computed tomography with monochromatic beam and chemical speciation



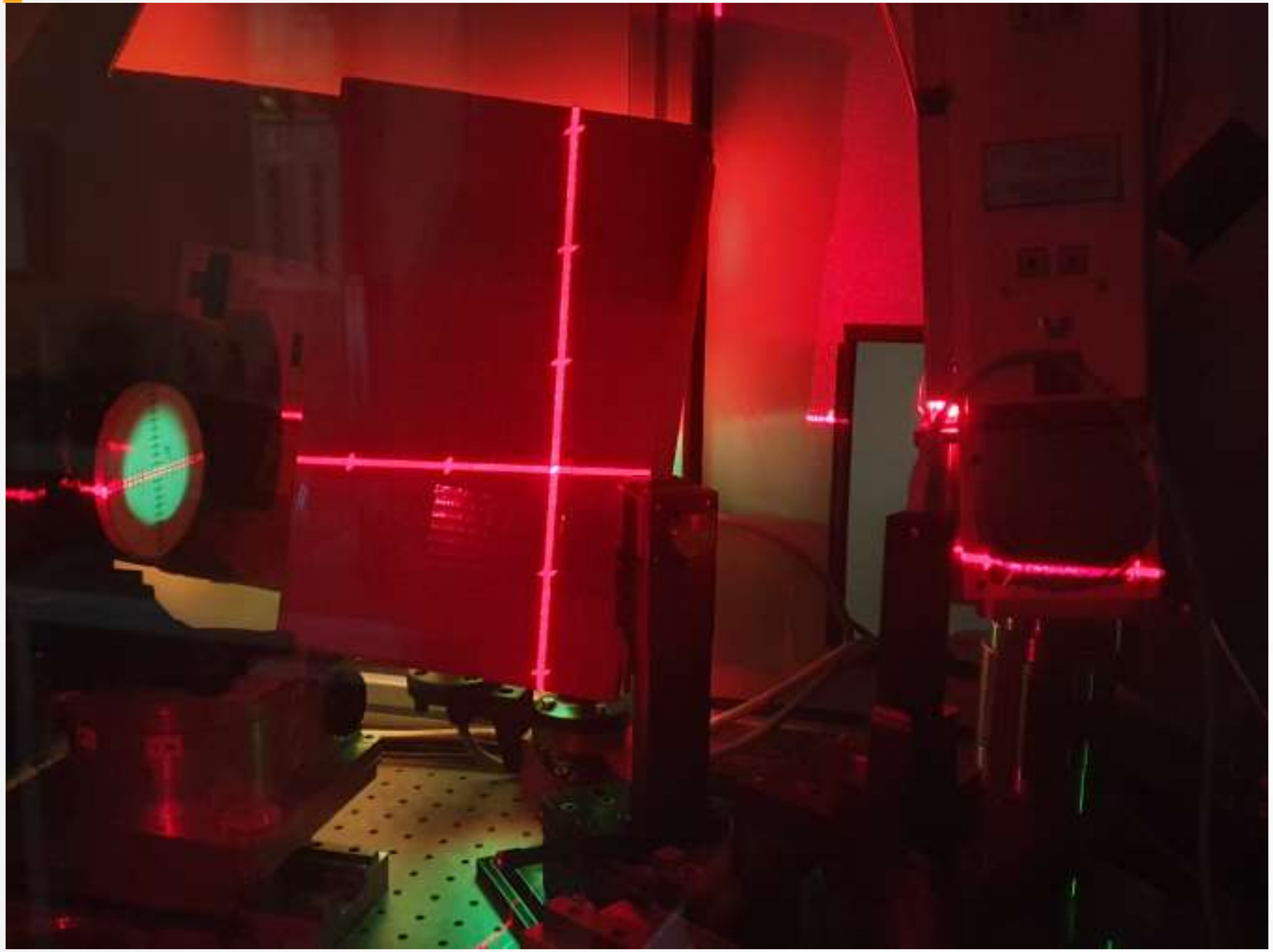



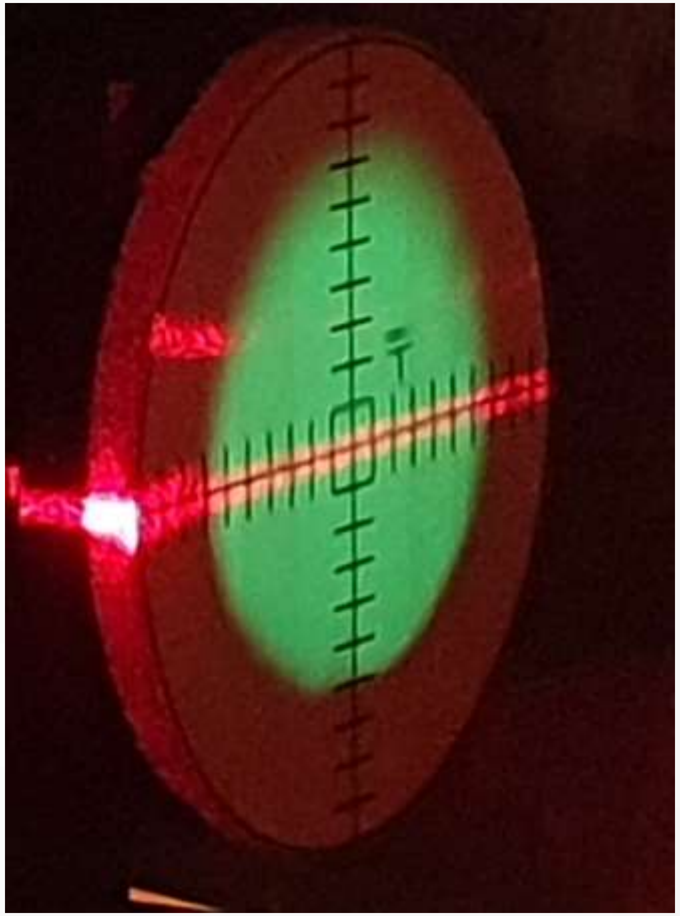

Ari-Pekka Honkanen and S. Huotari: **Monochromatic computed tomography using laboratory-scale setup: proof-of-concept**, **Scientific Reports** 13, 363 (2023); Salla-Maaria Latva-Äijö et al.: **Inner product regularized multi-energy X-ray tomography for material decomposition**.

