Enabling investigations of liquids and liquid-solid interfaces with soft X-ray excitation at UHV conditions

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BLiX
Berlin Laboratory for innovative X-ray Technologies

Outline

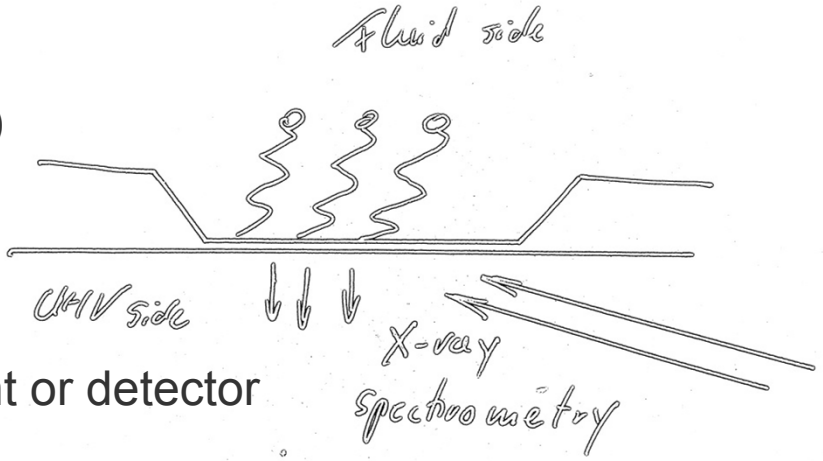
- Motivation for developing a liquid cell
- Challenges for constructing the liquid cell
  - Geometry, thickness and bulging of the window
  - Pressure compensation and degased sample solution
- Construction and design
- First experiments
- Summary
- Perspective

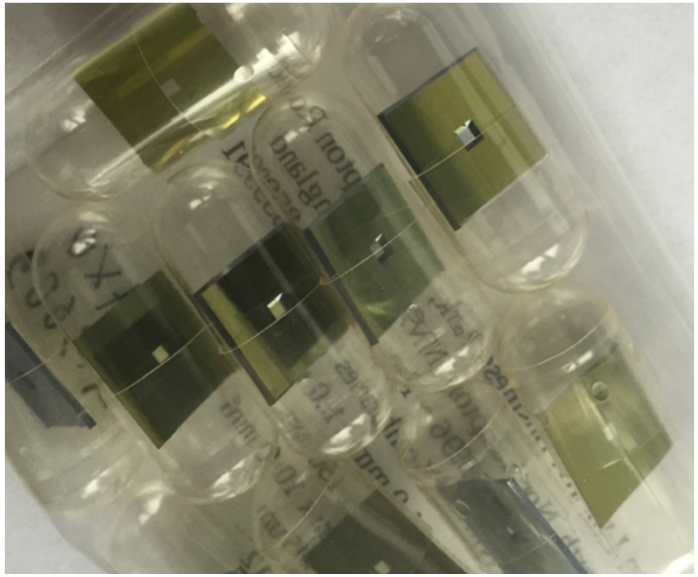
Developing a liquid cell for soft X-ray (< 1 keV) spectroscopy (NEXAFS)

Requirements:

- Investigation of liquids and liquid solid interfaces
- Vacuum-tight but soft X-ray transparent window
- Enabling measurements in emission (reflection) and transmission geometry
- Compact dimensions
- Easy to handle
- Reproduceable measurements

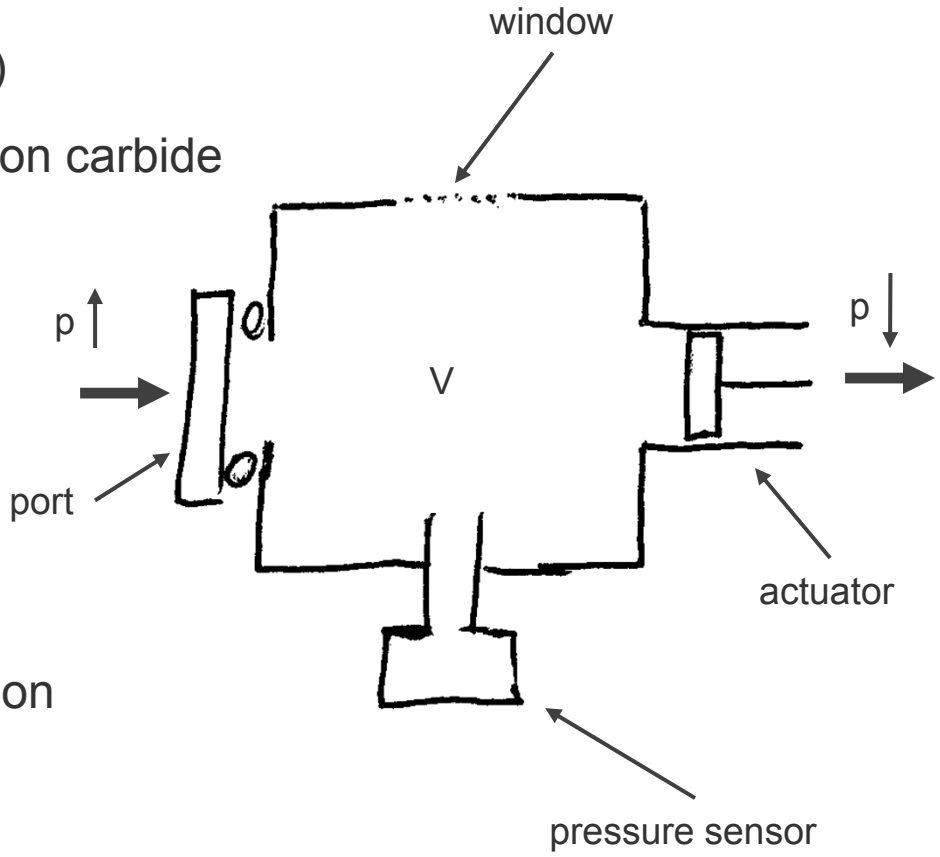
- X-ray analysis in UHV (ultra high vacuum)
  - Reduce absorption
  - Cooled, windowless detector
  - Contamination of sample environment or detector
- Risk of window rupture
- Bulging of window hampers analysis

