Surface analysis for CERN: a wish list

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-New XPS
-Repair SIMS
-Kelvin Probe
-UPS

Surface analysis lab

Typical useful information for a surface:

-identification of elements present on the surface and quantification (elemental surface concentrations)

-identification of chemical groups/bonds present on the surface

-concentration profile in depth

-Other surface properties: work function, secondary electron yield, surface energy

Identification of elements (in the topmost 1 nm layer)

Presently at CERN lab (101):

-**XPS** (30 years old), lateral resolution 1-4 mm (XPS)
-**AES** (25 years old), lateral resolution 0.1-0.2 mm (AES)
-detection limit around 0.5-5% depending on element (except H)
Typically 150 jobs/year or 700 measurements. The instruments (especially the frequently used XPS) need often maintenance due to their age

Lateral resolution requirements for a new machine

- For most of the applications (contamination detection, NEG activation control, coatings control ….) high spatial resolution would be helpful, but is not mandatory
-The request for spatial resolution comes mainly from the experiments (contamination on chip contact pads and similar): few requests per year

Existing commercial standard instruments:

-0.003-0.1 mm lateral for XPS
-20 nm lateral for AES
-Detection limits are similar as old instruments, but with more efficiency (faster acquisition, less sample irradiation)

Further requirements for a new XPS machine:

-**base pressure** of the instrument should be sufficiently low for example to enable clean activation of NEG (low 10^{-10} mbar range)

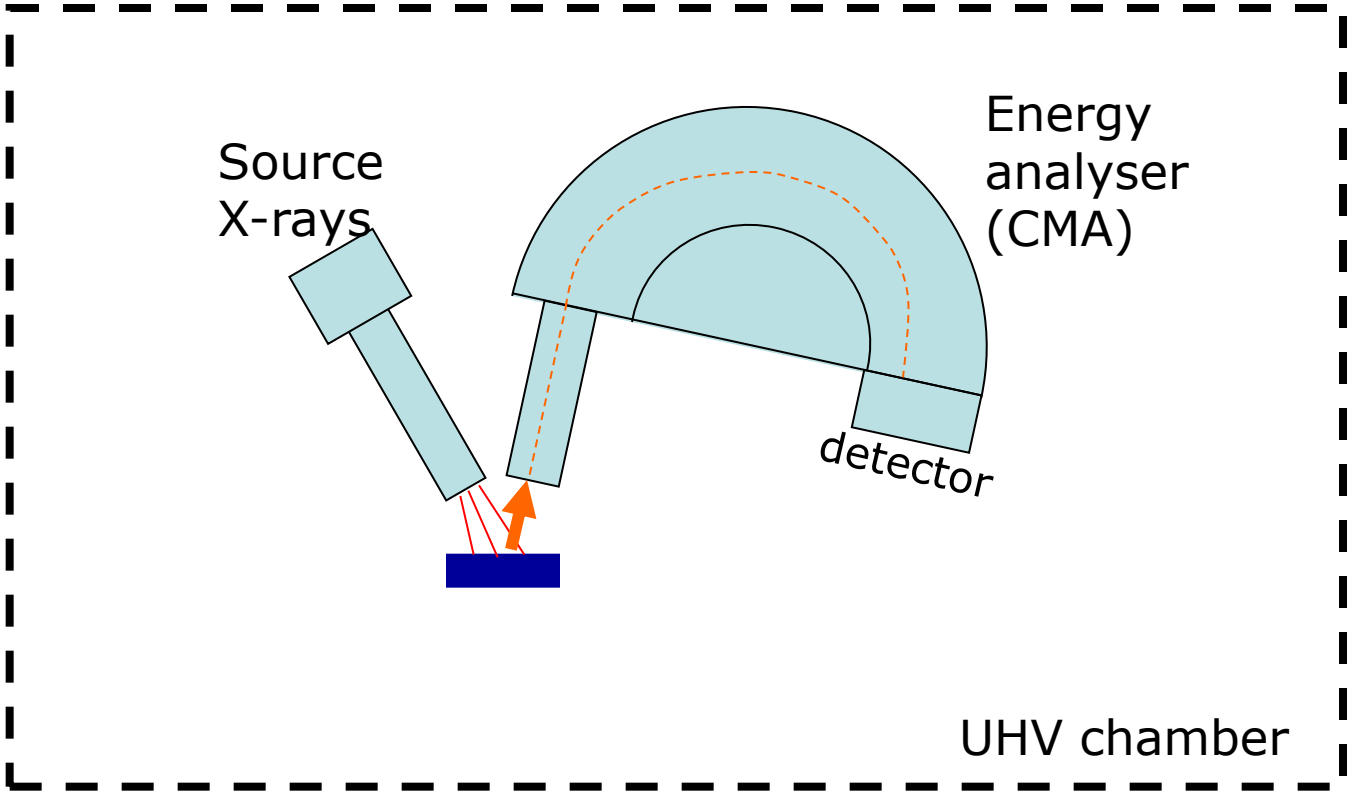
-**heatable manipulator** should have low outgassing (residual pressure < 10^{-8} mbar at 250C)

-**flexibility** to connect other (home made) devices

-larger sample insertion port (DN63 instead of DN40)

