Chemical and surface analysis at TE-VSC-SCC

Marcel Himmerlich on behalf of the TE-VSC-SCC team

Chemical Analyses – Quality Control and R&D

The Chemical Analysis team provides service material analyses and contributes to CERN R&D and scientific studies.

We operate standard characterization systems for gaseous, liquid and condensed matter and develop routines for detection and quantitative analysis.

Benoit Teissandier

Colette Charvet

Daria Ternova

Analysis techniques at TE-VSC-SCC Chemistry lab I

Optical Emission Spectroscopy

*e.g.: **Lead** detection in CERN buildings*

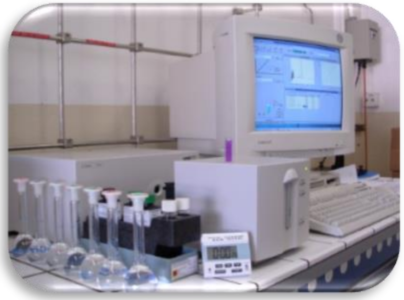
Atomic Absorption Spectroscopy

*e.g.: Superconducting cable **composition***

Potentiometric titration

*e.g.: Quality control of **surface treatments bath***

UV-Visible spectroscopy



*e.g.: Water analysis from **STEP***

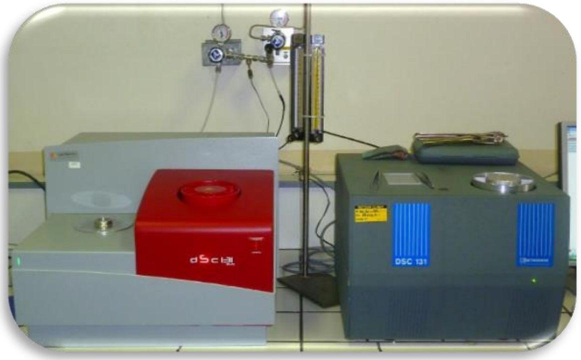
Quality control of water, surface treatment baths, analysis of metal ions after STEP treatments

Analysis techniques at TE-VSC-SCC Chemistry lab II

FTIR spectroscopy

*e.g.: Evaluation of surface cleanliness for **UHV applications, Polymer identification***

Differential Scanning Calorimetry



*e.g.: Polymer **Tg Measurement***

Thermogravimetry

*e.g.: Mineral filler quantification in **polymers***

Analysis techniques at TE-VSC-SCC Chemistry lab III

X-ray fluorescence spectroscopy

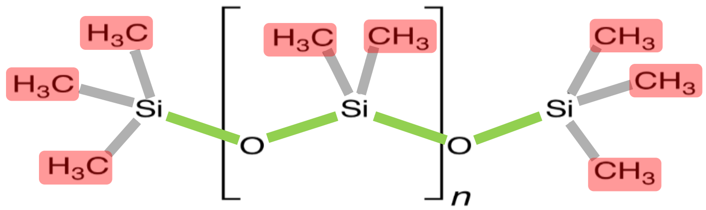
e.g.: Elemental composition of metallic parts, In-situ thickness measurement of coatings

Karl Fischer Coulometry

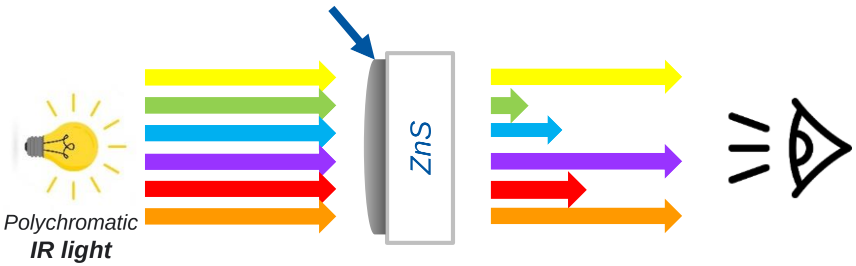
Gas Chromatography

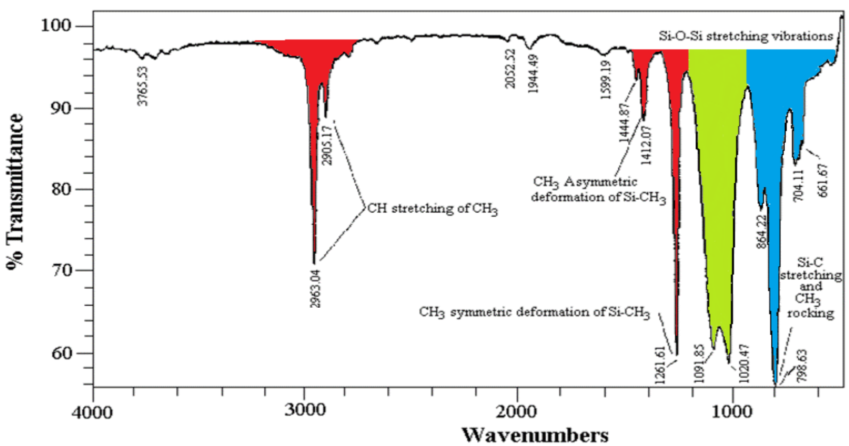
e.g.: Quality control of the ***LHC experiments gas and/or cooling fluid***

Analysis of organic compounds by IR spectroscopy



e.g.: Silicone oil





Lab. Spectrometer : Bruker Vertex 70

Handheld : Agilent Exoscan 4100

Characterization of solids, liquids & gases

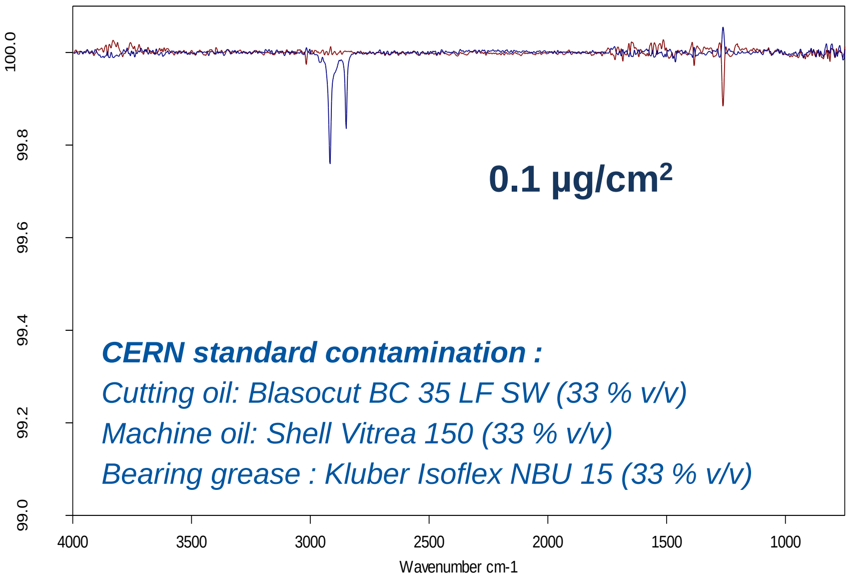
- "Silicon free" - Quality control of pipes used to build gas detectors
- Cooling fluids (and gas) identification and quantification of contaminants
- Identification of Polymers

Quantification to ppm level (after calibration)

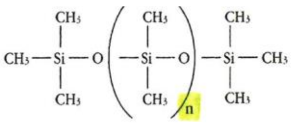
- Cleanliness assessment for gas system detector or UHV applications
- Cooling fluids purity

Quantification and detection limit by IR spectroscopy

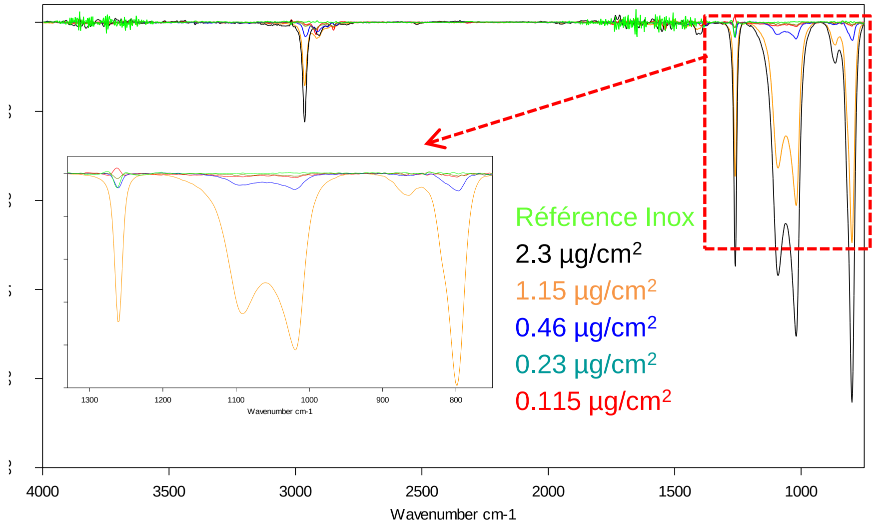
*Detection limit of **hydrocarbon contamination** on stainless steel surface*



*Detection limit of **Dimethylsiloxane** on stainless steel surface*



n ≈ 1235



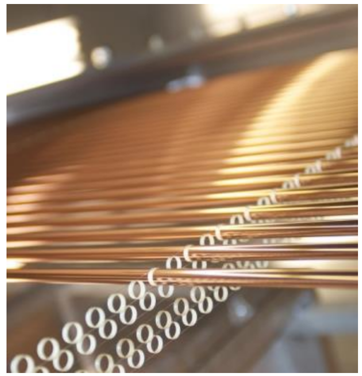
Detection limit ≈ 1 molecular layer

Report : EDMS 1332721 (B. Teissandier)