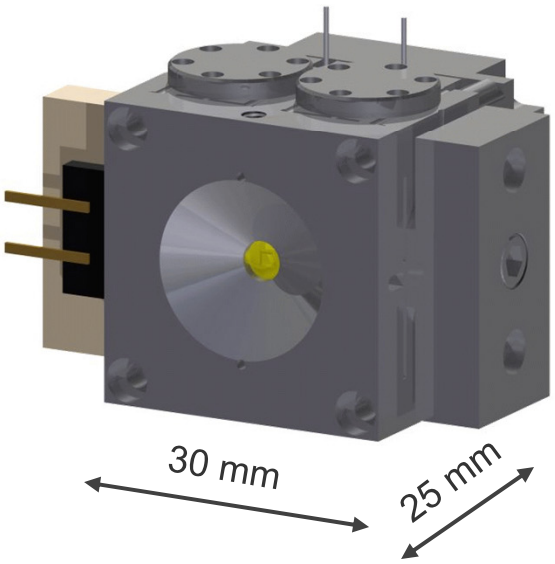


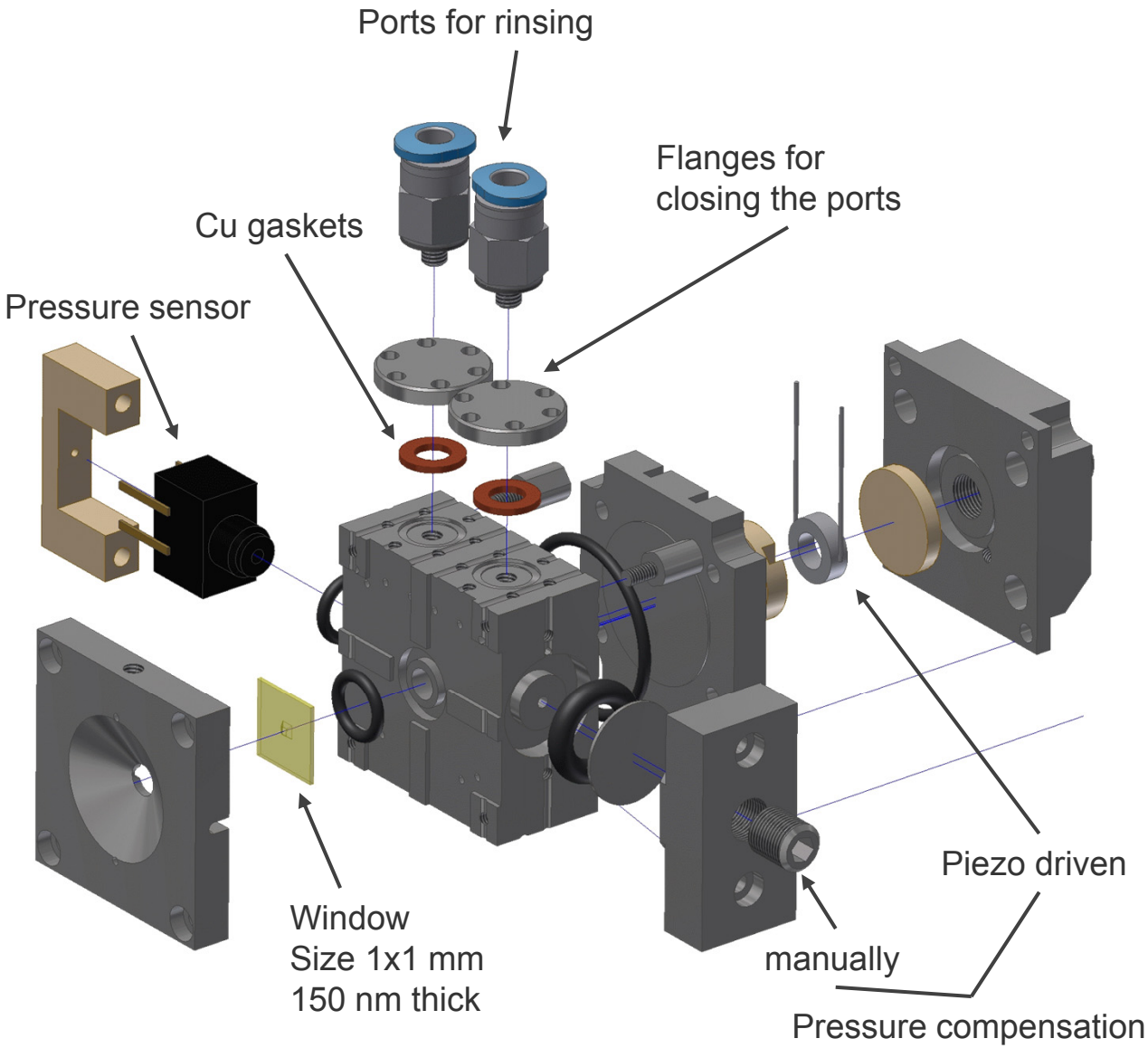


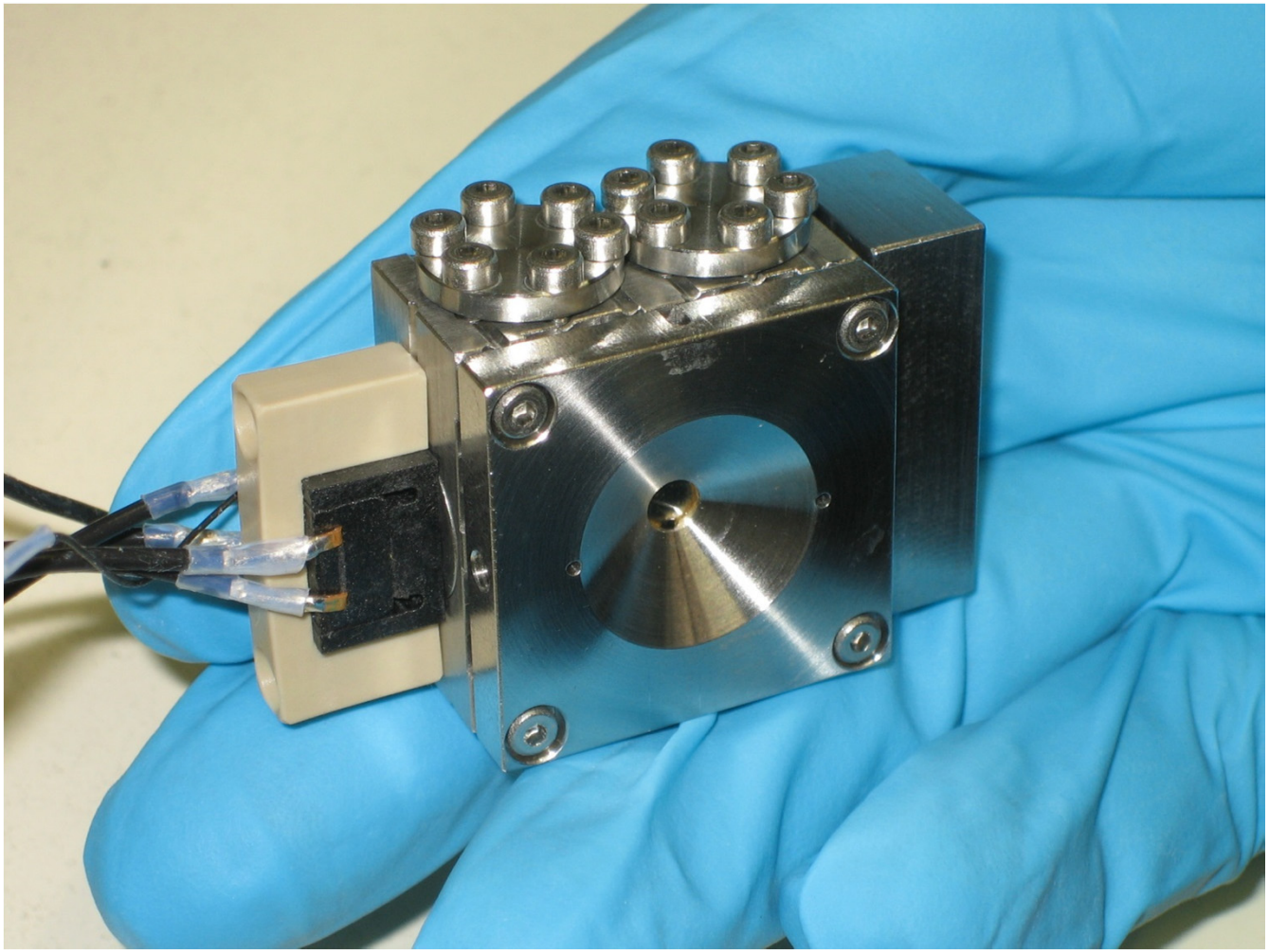
- Ultrathin window (100...150 nm)

  made from silicon nitride or silicon carbide
- Reduce the inner pressure
  - Reduced window bulging
  - Reduced risk of rupture
- Pressure compensation
  - Sensor and actuator
  - Use degased sample solution
  - Filling without bubbles



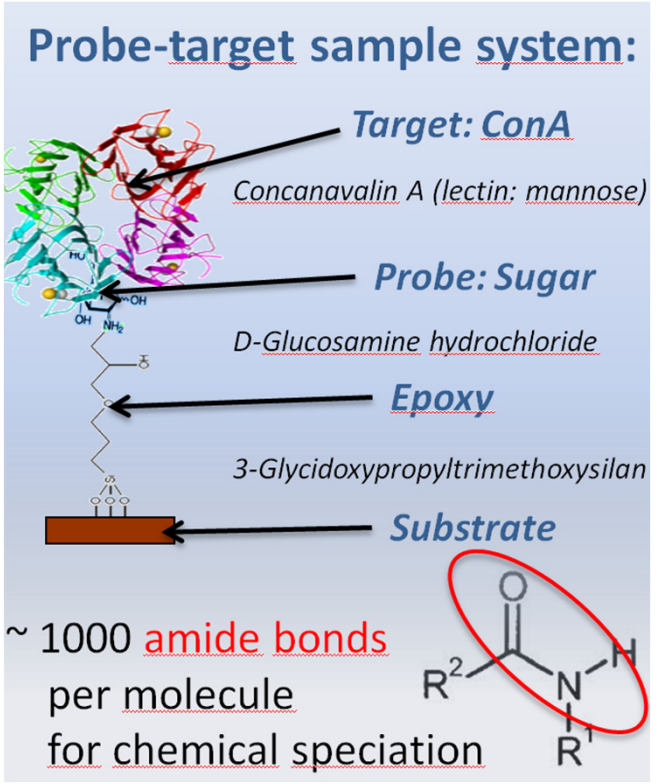

30 mm
25 mm


Ports for rinsing
Flanges for
closing the ports
Cu gaskets
Pressure sensor
Window
Size 1x1 mm
150 nm thick
Piezo driven
manually
Pressure compensation



