Surface finishing and coatings for accelerator vacuum applications

M.Taborelli, TE-VSC-SCC CERN

cleaning

plating

coating

Why to care about treating the surface?

- the **thermal outgassing** and **particle induced outgassing** (electrons, photons… hitting the surface) in vacuum is determined by the surface composition and cleanliness (with the notable exception of H_2)

- **electron multiplication** (electron cloud) depends on surface properties

- **adhesion** of thin films and peel-off, depends on the surface state of the substrate

- the performance of superconducting thin films on **RF cavities** depends on substrate surface preparation

- **impedance** seen by the beam depends on surface conductivity (within skin depth)

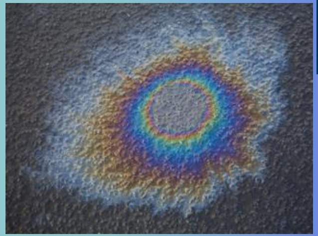
- **corrosion** starts at surfaces/interfaces

Cleaning

P.Mondrian
Composition No. II

Cleaning

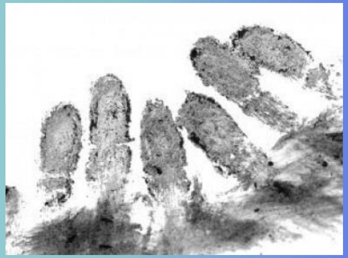
The definition of cleanliness depends on the application



In accelerator technology and **ultra-high-vacuum** it means to get rid of :

- **hydrocarbons**, oils, lubricants, fingerprints, glue, marker traces (vacuum, surfaces for welding and vacuum brazing)

- **halogens as Cl**, F, I; sulphur...., from lubricants and flux fluids for soft brazing, fingerprints (corrosion)
- **silicones** from lubricants (vacuum, formation of insulating layer upon irradiation)

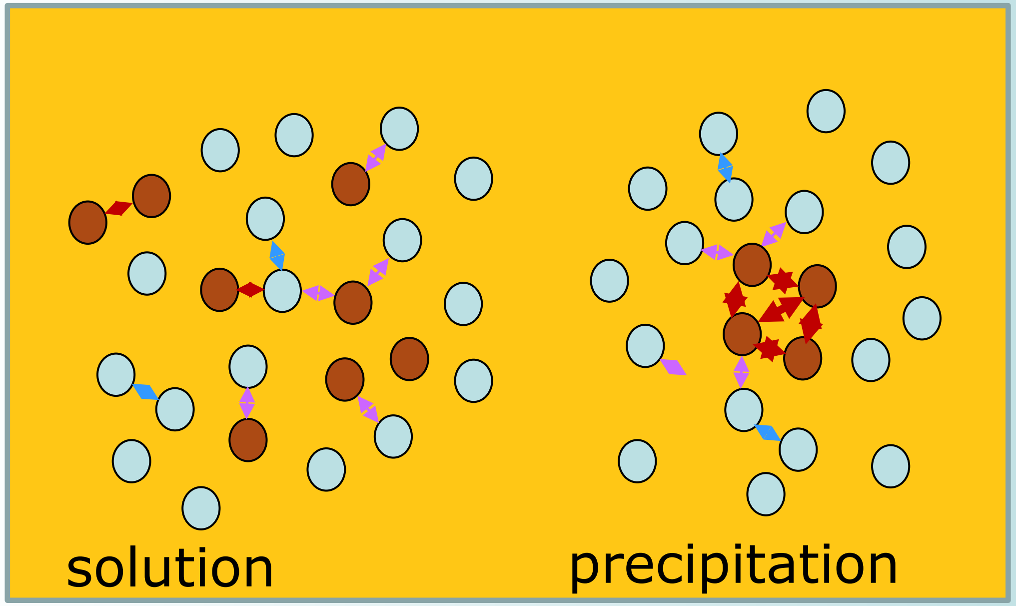


- metals with high vapour pressure (Cd, Zn 10^{-7} and 10^{-9} mbar at 100C)

Precision cleaning <1 µg/cm² (< 3×10^{15} molec/cm² of $C_{12}H_{14}$ roughly one molecular layer)

Solvents

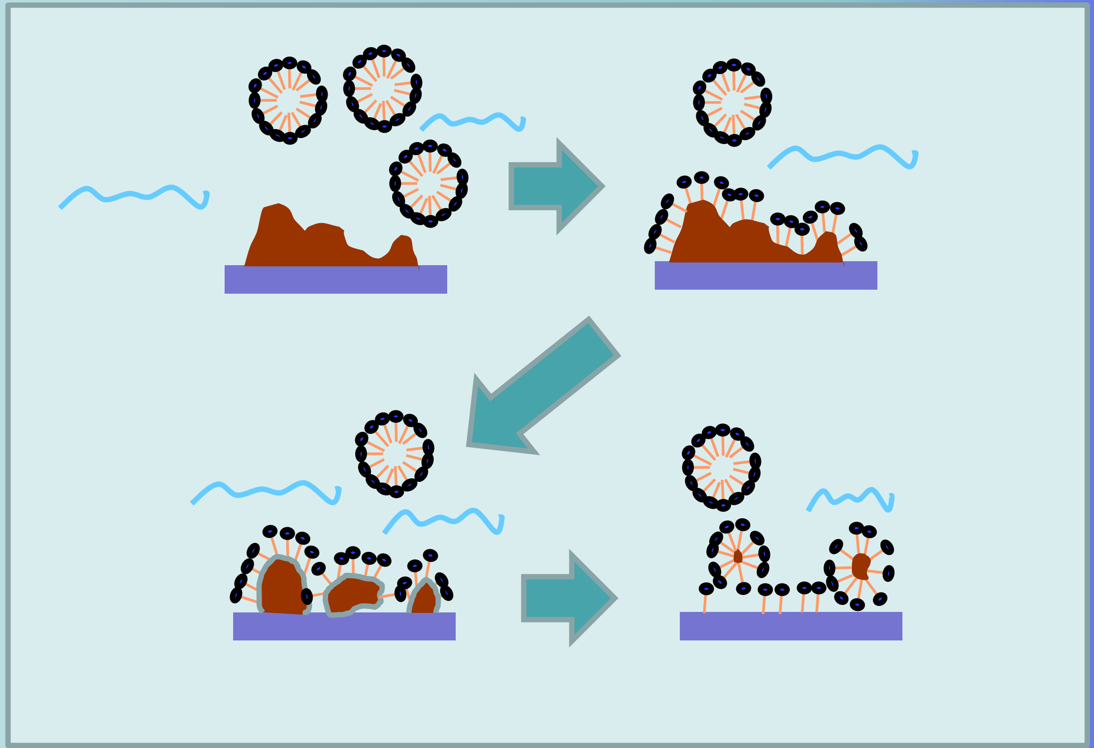
The contamination is put in solution.



"like with like" : polar dissolves polar and ionic, non-polar dissolves non-polar etc…

Detergents:

A detergent can wet any surface (surfactant). Is an **amphiphilic** molecule with polar head and non-polar tail, **soluble in water and organic solvents**, can incorporate the non-polar hydrophobic material which can thus be dissolved (formation of micelles).



Cleaning by solvent:

Which fluids?

- Ethanol (ATEX!), modified alcohols (having polar and non-polar components R′-O-R′′-OH), supercritical CO_2 …….
- **Volatile** solvents are used: a **closed plant is necessary** to avoid loss of solvent (safety and environment)

By immersion:

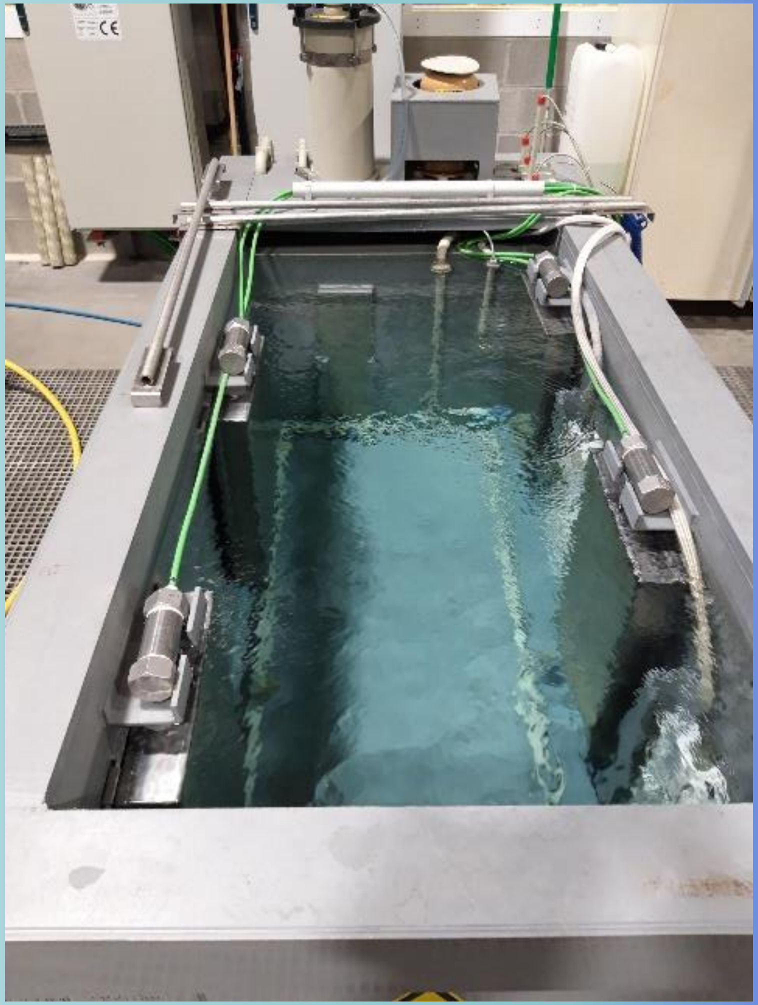
- Dip the part to be cleaned in the solvent bath with ultrasonic agitation.
- Final rinsing with pure solvent and drying by evaporation.

Without immersion (vapour degreasing):

- Keep the cold workpiece above the bath, in the vapour phase to condense the solvent on it
- Continuous distillation of the condensed solvent removes dissolved contamination
- Sometimes a further passage in an air oven is necessary to completely remove the solvent

Cleaning by detergent: typical procedure

warm water based detergent bath
(50°-60°C)
with **ultrasonic** agitation
(or turbulent flow circulation for long pipes
which cannot be immersed)
+
rinsing bath (demineralized and/or tap water
with ultrasound)
+
rinsing with demineralized water
bath (conductivity <5 μS cm^{-1})
+
drying (hot air oven or blowing with dry
nitrogen)



NB: simple control by a verification of wetting of the surface with the rinsing water

Solvents

+ can in principle evaporate from pores, traps (bellows), still further heating in air oven is often required

+/- chemically inert on metals/oxides

+ can dissolve silicones

- requires more complex cleaning machine

Detergents:

- complex shapes difficult to rinse and dry

+/- pH is alkaline, surface oxides and some alloys (Ag/Cu brazing, NEG, Al, alloys…) can be slightly etched; test for your workpiece material or look for stability in basic pH

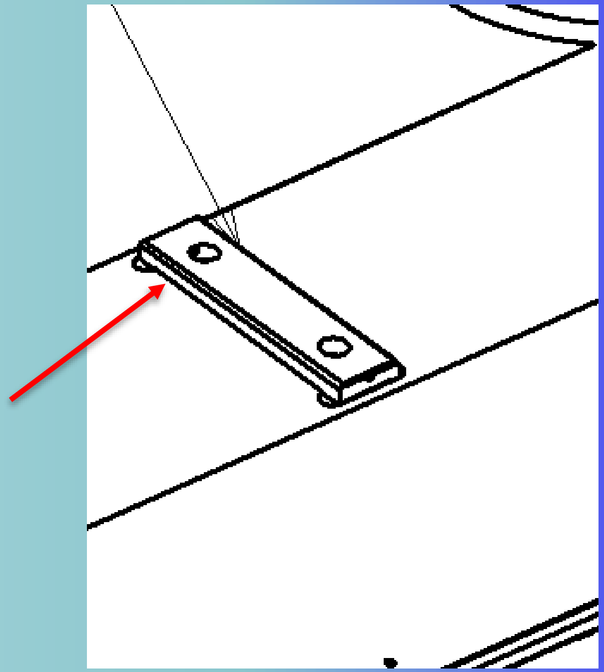
- does not eliminate silicones (they float on the bath surface and are recollected)

A priori there is not one option which is better than the other

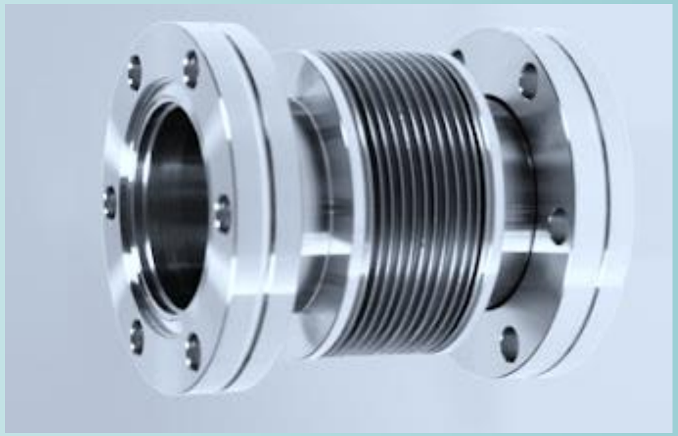
Design and manufacture cleanable parts !

-non-penetrated weldings, « pockets », are traps for contamination and liquids that cannot be properly rinsed
-tapped blind holes do not help, but are unavoidable

-avoid to produce inclusions (from brushing, grinding, sand-blasting)
-do not leave cutting fluids for long time on parts
-avoid stickers on functional surfaces
-avoid the use of solid lubricants (MoS_2, graphite etc...) before cleaning



Other:
-do not re-clean edge welded bellows



Uncleanable contamination: boron nitride

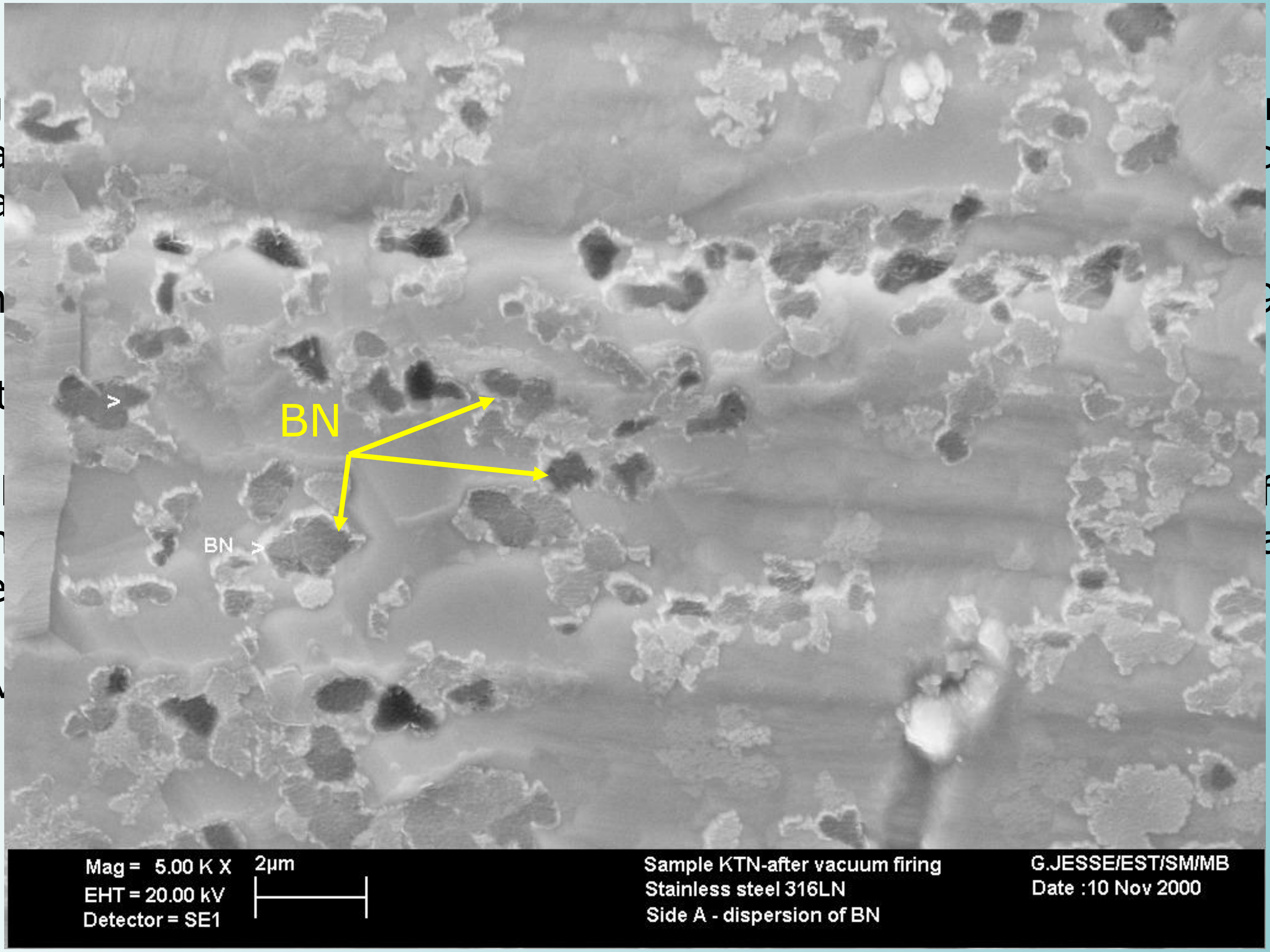
-B segreg … ring
(950°C) a … crease
hot worka…