-if we want also **UPS** (see later) we need an excellent shielding from magnetic fields and a suitable electron energy analyser (energy resolution) : vacuum chamber in mu-metal

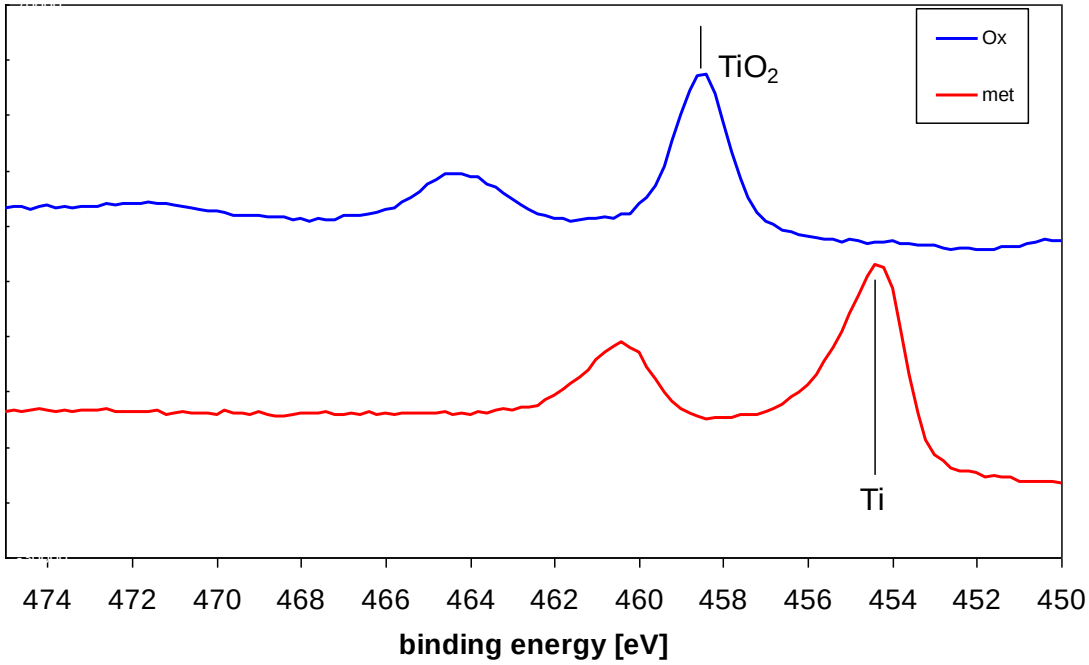
XPS principle



Identification of chemical bonds

Present situation at CERN labs (101+10):

-Non-monochromatized XPS through energy shift of the lines: works for many metal/oxides with the present instrument, more difficult for organic bonds in adsorbates (**contamination**), carbon….Impossible for silicone/silicates



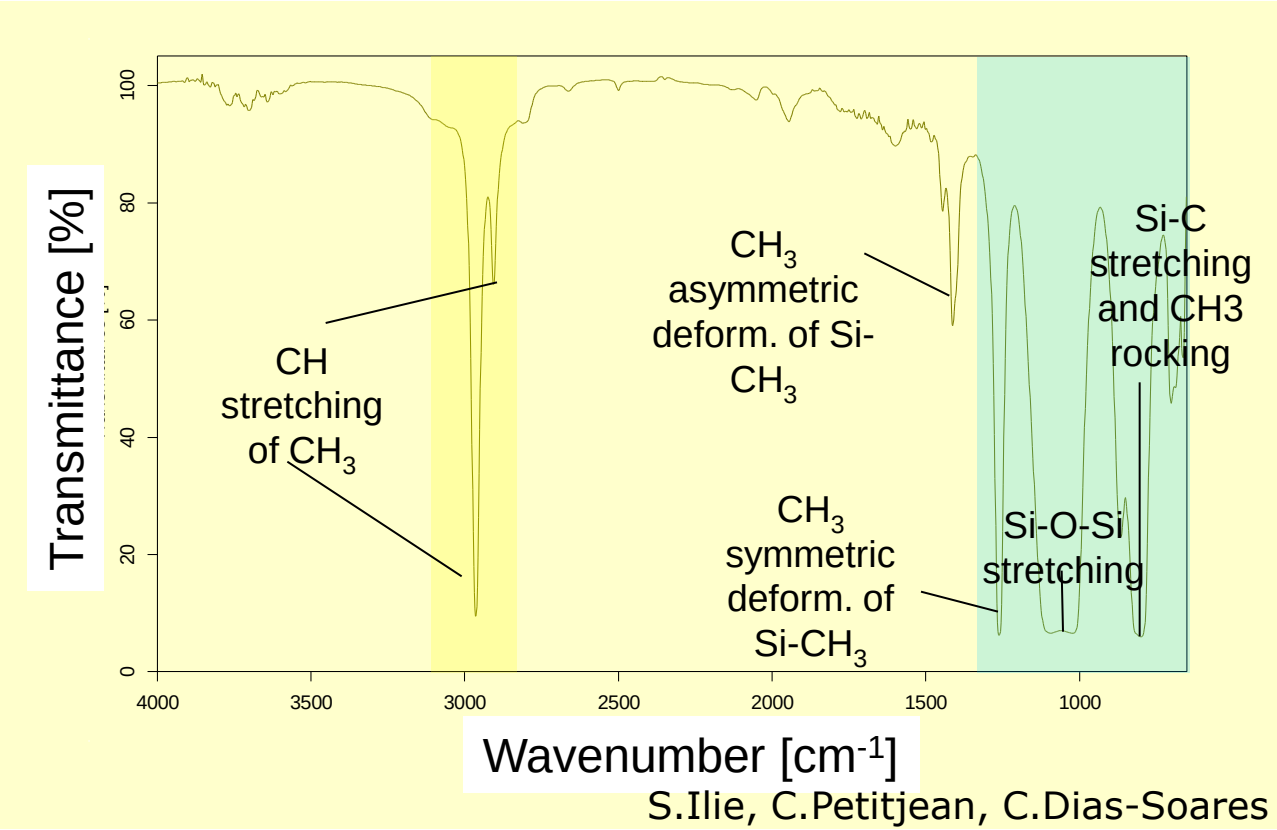
-For soluble organic or silicone contamination: elution in hexane subsequent **FTIR** (absorption spectroscopy of a drop re-deposited on transparent substrate); can be done if the surface is sufficiently large to provide enough eluted material