Investigating capture molecule for medical point of care diagnostic sensor

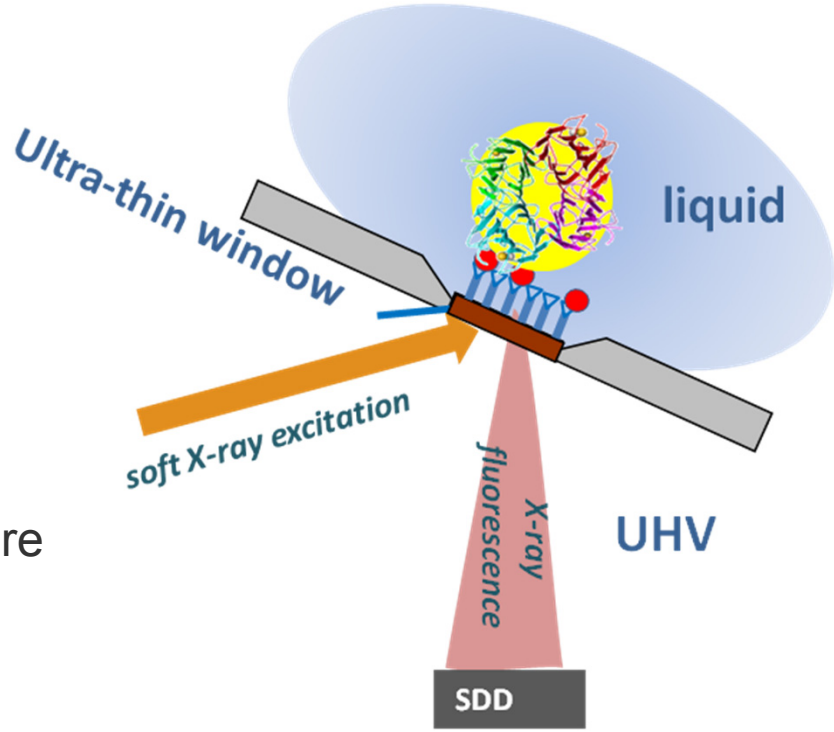
- Capture molecule binds selective and sensitive target molecule to a membrane
- Detection of target molecule by optical method or natural vibration frequency
- Characterization of the probe-target system by X-ray spectroscopy
  - Orientation
  - Chemical state
  - Deposition
- Beamtime BESSY II – PTB Beamline PGM



Paul Dietrich, ECASIA 2013, *Sessions Life Science & Biosurface 2*

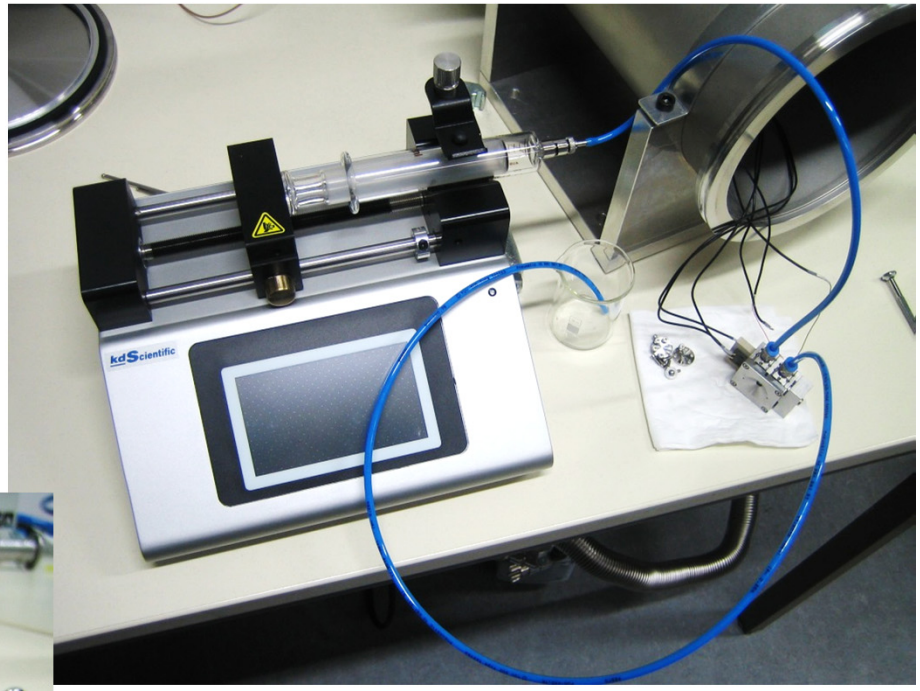
The liquid cell enables investigations of biomolecular films at liquid-solid interfaces

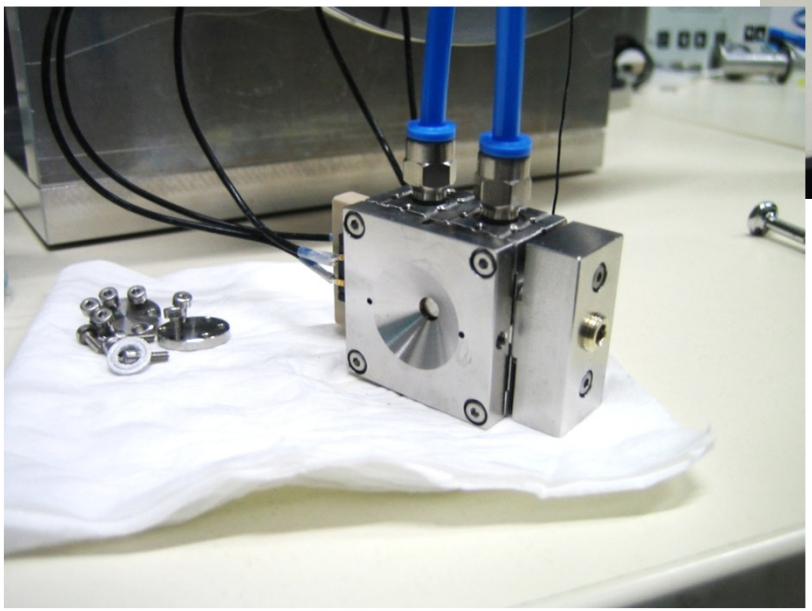
- In situ preparation of probe-target system
- In situ detection of the capture molecule with soft X-ray NEXAFS
- Excitation from different angles
- Measurement under UHV atmosphere
- Reduction of window bulging



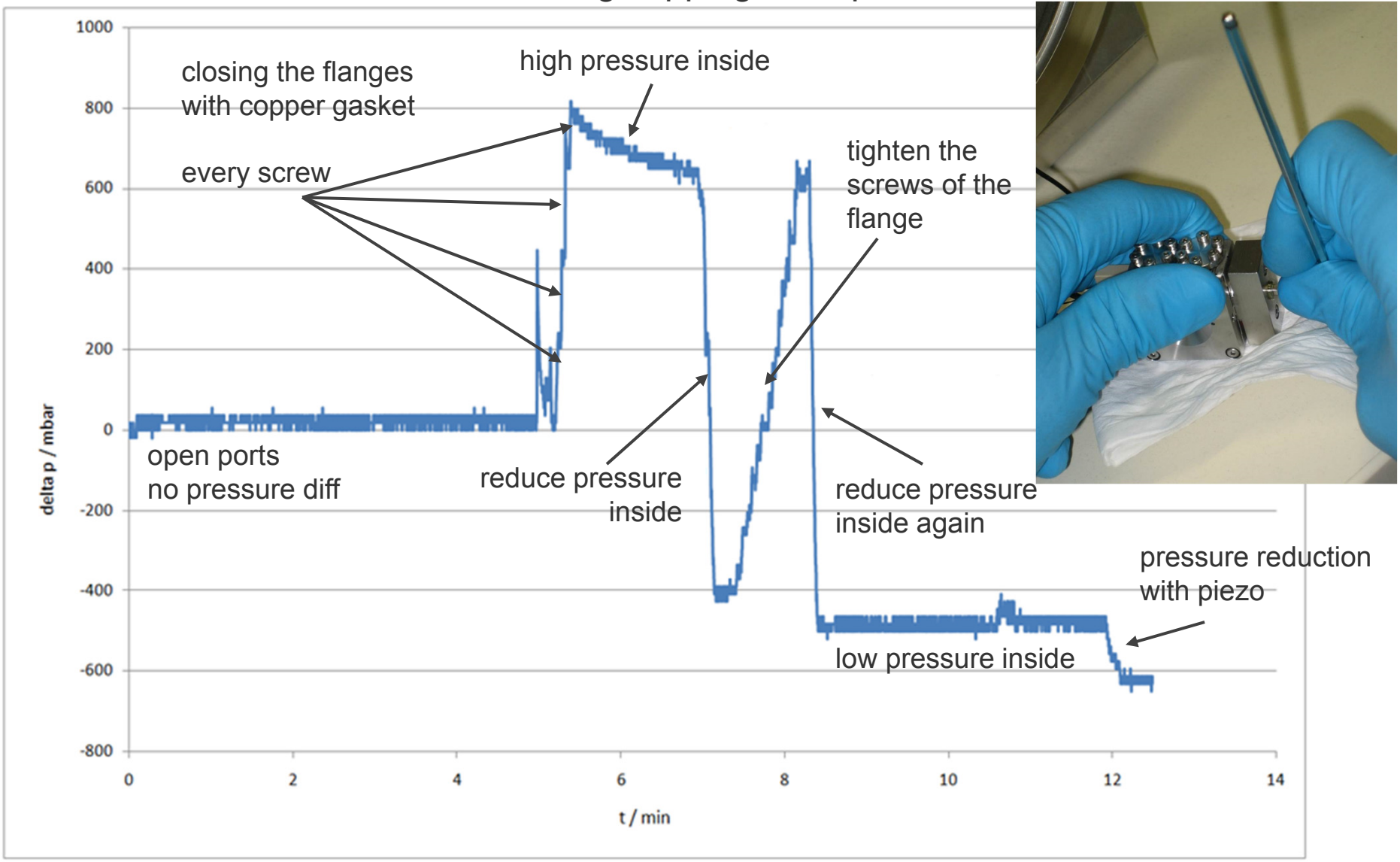
Cornelia Streeck, ECASIA 2013, *Session Solid liquid interfaces*