- BN form … 9 ppm wt

-BN is not…

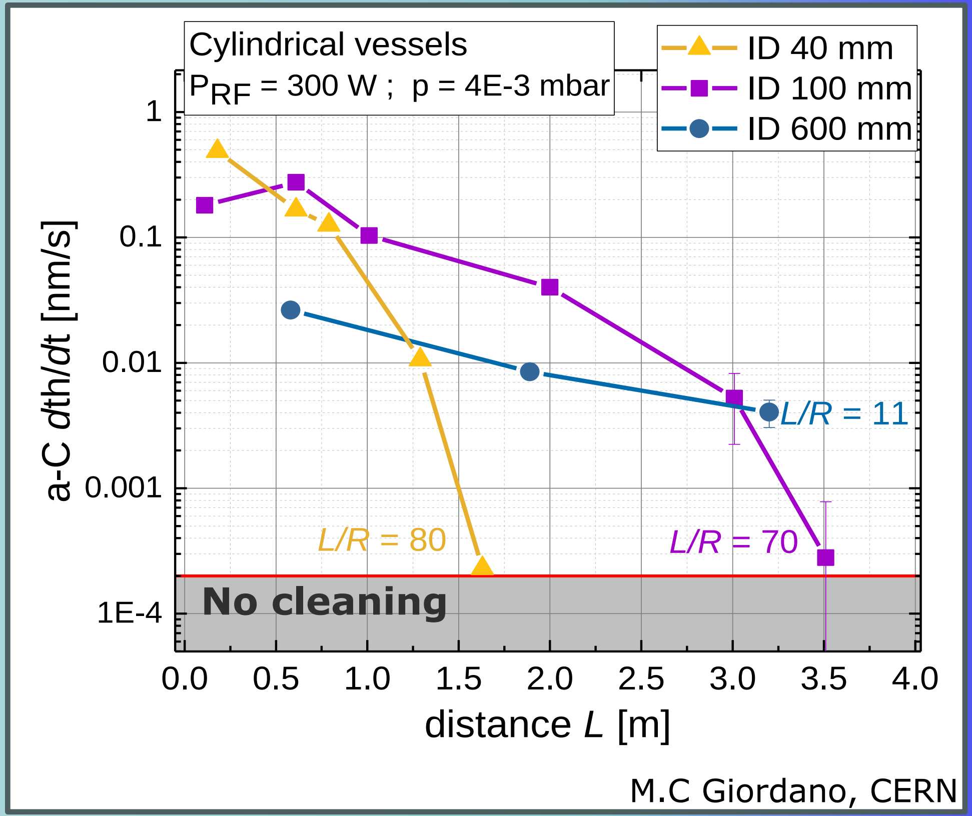
-It is not … face
energy an … and will
readily de…

- is remov…



O_2 plasma cleaning, dry

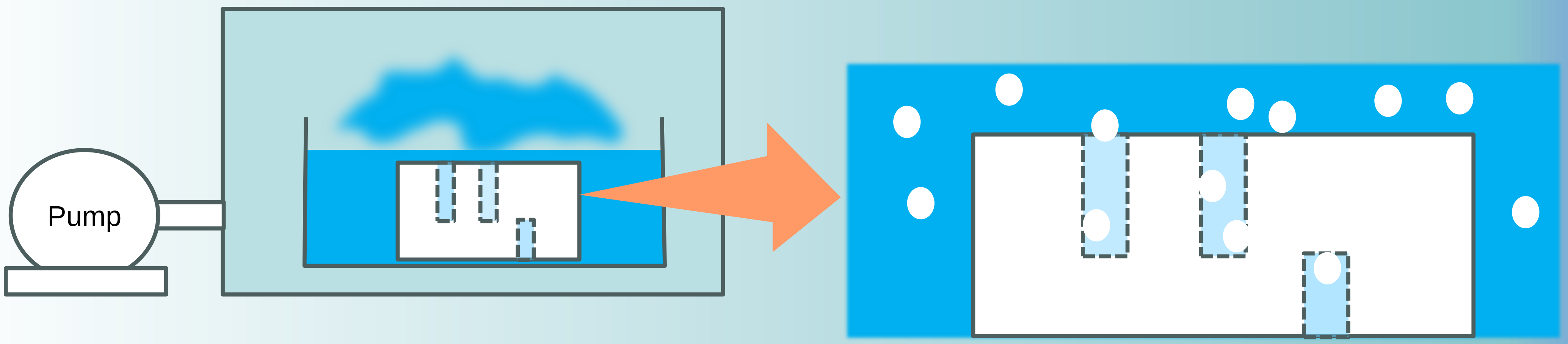
- ICP O_2 plasma source
- For organic contaminants and low contamination level, oxydation of CxHy to volatile species
- High dose can oxidise the surface (on copper)
- ...work in progress



Related technique: Ozone produced by UV-lamp see J.R.Vig JVST A3, 1027 (1985)

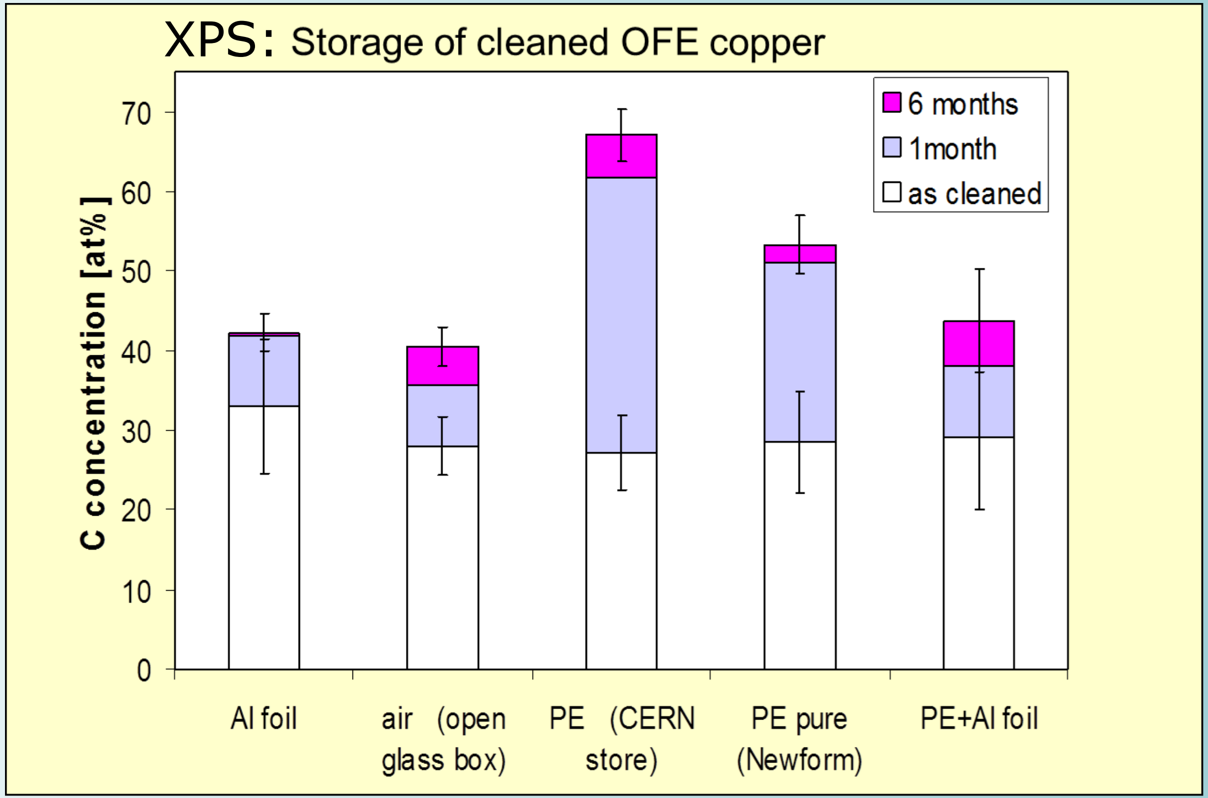
Cyclic Nucleation Process/ Vacuum Cyclic Nucleation

- Reducing the total pressure in controlled environment chamber with the parts to be cleaned immersed in a solvent or aqueous solution → **vapour bubbles in crevices, pores, defects, contamination….**
- **Pulsing** or continuous evacuation to facilitate mass transfer

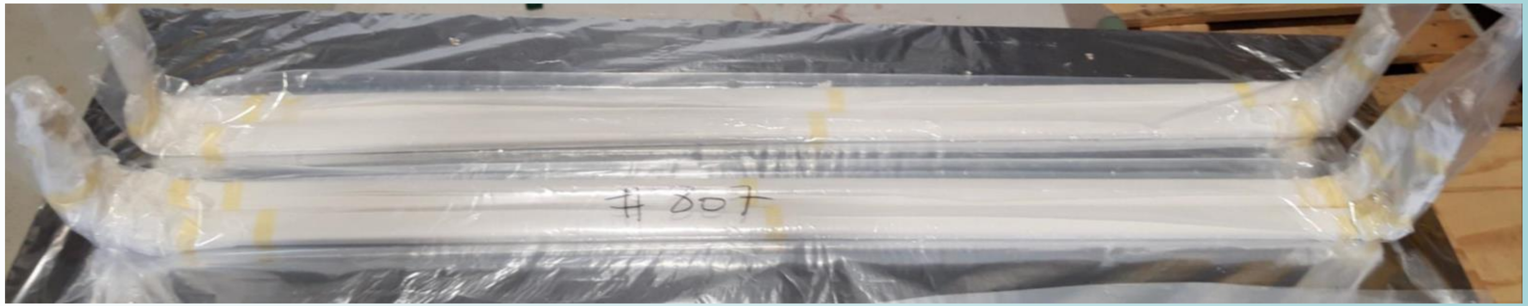


Effect of storage in different packaging after cleaning

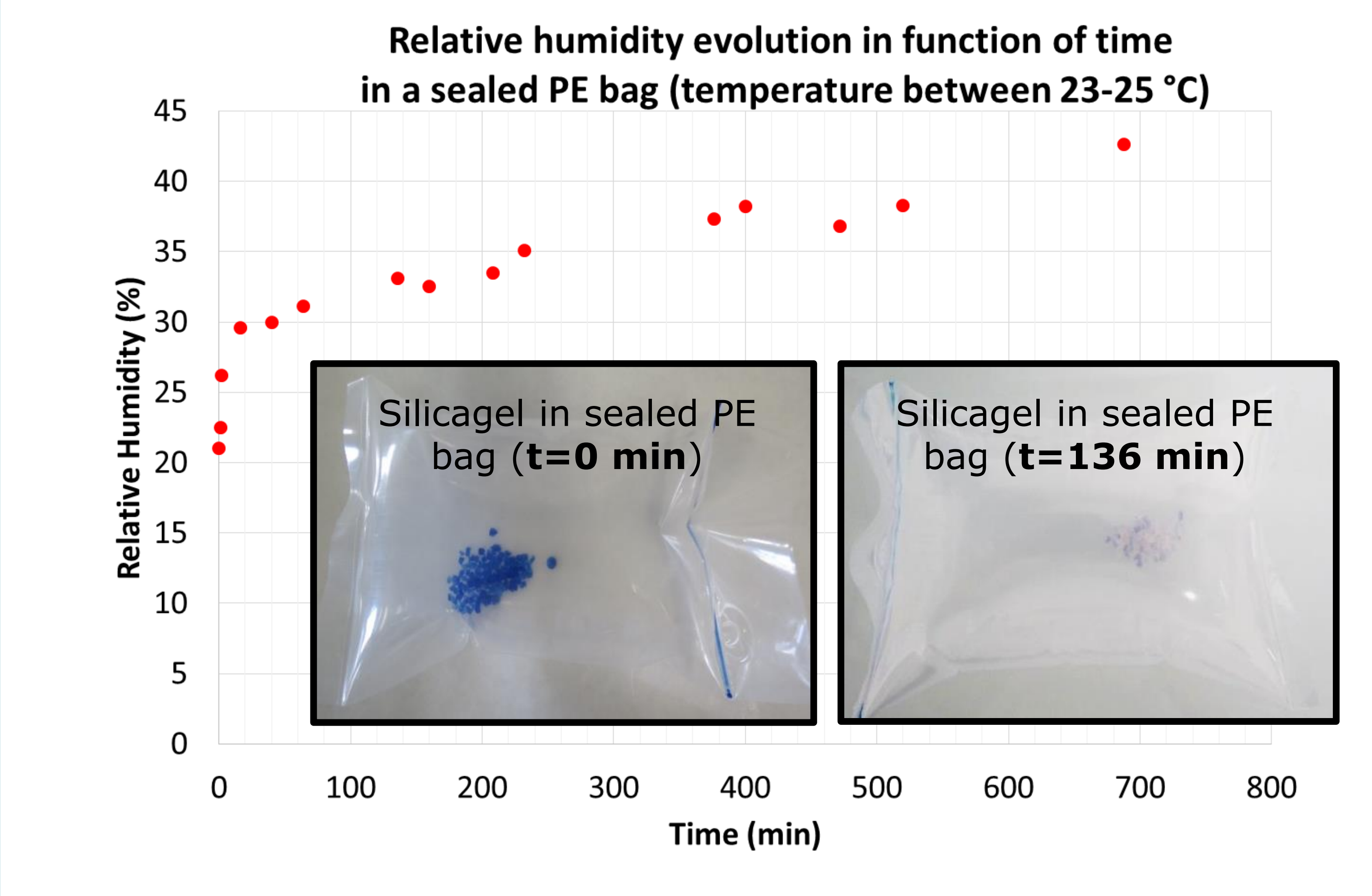
Aluminium foil is the best, but should not be used for **copper** parts in presence of humidity



C. Scheuerlein et al. Appl. Surf. Sci. 252 (2006) 4279-4288



Storage and humidity: polyethylene bag



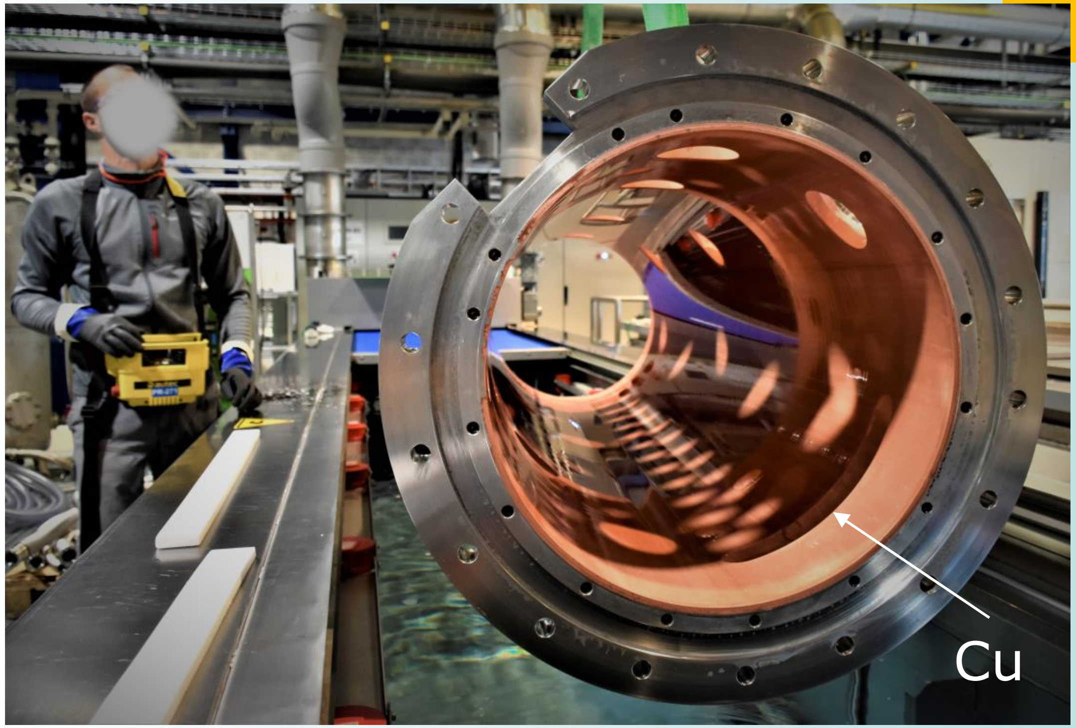
The PE bag is a good barrier against macroscopic contamination only