# OUTLINE

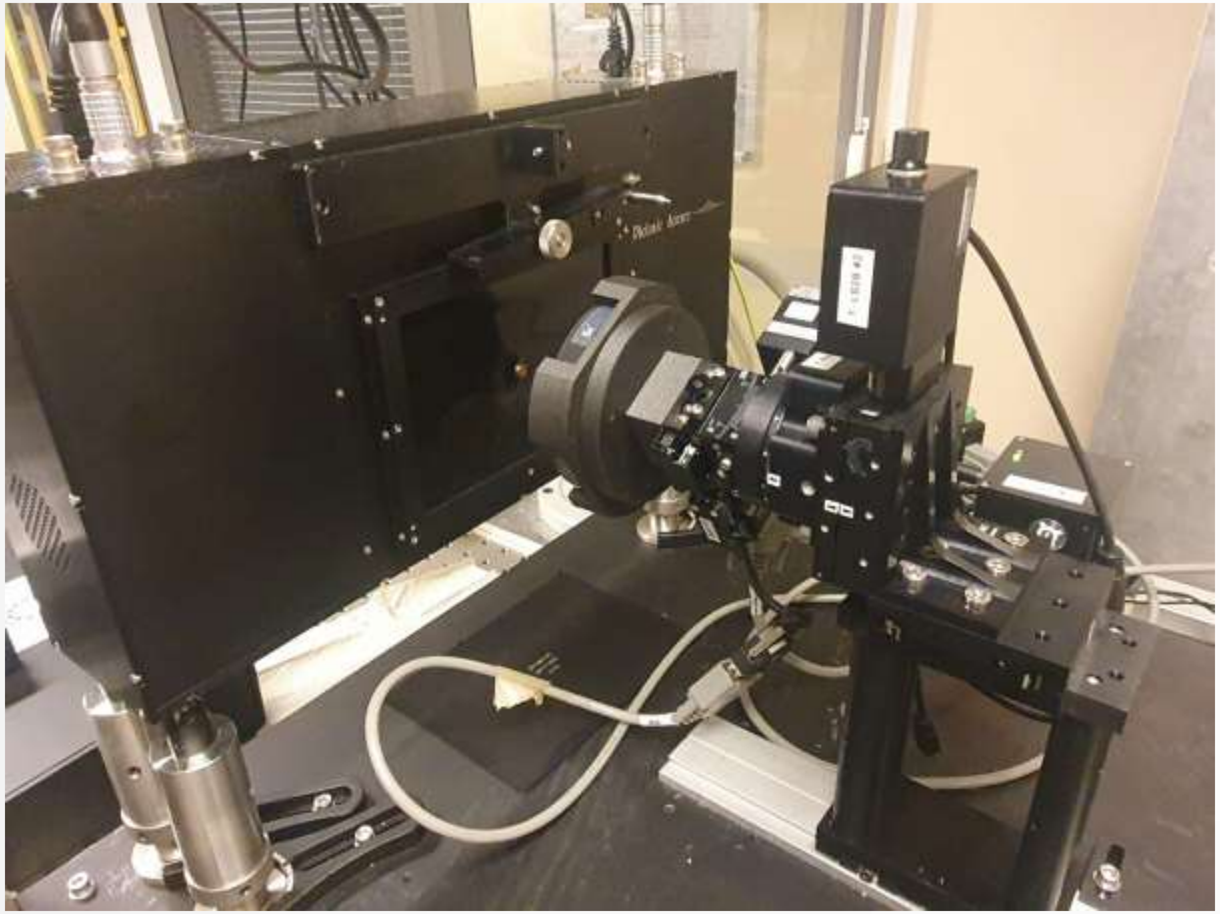
1. User statistics and recent publications
2. Auxiliary equipment (Laue, optical test bench etc.)
3. Extending the energy range
4. Simultaneous measurement of $I_0$
5. New *operando* sample environment designs

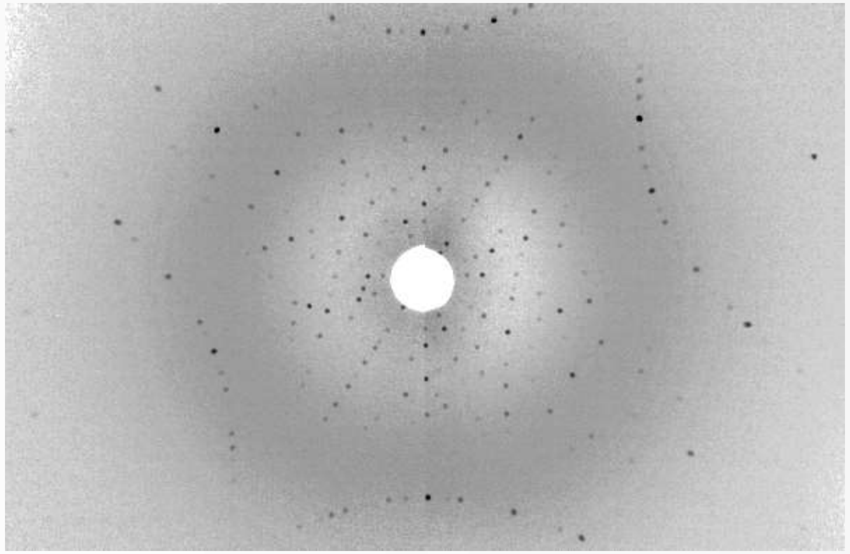
# Optical alignment with fluorescence screens