- In situ sample preparation
- syringe pump for rinsing the window with sample and flushing solutions

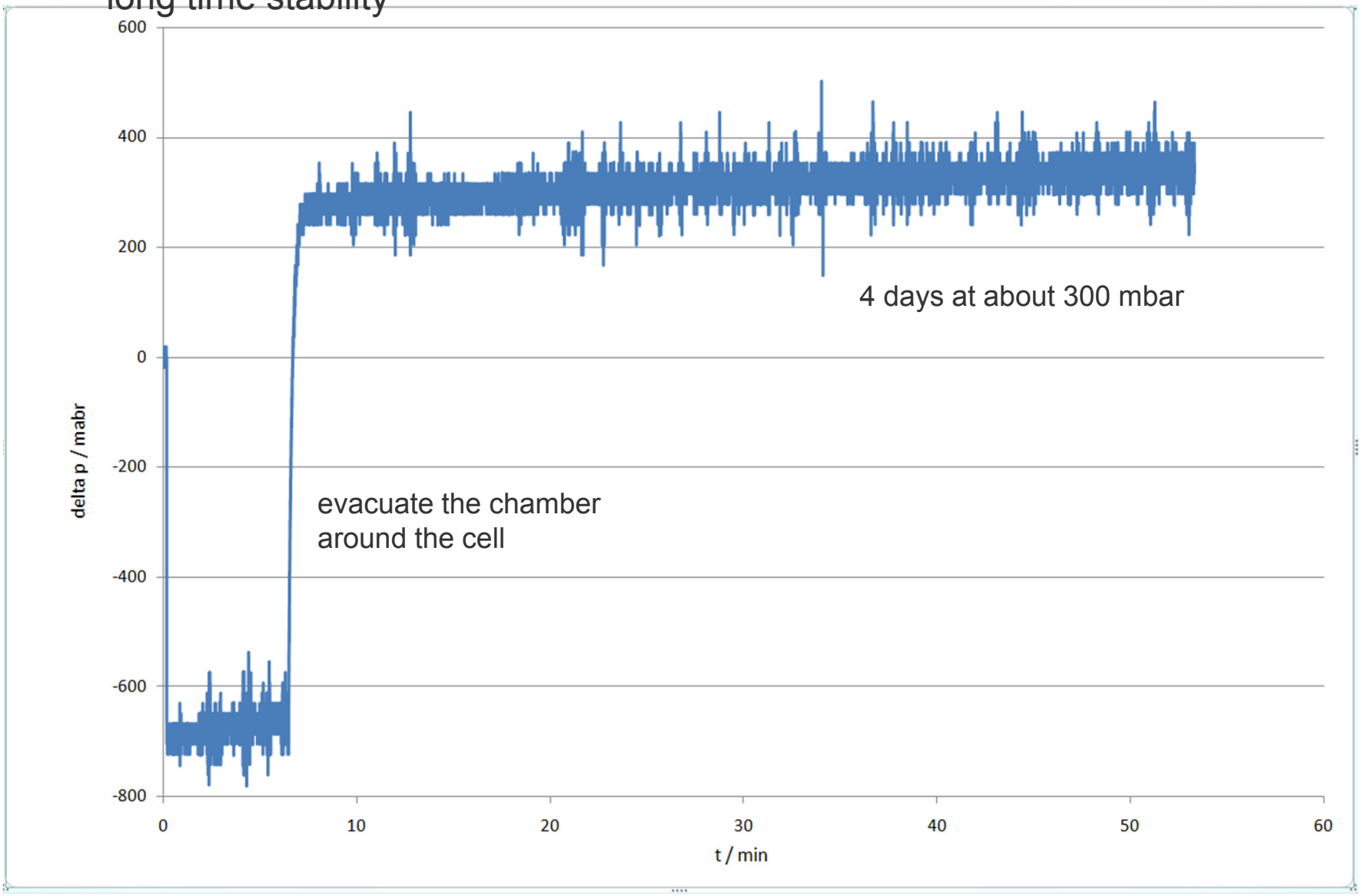




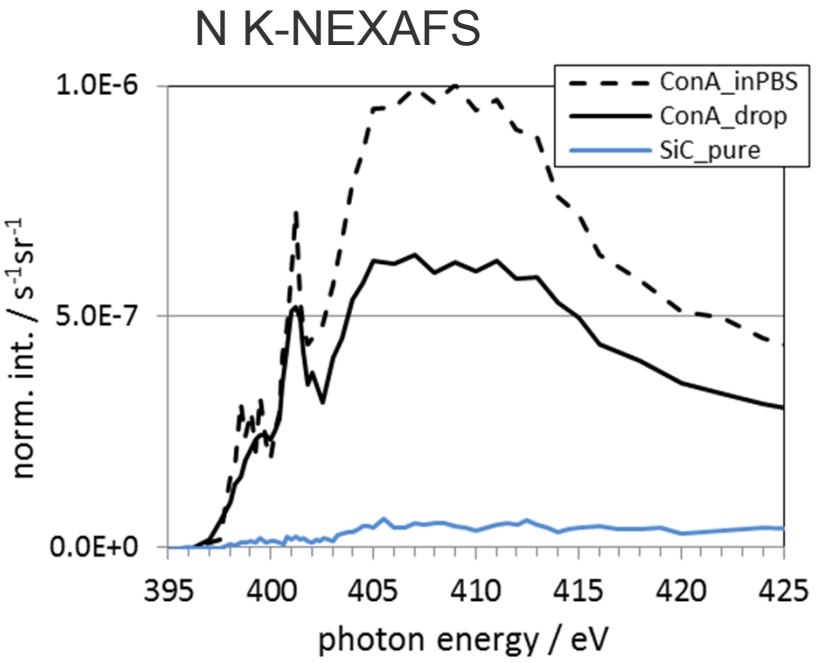
Pressure characteristics during capping the liquid cell



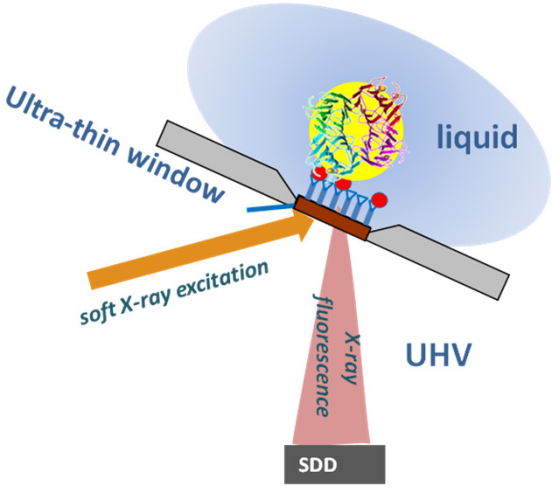
long time stability



NEXAFS investigation of capture molecule (ConA) in liquid environment with the liquid cell

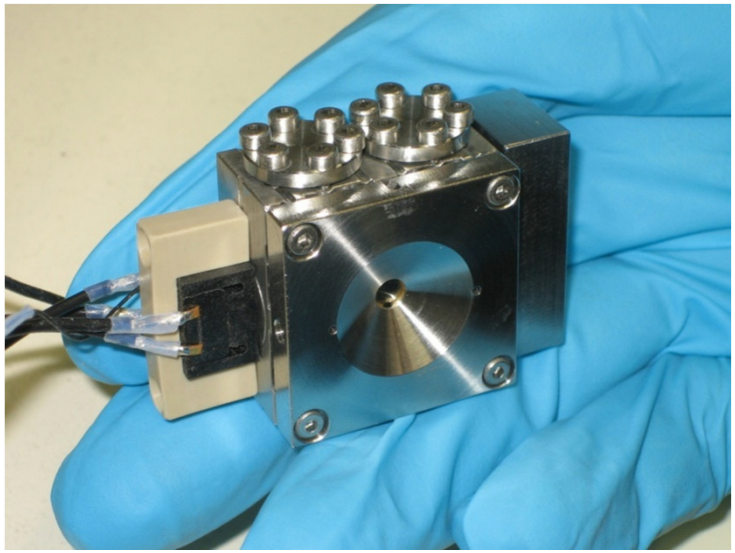


Window material	C K-NEXAFS	N K-NEXAFS
Si_3N_4	✓ Limited by carbon contaminations	✗ Limit of detection due to nitrogen in the window
SiC	✗ Limit of detection due to carbon in the window	✓ Limited by count rate of nitrogen K α fluorescence line