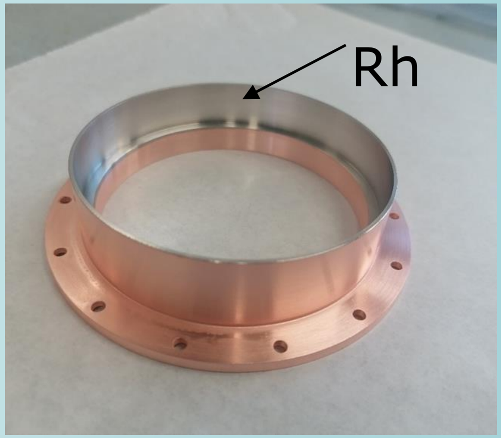
Only detergent and solvent cleaning were discussed, but sometimes
-chemical etching (before vacuum coating),
-electropolishing (before superconducting cavity coatings),
-passivation (before coatings)
-….
…….must be used

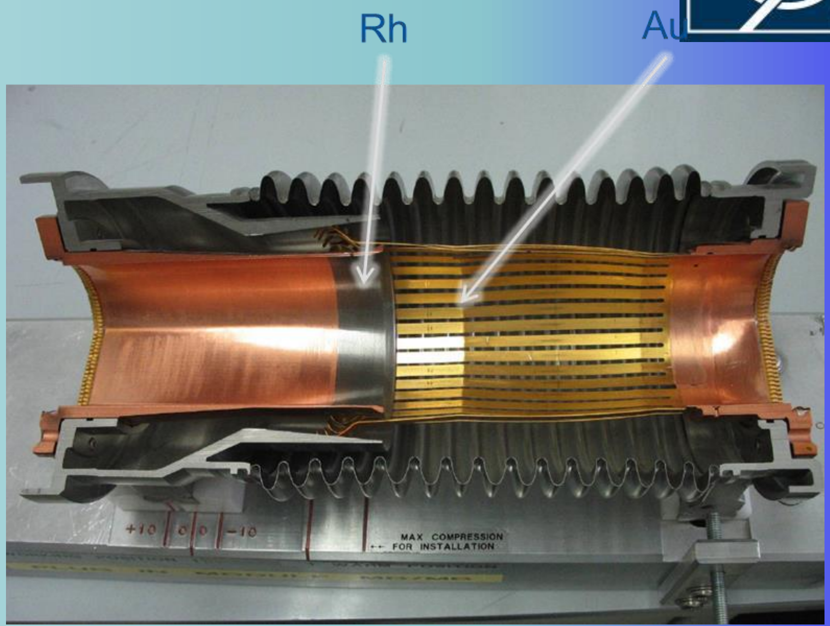
Galvanic deposition, electrochemical coating, electroplating, plating

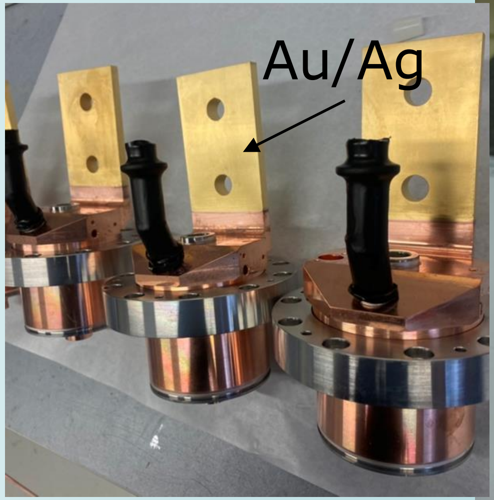
San Marco, Venezia

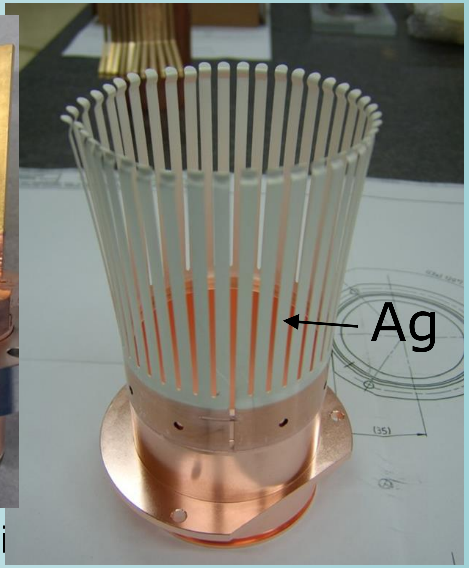
Examples

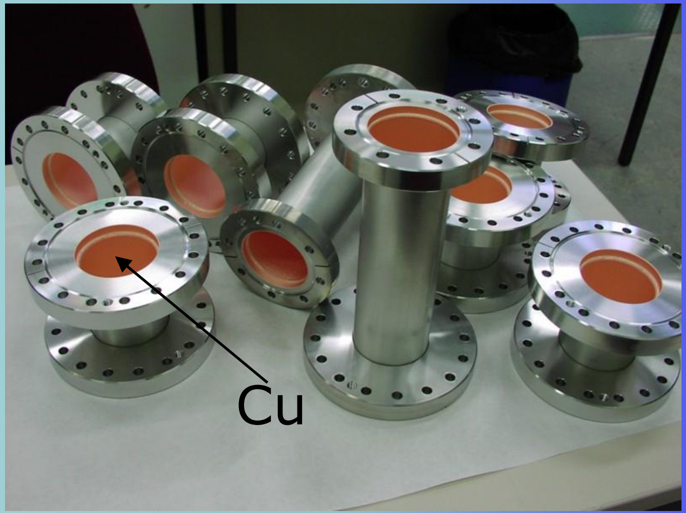












Courtesy of CERN

Plating

Applications:

- Provide electrical surface conductivity (impedance, flow of the image current) (*Cu)*
- Prevent cold welding, seizing, *(Ag on nuts/bolts of flanges)*
- Enable electrical (mobile) contacts *(Au, Ag, Rh/Cu; in general hard on soft to avoid adhesion and obtain a large contact surface)*
- Build wetting layer for brazing *(Ni) or* diffusion barrier *(Cu on Glidcop)*
- Protect against oxidation
- …..

Typical thickness range: few um – few mm

Typical substrates:
-Copper, CuBe, StSt, Aluminium,…polymers (not for vacuum!)
-some substrates require a pre-layer (or adhesion layer) as Ni or Au on StSt; Au on μ-metal; zincate on Al…….

Plating with non-soluble anode

Conducting electrolyte

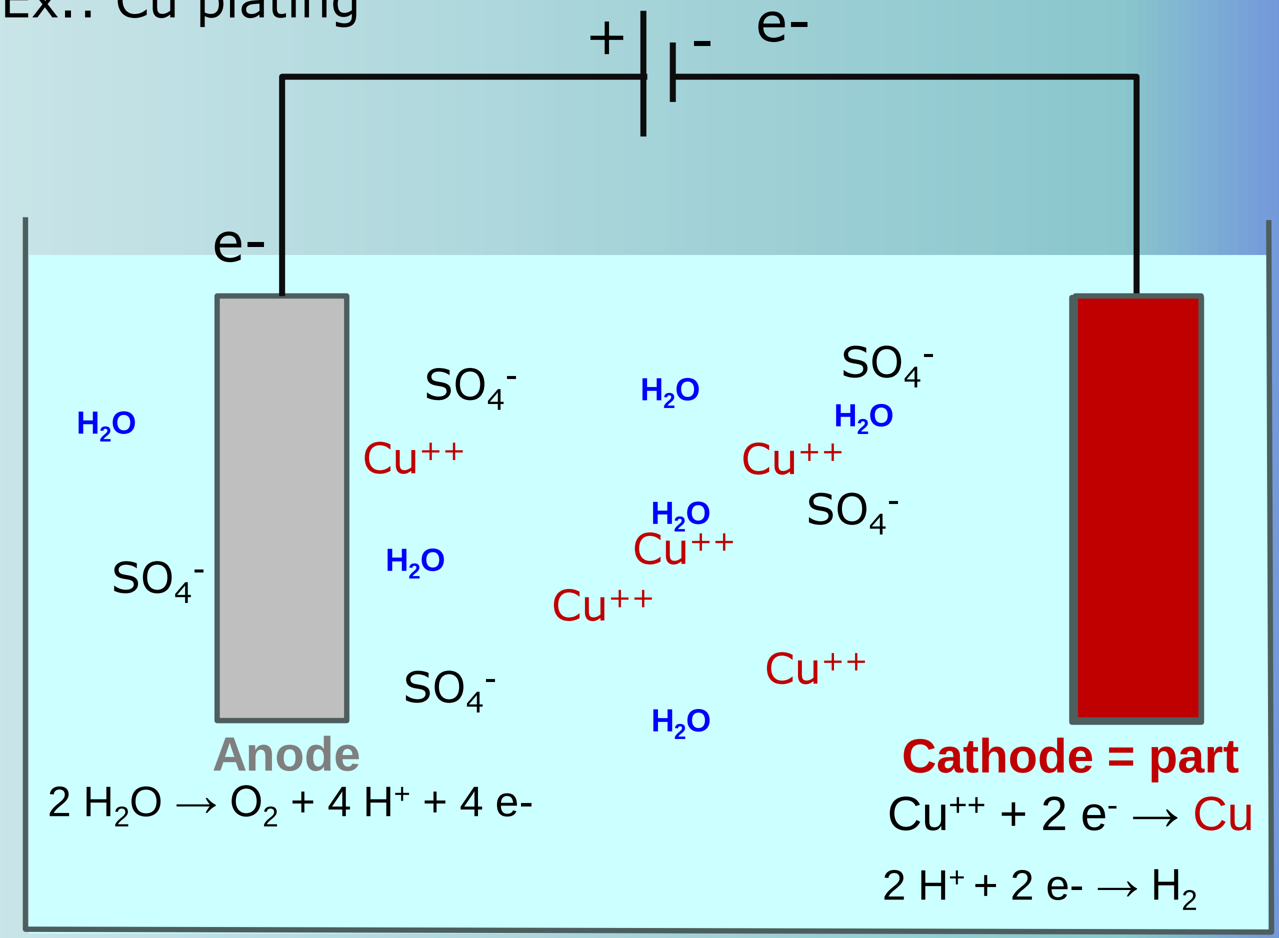
The metal to be plated must be present as **ion** soluble in water; ionic liquids are possible solvents, but still in R&D phase

DC power: the deposited amount of material is proportional to the transferred charge (Faraday)

Agitation: to make the process more uniform (air bubbling)

Adapted pH to stabilize the ions

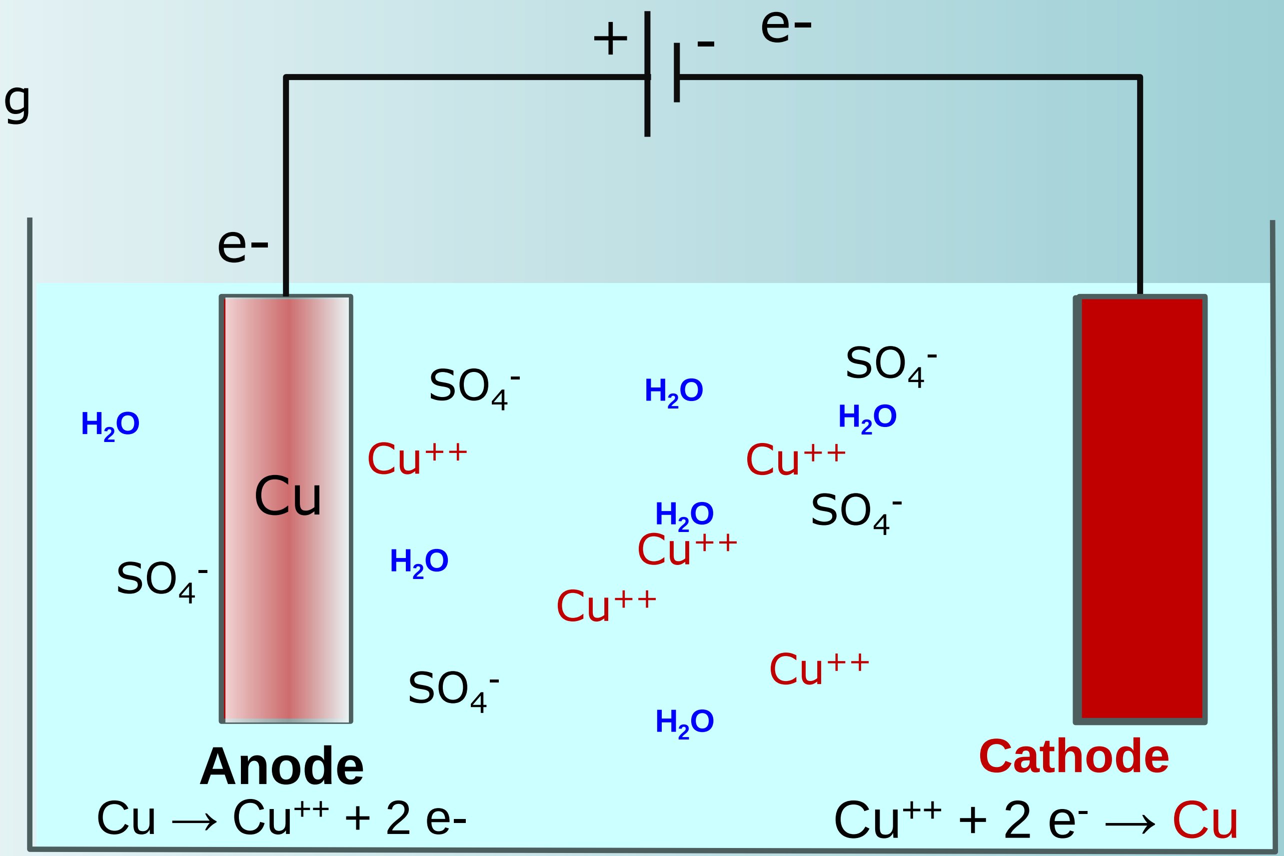
Ex.: Cu plating



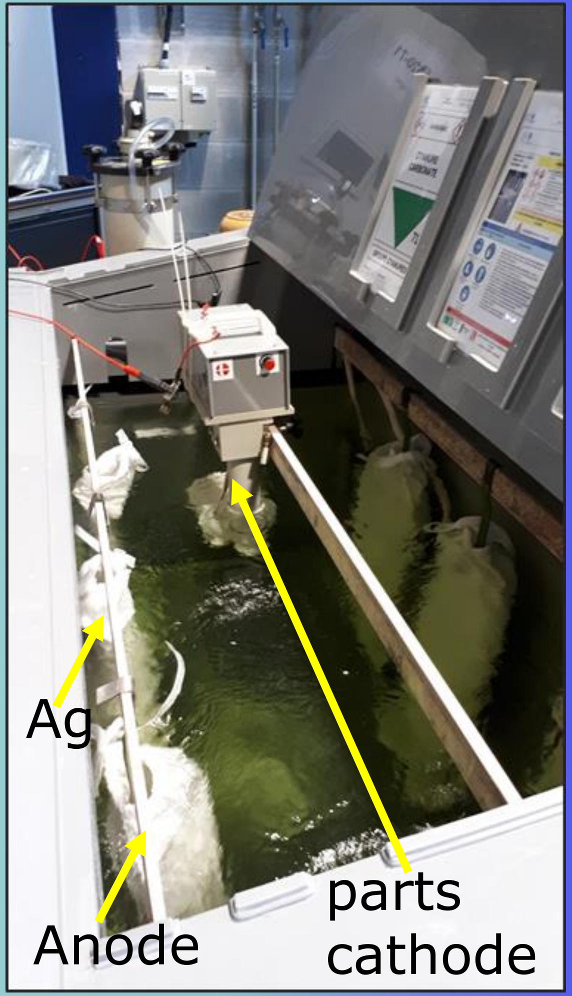
- The metal ions to be transported are added to the solution, which must be reloaded