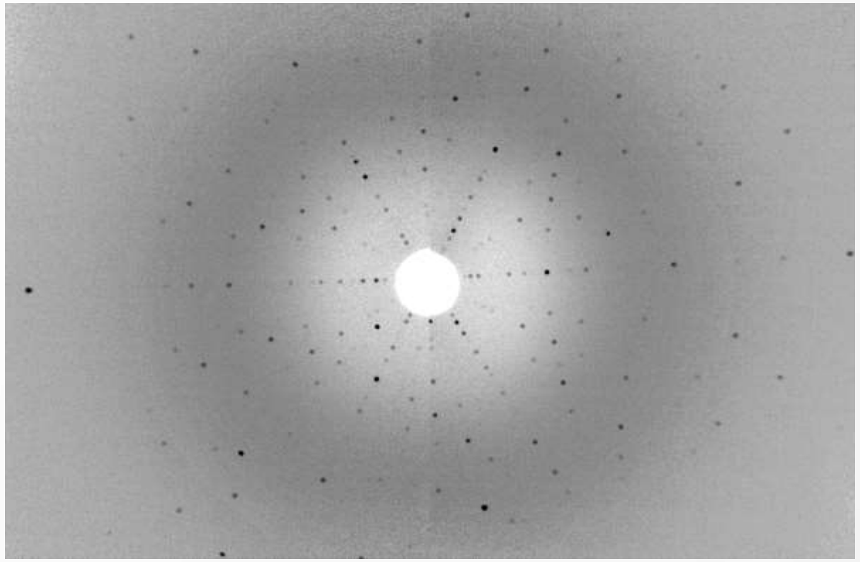




# Laue camera for monochromator orientation



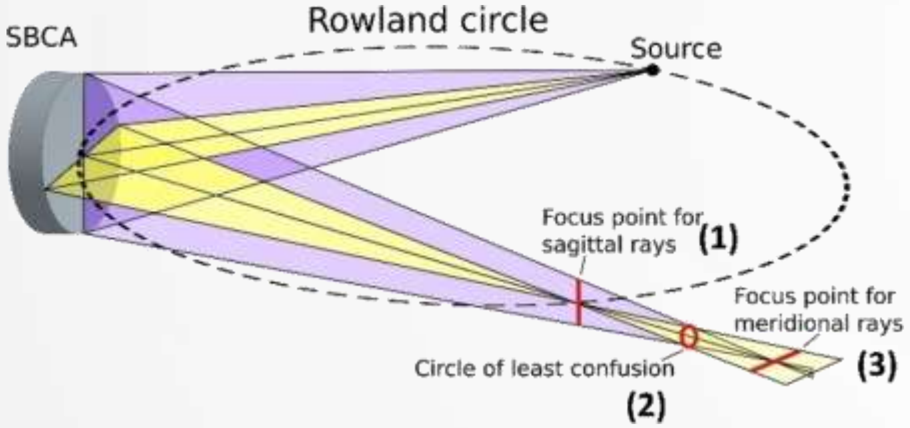


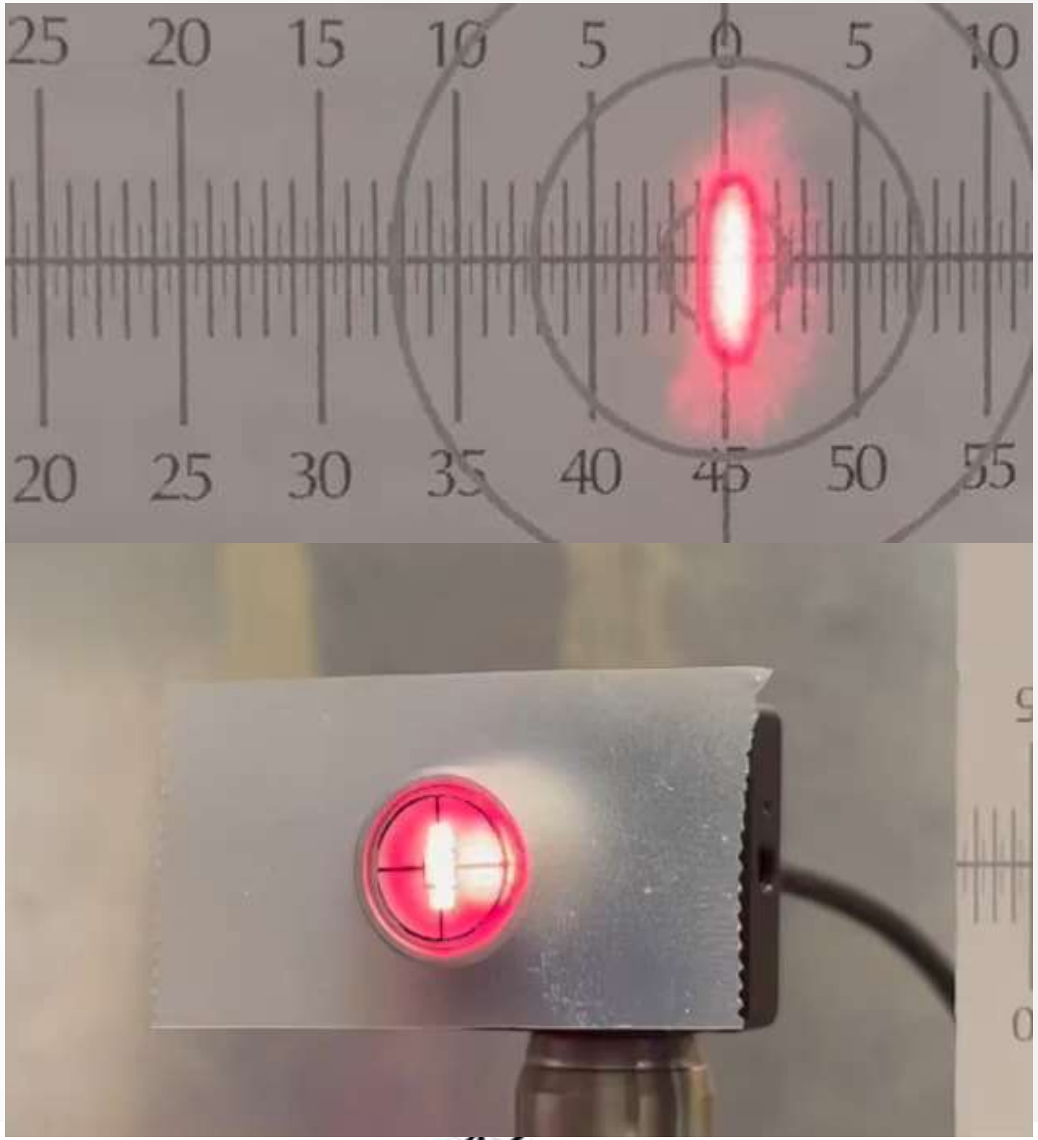


HELSINGIN YLIOPISTO
HELSINGFORS UNIVERSITET
UNIVERSITY OF HELSINKI

Center for X-ray spectroscopy

# Optical bench for crystal focal testing



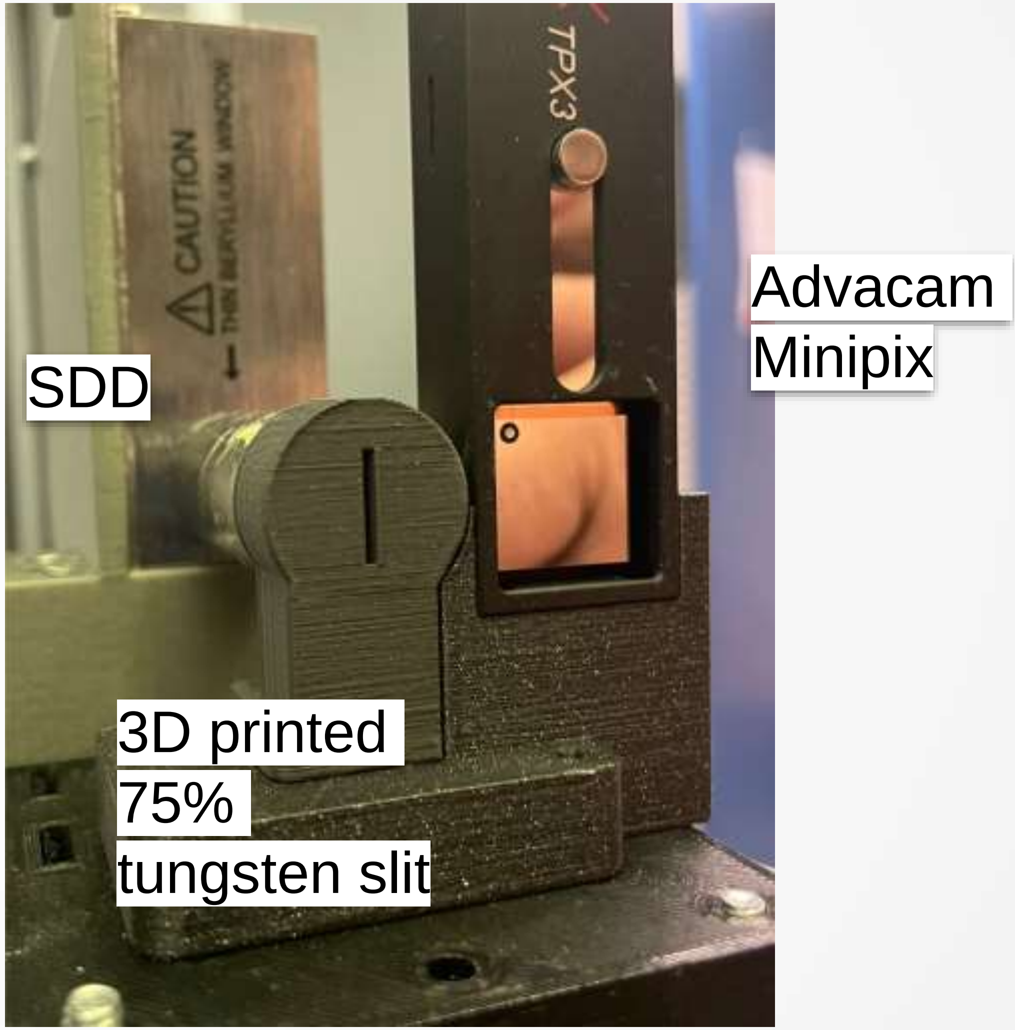



- Matte-finish Scotch tape to diffuse the laser light
- Determination of SBCA bending radius
- Demonstrate optical effects of analyzer crystals

# Tungsten filament for 3D printing

## Prusament PETG Tungsten 75% 1kg

Parameters | Prusament | Grey / Silver | Filled





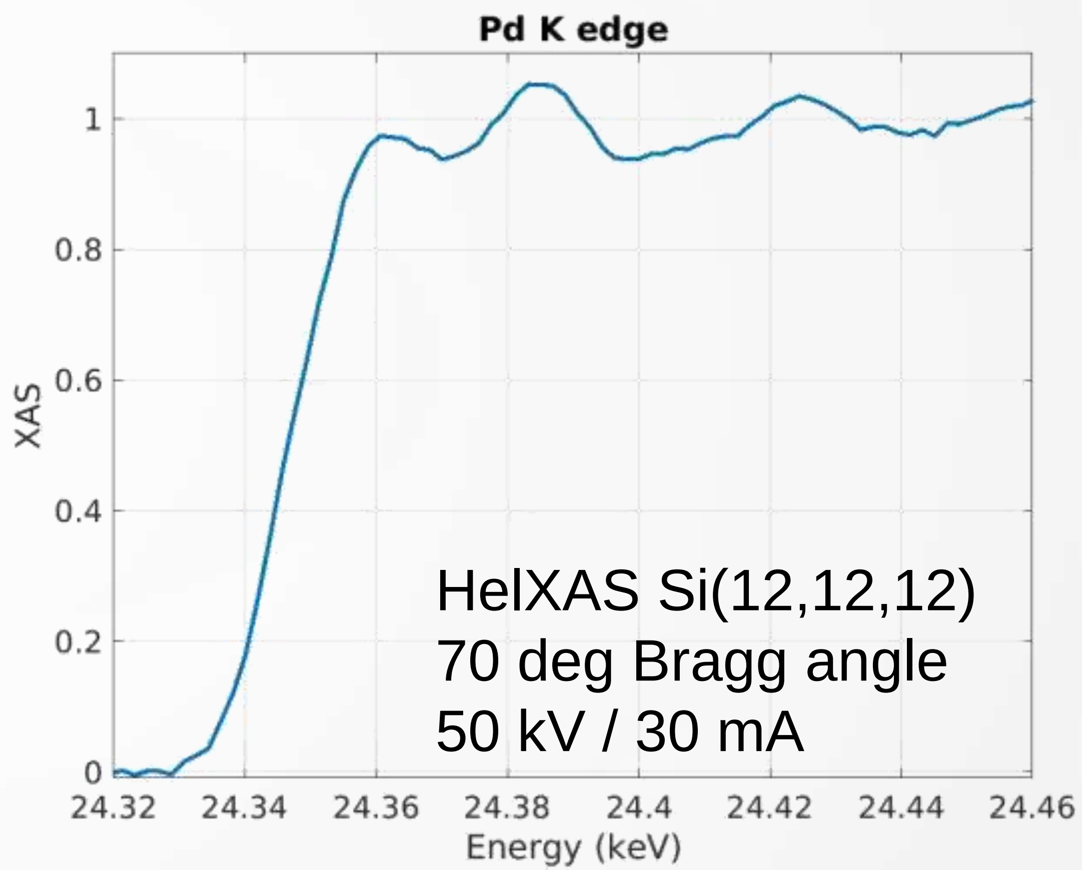

https://www.prusa3d.com/product/prusament-petg-tungsten-75-1kg/

# OUTLINE

1. User statistics and recent publications