Hostaphan® (PET) foils with Cu/Au coatings (NA62 - Straws Tracker)

Thickness measurement of Au & Cu coatings

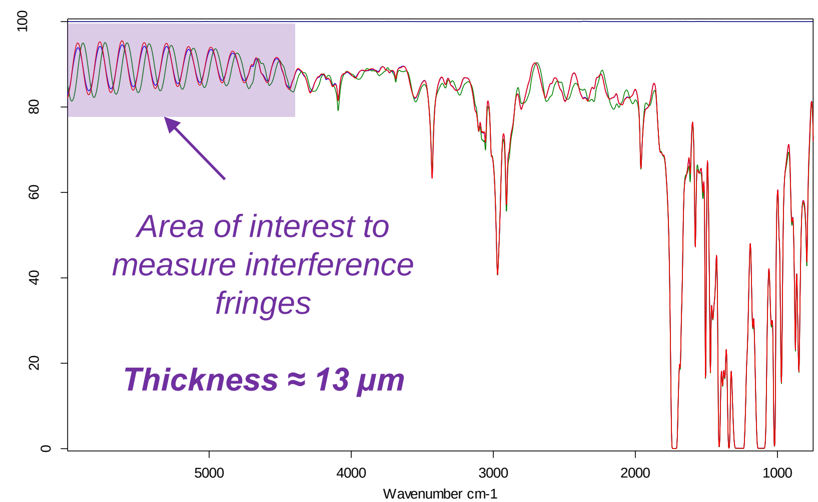
1. Chemical dissolution of metallic coatings with aqua regia (on defined area)



2. Quantification of Au and Cu by ICP-OES spectroscopy

Thickness measurement of Hostaphan foil

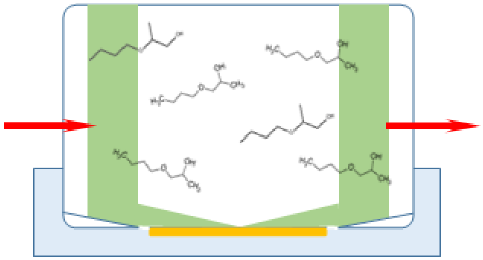
1. Chemical dissolution of metallic coatings with aqua regia
2. Infrared spectroscopy analysis in transmission mode



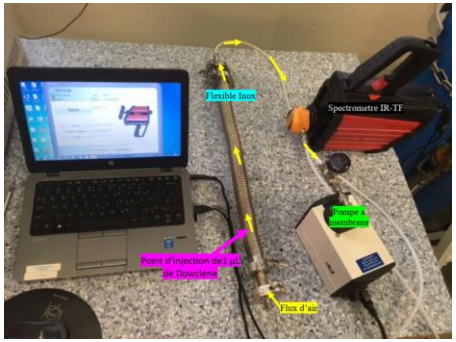
Analysis report : EDMS 2747287 & 2823835 (B. Teissandier)

Search for residual cleaning solvent (Dowclene 1601) in CMS Resistive Plate Chamber (RPC) gas system

Lab-based validation

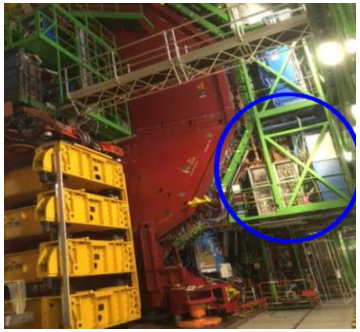


Principle of FTIR gas cell

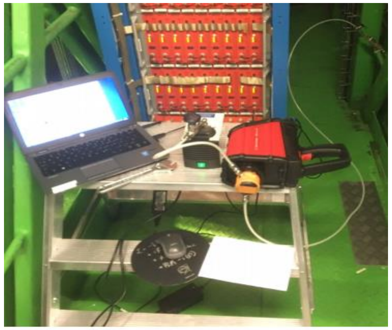


Dowclene detection by FTIR

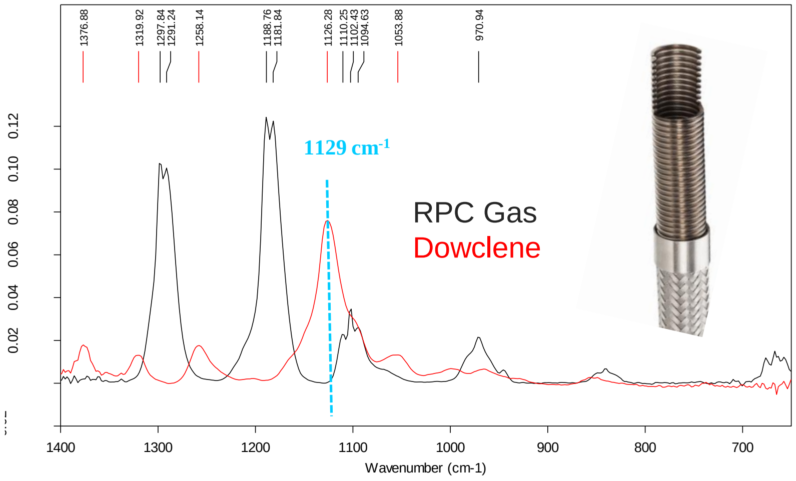
Measurements in CMS RPC gas system

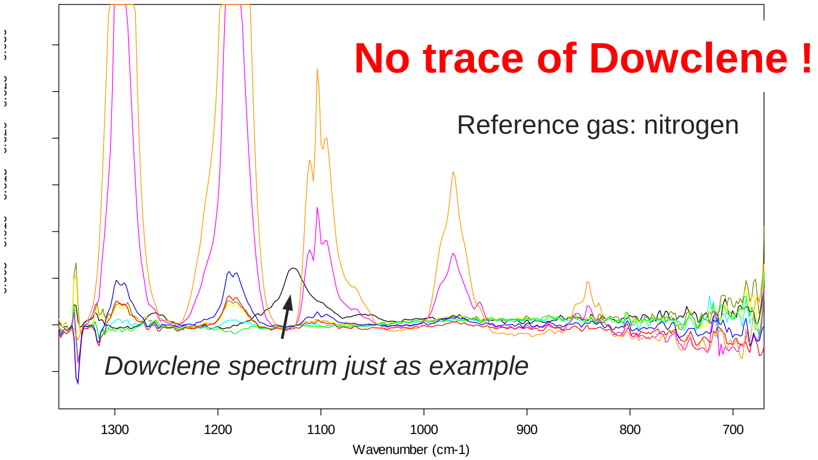


Sampling in CMS



FTIR on CMS RPC gas system



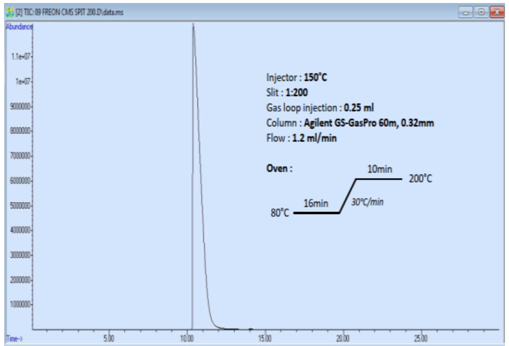


RPC gas: CH_2FCF_3 / SF_6 / C_4H_{10}

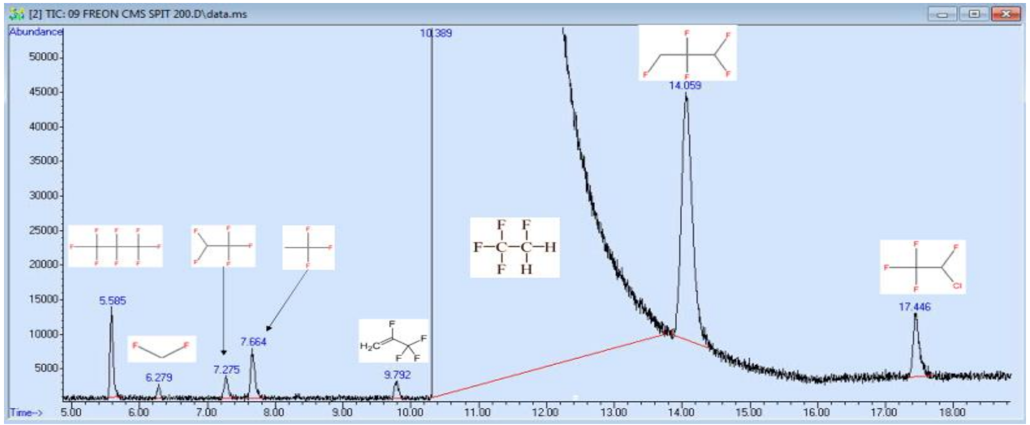
*Analysis report : EDMS **2716850** (B. Teissandier)*

R134a GC/MSD Analysis (CMS RPC)