Plating with soluble anode

Ex.: Cu plating



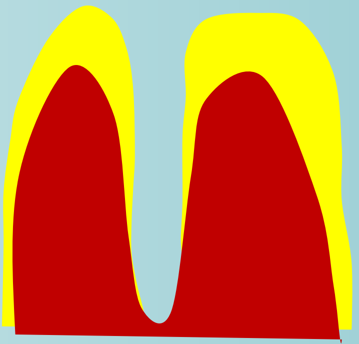
Ex: Ag bath



- The metal ions to be transported are provided by the anode, which gets dissolved (oxidation)
- The metal is deposited on the cathode (reduction)
- The anode must be replaced

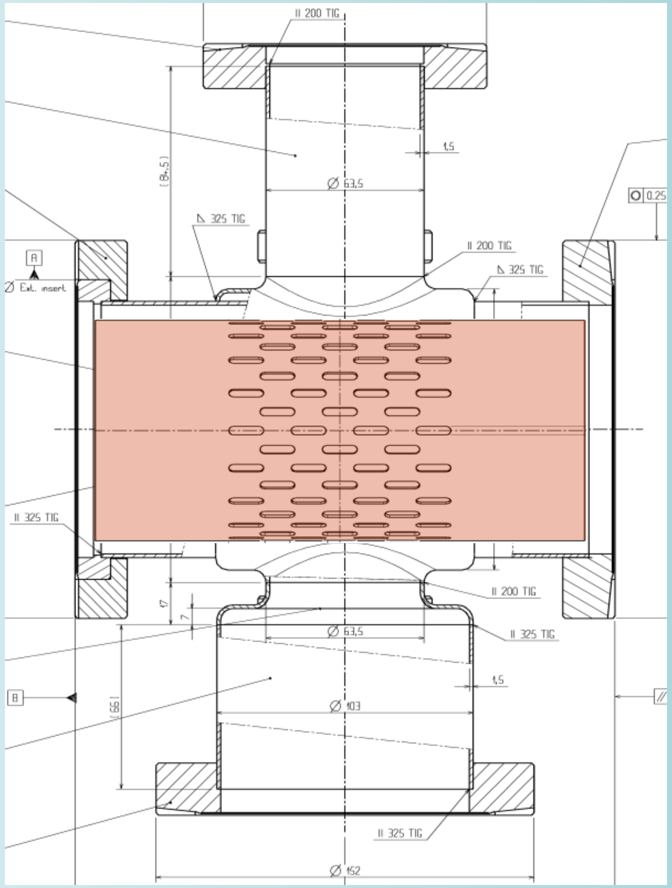
Uniformity issues

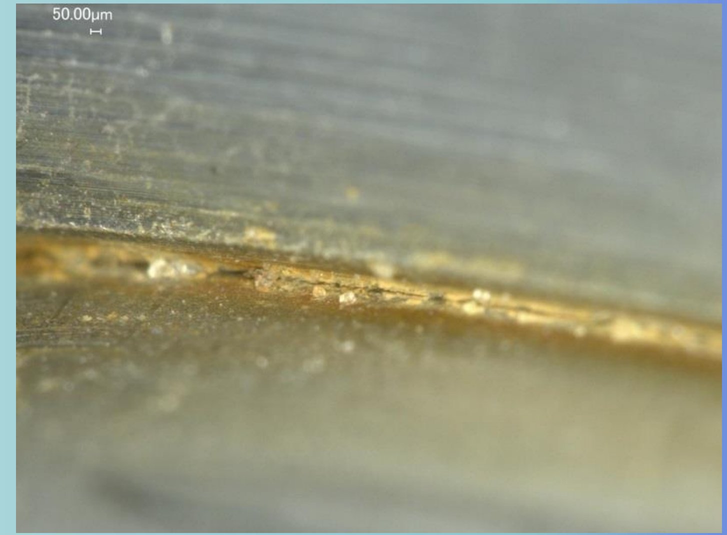
Issues:
-not all metals can be plated
-uniformity depends on shape (ionic transport, development of gases) and spatial distribution of the potential
-design parts adapted to plating
-high aspect ratio StSt pipes are an issue (adherence of Ni pre-layer on StSt…)



The Cl in the story…or how to do it wrong

An original piece all in StSt was re-used after copper plating (Ni underlayer) → the Ni bath contains HCl and the part was not conceived for plating →leak during operation





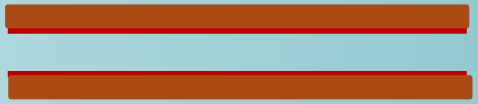
Probable origin of the leak: stress corrosion cracking, presence of Cl

Electroforming

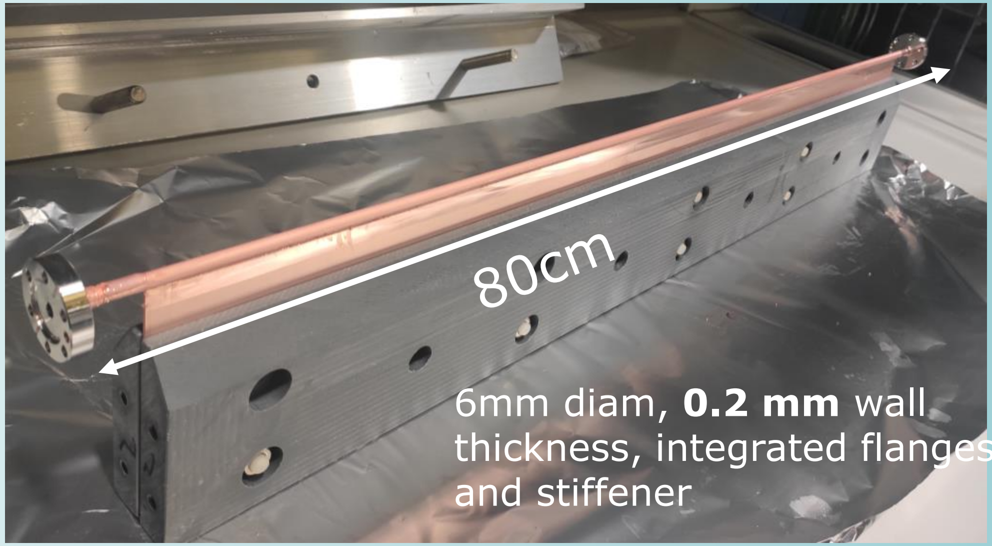
Al mandrel

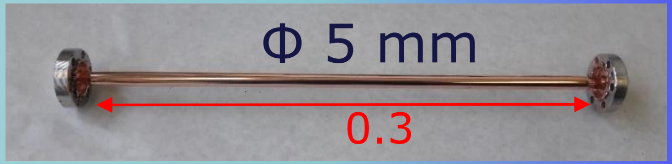
PVD copper layer

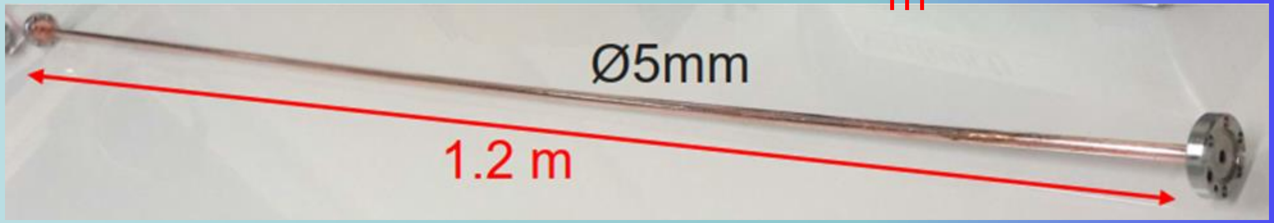
Electroformed layer



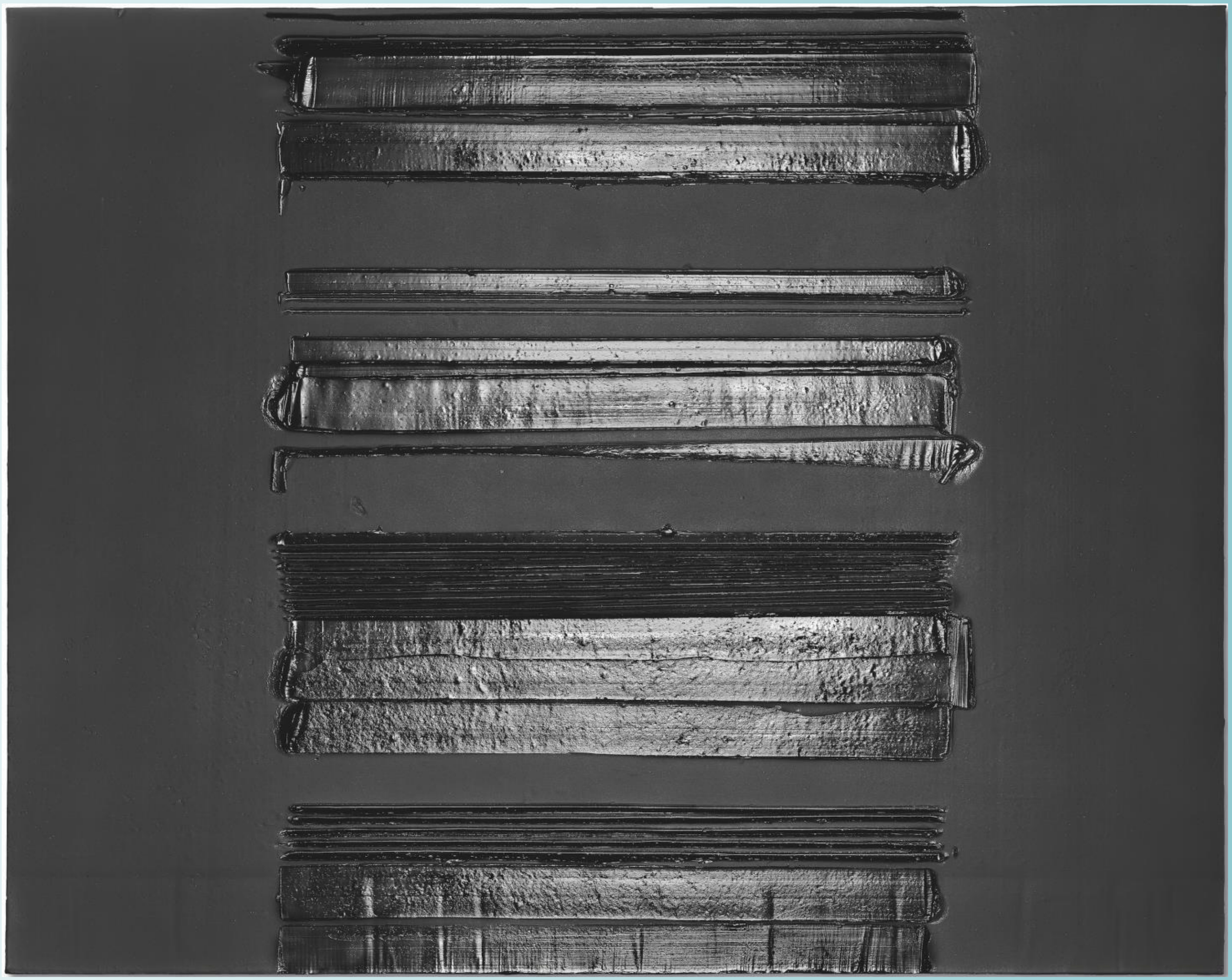
Mandrel removal by chemical etching







Coating



Pierre Soulage,
Peinture

Thin films coating by vacuum processes (PVD, CVD, ALD)

-evaporation: mostly low melting point metals; adhesion is sometimes difficult (atoms landing on the substrate with low energy (~100 meV)

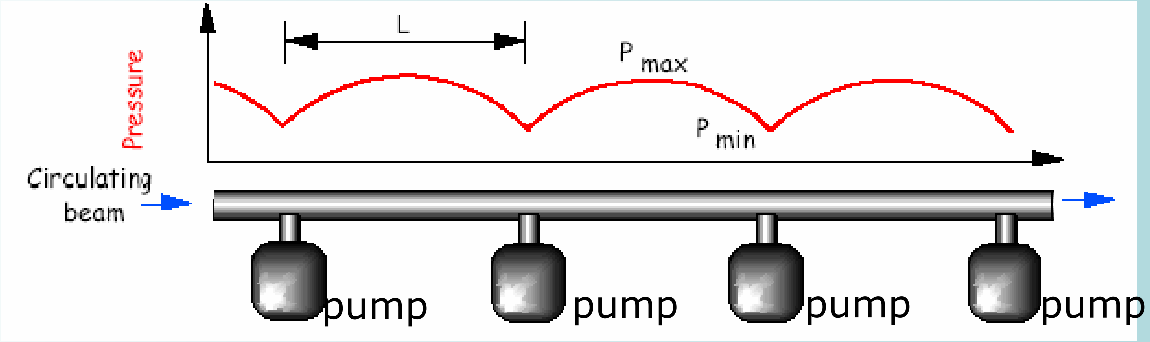
-**sputtering**: almost all metals including alloys, several oxides/nitirdes (reactive sputtering); ion bombardment of a target; different modes as diode, hollow cathode, magnetron, HIPIMS (High-power Impulse Magnetron Sputtering), HIPIMS with positive pulse; **good adhesion** since atoms land at higher energy (> 10 eV)

-CVD (Chemical Vapour Deposition): oxides, carbides, nitrides, diamond-like carbon, organic molecules; reactive species (sometimes produced in the plasma=PECVD) bind chemically to the (often hot) substrate

-ALD (Atomic Layer Deposition): oxides, nitrides, more rarely metals; a single lazer of precursor reactive species bind chemically to the activated substrate; **excellent layer by layer deposition, conformal coating** needs specific chemical precursor

Most of those processes are used at industrial level

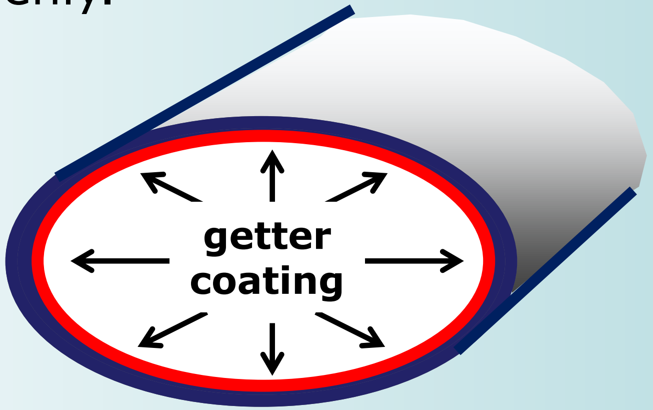
Application: distributed pumping with Non-Evaporable-Getter (NEG) thin films in beam pipes



Accelerators have low conductance (long narrow pipes)

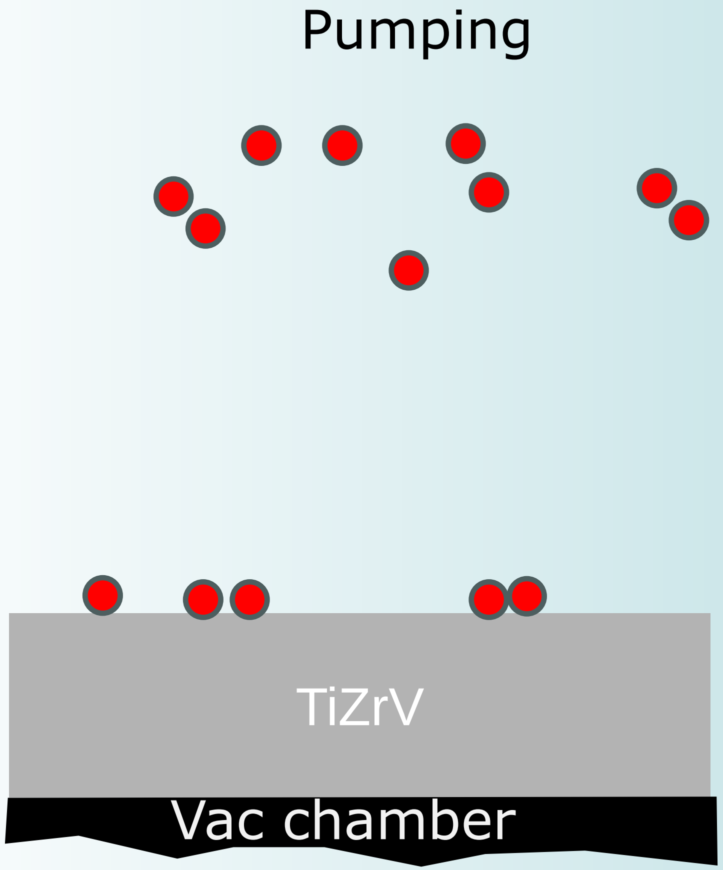
Pumps efficiency is limited by space hindrance and conductance

Bring the pump closer to the outgassing source and distribute the pumping speed evenly.