Detection of silicones by FTIR

- ❖ Elution of contaminant from the "cleaned" part (tube, valve ,..) with a defined quantity of hexane per surface area
- ❖ Deposition of a drop of solution on a ZnS window (transparent to IR)
- ❖ Measurement of transmittance after evaporation of the hexane

Sensitivity depends on the area used for the elution (various drops can be cumulated if necessary to increase concentration)

Problem: Uncertainty on the effectiveness of elution



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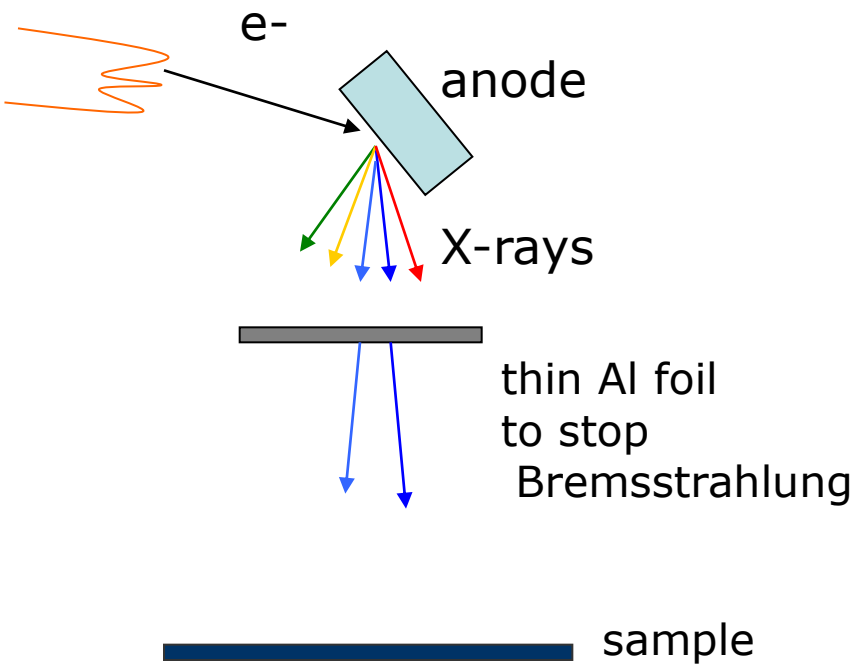
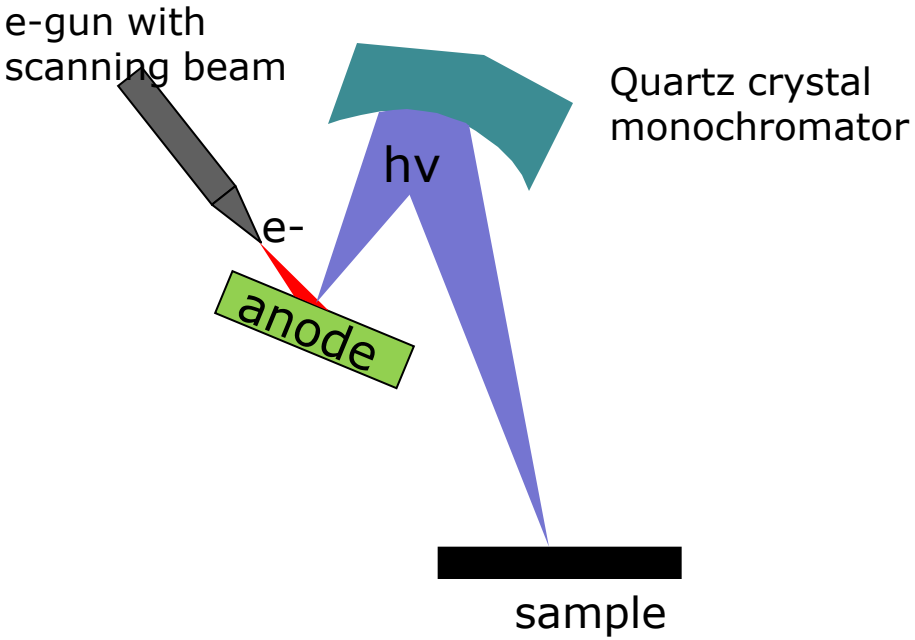
Non-monochromatized vs monochromatized X-ray source

