New developments at the INE-Beamline for Actinide Research at ANKA

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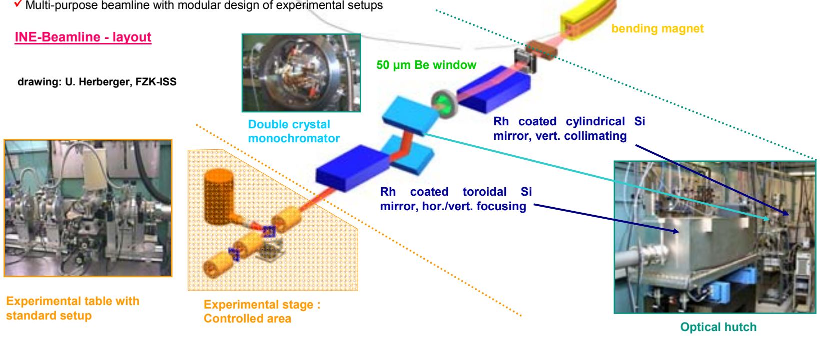
INE-Beamline Characteristics

The INE-Beamline is an experimental synchrotron X-ray station dedicated to actinide speciation investigations related to nuclear waste disposal as well as applied and basic actinide research.

- ✓ On-site (FZK, KIT north campus), backed by decades of know-how and infrastructure to handle radioactive materials
- ✓ Access to INE laboratories for preparation and characterization of samples
- ✓ Studies with activities up to 10^6 times the exemption limit allowed
- ✓ Safe and flexible containment concept
- ✓ Multi-purpose beamline with modular design of experimental setups

INE-Beamline - layout

drawing: U. Herberger, FZK-ISS

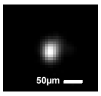


Standard methods	**monochromatic beam**
XAFS	characterization of bulk species
XAFS/XRD	correlate phases with pair distributions
TEY / FluoXAFS	for non-transmission experiments
Surface sensitive	**grazing incidence technique**
GI-XAFS	characterization of surface sorbed species
Standing wave	characterization of atomic positions at surfaces
Spatial resolution	**focused beam for "micro" or µ-technique**
µ-XAFS	chemical state imaging
µ-XRF	elemental mapping
µ-XRD	identification and distribution mapping of phases
Energy resolution	**secondary monochromator (Johann spectrometer)**
HRXES	high resolution X-ray emission spectroscopy
RIXS	resonant inelastic X-ray scattering
Combination of methods	**combined x-ray methods or combination of x-ray method & other techniques, e.g., laser spectroscopy, UV-Vis, Raman, etc…**

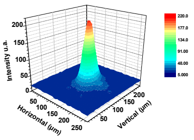
Spatially Resolved Studies : combined µ-XAFS and µ-XRD High Pressure Diamond Anvil Cell (DAC) experiment with 243-Am

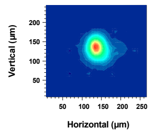
Characterization of a new single bounce capillary (SBC) at 18.5keV by registering the beam spot at the focal distance with an X-ray camera. This SBC is specially designed to adapt to the high horizontal divergence of the beam.

Camera in SBC focus

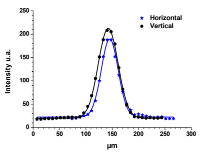


Camera output

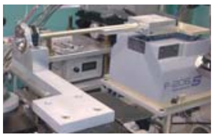




Digitized beam intensity cross-section and 3D view



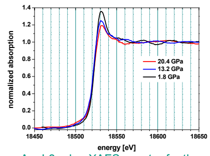
Beam dimensions at 18.5keV: focal length 3mm, FWHM 33µm horizontal and 37µm vertical



Single-bounce capillary installed at the INE-Beamline for DAC experiment

243-Am phase transitions from the AmI phase (dhcp), to AmII (fcc), to AmIII (face centered orthorhombic Fddd) to the highest known pressure AmIV phase (Pnma) at nominal pressure up to 25 GPa in a high pressure DAC are studied. At discrete pressures an XRD pattern is recorded to validate the Am phase and an Am L3 edge XAFS spectrum is recorded in transmission geometry.

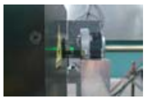
Setup for µ-XAS



Am L3 edge XAFS spectra for three different pressure

Setup for µ-XRD

The pressure inside the DAC is measured by in situ monitoring of wavelength changes in the fluorescence emission line of a ruby crystal.