Instrumentation & method

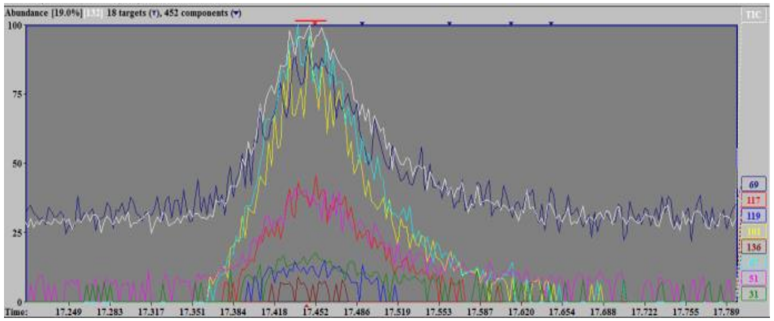


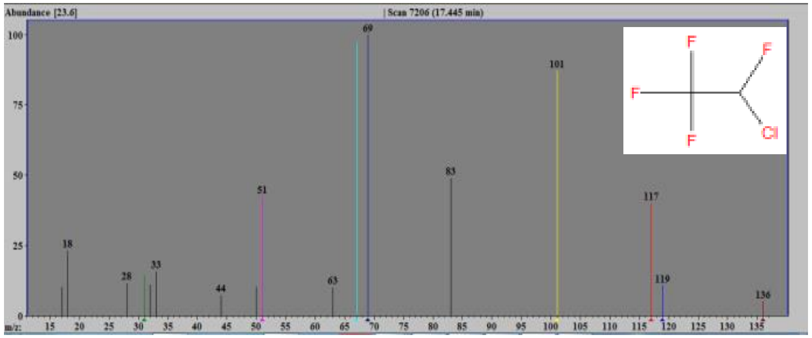
Impurities in CH_2FCF_3



Example of gas traces identification

@17.4 min, identification of C_2HClF_4





Colors indicate signals from C_2HClF_4

R134a = CH_2FCF_3 (tetrafluorethane)
C_2HClF_4 (Chloro-tetrafluorethane)

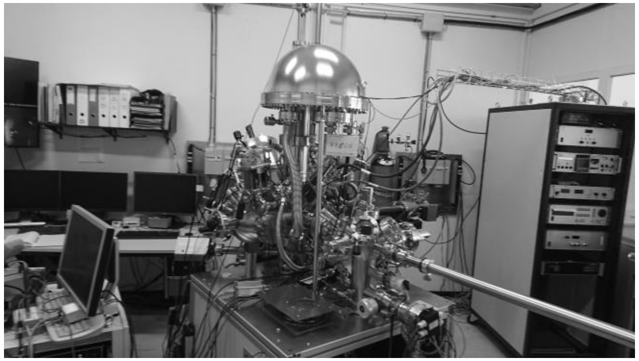
Surface Analyses – Quality Control and R&D

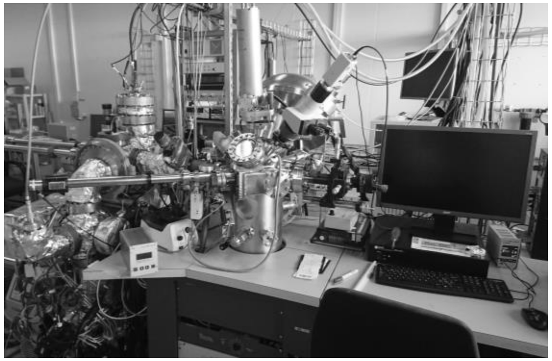
The Surface Analysis team provides service material analyses and contributes to CERN R&D and scientific studies.

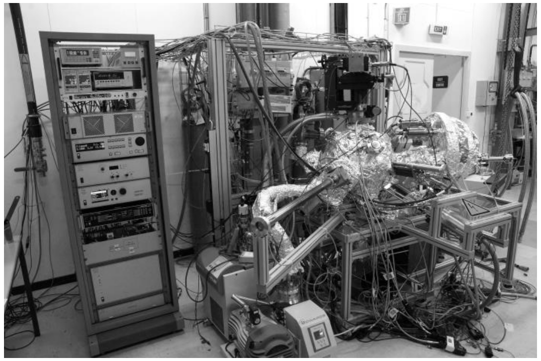
We operate UHV systems for surface spectroscopy and thin film characterization on small test samples.

Main methods:

- Secondary Electron Yield (SEY) measurements
- X-ray Photoelectron Spectroscopy (XPS)







Surface Analyses – Quality Control and R&D

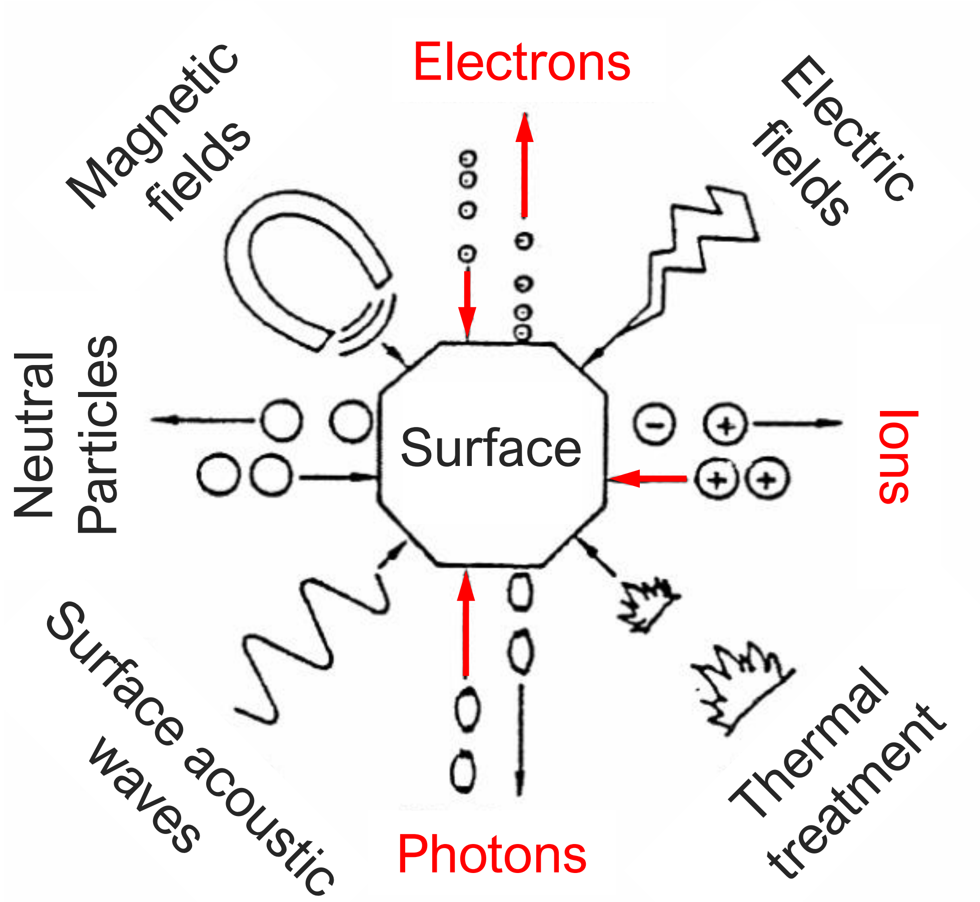
- We provide surface and thin film analysis expertise for the CERN community and projects.

- If a surface or thin film analysis technique does not exist at CERN
  → we advise and mediate tests at external partners and institutes

Examples: Secondary Ion Mass Spectroscopy profiling &
Ion Scattering Spectroscopy for Hydrogen content in thin metal films

Laterally resolved Auger Electron Spectroscopy depth profiling
for surface composition analysis of superconducting cables

The «playground» of surface analysis



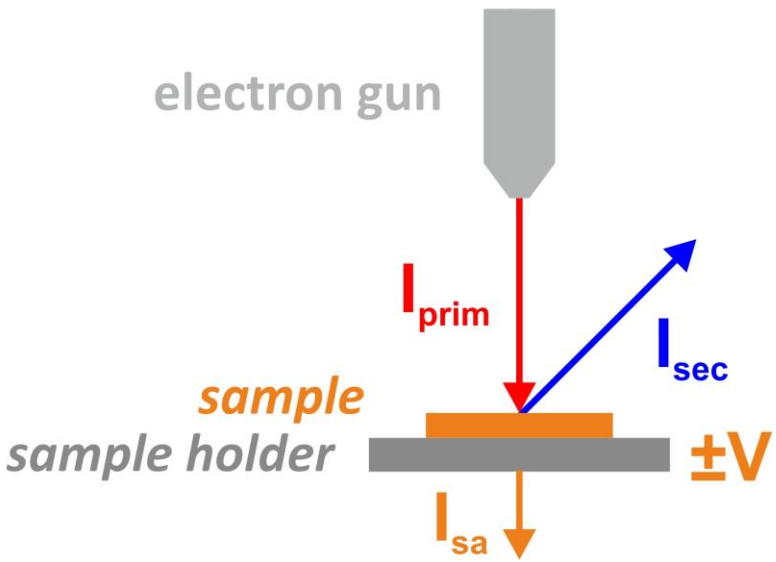
Laterally resolved analysis
→ Microscopy