Non-monochromatized (present CERN source)



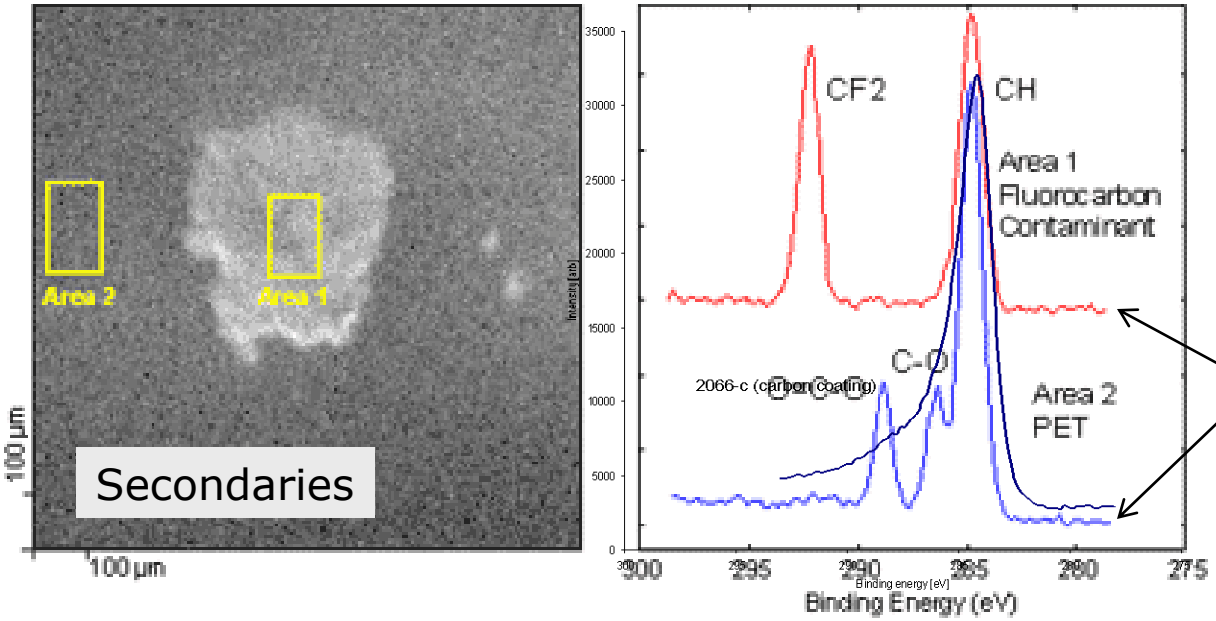
Source gives a spectral line (ex.AlKα with its satellites Kβ etc..)

Monochromatized , with in addition spatial resolution



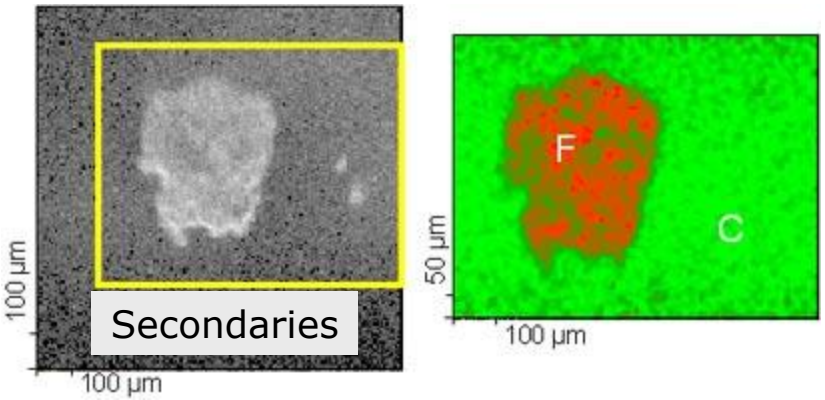
Source gives only one line (ex AlKα)