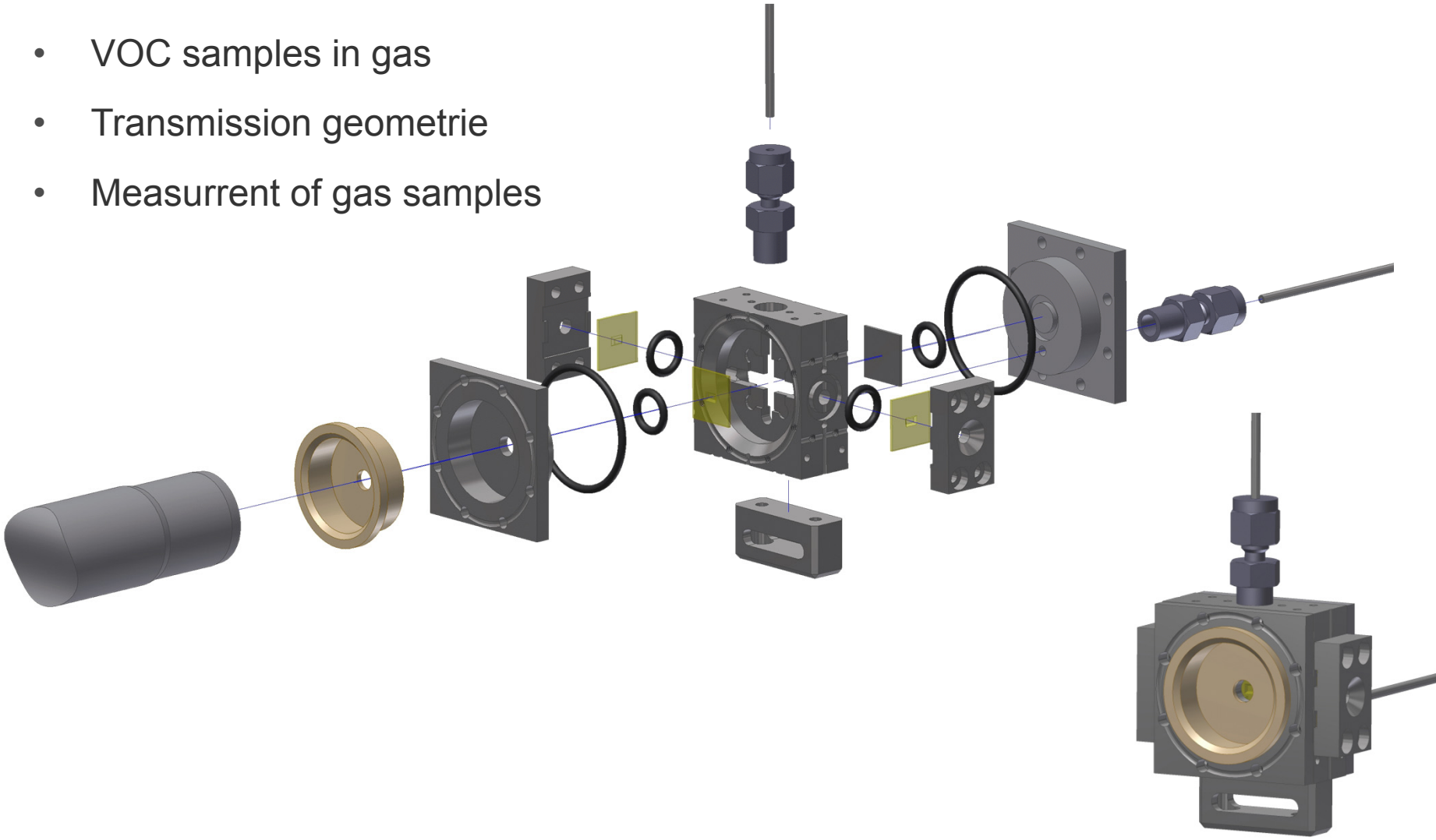


Analysis of liquids and liquid-solid interfaces is now possible with the liquid cell

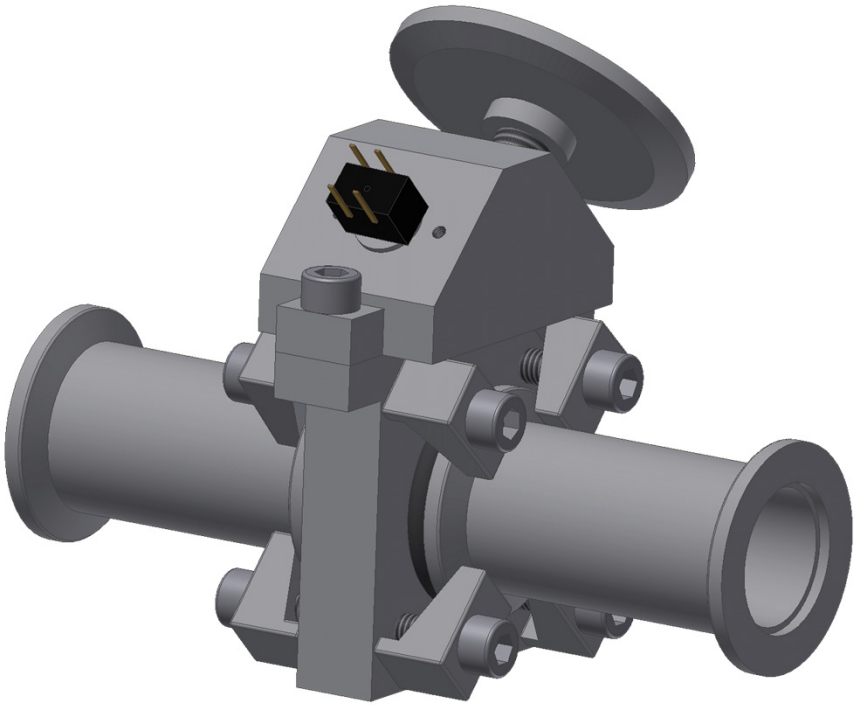
- In situ preparation of molecular films
- Easy and safe handling of liquids in UHV
  - Fast filling
  - Low risk of window rupture
  - Stable over typical period of experiment
- Compact sample holder