Spectrally resolved analysis
→ Spectroscopy

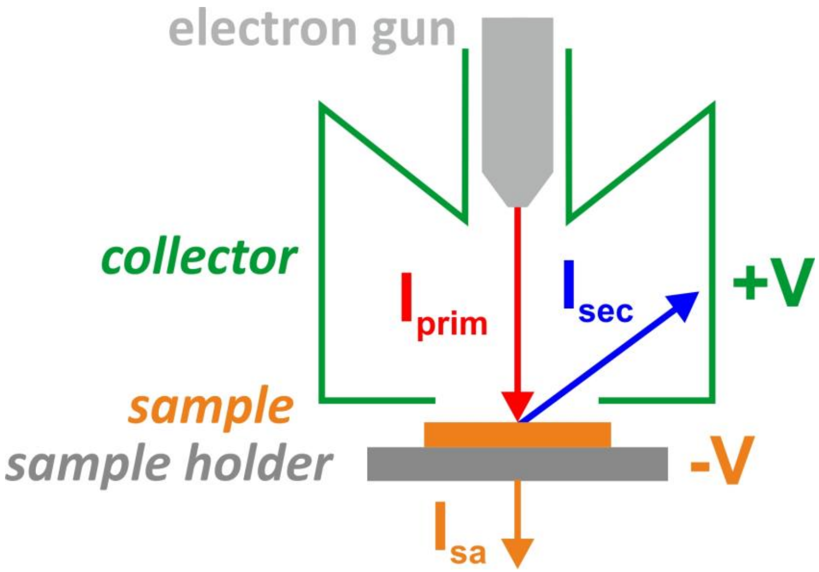
Combination of lateral magnification and spectral selection
→ Spectromicroscopy
→ Microspectroscopy

adapted from M. Henzler and W. Göpel, Oberflächenphysik des Festkörpers

Angle-integrated **S**econdary **E**lectron **Y**ield

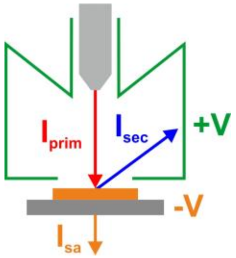


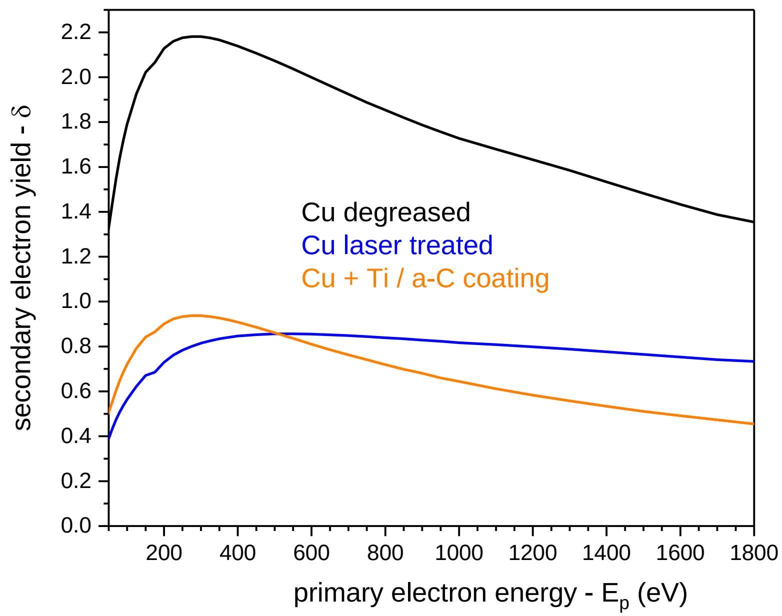
$$\delta(E) = \frac{I_{sec}(E)}{I_{prim}(E)} = \frac{I_{+V} - I_{-V}}{I_{+V}}$$

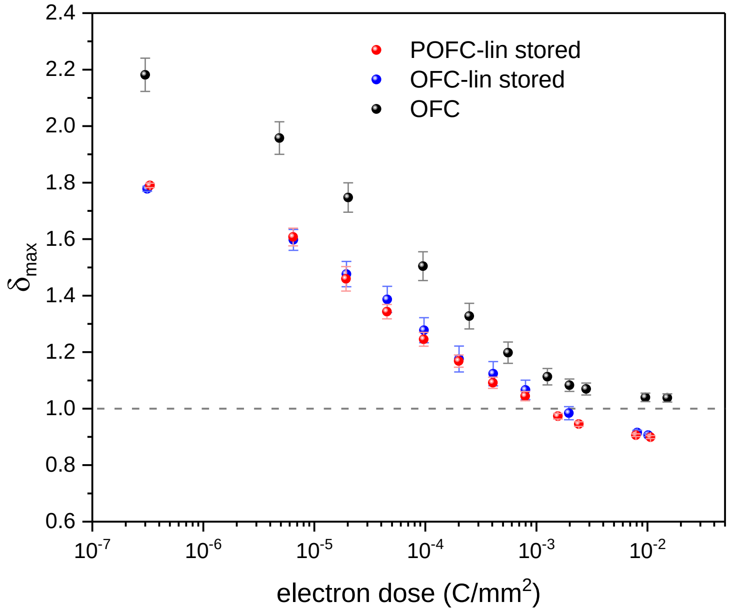


$$\delta(E) = \frac{I_{sec}(E)}{I_{prim}(E)} = \frac{I_{col}}{I_{col} + I_{sa}}$$

Secondary Electron Yield & Conditioning



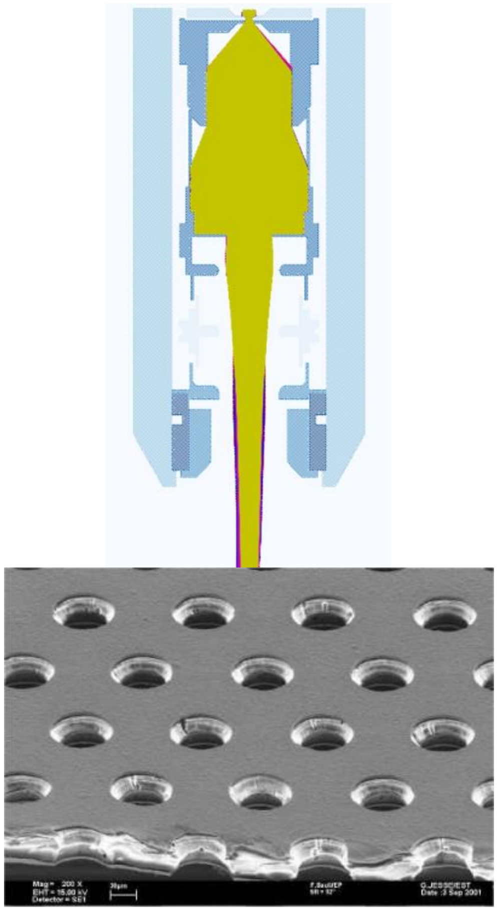




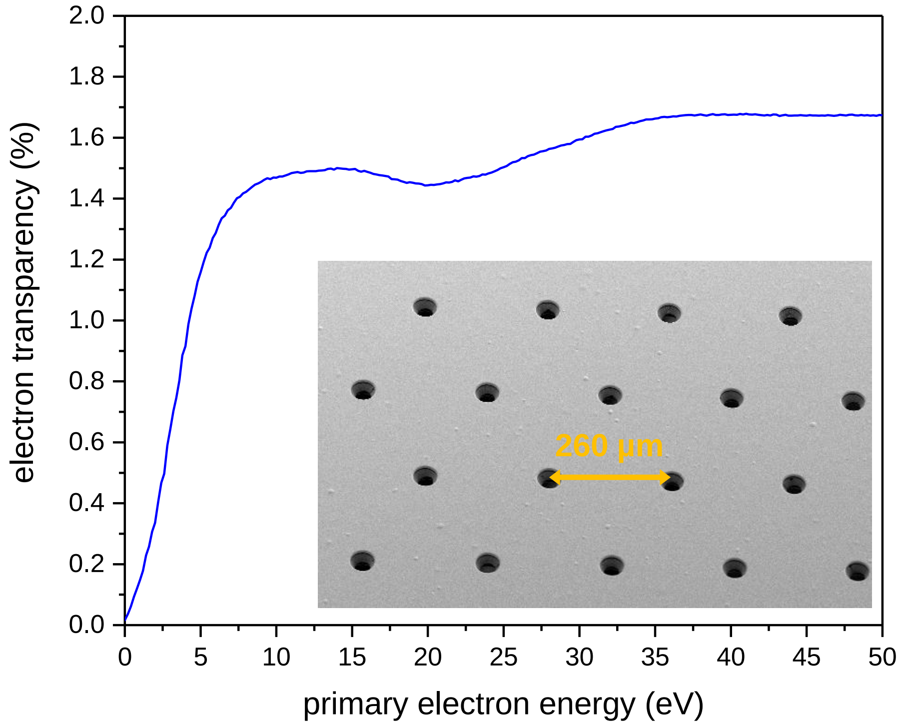
Other options:

- Electron induced surface modification (conditioning)
- Work function measurements
- Incidence angle dependent SEY analyses
- SEY measurements of insulating samples