Advantages of a monochromatized source



Monochromatized source

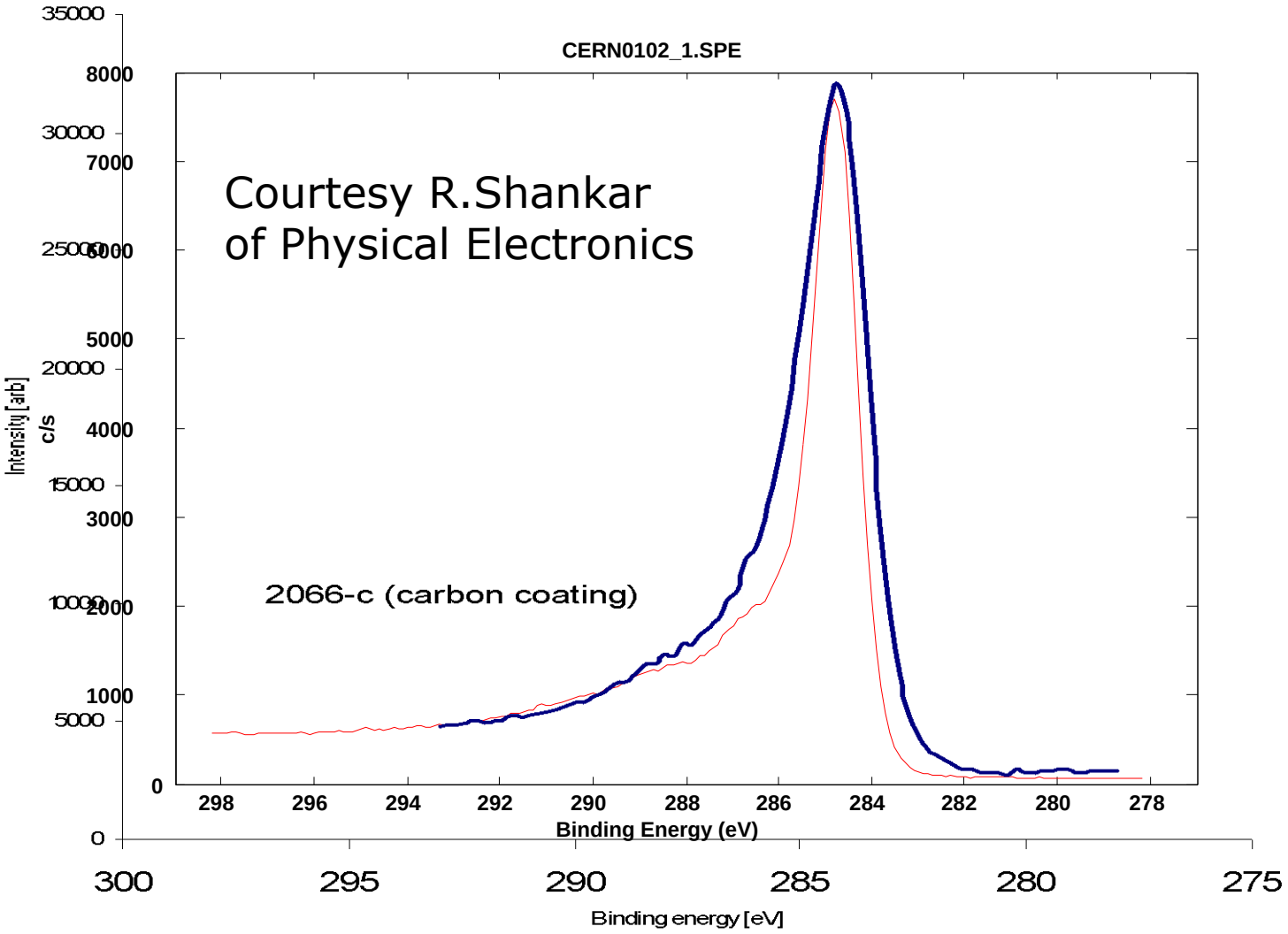
High resolution carbon 1s spectra from the same selected areas that show the presence of a fluorocarbon contamination in localized areas on the polymer surface.



Interpretation and fitting of the various components is easier!

It would be a step back in time to buy a non-mono. Source.