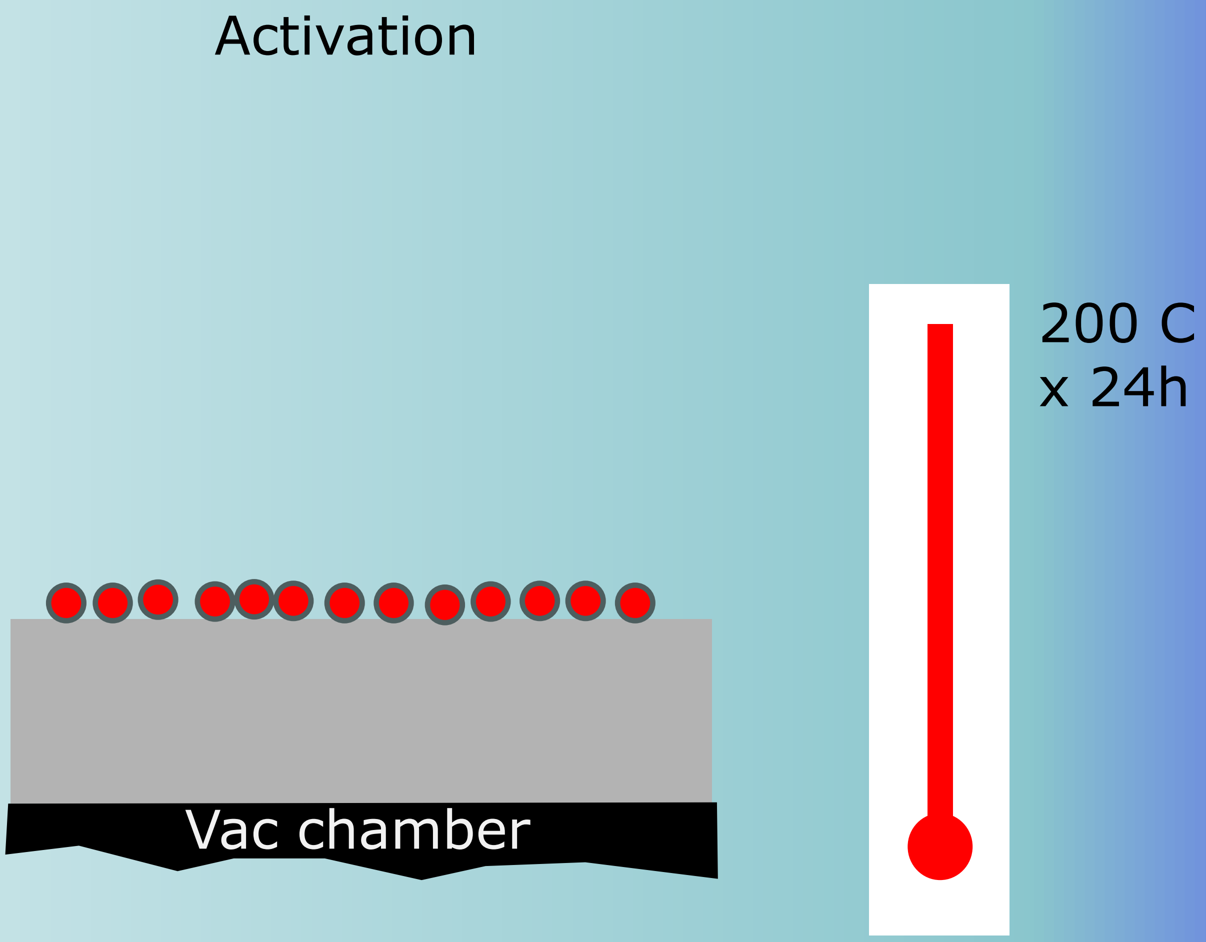
➔ transform the entire vacuum chamber in a pump by ex-situ coating of the vacuum pipe with a getter thin film acting as a pump

Principle of NEG pumping and activation



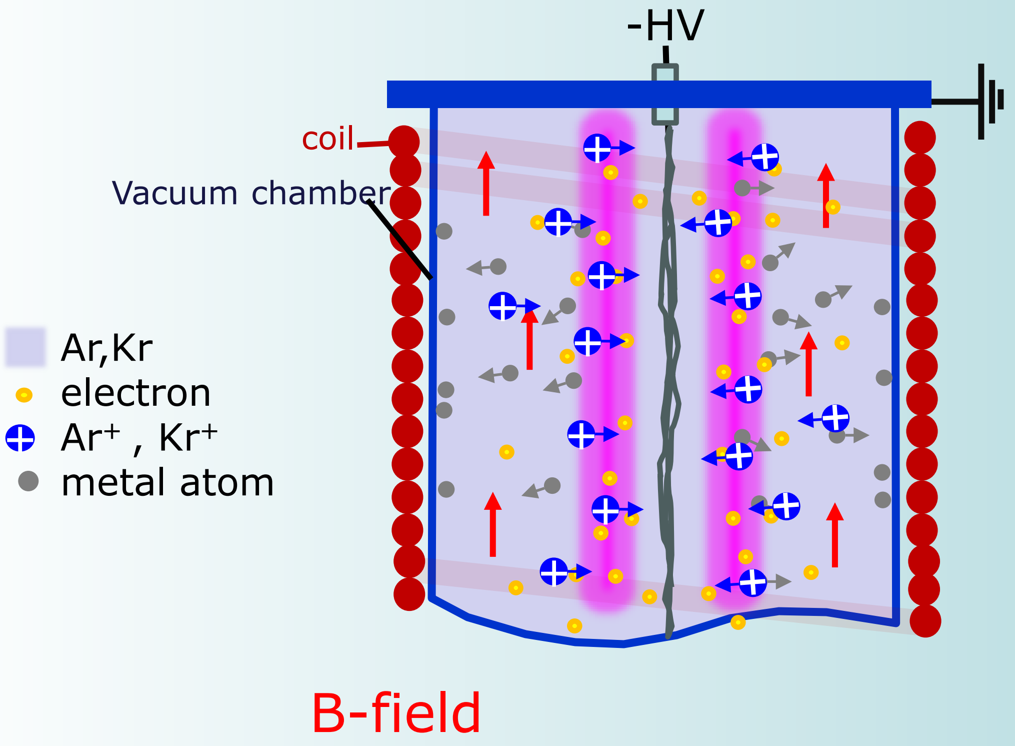
For CO, CO_2, H_2O, H_2

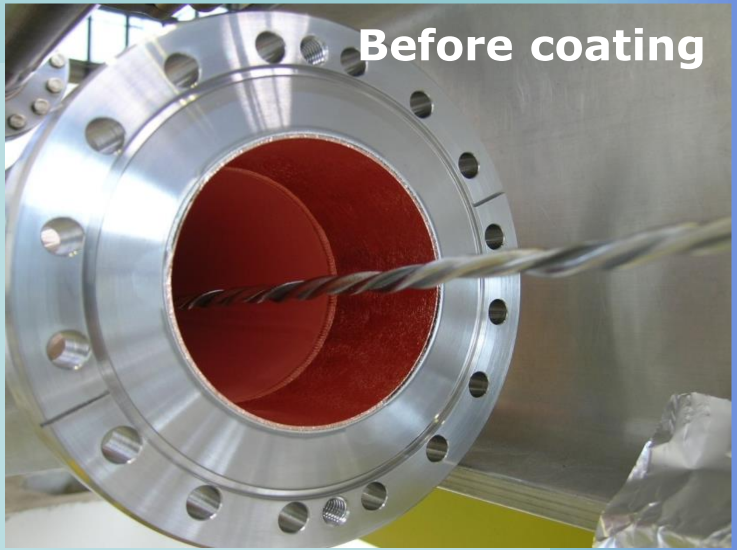
...not for He, Ar, CH_4...



Coating method for vacuum pipes

TiZrV (TiZrVHf, Zr,…) alloy is deposited by DC-magnetron sputtering with a single target made of intertwisted wires of titanium, zirconium and vanadium





Coating after pumping and bake out (below 10^{-8} mbar base pressure)

Tested for 0.2-3 μm thickness

CERN: fixed coil

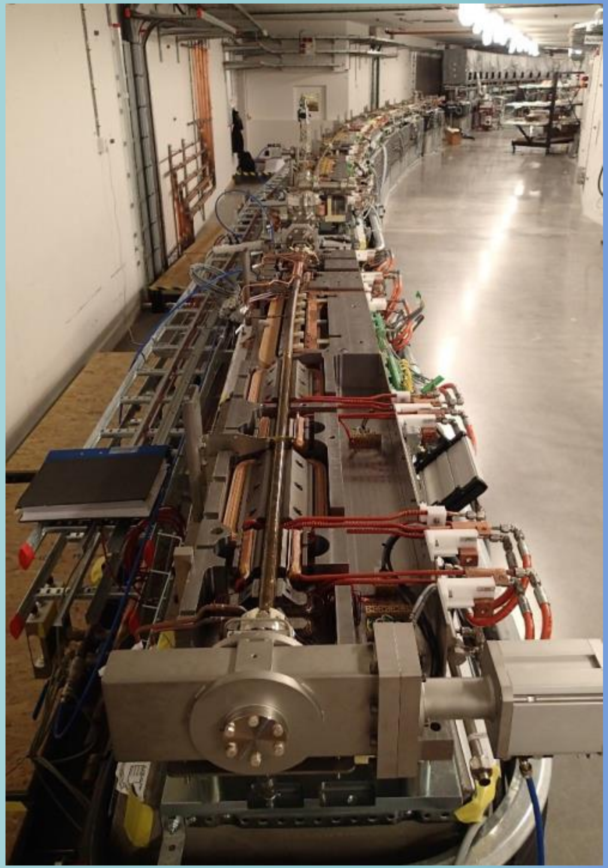
ESRF Grenoble: movable coil

Examples

LHC, Geneva
MAX IV, Lund
ESRF, Grenoble
Soleil, Orsay
Sirius, Brazil
Alba, Barcelona
Desy, Hamburg
ANL, USA
BNL, USA
KEK, J
.....

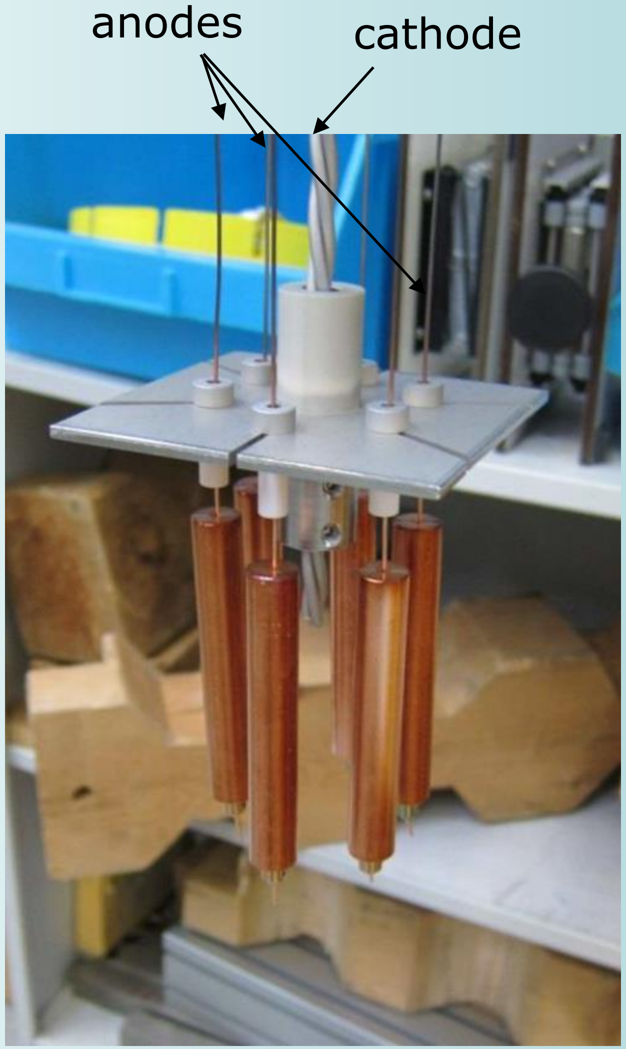
Soon in:
Elettra, I upgrade
SLS , CH upgrade
Diamond, UK
....
Commercially available

LHC long
straight section



MAX IV

Coating of ceramics for RF applications and «pulsing» magnets



Tuning the resitivity

Ti thicker layers
-Typical R_s square 20-200 Ohm (after air exposure)
-mitigates surface charging

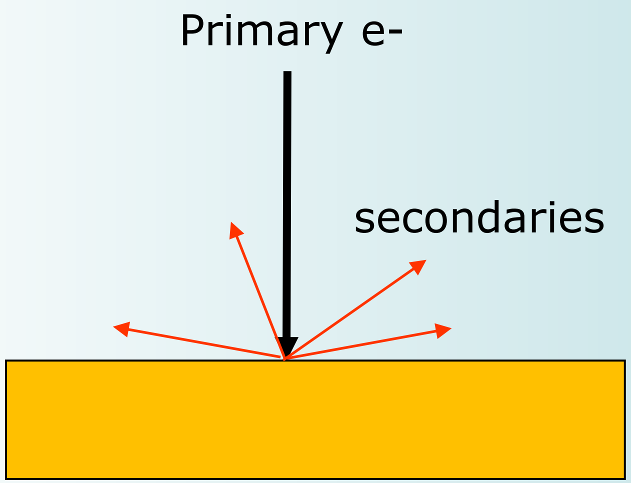
Ti very thin layers
-Typical R_s (R_{square} or R_{sheet}) 10-20MOhm before air exposure and GOhm after air exposure
-reduces the SEY of alumina

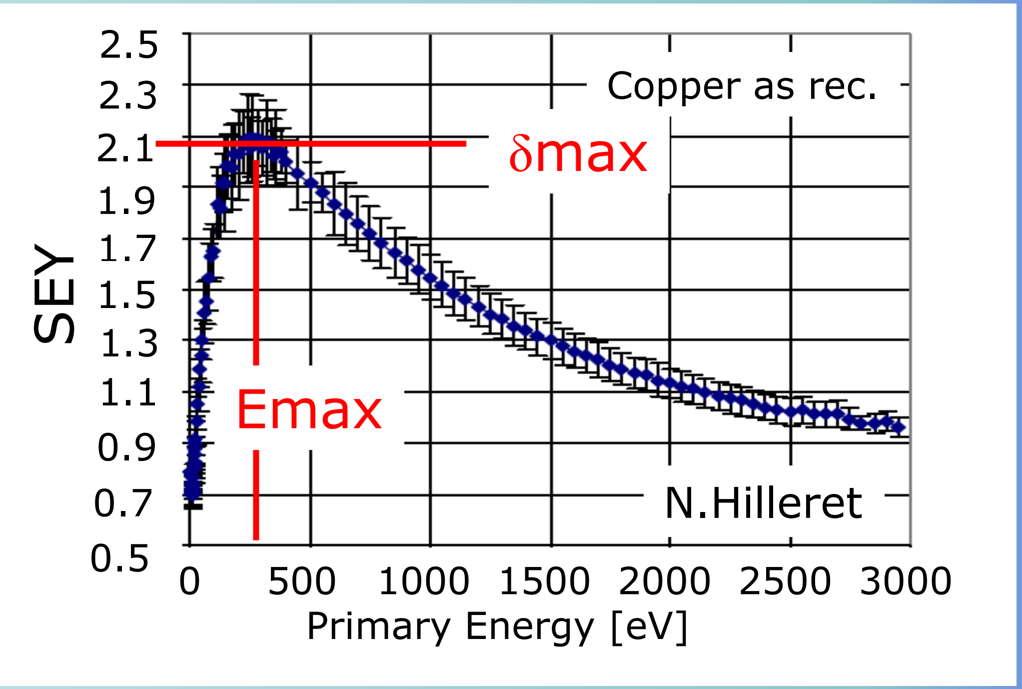
Square or sheet resistance R_s:

$$R = \frac{L}{w}\frac{\rho}{th} = \frac{L}{w} R_s$$

Coatings for low secondary electron yield: SEY

$$SEY = \frac{\text{number of emitted electrons (secondary)}}{\text{number of impinging electrons (primary)}}$$