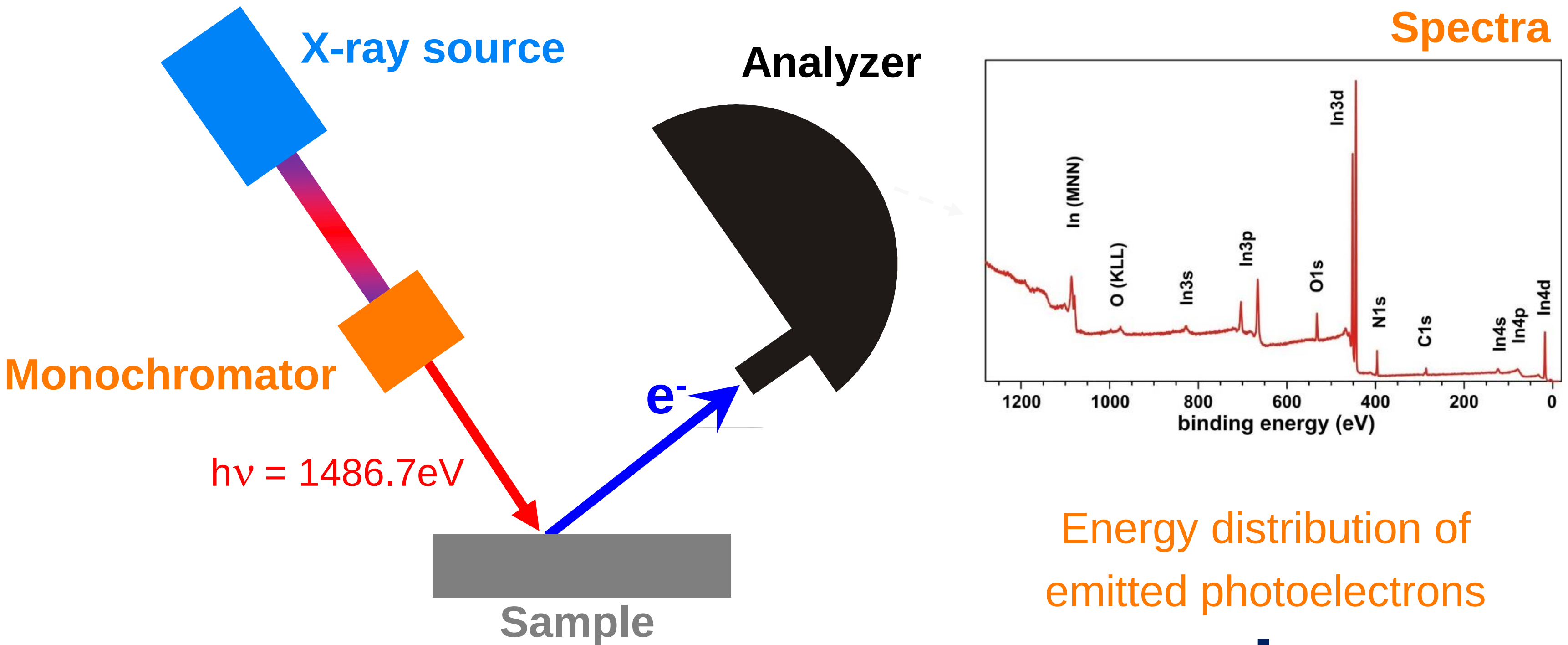
Electron transmission through GEM foils and graphene layers



Adaption of UHV setup with versatile electron source for transmission (current) measurement



X-ray Photoelectron Spectroscopy



Energy distribution of emitted photoelectrons

↓

Represents the element-specific electron distribution

Results from **P**hotoelectron **S**pectroscopy

Surface chemical composition

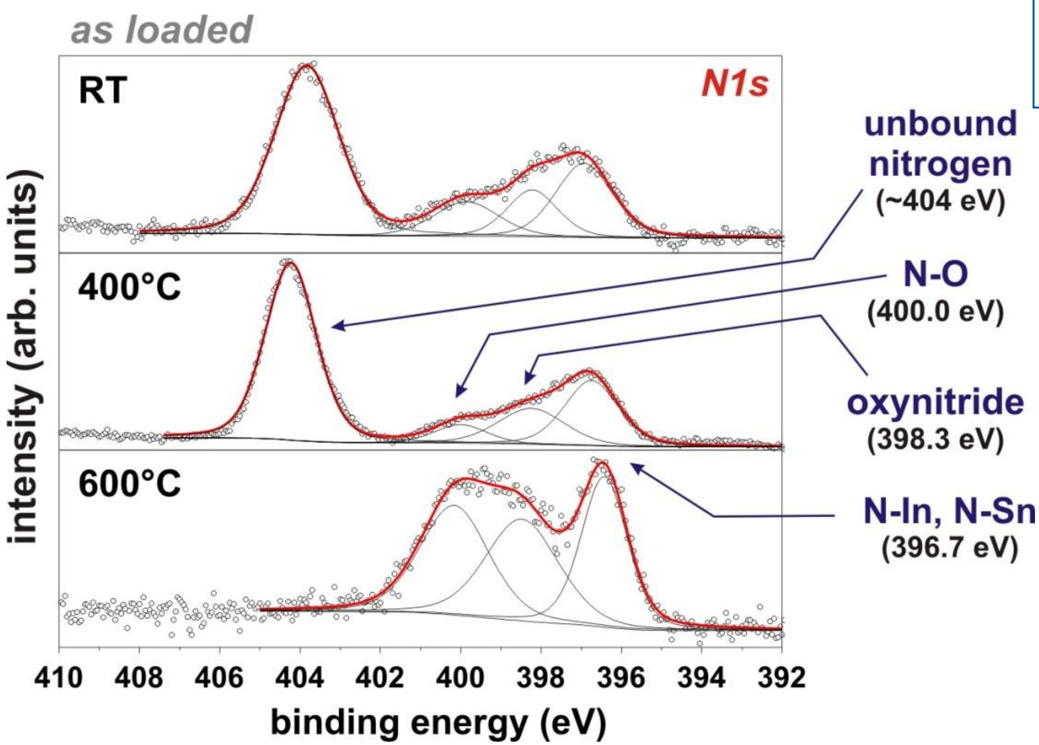
- Surface and film stoichiometry (elemental composition)
- Adsorbates, contamination & surface functionalization
- Chemical modification of surfaces
- Degradation & passivation

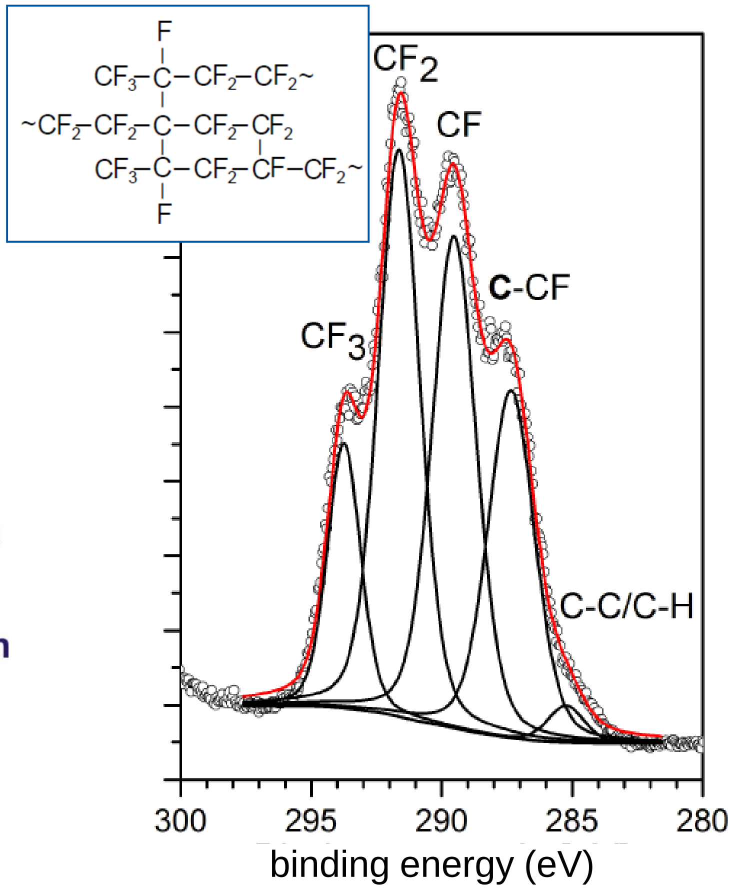
Surface electronic properties (in-situ studies)

- Valence band density of states
- Work function, surface band bending, surface dipoles
- Band offsets at interfaces
- Charge transfer processes