2. Auxiliary equipment (Laue, optical test bench etc.)
3. Extending the energy range
4. Simultaneous measurement of $I_0$
5. New *operando* sample environment designs

# Reaching out to higher energies: Pd K (24 keV)

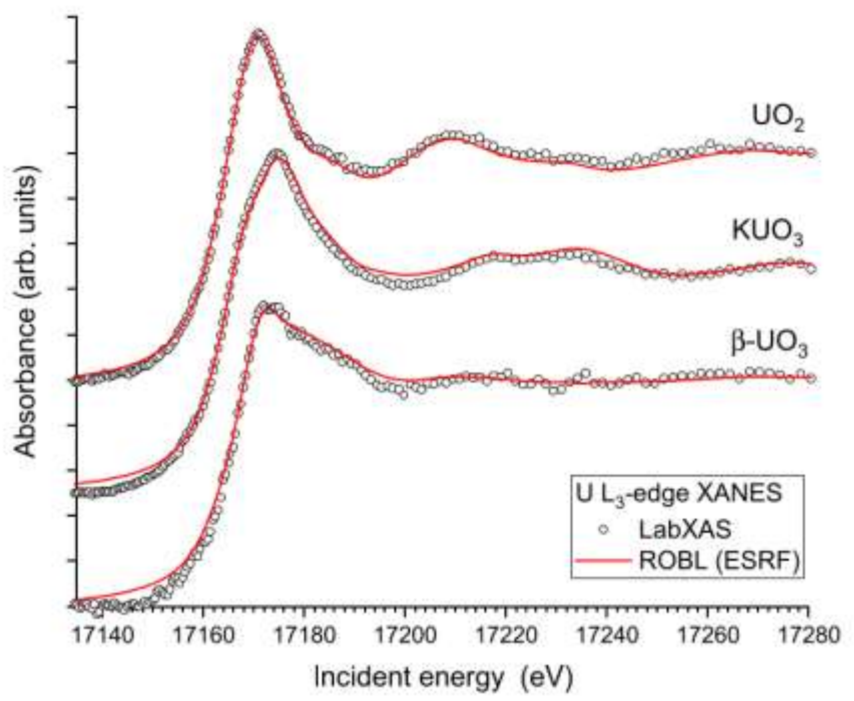
- Lots of reasons for investigating Pd K edge
- With high symmetry reflections using very high harmonics, the lower harmonics may contribute strongly to the detector dead time -> filtering
- Using a low-symmetry reflection such as Si(15,15,1) should be better
- Fluorescence mode needed for low-concentration samples, low-symmetry reflection then mandatory (to avoid excitation by e.g., 13,13,13)
- CdTe or Ge detector necessary
- Radiation shielding issues become important when using high x-ray source voltages
- Up to now, no useful data from low-concentration (1wt-%) samples