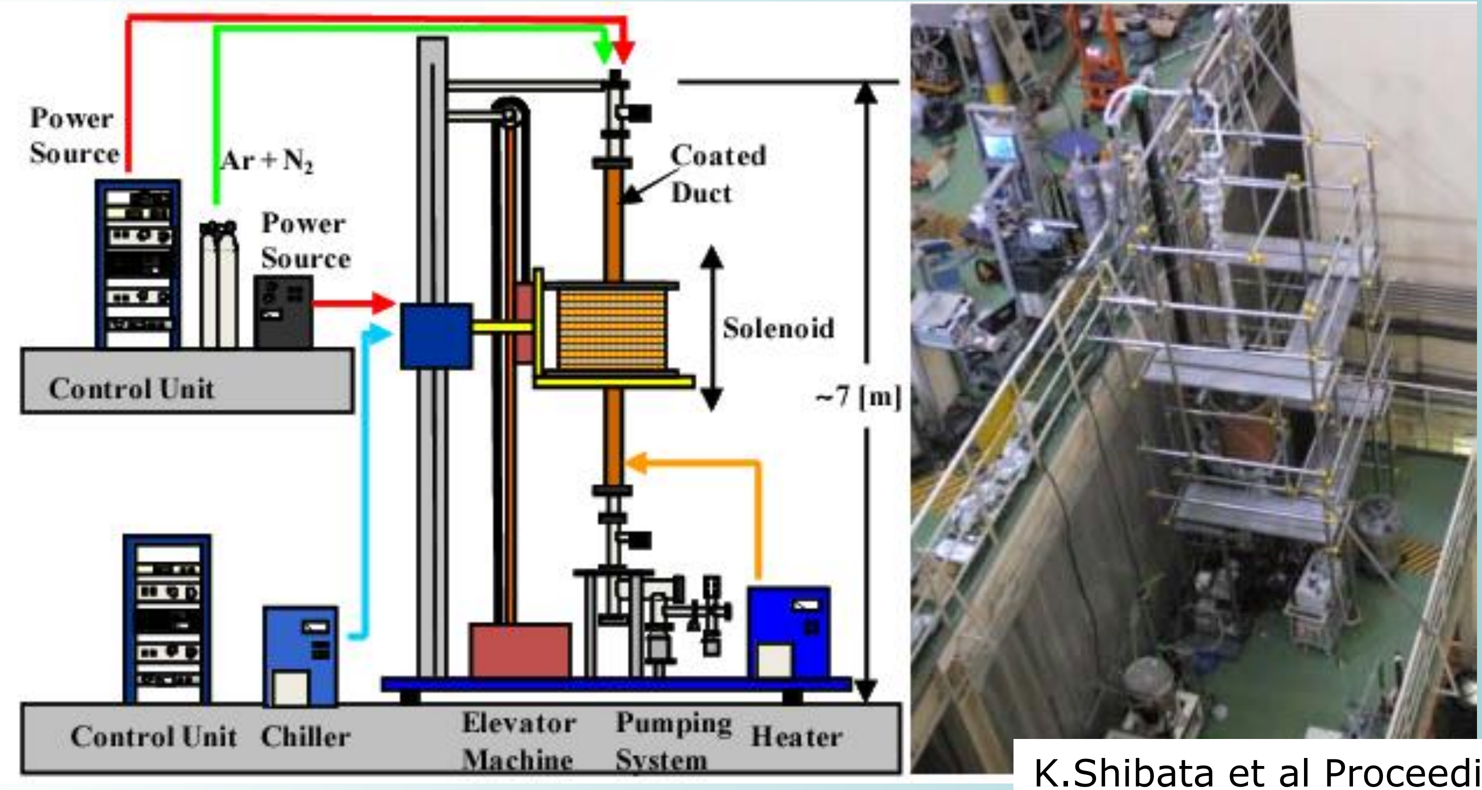




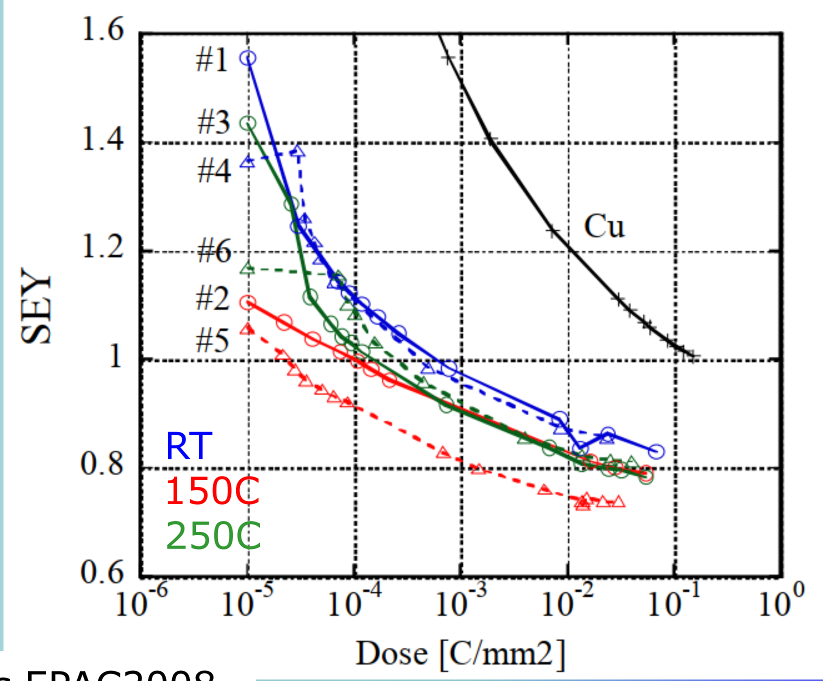
δ_{max} or SEYmax = maximum value as a function of **primary** energy
E_{max} = **primary** energy of the maximum

The electrons in that energy range escape from less than 20 nm: **SEY is a surface property**

TiN coating to reduce SEY



Conditioning curves

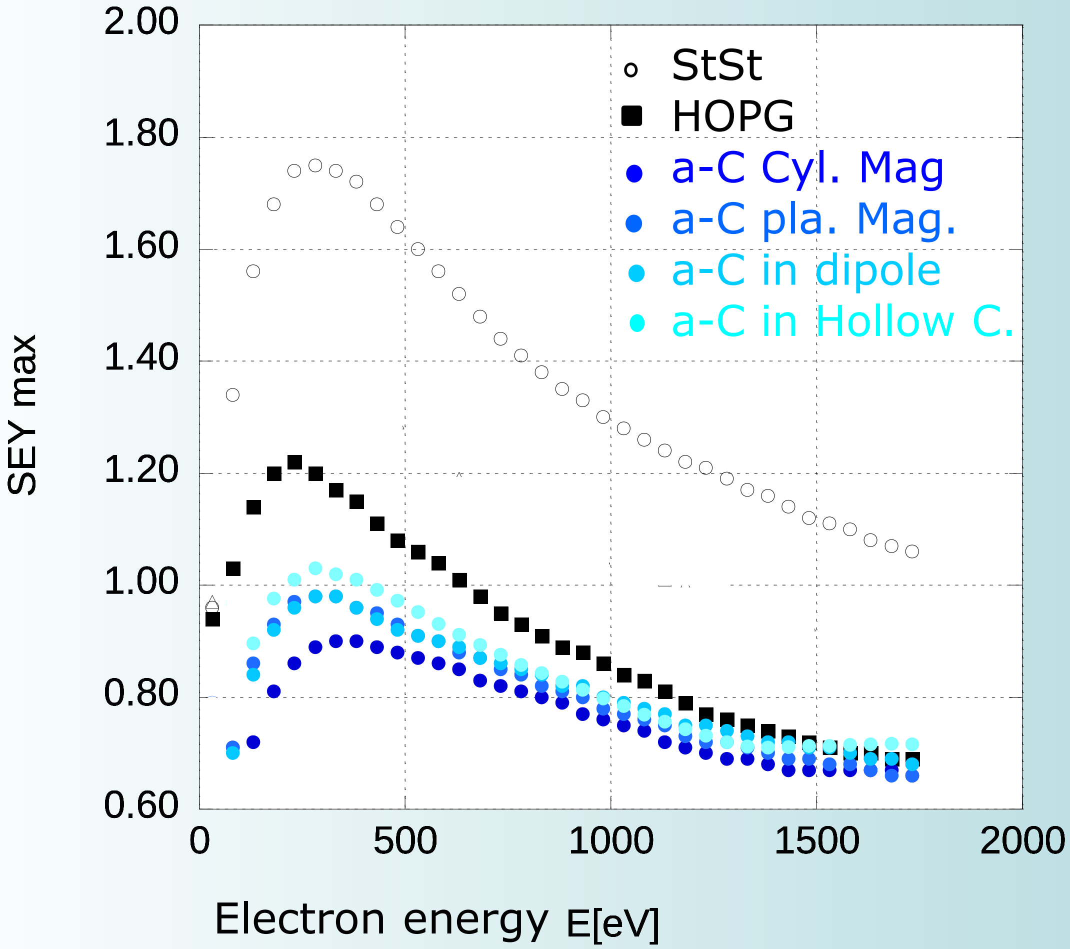


K.Shibata et al Proceedings EPAC2008

-reactive sputtering in N_2:difficult to get the stoichiometry, since there is a pressure profile along the tube during coating; SEY sensitive to coating temperature, resulting roughness etc

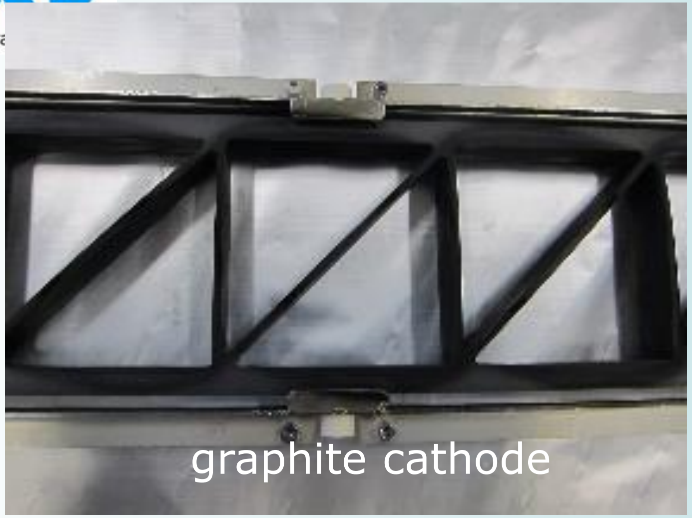
-needs some conditioning to get low SEY

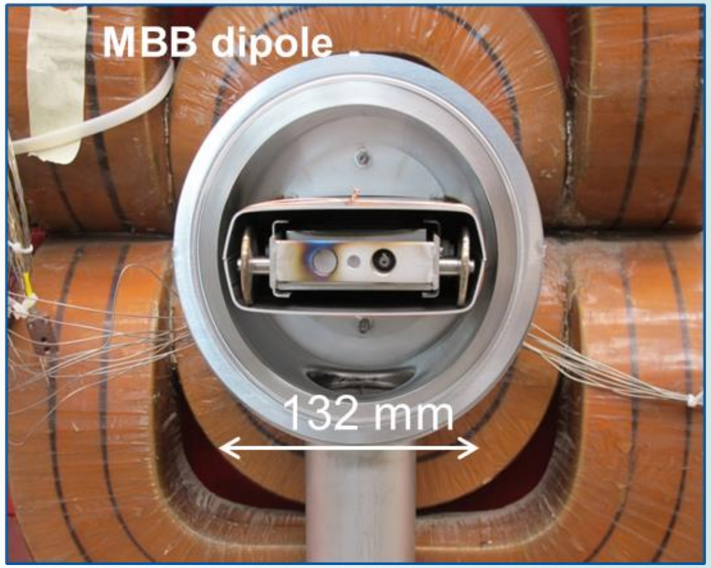
Low SEY carbon films



- Can be used on unbakable systems (ex: cryogenic UHV), since it maintains the low SEY after air exposure
- Coating in the lab based on standard magnetron sputtering of graphite target
- Coating in situ (parts installed in the accelerator) with suitable "trains"