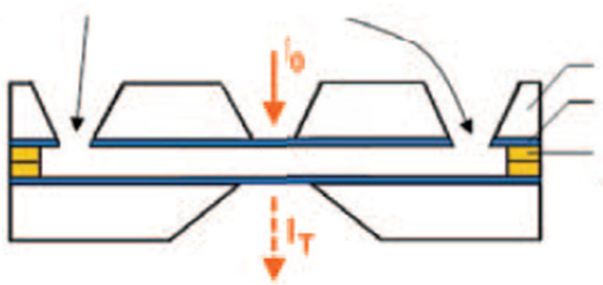


- VOC samples in gas
- Transmission geometrie
- Measurrent of gas samples

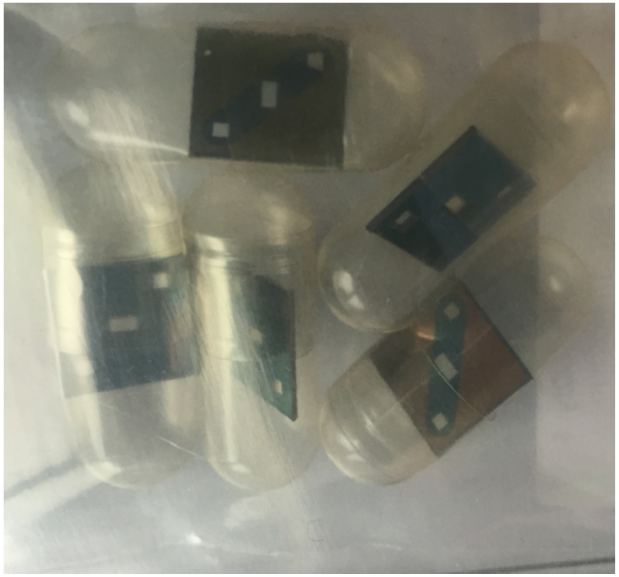


Development of a liquid cell for transmission geometry



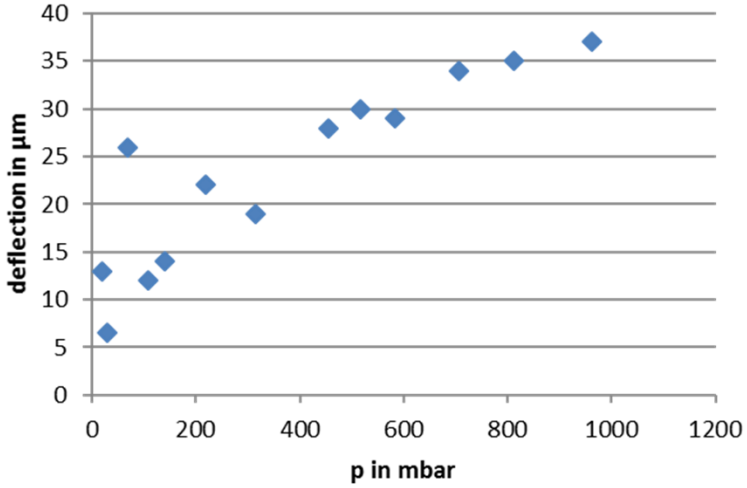


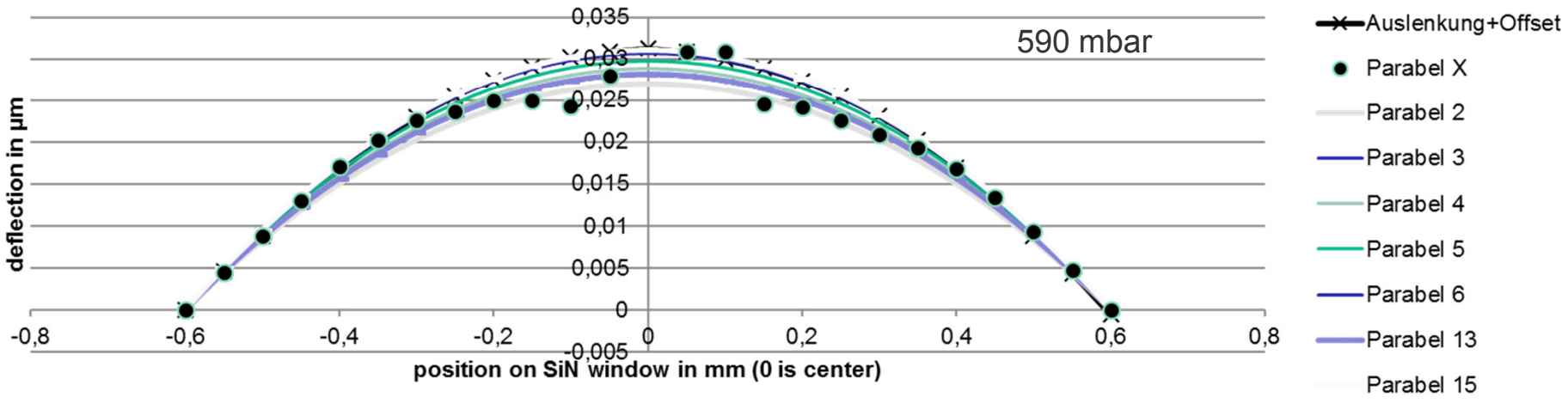
Simon Schreck, Rev. Sci. Instrum. **82, 103101 (2011)**



design done by Slava Martyanov

deflection/ bulging of SiN windows





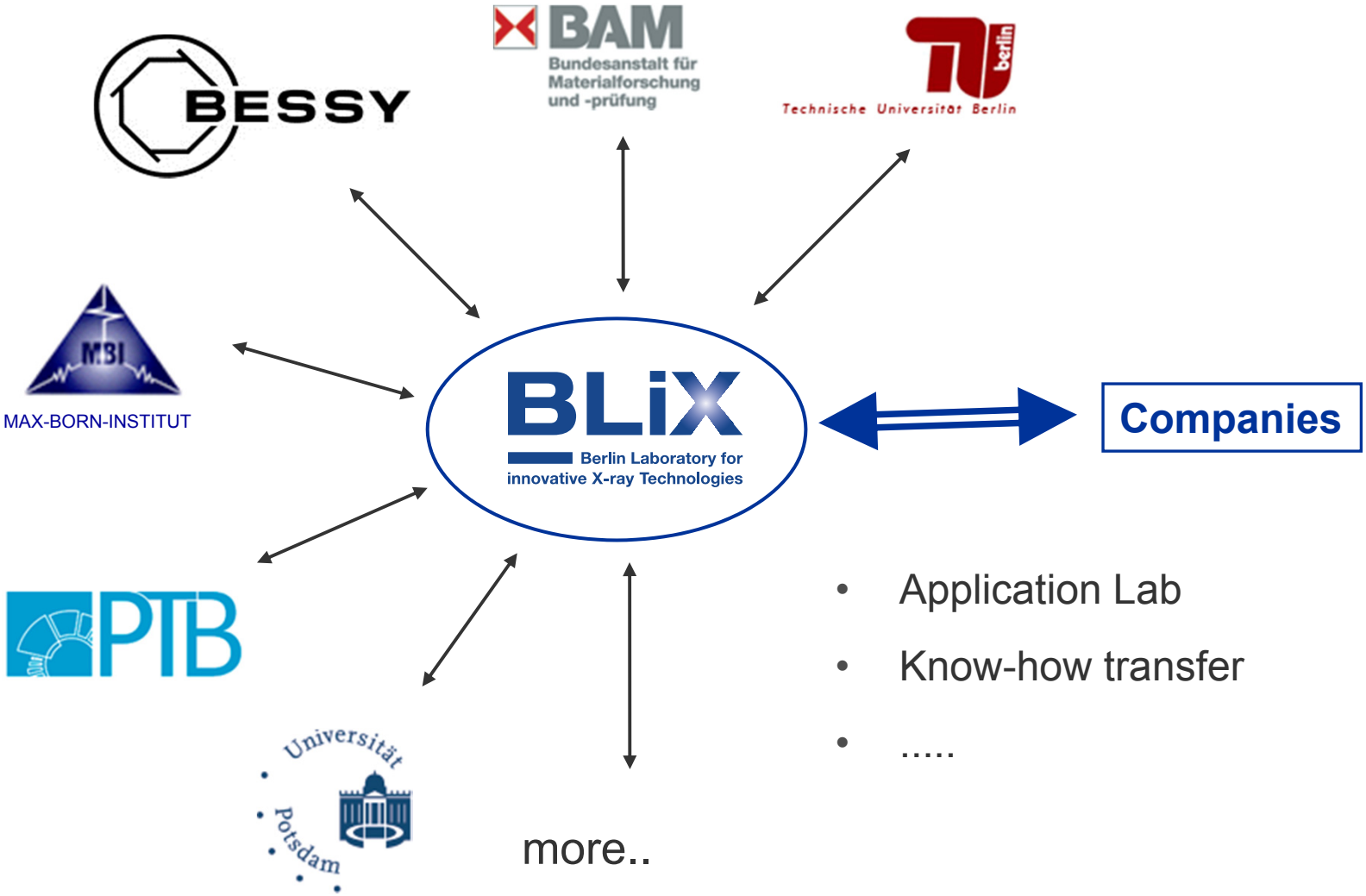
Further developments:

- Enlarged window for excitation and detection under shallow angles
- Advanced pressure compensation
- Implementing Temperature controlling
- Implementing electrical contacts for investigation under exterior voltage
- Investigations of batteries during cycling
- Complementary methods (IR, Raman)

To all colleagues who are involved in this work

- AXP research group: Birgit Kanngießer, Katharina Witte, Wolfgang Malzer, Ioanna Mantouvalou, Slava Martyanov, Janina Lebendig Kula, Adrian Jonas,
- The group of Burkhard Beckhoff (PTB): Cornelia Streeck, Janin Lubeck, Andreas Nutsch, Jan Weser
- Colleagues from BAM: Carolin Nietzold, Wolfgang Unger, Paul Dietrich
- Our mechanical workshop at IOAP: Irene Abendroth, Frank Röhrbein, Jörn Six, Fabian Sielaff
- Max-Planck-Institute for Chemical Energy Conversion: Serena DeBeer