# Recent developments and results on Uranium

## Johann spectrometer optimized for actinide studies

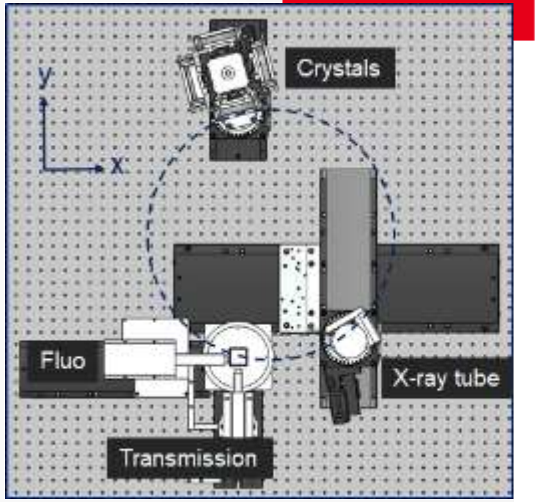
- HotXAS : instrument developed for CEA Atalante facility (hot laboratory in CEA Marcoule):
  - nuclear fuel studies → very limited access to synchrotron due to radioactivity & Pu related limitations
  - Actinide's energy range between 16 and 20 keV for L3-edge
  - **feasibility firstly demonstrated in HelXAS in 2018** :
    - Ge(9 9 9) & 30 kV / 10 mA
    - 300 W = ~700 cps → 24 hours / XANES




- Requirements:
  - special sample environment (under development at CEA)
  - sample position fixed for safety reasons
  - moving X-ray source :
    - air cooled / low-power (~25 W) → 10 days / XANES ?!

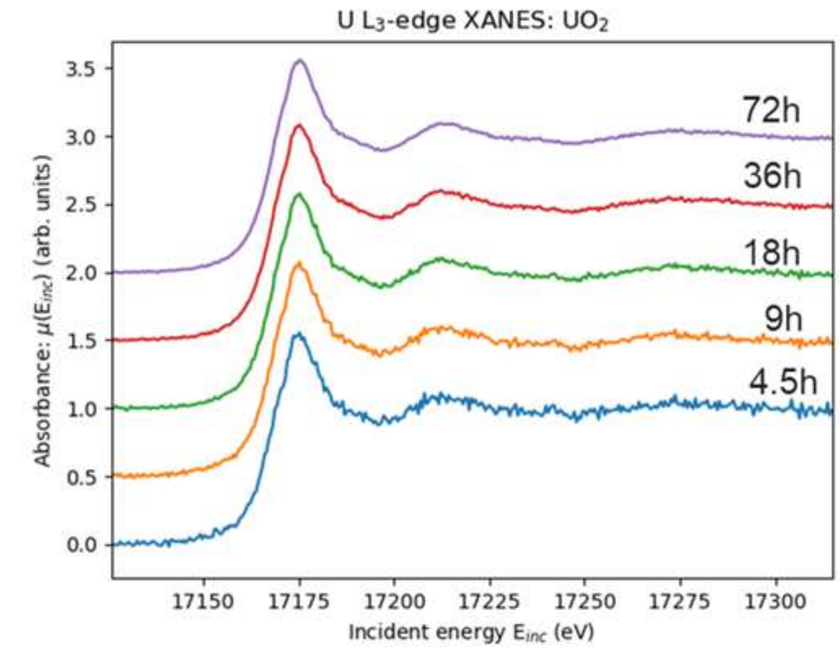
**→ Improved measurement time (better flux) needed to be realistic !**

# Recent developments and results on Uranium

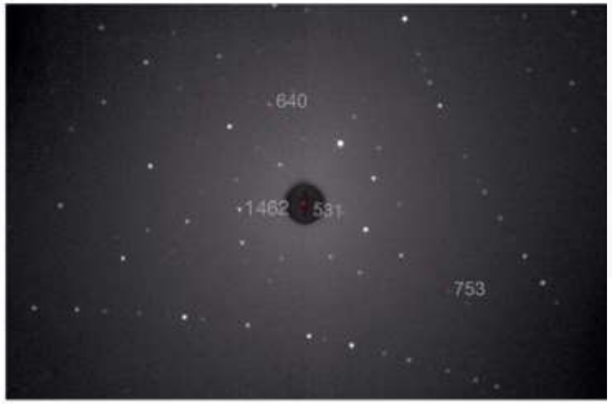


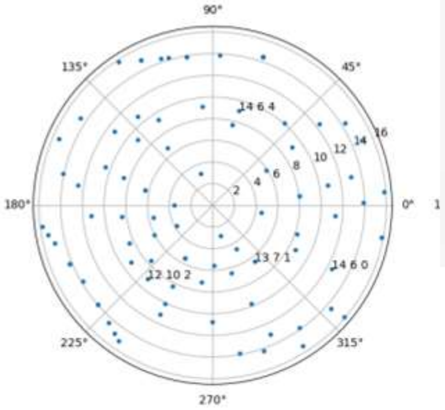

## Johann spectrometer optimized for actinide studies

- Setup developed through S. Orlat's PhD thesis
- Flux significantly improved from better reflection choice Si(12 8 4):
  - same Bragg angle = no energy resolution loss !
  - form factor: Ge(9 9 9) / Ge(1 1 1) ~0.04 % vs Si(12 8 4) / Si(1 1 1) ~0.31 %
  - U L3-edge XANES spectrum collected in few hours with 12x less power !
    → Can still be improved with better detector, e.g. 1 mm thick SDD