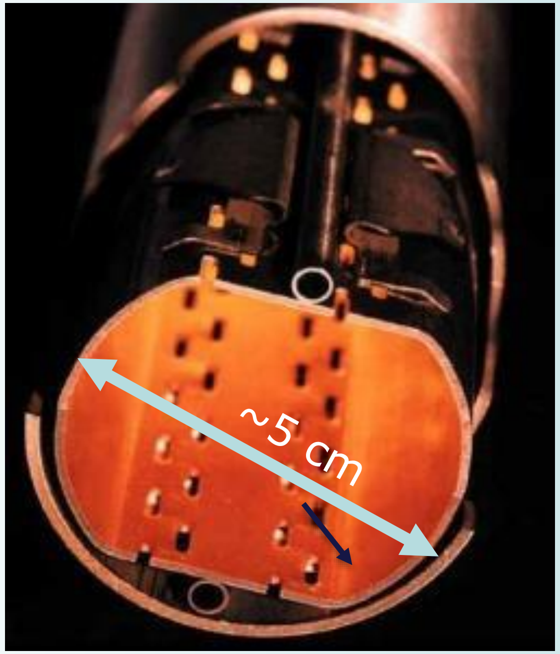
a-C coatings in situ: cathode trains

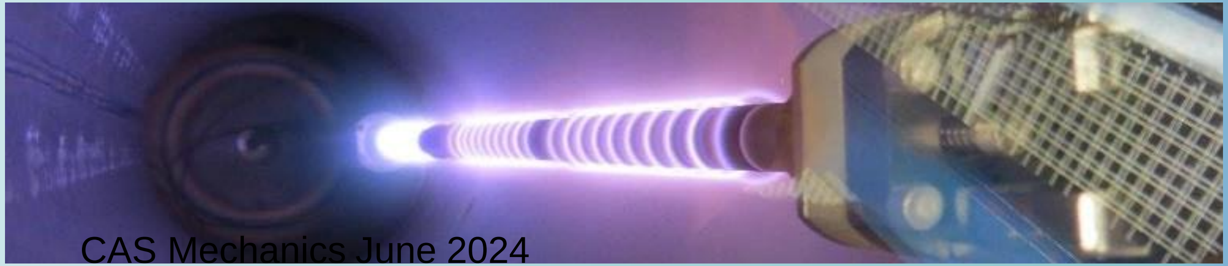




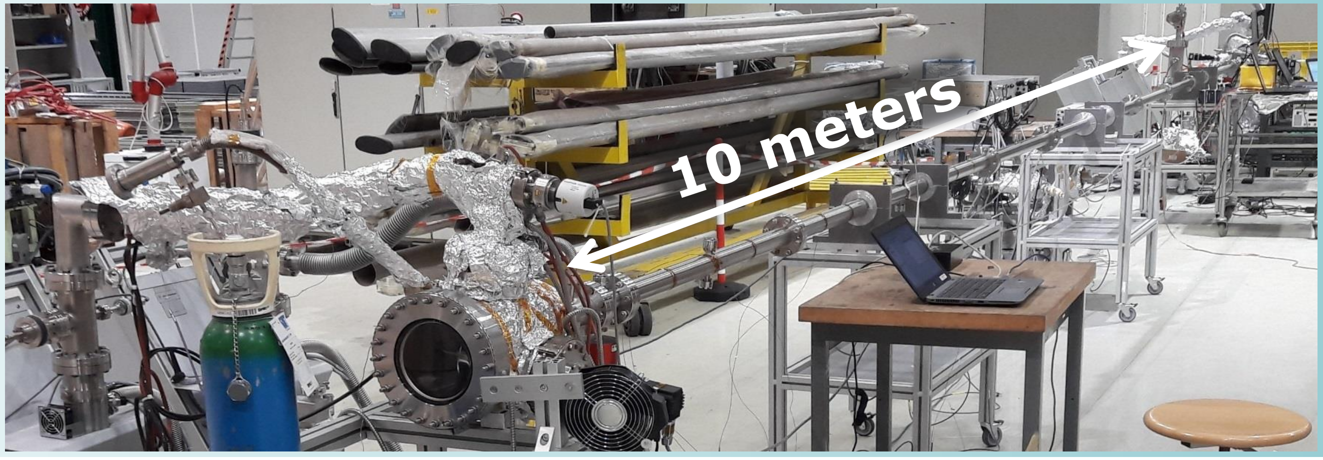
Carbon coatings in situ II: mini-train

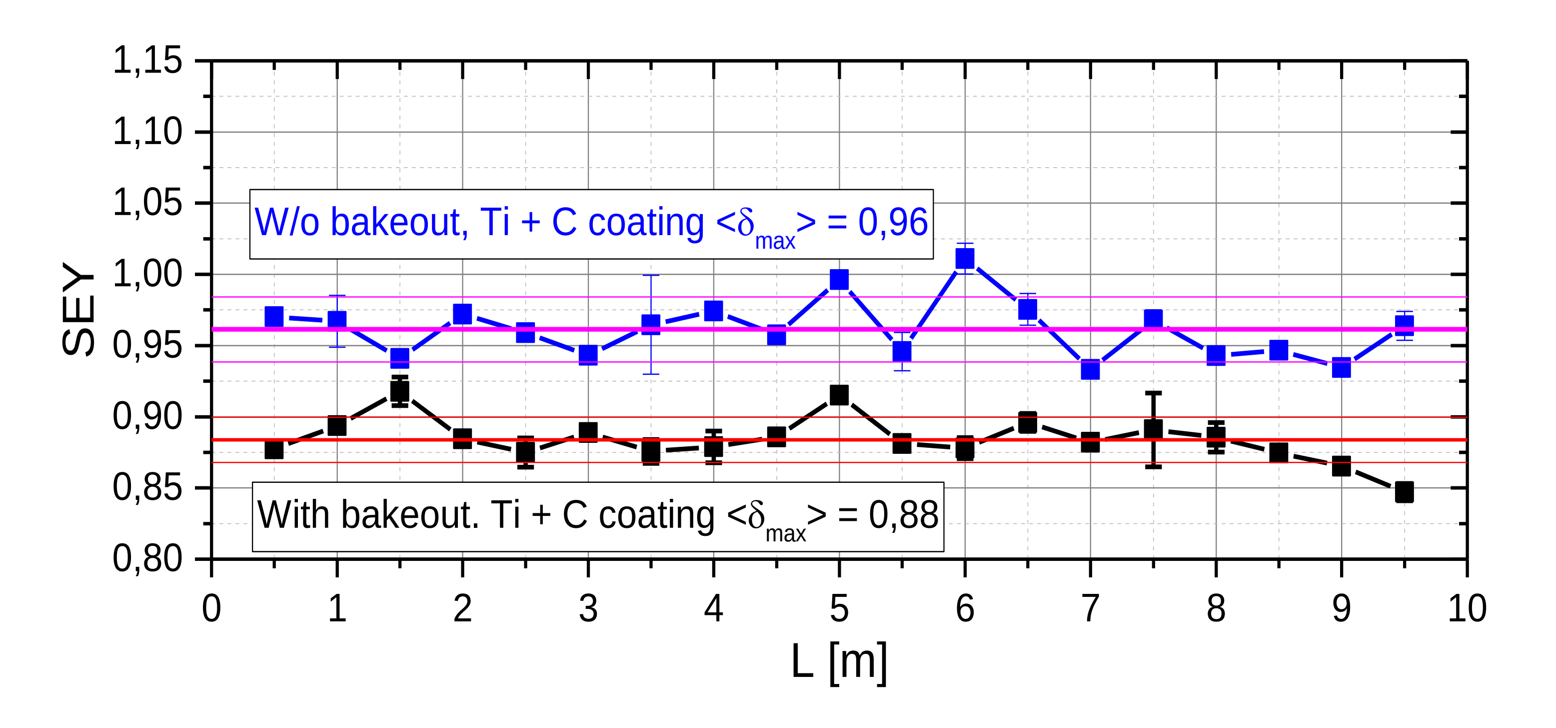
- Example of "modular sputtering source" that can be assembled, inserted and pulled by cables all along a magnet
- Combined coating with a-C and Ti cathodes to reduce outgassing in sequential coating process

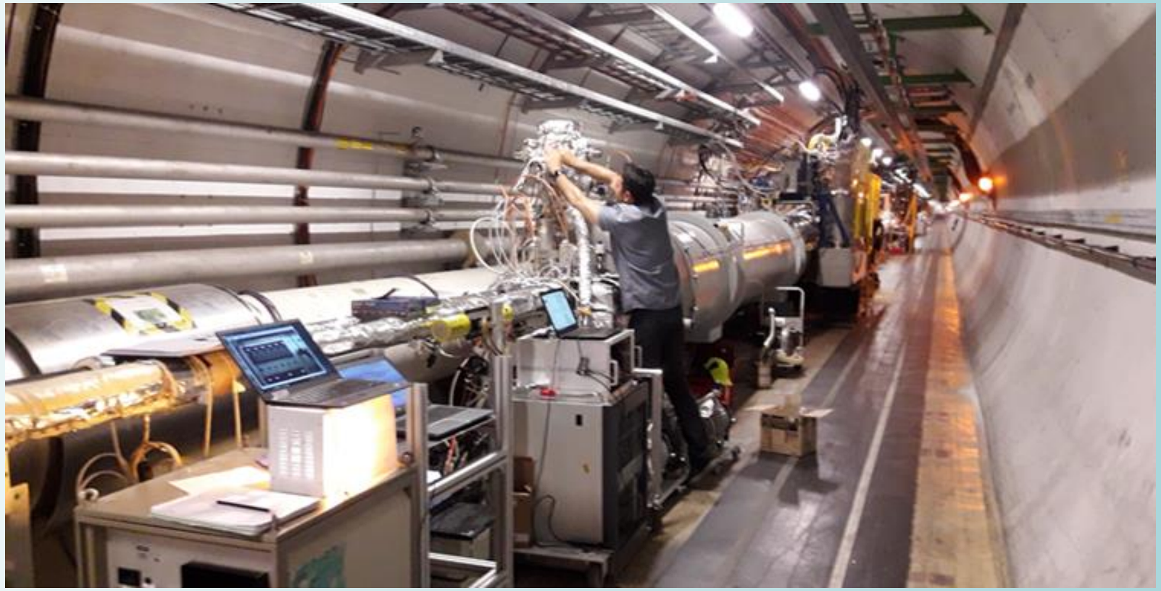


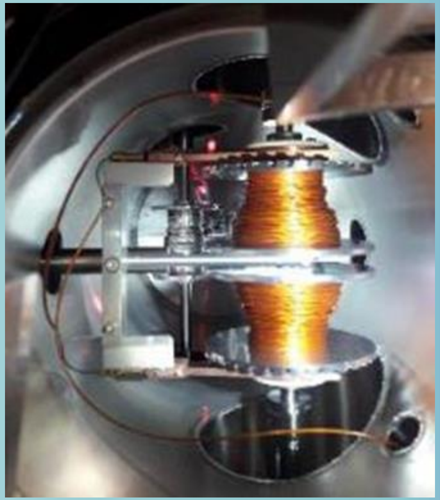


Travelling 10 m

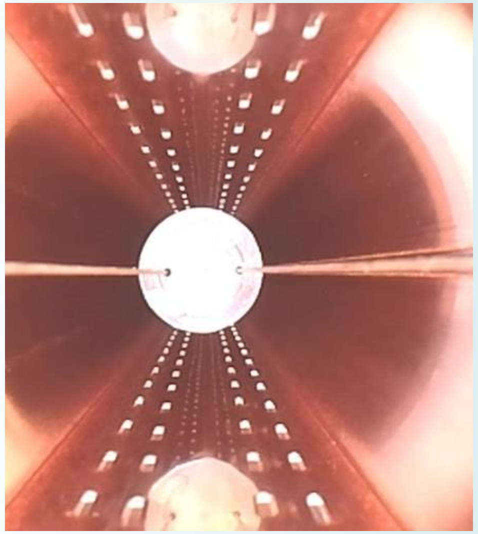




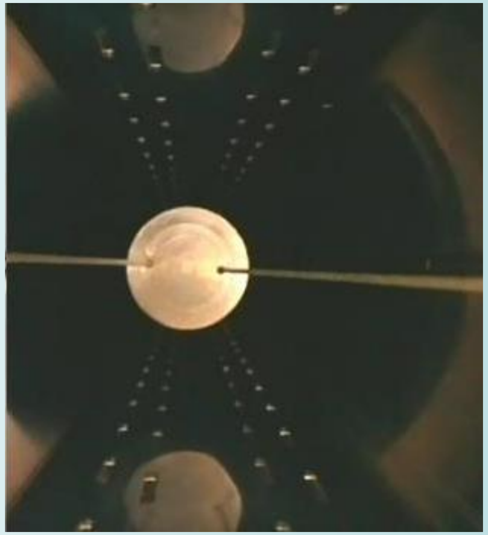


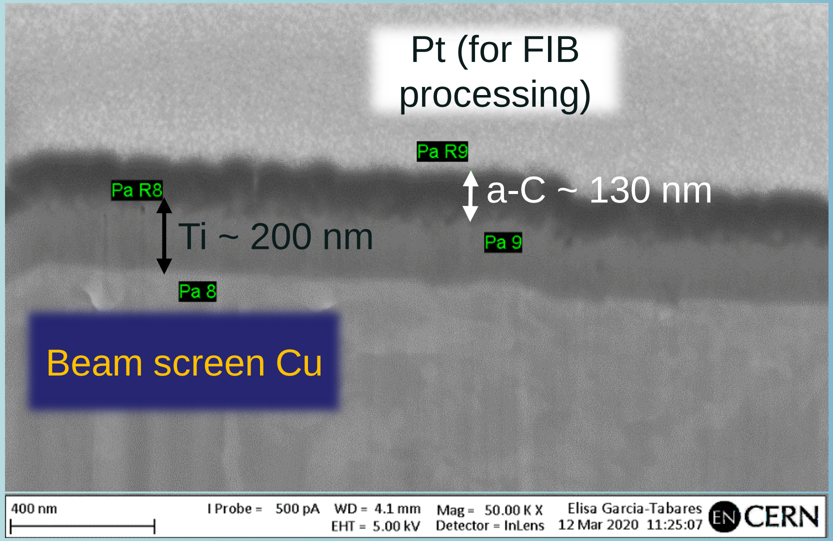


Before coating



After coating





The surface is delicate

The last step in the fabrication process is the one which defines the surface state.

Therefore ideally the **final step should be the surface treatment (or thermal) and not** a machining, joining, welding, forming process...

Its state should be **preserved** and protected

THANK YOU FOR YOUR ATTENTION!

Surface treatments and coatings related to accelerators

Cleaning and its assessment:
C. Scheuerlein et al. Appl. Surf. Sci. **252** (2006) 4279-4288;
M.Taborelli, CAS Vacuum for Particle Accelerators, Glumslov, Sweden, 2017
K.J.Middlemann, Vacuum **81**, 2007, Pages 793-798

Surface treatments
L. Lain Amador et al. *J. Vac. Sci. Technol.* ***A*** **36**, 021601 (2018)
L.Lain Amador et al. Phys. Rev. Accel. Beams **24**, 082002 –2021
Paper Leonel electropolishing?
Gloria proceedings?

a-C coatings:
C. Yin-Vallgren et al. Phys. Rev. ST Accel. Beams **14**, 071001, 2011 ;
W.Vollenberg et al. proceedings IPAC 2021 3475-3478;
P. Costa Pinto et al Vacuum **98**, 2013, 29-36
P. Costa Pinto, CAS Vacuum for Particle Accelerators, Glumslov, Sweden, 2017

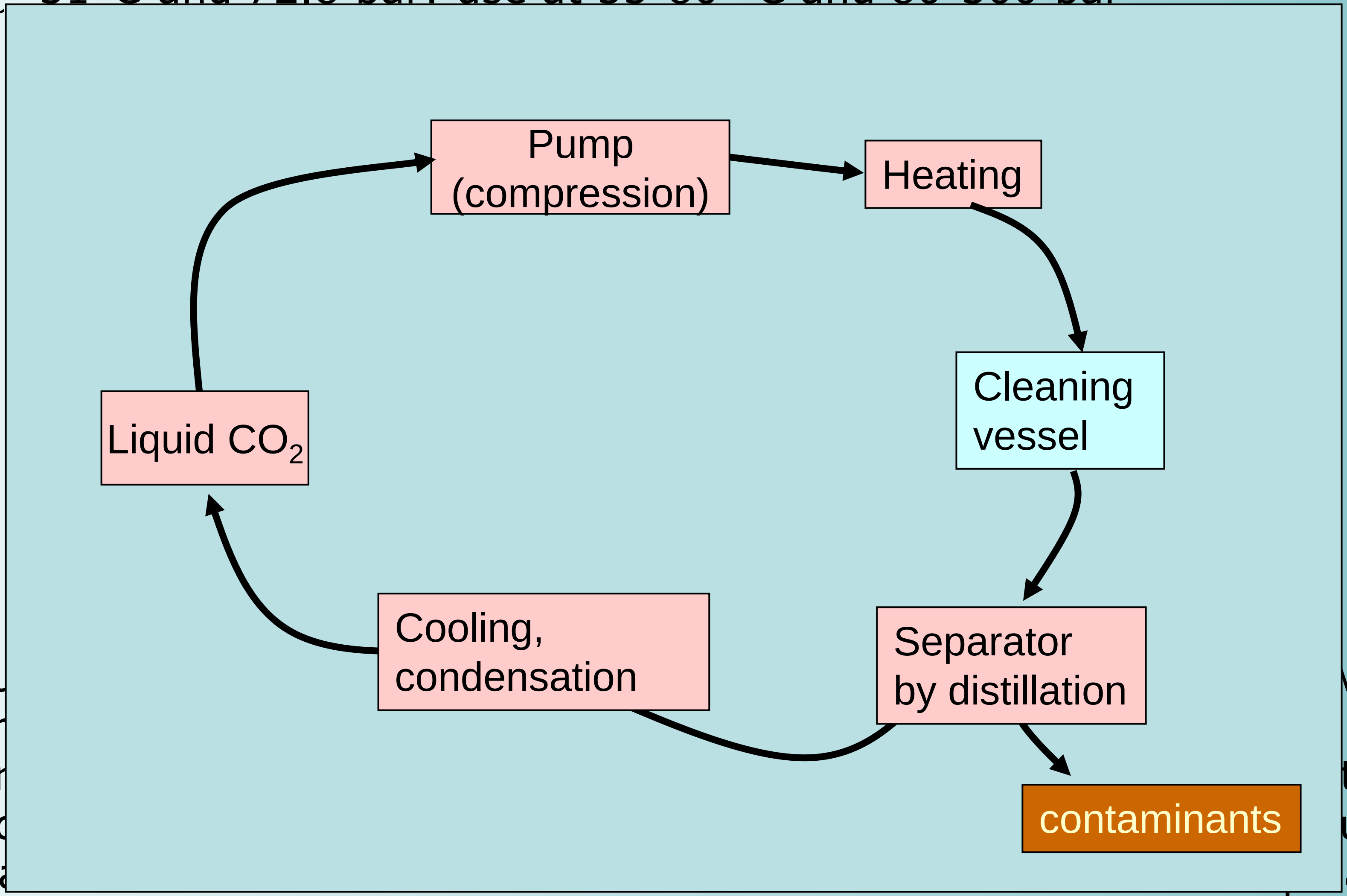
NEG coatings:
P. Costa Pinto, CAS Vacuum for Particle Accelerators, Glumslov, Sweden, 2017;
C.Scheuerlein et al. Appl. Surf. Sci. **172** (2001) 95-102;
M.Eriksson et al. Proceedings of IPAC2016, 11-15;
R.Sirvinskaite et al. Vacuum **179** (2020) 109510;
O.B. Malyshev et al. Vacuum **86**, Issue 12, 2012, 2035-2039

Ti, TiN coatings:
W.Vollenberg, Proceedings of IPAC2015, 3148-3150
K.Shibata, Proceedings EPAC08

SPARE SLIDES

Supercritical CO_2 (SCCO2):