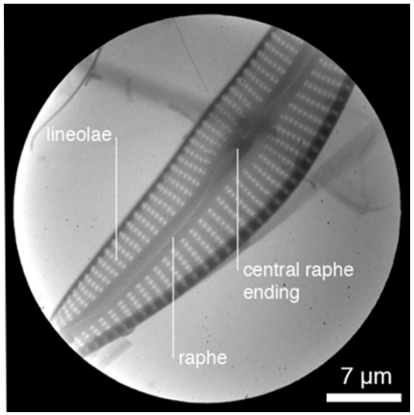
Thank you for your attention



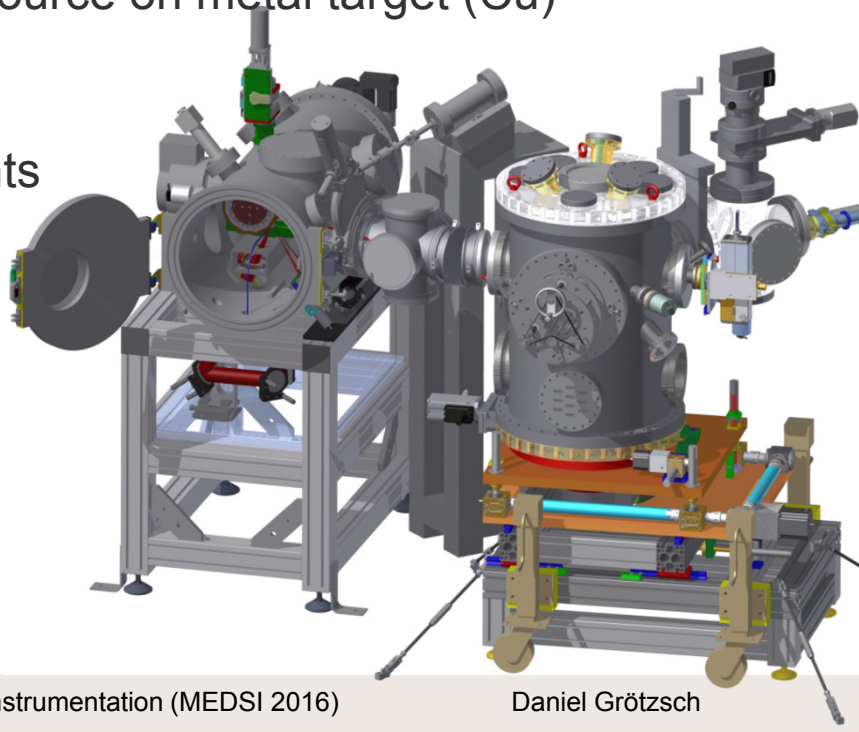
- Application Lab
- Know-how transfer
- .....

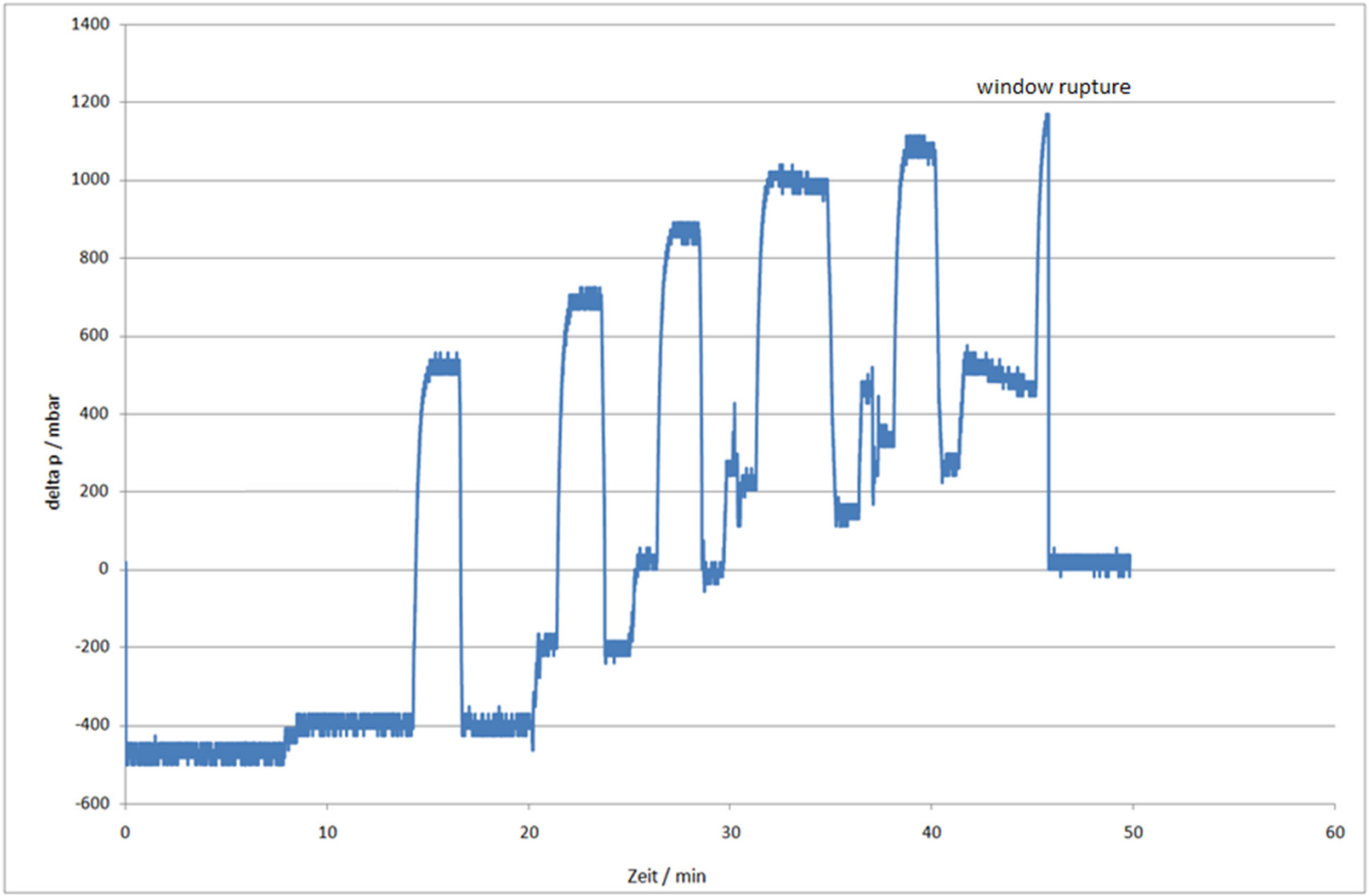
http://www.blix.tu-berlin.de/

- X-ray microscopy
  - Soft X-ray: laser produced plasma source on nitrogen jet
  - Hard X-ray: excitation by X-ray tube
- X-ray spectroscopy
  - Soft X-ray: laser produced plasma source on metal target (Cu)
  - Hard X-ray: excitation by X-ray tube
  - Different methodes and arrangements