- **Could we get similar results for Pu and Am ?**
  - best reflection(s) not available directly → asymmetric Rowland !
  - On-going extensive Laue characterization of our crystals
  - First promising results on U : same flux using (12 8 4) from Si(953)

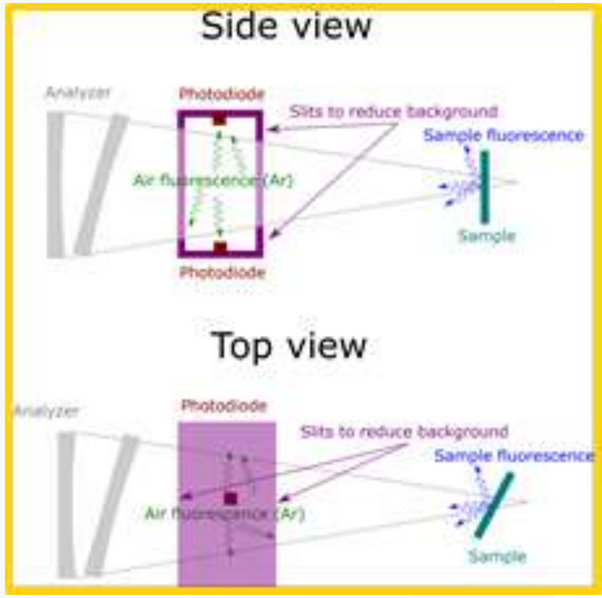


# OUTLINE

1. User statistics and recent publications
2. Auxiliary equipment (Laue, optical test bench etc.)
3. Extending the energy range
4. Simultaneous measurement of $I_0$
5. New *operando* sample environment designs

# $I_0$ simultaneous measurement




**How to measure simultaneously incoming and transmitted beam intensities?**

- Would significantly save measurement time
- Requirements:
  - good energy resolution (<500 eV) to separate harmonics
  - large active area (1-2 cm2) to be positioned off-Rowland
  - semi-transparent (~10%) to limit photon loss

- Usually performed with ionization chamber: not very practical on Johann spectrometer
  - Instrument compactness and required energy resolution are limiting factors

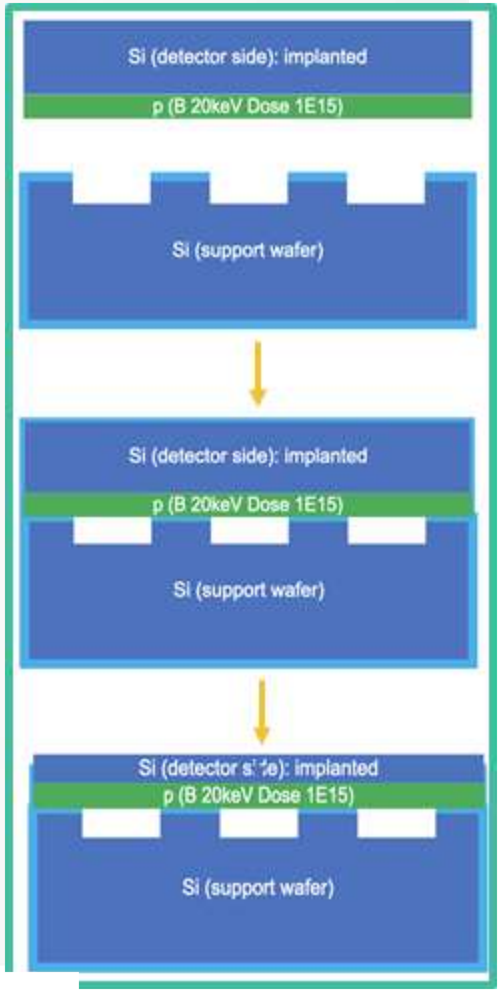
- Several possibilities:
  - harmonic approach : working but not applicable in all cases :(
  - scattering foil : first tests using kapton + SDD aside not conclusive → very weak signal :(
  - **Ultra-thin SDD :  not available on the market :( → HIP detector laboratory !**
  - Other alternatives: air ionisation chamber, beam-chopper, annular SDD, etc.. → to be evaluated

# $I_0$ simultaneous measurement

**Development of ultra-thin SDD for I0 measurements with HIP detector laboratory**

- Goal is 30 µm thin SDD with concentric hexagonal structures.
- Collaboration with Okmetic Oy using BSOI technology.
- Current status:
  - Wafers (n-type FZ) received, backside boron implant.
  - **Bonded to carrier wafers and thinned down** to desired thickness.
- Simulations ongoing for optimized design :
  - Must fulfill the objectives of transparency, energy resolution and large area
  - Geometry (Sentaurus TCAD): thickness, patterning and doping ?
  - Processing (ICECREM) : thermal budget, dopants ?
  - Low noise potential JFETs to select the best one(s) for future prototype(s)

  → **First prototype expected in 2025**



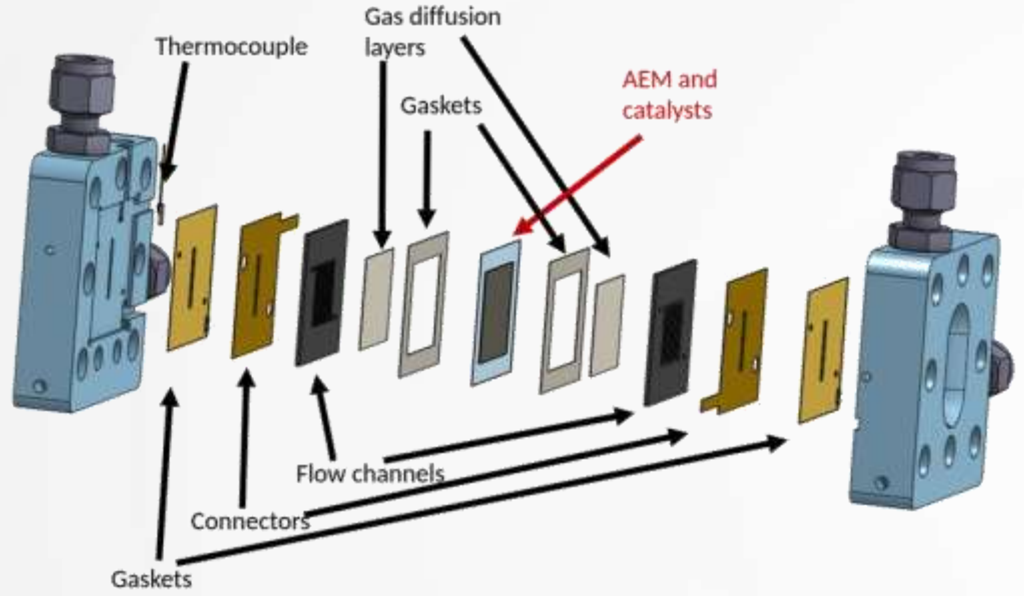
# OUTLINE

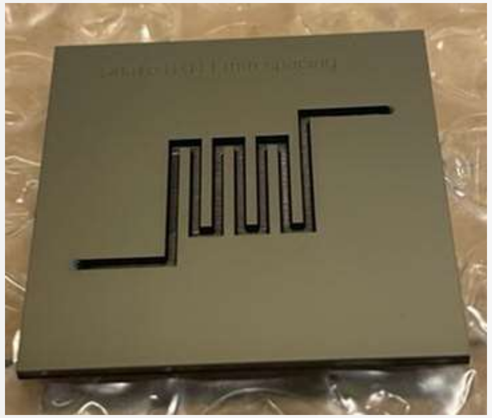
1. User statistics and recent publications
2. Auxiliary equipment (Laue, optical test bench etc.)
3. Extending the energy range
4. Simultaneous measurement of $I_0$
5. New *operando* sample environment designs