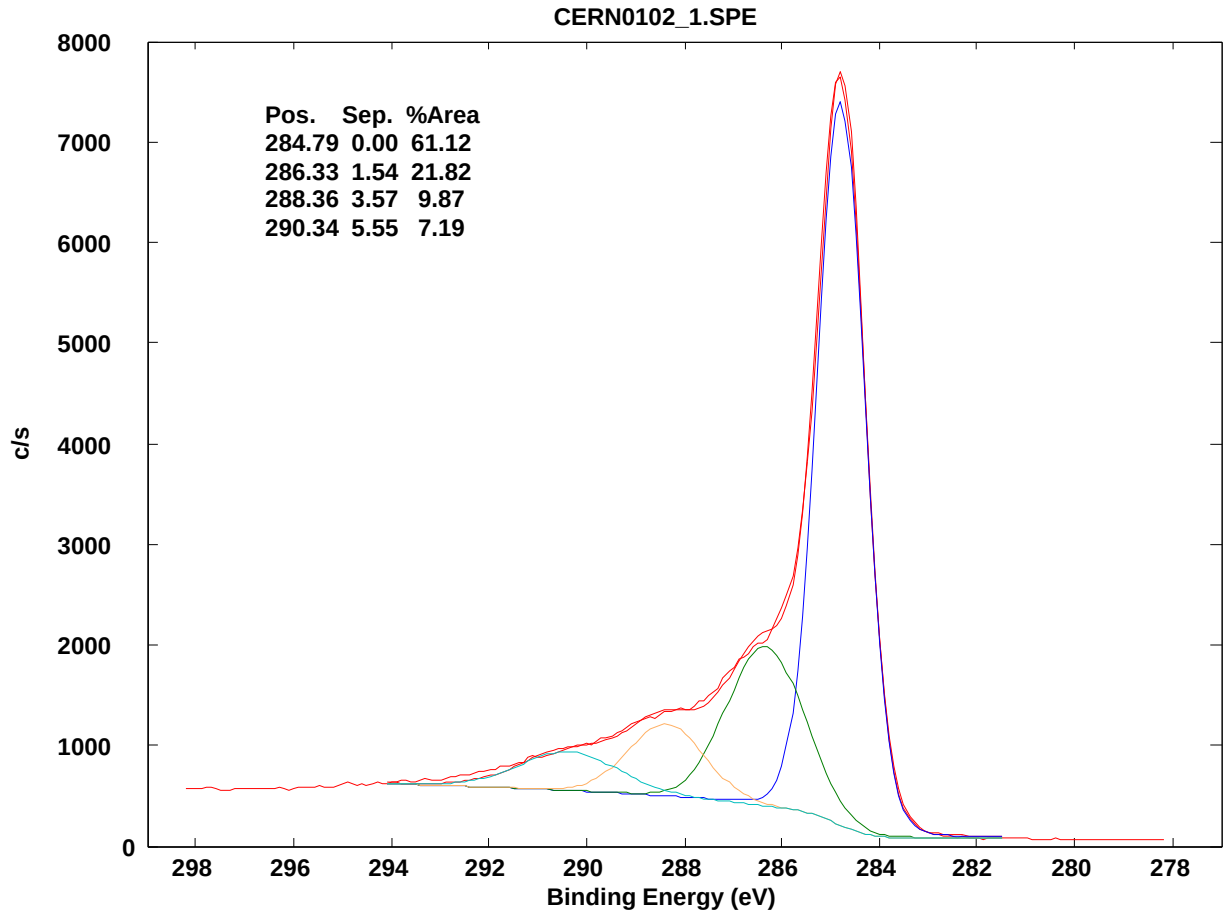
On a-C coatings



CERN0102_1.SPE: CNe35 - Carbon coating PHI

2010 Mar 23 Al mono 98.9 W 100.0 µ 45.0° 11.75 eV 8.38 min

C1s/Area1/1 (Shft)

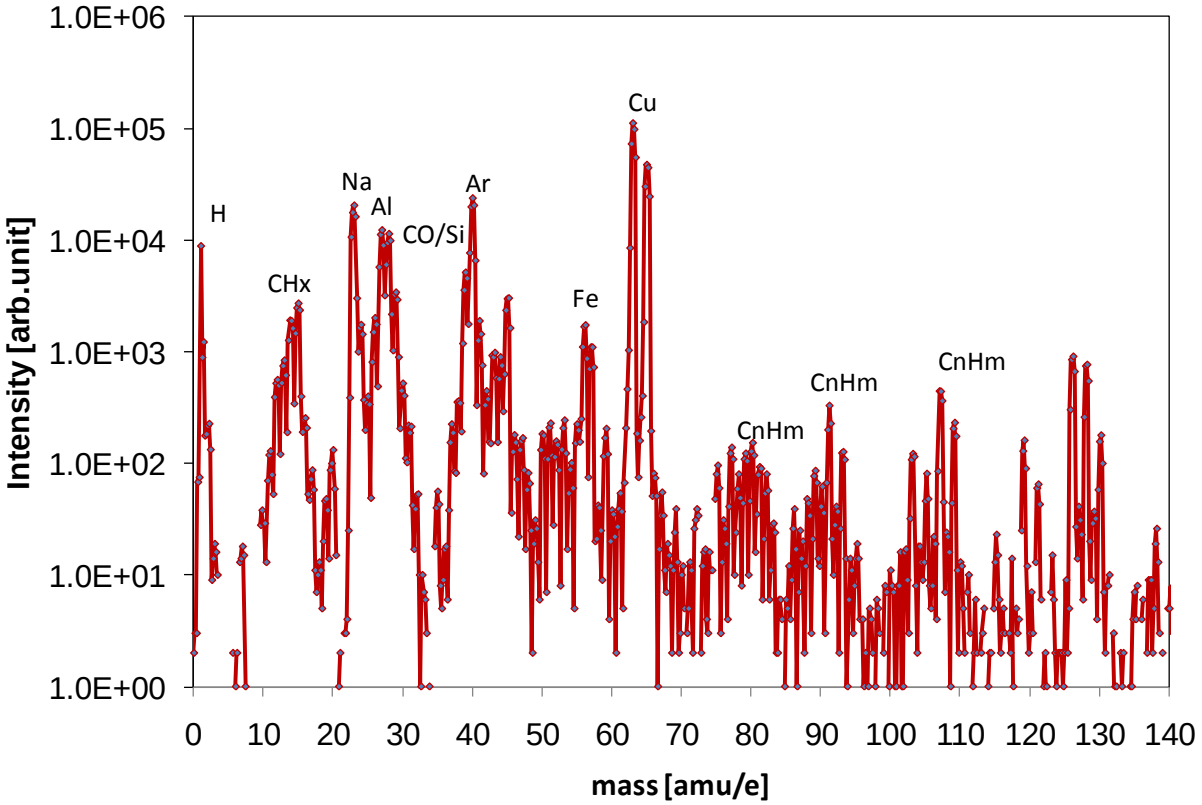


One step further: SIMS (Secondary Ion Mass Spectroscopy)