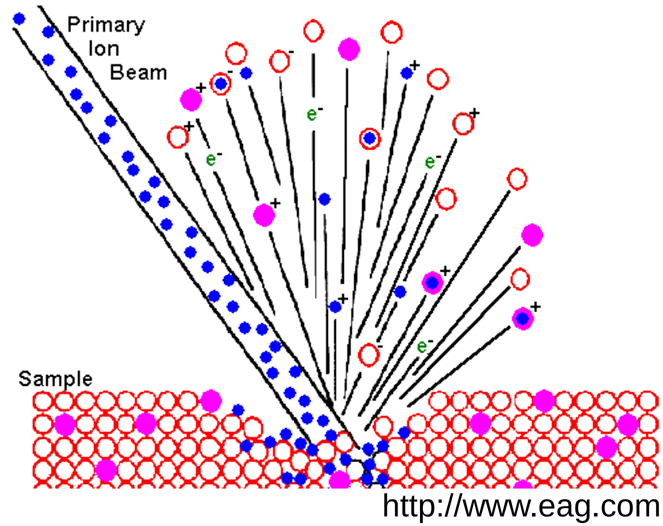
Analysis of chemical states

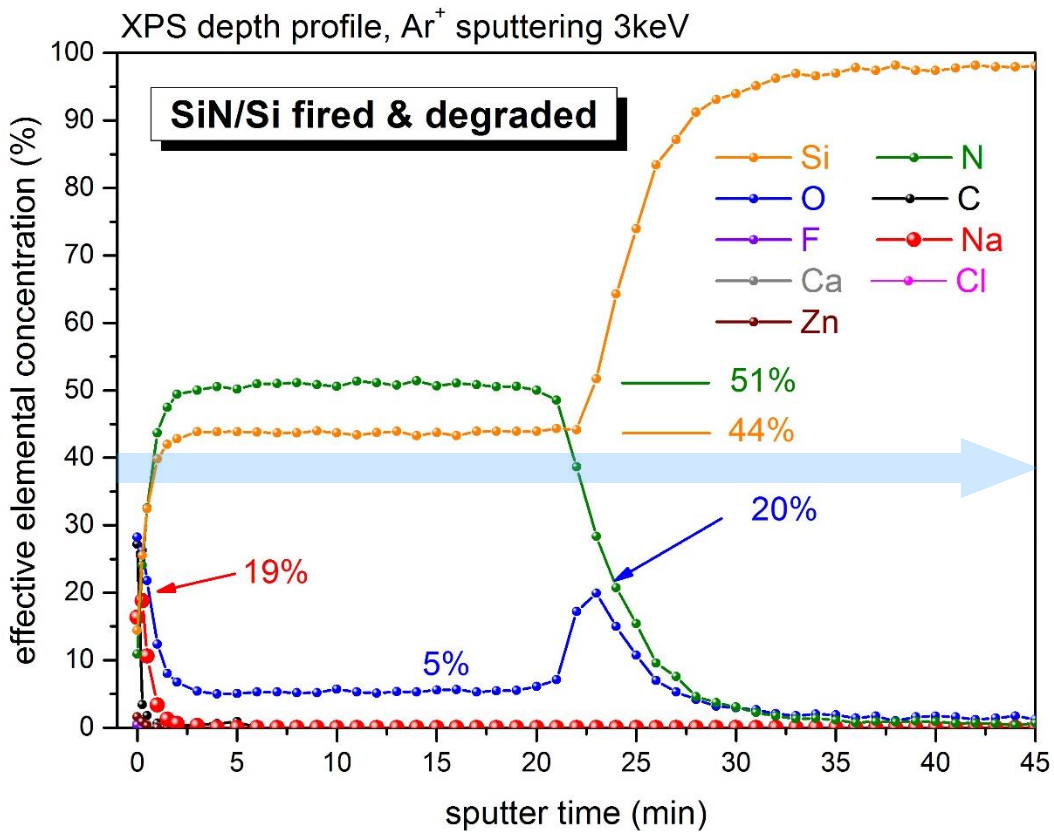
Electron binding energy depends on the actual chemical bond configuration of the material and the nature & electronegativity of the neighboring atoms





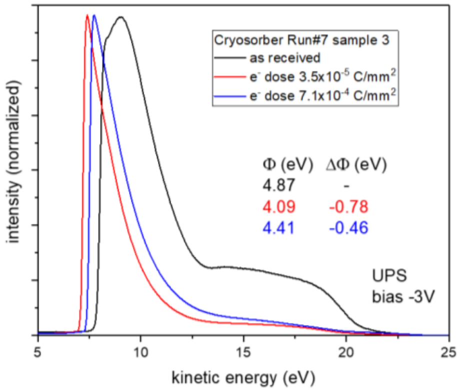
Sputter depth profiling



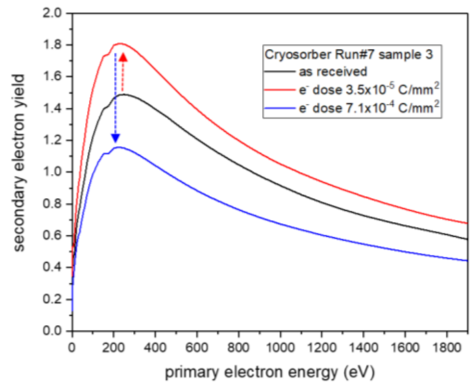


UV or e⁻ induced electron spectroscopy

- UV source to measure work function and valence band



Φ ⟷ δ



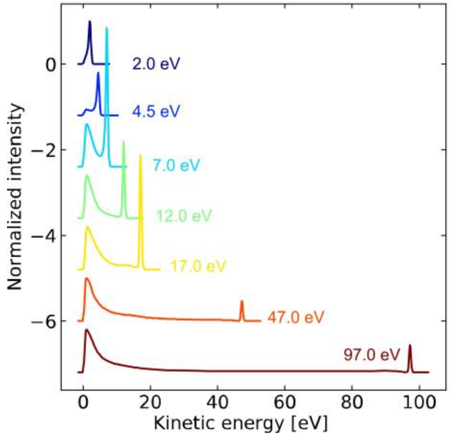
E_{photon}

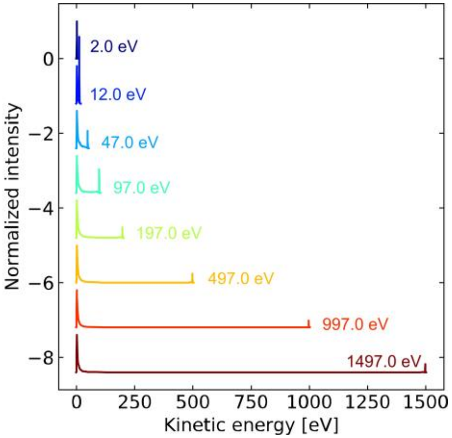
21.2 eV

&

40.8 eV

- Electron source to measure angular-resolved SE spectroscopy





$E_{electron}$

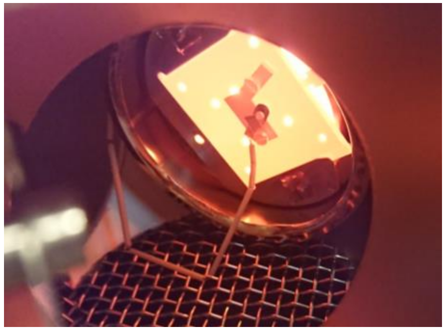
1 eV

-

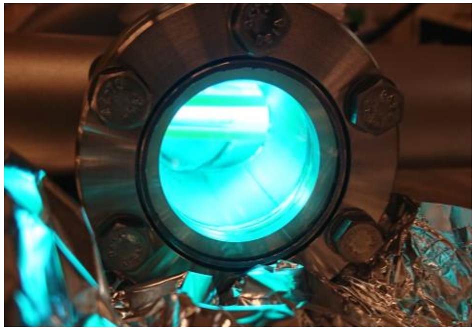
1500 eV

Sample preparation & surface modification

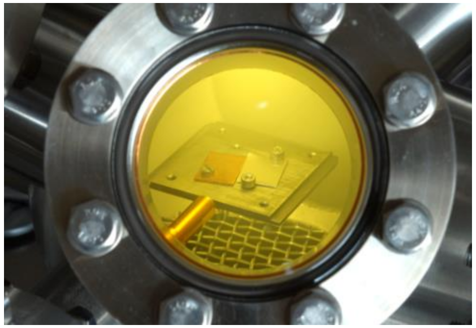
- Characterization of surface property changes during treatments in vacuum and/or reactive atmosphere (p ≈ 10^{-2} mbar)