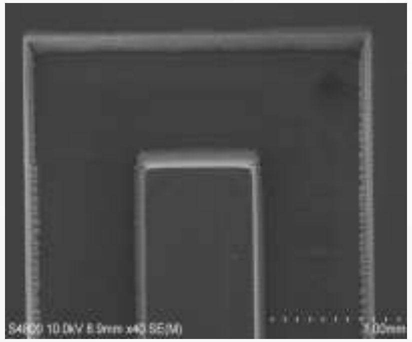
# Next-gen catalysis cell designs

Tested at ID26@ESRF

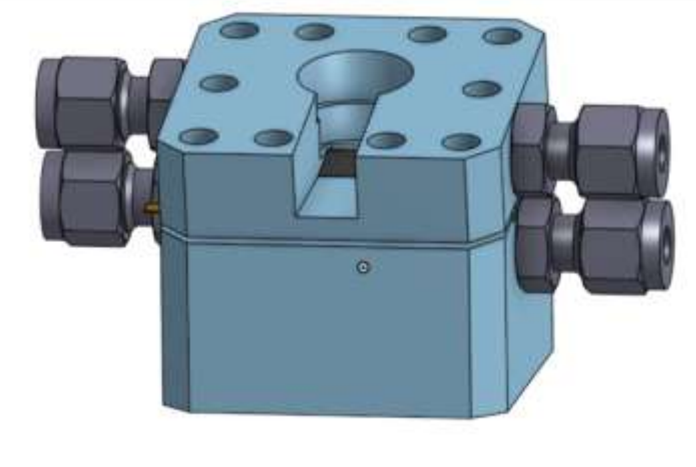
Transmission setup:



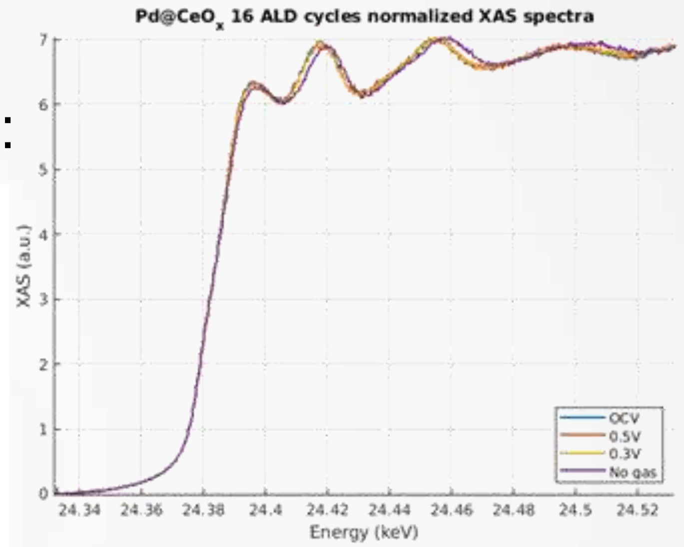



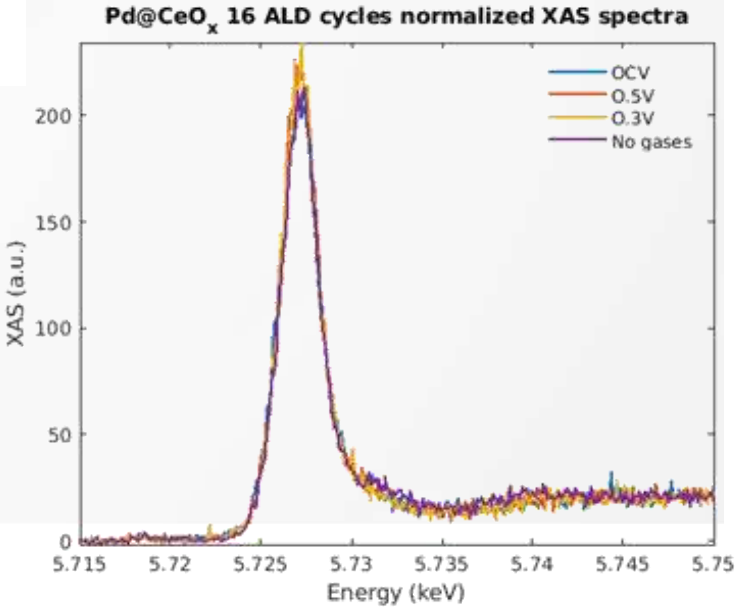


Fluorescence-mode setup for low concentration samples:

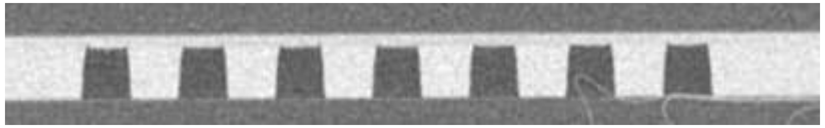


- 1-mm glassy-carbon plate, laser micromachined flow channel
- ~170 micron window thickness