Only meaningful after a preliminary XPS analysis

-detects molecular fragments with higher surface sensitivity, lower detection limit, depending on element/group and matrix , but typically below 1 0/00
-absolute quantification is difficult, due to matrix effects (sensitivity for A in B is not the same as A in C)

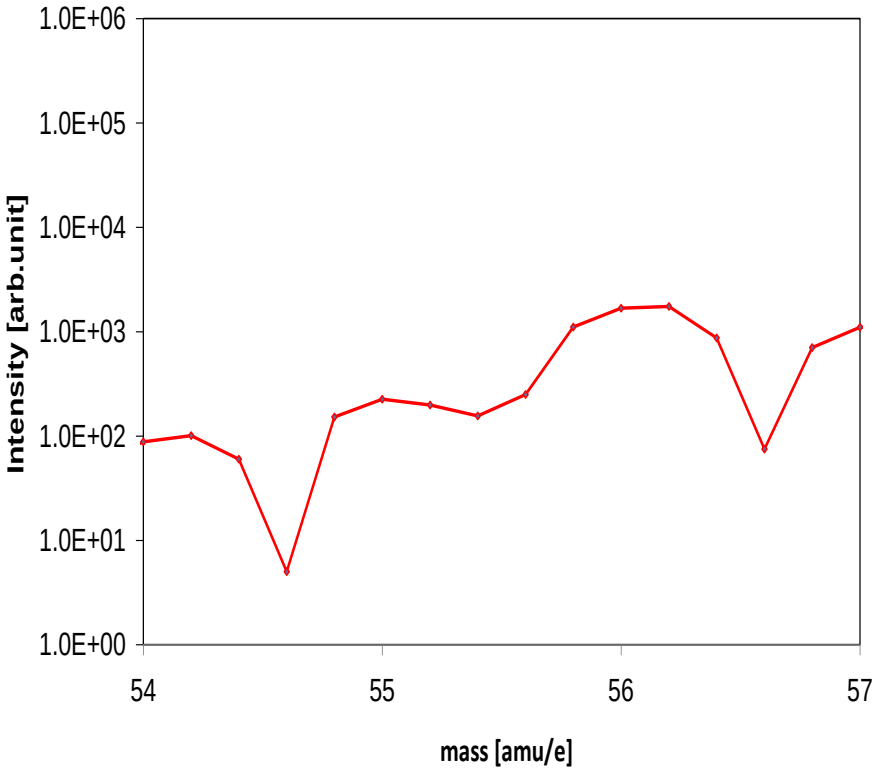
Present
CERN system
(not working
at the moment):
-Ar ion gun
-in the XPS chamber
-only dynamic, for high masses (>30-40)
-in principle one can do profiles….but not quantitative



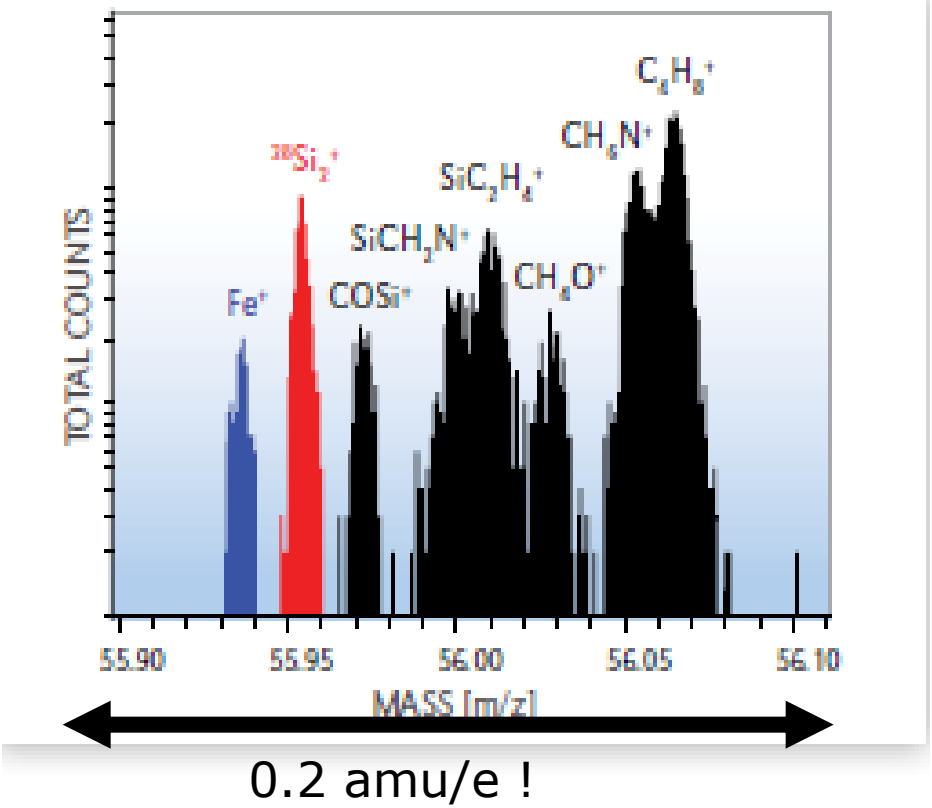
Typical performance of modern instruments

Modern TOF systems can distinguish between chemical groups which are very close in mass, with a resolution of m/Δm=10000

CERN system



TOF-SIMS



0.2 amu/e !