Heating up to 800°C



UV-C irradiation



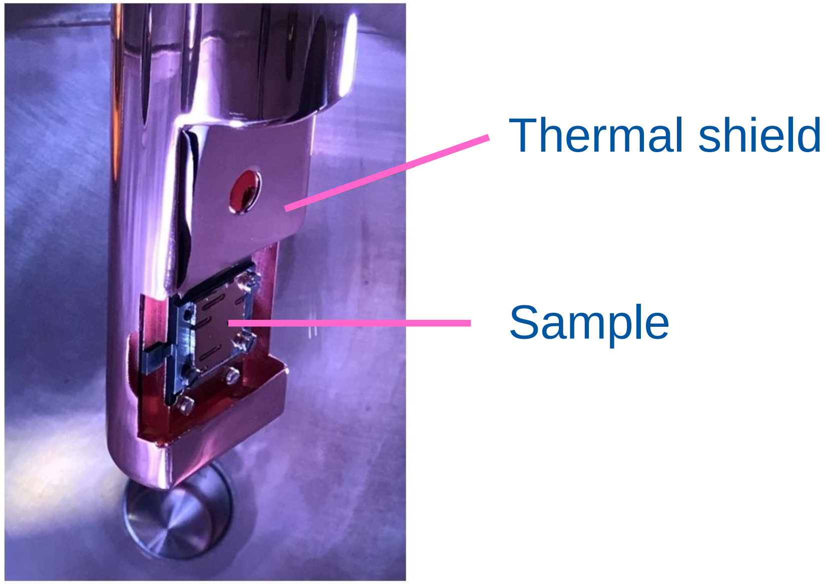
Plasma exposure

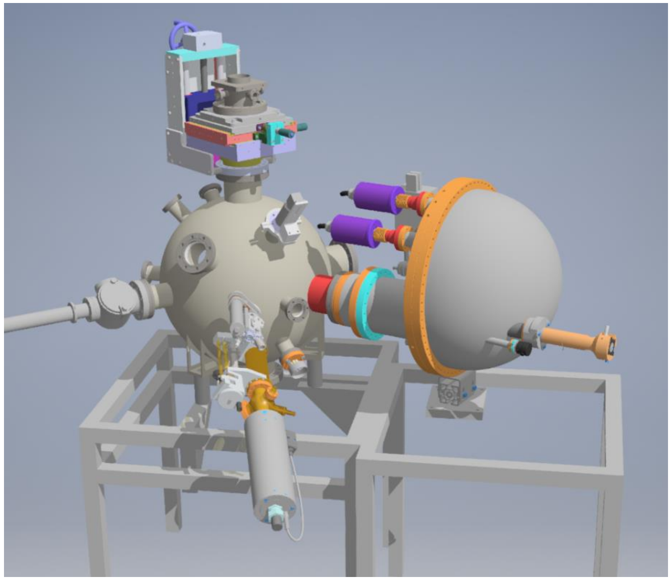
+ injection of gaseous species

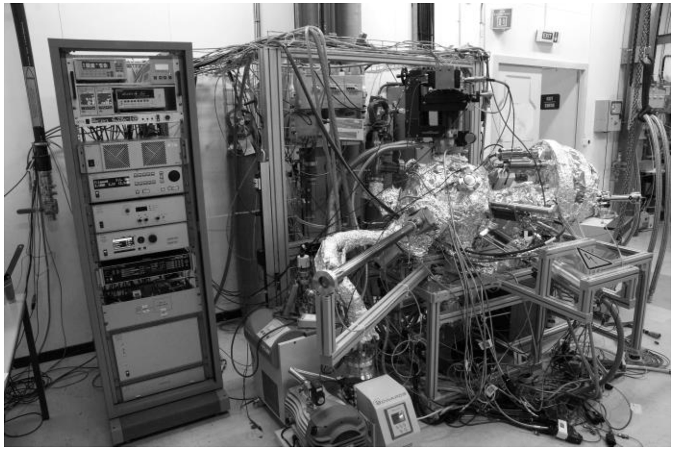
Characterization of:

- Chemical reduction/oxidation and functionalization processes
- Physical cleaning/etching of surfaces

Surface analyses at cryogenic temperatures







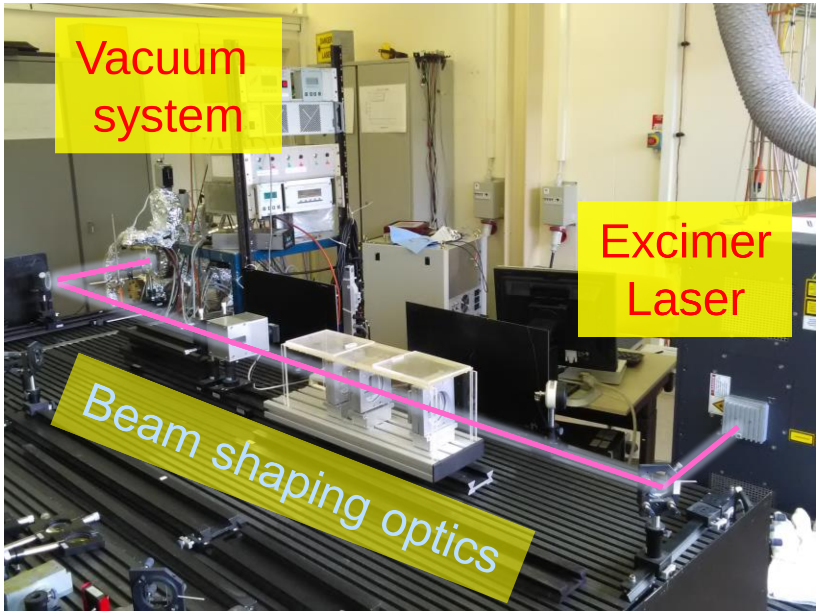
- Cryogenic cooling of samples to 15 K
- SEY, SES, conditioning and XPS analyses at variable temperature
- Optional injection of gases to characterize surface reactions

Pulsed laser ablation

- Ablation of thin films on metallic substrates in UHV by 248 UV laser
- Accumulation of the trapped noble gas in the ablation chamber
- Evacuation of the ablation volume via analysis chamber with a calibrated RGA allows to determine the gas quantity (p•V → number of gas atoms)
- Film thickness × ablated area (2 mm^2) → compute number of ablated atoms
- Gas content = $\frac{\text{\# noble gas atoms}}{\text{\# ablated atoms}}$

Options:

- laser-fatigue tests
- pulsed laser deposition from target



Key parameters:

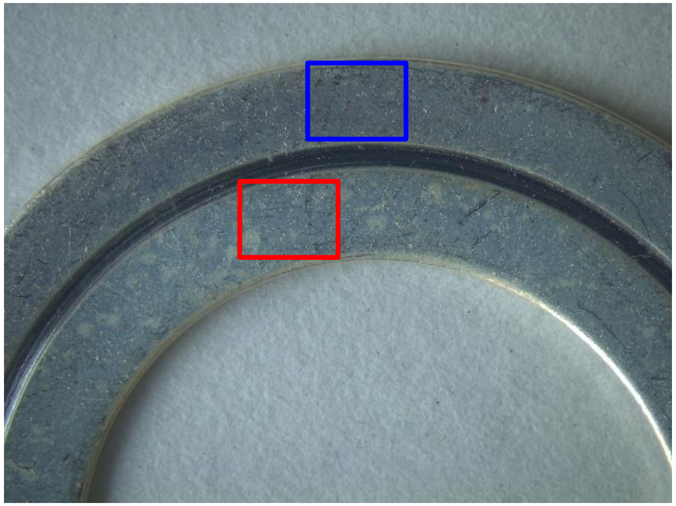
- Possibility to measure all noble gases trapped in thin films up to 5 µm thickness
- Gas content as low as 10 ppm detectable

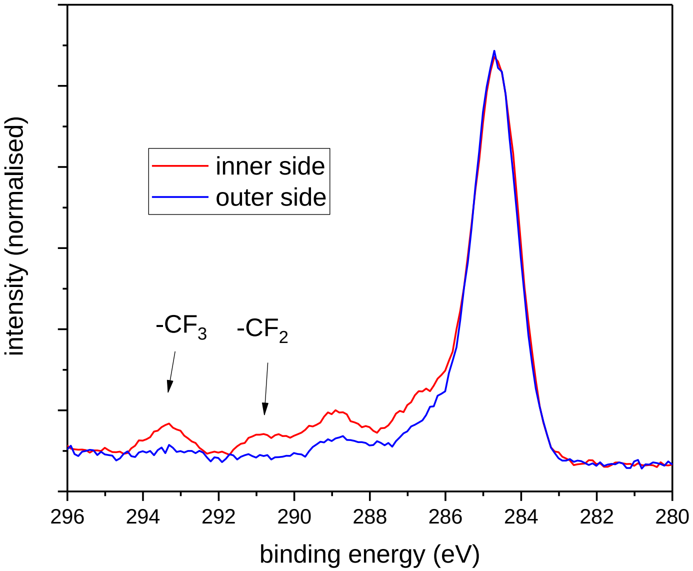
Typical surface analysis tasks

- Contamination analysis after cleaning or material processing
- Thin film composition characterization
- Identification of chemical bonds and adsorbates at surfaces
- SEY qualification of materials and surface processing including electron-induced conditioning tests
- In-situ modification of surfaces & model experiments to develop surface technologies
- Development of new routines for material characterization

XPS: example I

Impurities of Ag-coated gaskets from LHCb SciFi baby demo plant





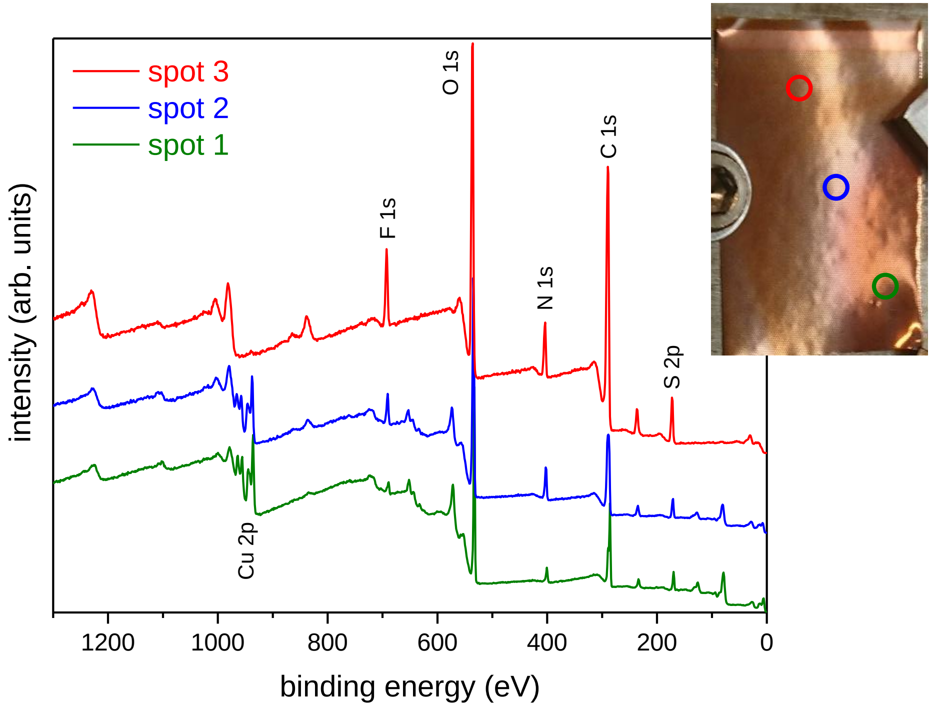
- Circuit operated with NOVEC 649 including *Dodecafluoro-2-methylpentan-3-one* ($CF_3CF_2C(O)CF(CF_3)_2$)