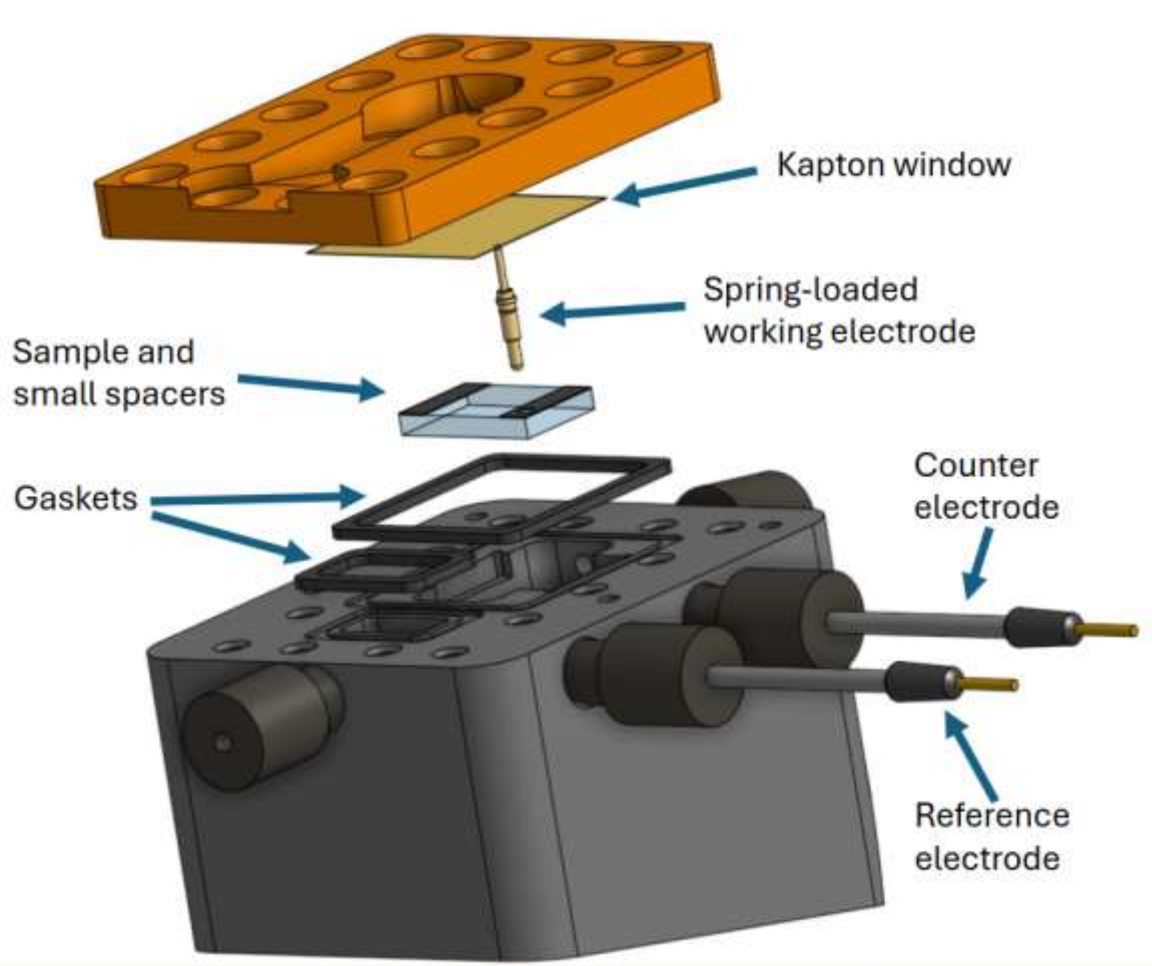




HELSINGIN YLIOPISTO
HELSINGFORS UNIVERSITET
UNIVERSITY OF HELSINKI

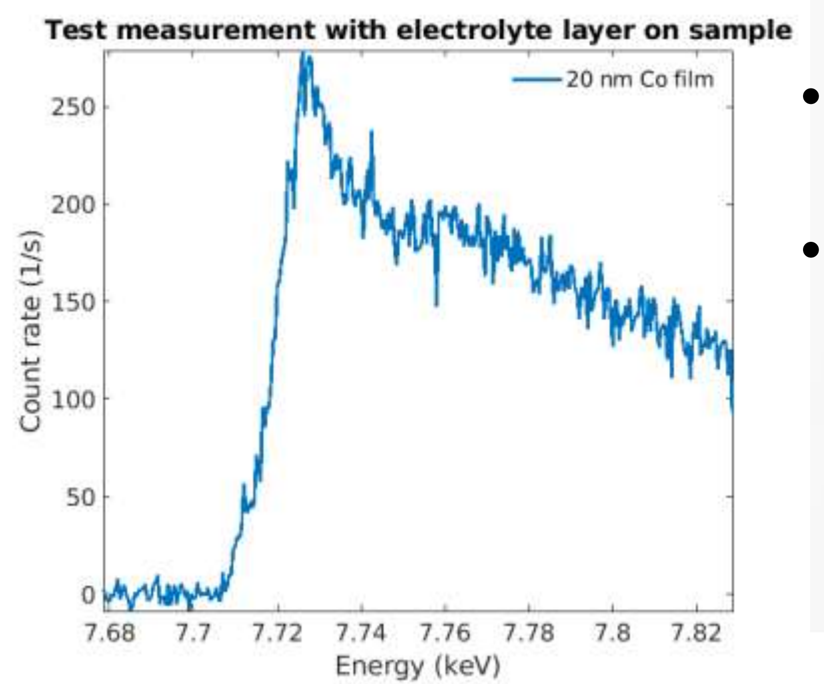


Center for X-ray spectroscopy

# 3-electrode cell for electrolysis studies




- Co/Fe/Ni ALD thin films grown on TFO glass
- 3-electrode cell
- Small rubber spacers to allow flow of KFO electrolyte
- Kapton window




Count rate from a single 10 min scan

- Fluorescence mode
- No need to deposit on glassy carbon or Kapton

# Conclusions

- During the recent year, activity of lab-based x-ray spectroscopy in Helsinki has been steady and development of HotXAS (CEA Marcoule, France) being done
- New industrial users would be welcome

- User and beamline scientist experience improves with auxiliary equipment for alignment, crystal testing, etc.

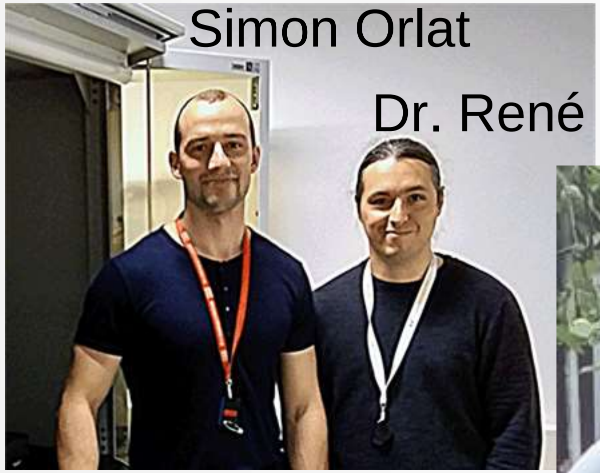
- Increasing the energy range from nominal 5-20 keV will remain a challenge, but some improvements have been made toward the high-energy side
- Toward lower energies?

- We are developing instrumentation for sample environments, simultaneous $I_0$ measurements, etc. More results on them in the next workshop ;)

# ACKNOWLEDGEMENTS

Antti-Jussi Kallio
(see his poster today)

Dr. Merja
Blomberg



Simon Orlat

Dr. René Bes

Dr. Heikki Suhonen

Dr. Nina S. Genz
Swiss Light Source

Morten Johansen
Aarhus University

Prof. Dr. Bert
Weckhuysen
Utrecht University

+ many others
+ you for your attention!