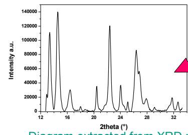
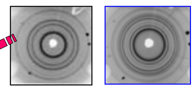


Diagram extracted from XRD ring pattern for the AmI (dhcp) phase



XRD ring pattern of the AmI (dhcp) phase left and AmIII phase right, exposure time 5min at 18.5keV (λ = 0.670185 Å)

This high pressure Am experiment is a cooperation with the European Joint Research Centre Institute for Transuranium Elements (ITU) ; G Lander, S Heathman and S. Surblé.

In-situ Studies : electrochemical cell

An electrochemical cell for in situ XAFS investigation of redox sensitive systems has been developed and, following successful tests with inactive Se, used for investigations of the redox chemistry of radioactive 237-Np. Np L3-edge XANES and EXAFS of pure 237-Np species prepared electrochemically in the same solution are recorded. A 1mM 237-Np solution in 1M $HClO_4$ is used as start point.

$$\mathrm{Np(V)} \xrightarrow[\text{Ag/AgCl}]{-0.3\ \text{V}} \mathrm{Np(III)} \xrightarrow[\text{Ag/AgCl}]{+0.2\ \text{V}} \mathrm{Np(IV)} \xrightarrow[\text{Ag/AgCl}]{+\ 1.0\ \text{V}} \mathrm{Np(VI)}$$

Electrochemical cell in use at the INE-Beamline

Characteristic spectral shapes and energies and relative edge energy shifts:

Edge calibration: Zr K at 17.998keV

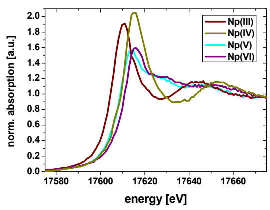
Ge(422) crystal pair in DCM

Np(V) = 17614.0eV

ΔE Np (V-III) ≈ + 3eV

ΔE Np (V-IV) ≈ - 1eV

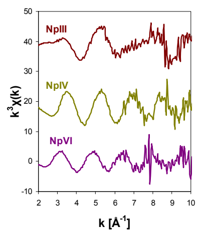
ΔE Np (V-VI) ≈ + 2eV

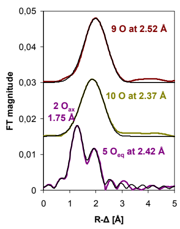


XANES spectra of different stabilized oxidation states of 237-Np recorded in fluorescence mode

EXAFS recording after

- exhaustive electrolyses for every valence
- no more changes observed on XANES spectra





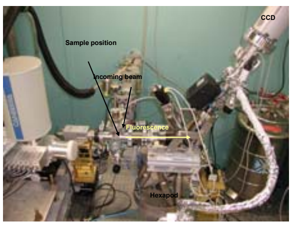
Fourier transform data & best fits using single scattering oxygen shells

High Resolution X-ray Emission Spectroscopy (HRXES)

HRXES improves spectral energy resolution of fluorescence emission by several orders of magnitude. This overcomes limitations of conventional techniques and provides electronic structure information for 4f and 5f elements.

HRXES spectrometer setup:

Photon fluorescence emission is energy dispersed by a bent Si/Ge crystal and focused onto a position sensitive detector. FWHM of the Fe $K\beta_{1,3}$ line is ~ 5eV.



Photograph of the spectrometer in use at the INE-Beamline

Photograph of the crystal bender

Photograph of the Spectrometer at a different Bragg angle

See poster of Vitova et al.

This work was performed during an ACTINET funded fellowship

Future Upgrades

Instrumentation development and upgrades planned for the near future at the INE-Beamline are related to **optimization of the µ-focus options at the beamline**, improvements of the **HRXES spectrometer,** and development of **new sample cells** for special user requirements. Specifically are planned:

- Eliminate horizontal beam drift during DCM crystal rotation (i.e., large energy scans) with high precision actuators tuning the second DCM crystal roll position.
- Extend the microfocus capabilities to confocal irradiation-detection geometry for additional resolution in the third (depth) dimension.
- First active measurements with the HRXES spectrometer, extension of attainable emission energy range, and upgrade to a new position sensitive detector.
- Combine the electrochemical cell with UV-Vis spectroscopy signal detection for a secondary in-situ verification of oxidation states.
- Adapt and test a liquid cell for high temperature, high pressure investigations.

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