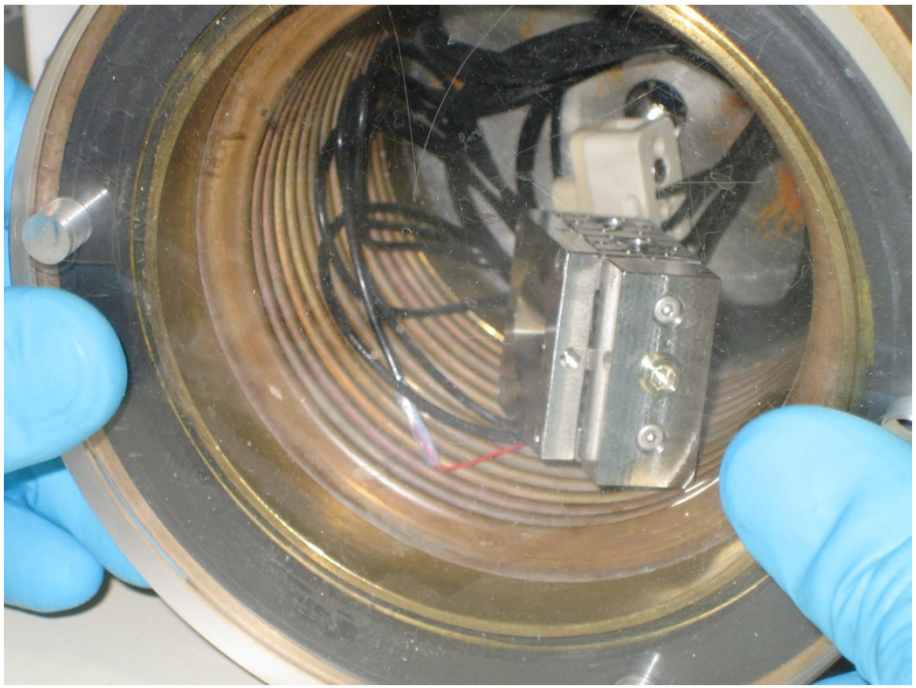


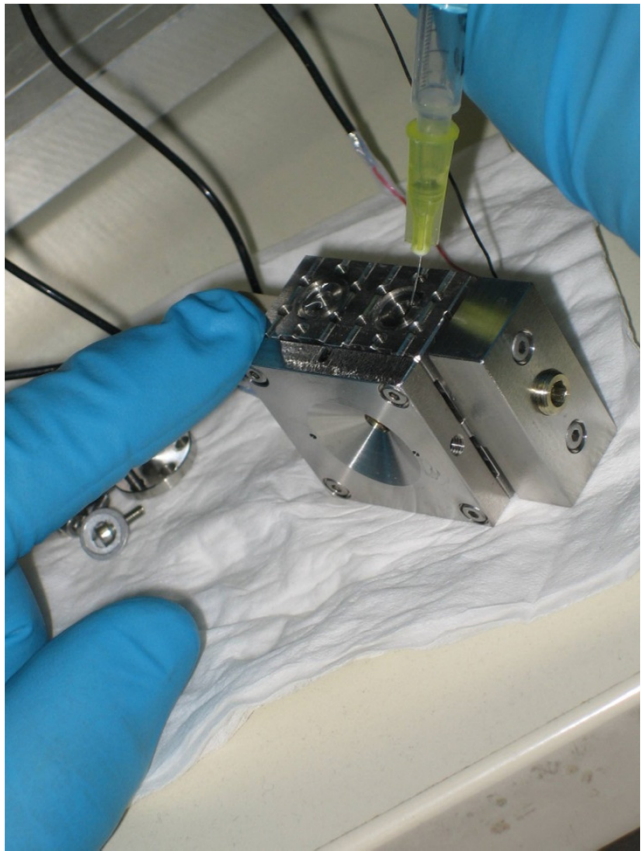
Diatom



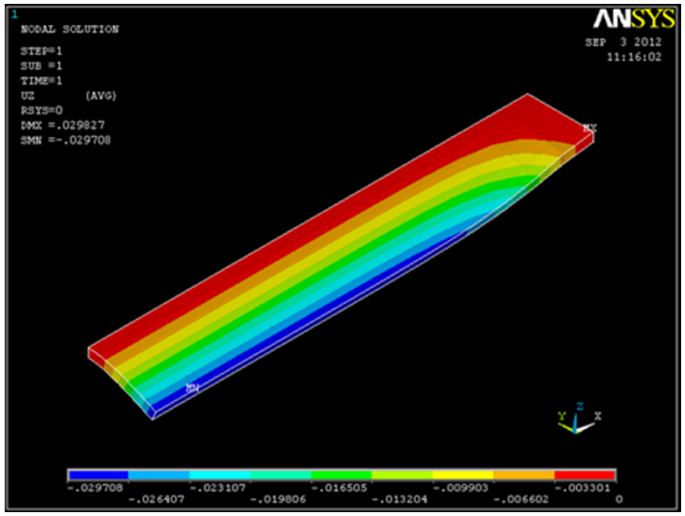

window rupture
delta p / mbar
Zeit / min
1400
1200
1000
800
600
400
200
0
-200
-400
-600
0
10
20
30
40
50
60

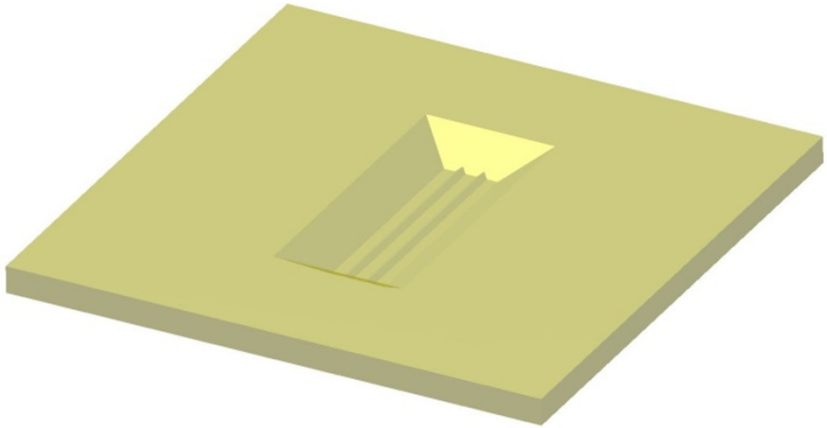
- Evacuate with open connectors
- Refill with degased solution
- Until no further bubbles show up





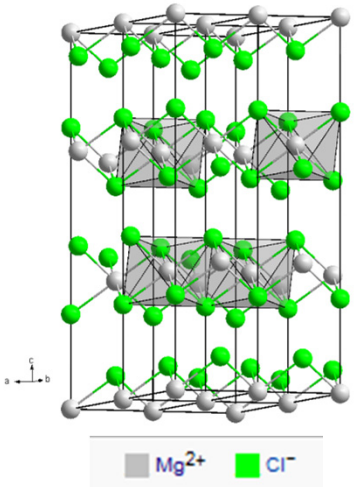
- Size and shape of siliconnitrid window
- Finite element method (FEM) simulation
- Rectangular shape for high sensitivity and stability
- Bars for stability of enlarged window





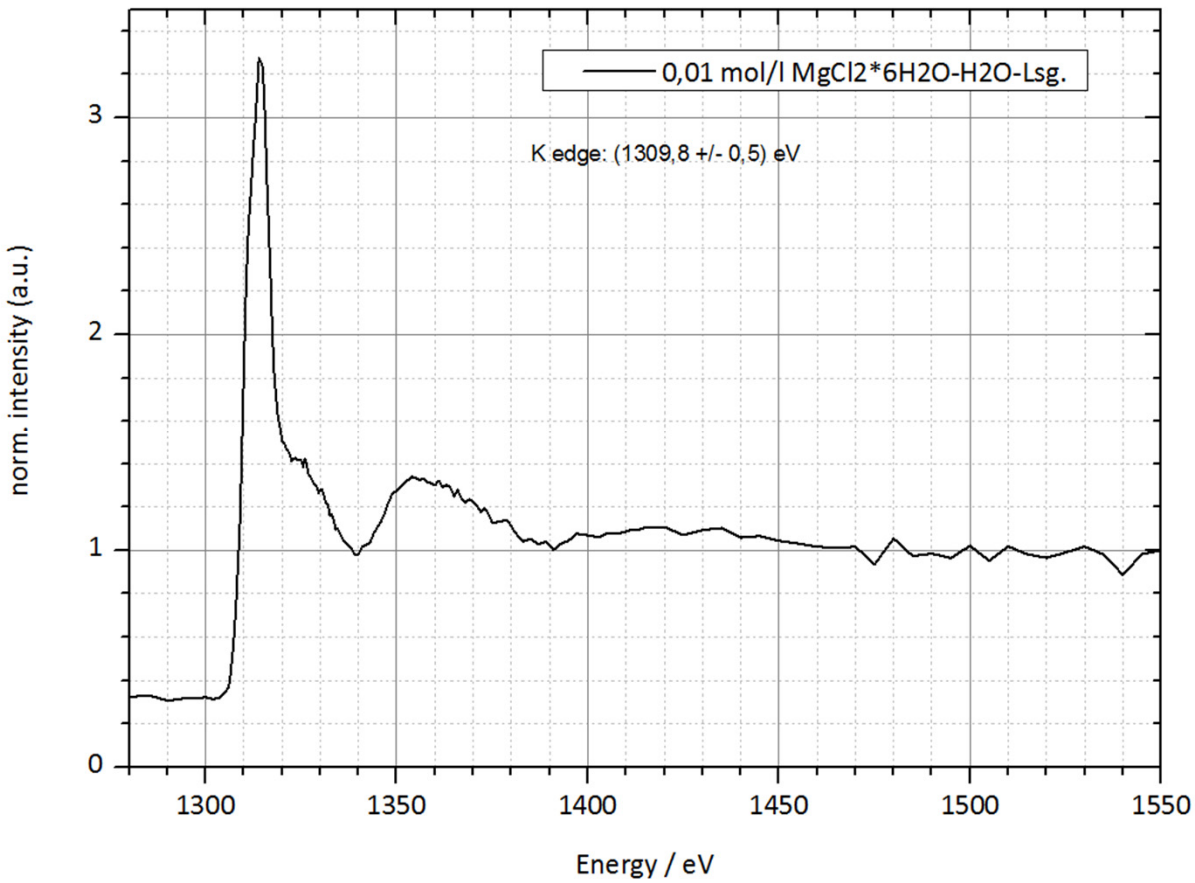
- Siliconnitridwindow
  - Window size 1x1 mm²
  - Thickness 150 nm
  - Frame 10 x 10 x 0,5 mm³
- Presure compensation
- Compact and completly sealed (no pipes)
- Rinsing the window inside the cell
- Measurement in emisson geometrie
  - 90° XRF
  - small angle excitation

- Beamtime BESSY II – PTB Beamline PGM (20 ... 1900 eV)
  - goal: Mg K-edge NEXAFS of Mg-salt in solution
  - Sample: $MgCl_2[H_2O]_6$ – H_2O – solution
  - concentration: 0,01 mol/l → 2,031 g $MgCl_2[H_2O]_6$ auf 1 l H_2O
  - Test system for Mg containing bio-molecules, e.g. Chlorophyll



Measurements done by Katharina Witte and Cornelia Streeck

- $MgCl_2[H_2O]_6$ – H_2O - solution



- success: observable Mg K-edge NEXAFS spectrum of low Mg-concentration solution!
- distinguishable XANES-features at Mg K-edge
- work in progress: interpretation and assignment of characteristical features
- work in progress: comparison to NEXAFS-calculation

Measurements done by Katharina Witte and Cornelia Streeck