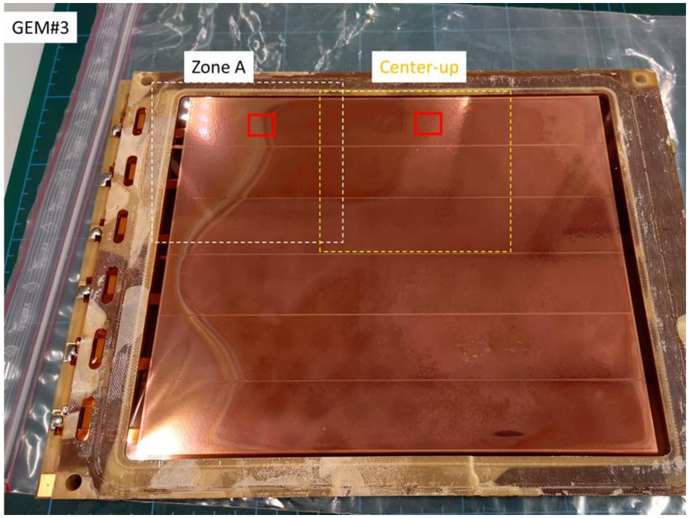
→ XPS spectra indicate absence of corrosion reactions but only stains from dryed operation liquid

see EDMS 2780062

XPS: example II

Analysis of triple-GEM detector after operation in LHCb with CF_4-based gas mixture (40% CF_4, 15% CO_2, 45% Ar)





N, S and C signals indicate polymeric contamination film

→ Same residuals found on glued frame

(see also EDMS 2802473 - SEM/EDX by A.T. Fontenla)

Thanks for your attention.

Analysis techniques at TE-VSC-SCC Chemistry lab

FTIR spectroscopy

e.g.: Evaluation of surface cleanliness for ***UHV applications, Polymer identification***

Optical Emission Spectroscopy

e.g.: ***Lead*** *detection in CERN buildings*

Atomic Absorption Spectroscopy

e.g.: Superconducting cable ***composition***

Differential Scanning Calorimetry

e.g.: Polymer ***Tg Measurement***

Potentiometric titration

e.g.: Quality control of ***surface treatments bath***

X-ray spectroscopy

e.g.: Composition of metallic parts, In-situ ***Thickness*** *of coatings*

Karl Fischer Coulometry

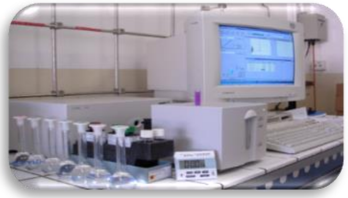
Gas Chromatography

e.g.: Quality control of the ***LHC experiments cooling fluid***

Thermogravimetry

e.g.: Mineral filler quantification in ***polymers***

UV-Visible spectroscopy

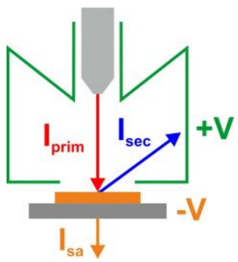


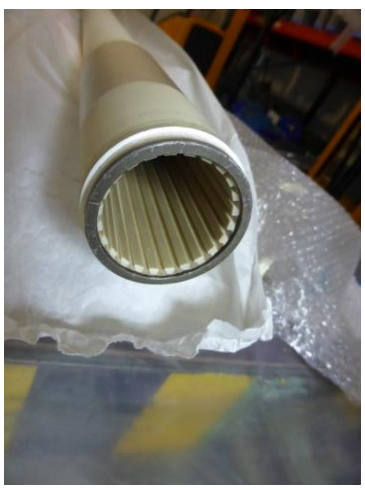
e.g.: Water analysis from ***STEP***

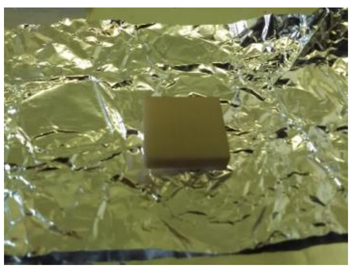
Pulsed SEY for Insulators

Problem: - Difficulties to measure continuous-current SEY on insulators due to surface charging

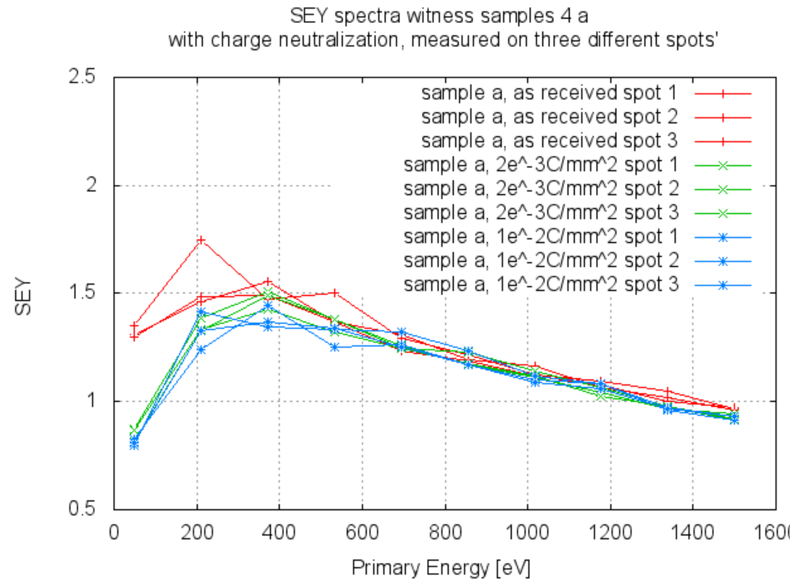
Solution: - Exposure to 30 µs long electron pulses (2×10^{-12} C per data point) on a spot of about 10 mm^2 to minimize charging
- Time-resolved measurement of primary and secondary electron current
- Neutralization with low energy electrons after each pulse to compensate positive charges







Coated Ceramic chamber for LHC injection kicker magnets and witness sample (Photos courtesy M. Barnes SEY_861)



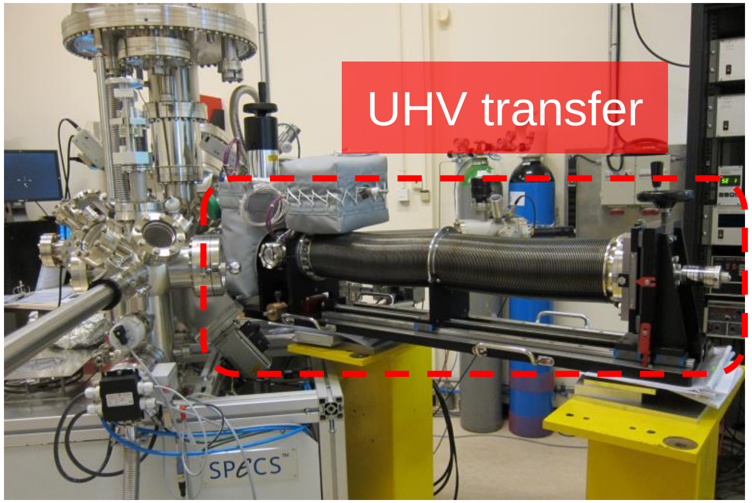
SEY spectra on witness sample with two conditioning steps

XPS: Practical and technical aspects

- Depth of information in XPS: 5-10 nm
- Detection limit 0.01 – 0.1 at.%
- Lateral resolution limited to 200 µm
- Depth profiling up to 2 µm
- Samples must be vacuum-compatible (low vapor pressure, no pencil marks, no fingerprints, contamination- and oil-free)
- Flat samples preferred & maximum sample thickness ~1 cm
- Minimum sample size 4×4 mm^2, maximum 45×45 mm^2

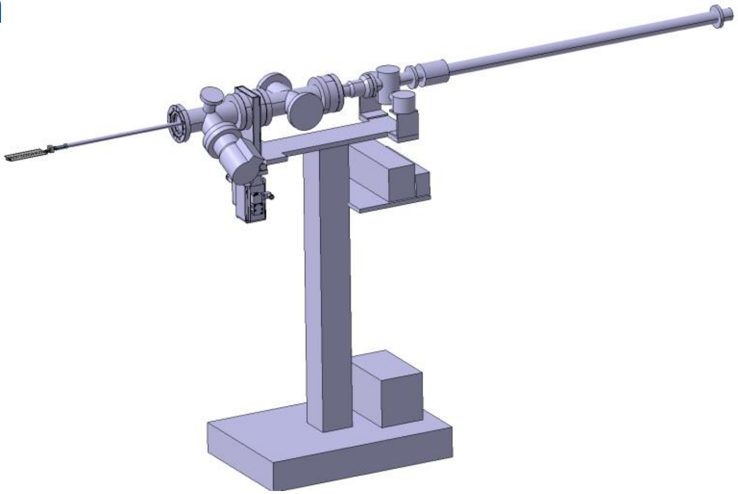
- Hydrogen not directly detectable
- Some organic materials are sensitive to X-ray damage
- Insulating samples: limitations in analysis of bond configuration

Vacuum Transfers for Surface Characterization



Characterization of Photocathodes with SY-STI-LP

- ✓ Vacuum transfer systems for sensitive and reactive samples are essential to avoid surface oxidation and adsorption of ambient species
- ✓ Solutions exist for analysis of photocathodes, samples from the SPS to study beam-surface interaction



Vacuum transfer solutions can be adapted to new needs and geometries.