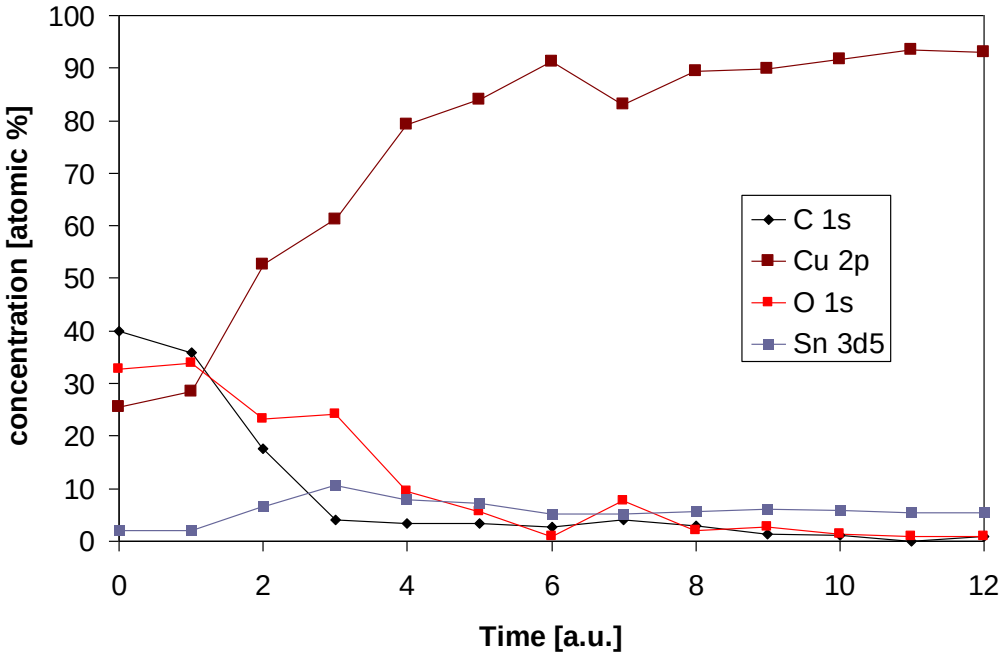
For us a **Static SIMS** would be useful (changes of the surface influencing SEY) since it has even more surface sensitivity than XPS and it does not damage the surface

Depth profiling

Present situation:

-with XPS up to 30 nm depth and AES to 100 nm depth, with Ar ions

-used to detect inter-diffusion in layer on layer systems or to measure relative oxide thicknesses



Note: The speed/depth is limited by the signal to noise (acquisition time) and the performance of the ion gun. In fact indirectly is limited by the lateral resolution of the technique: the sampling spot defines the maximum ion current density that the ion gun can achieve

Commercially existing improvements:

- Ion guns with different ions (as exotic as C60) and Zalar (azimuthal) sample rotation to avoid "cratering" effect of the beam

Work function measurements

Present situation:

-Relative work function measurements can be done in principle with the XPS system by looking at the low kinetic energy tail. Not routine.

-Possible applications: useful to understand mechanisms of physisorbed layers on SEY (also cold SEY) and on spark test samples (influence on field emission)

Improvements:

-**Kelvin probe**: cannot be installed in the old XPS (no free flanges) , but possibly in the SEY system . Home made or commercial.

Or:

-Measure workfunction with **UPS** (ultraviolet photoemission spectroscopy) by taking the length of the energy spectrum. Needs a UV lamp and an electron analyser with sufficiently good energy resolution (available on most XPS analyzer as further option)

-UPS enables to measure **valence band spectra**: interesting for adsorbates (often molecular orbitals can be identified, provided that one species only is present), coatings with different electronic/electrical properties depending on deposition parameters (TiN, a-C…)

Secondary electron yield

Presently at CERN (101 and 30)
-System for measuring SEY from 50-2000eV (20-2000 eV) primary energy
-on conductors only
-at RT and down to 8K on conductors

Improvements:
-pulsed beam with shorter pulses to measure on insulators: hardware available, needs some testing, programming, etc…
-8K down to 4.2K foreseen
-measurements at lower primary energy (0-10eV) would be interesting, but are and experiment in itself

No commercial systems with collector geometry, only electron guns are commercial

Surface energy …or something related to it

Contact angle measurements :
-presently only some temporary “bricolage” with microscope, CCD and syringe
-commercial devices exist

-applications would be mainly for control of surface processes (cleaning, CO2 jet cleaning, glow discharge cleaning…) to enhance wettability and adhesion of coatings

NB: absolute measurement of surface energy is extremely complex and implies the knowledge of the interaction energy of the liquid with the surface (not only surface energy of the liquid). In general it is extrapolated from many measurements with different liquids (for polymers)

Conclusion

Minimum requirements
-XPS with monochromatic source, with an energy analyzer which is good enough for UPS and improved data handling
-evaluate a repair of existing SIMS (Bdg 101)

Further upgrade
-add UV source for UPS
-ion gun for depth profiling on th new XPS
-Kelvin probe