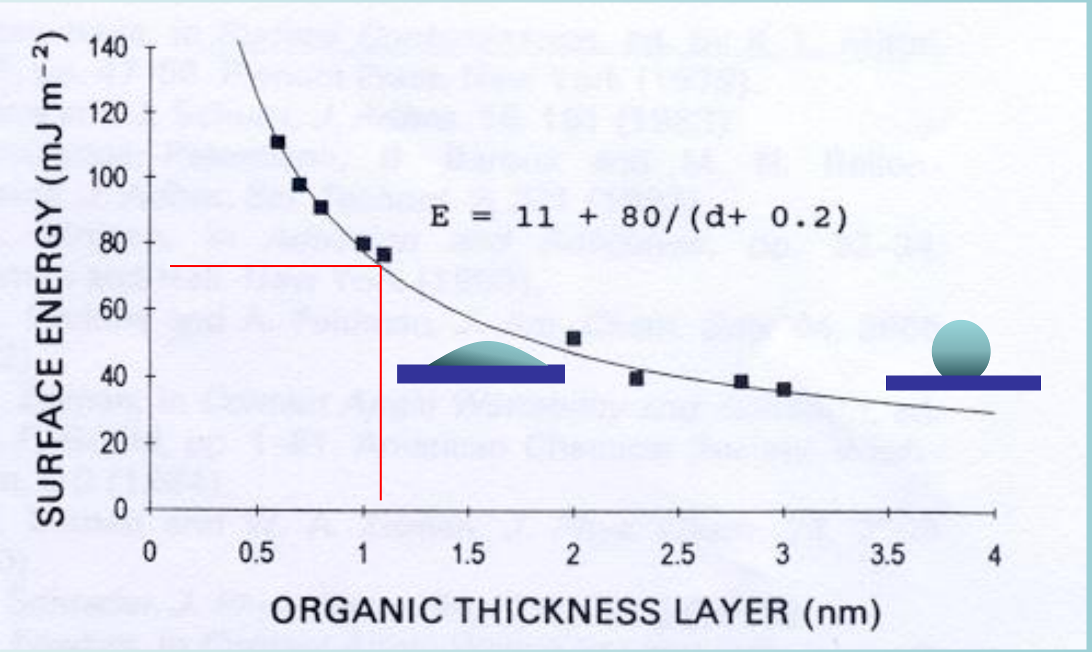
-T_C=31°C and 72.8 bar: use at 35-80° C and 80-300 bar



-Su ... ver
sur
per ... ty
and ... ure)
- ca ... ar
molecules and ionic species

Wetting and cleanliness

-Contamination has low surface energy (~25 mJ/m^2 for alkanes , 20 mJ/m^2 silicone oil, 72 mJ/m^2 for water, 1850 mJ/m^2 for Cu, 100-1000 mJ/m^2 for most oxides) and can adsorb easily on metallic surfaces and oxides

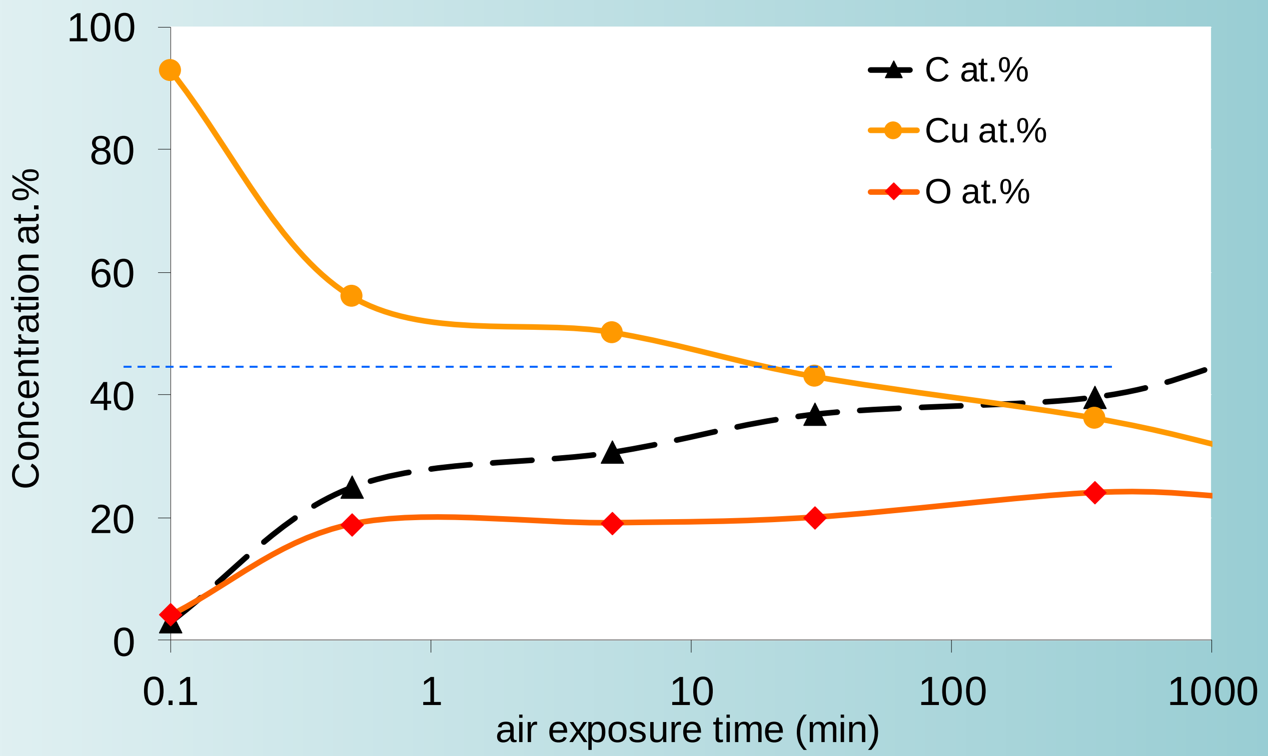


Hydrocarbons on stainless steel:
Mantel and Wightman Surf. Interf.An. 21, 595 (1994)

-the contact angle measured after cleaning depends on cleanliness, but also on the roughness and surface reactivity to air exposure

How clean can we clean?

Start with a sputter cleaned copper (highly reactive) surface and see how fast the airborne contamination increases. Hydrocarbon re-adsorption on sputter cleaned copper surface



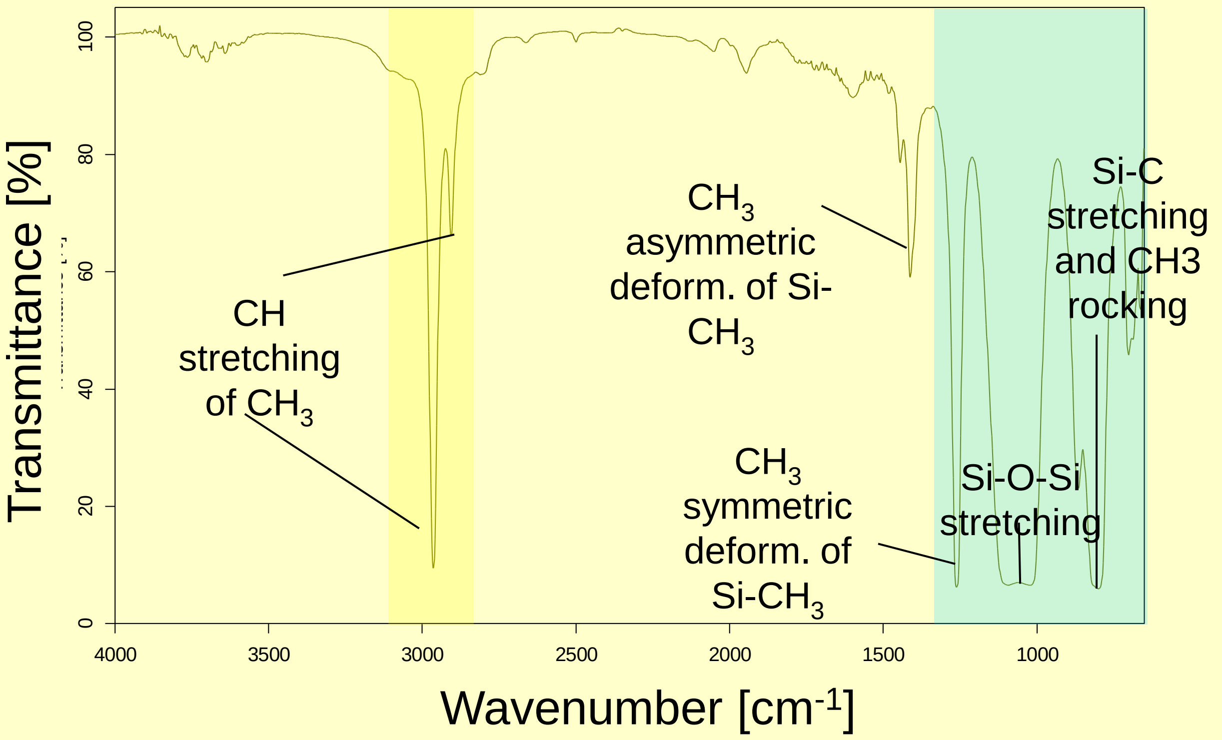
Trials of cleaning and keeping the sample in the rinsing water up to insertion in XPS does not improve the situation

Cleanliness

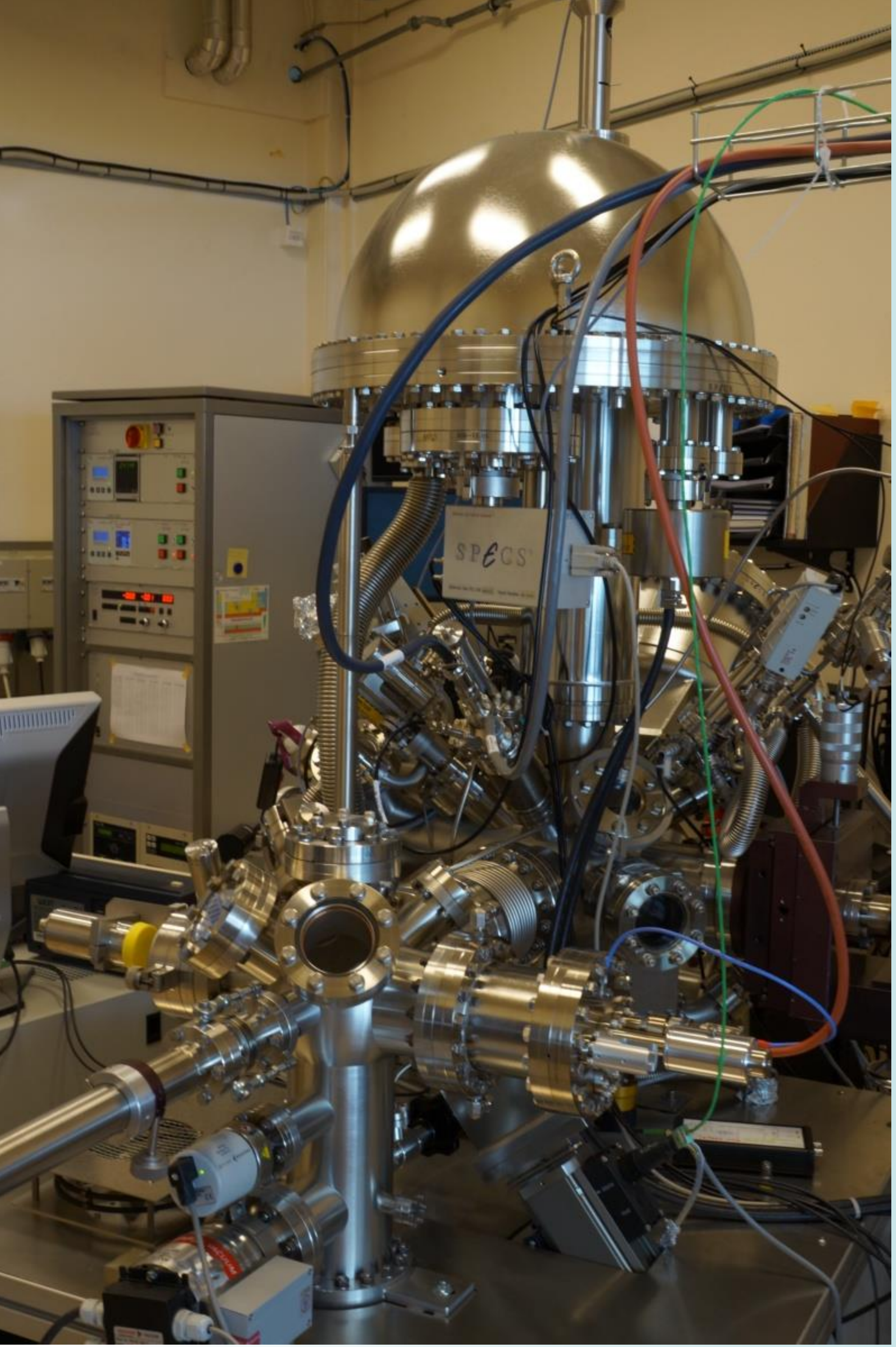
- ❖ Elution of contaminant from the “cleaned” part (tube,..) with a defined quantity of hexane per surface area
- ❖ Deposition of a drop of the resulting solution on a ZnS window (transparent to IR)
- ❖ Measurement of transmittance after evaporation of the hexane

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

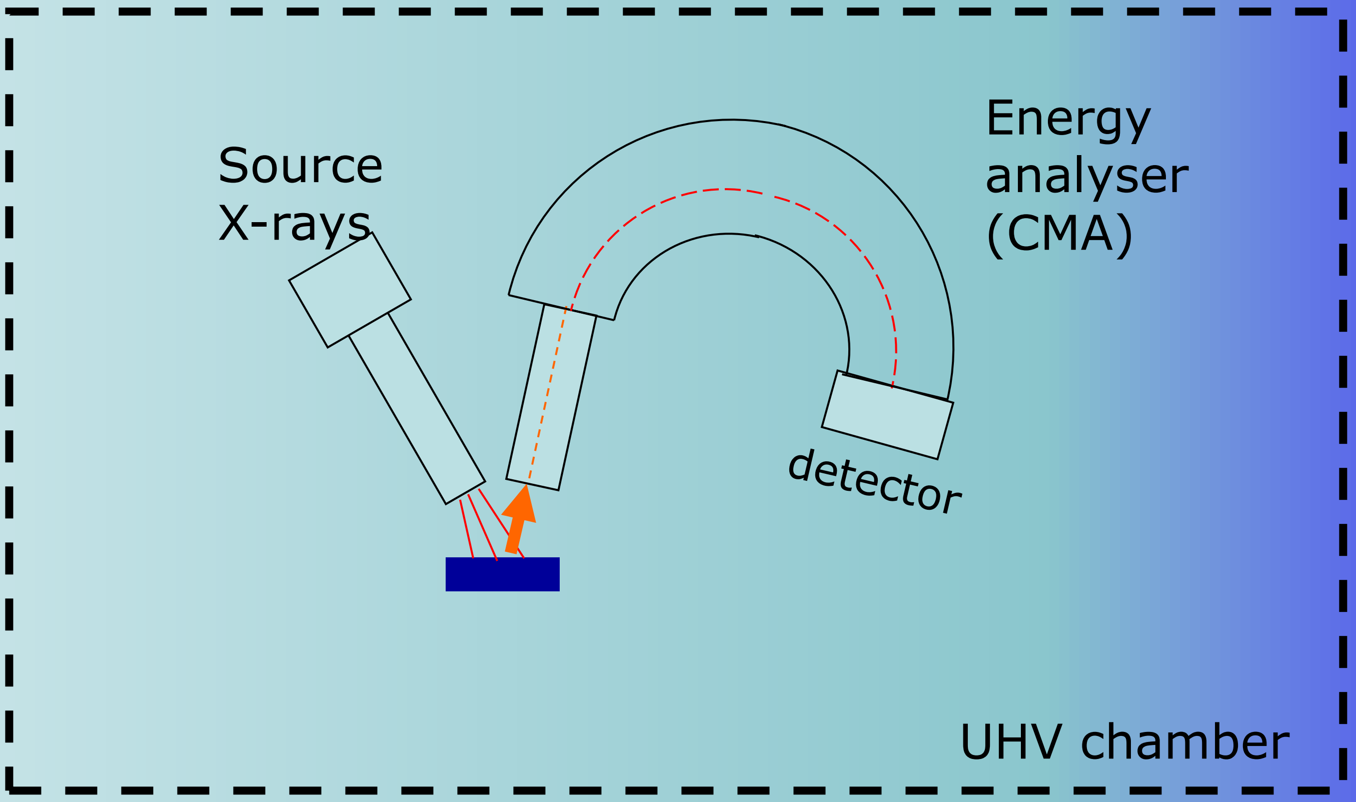
Problem: you get only what is eluted



S.Ilie, C.Petitjean, C.Dias-Soares

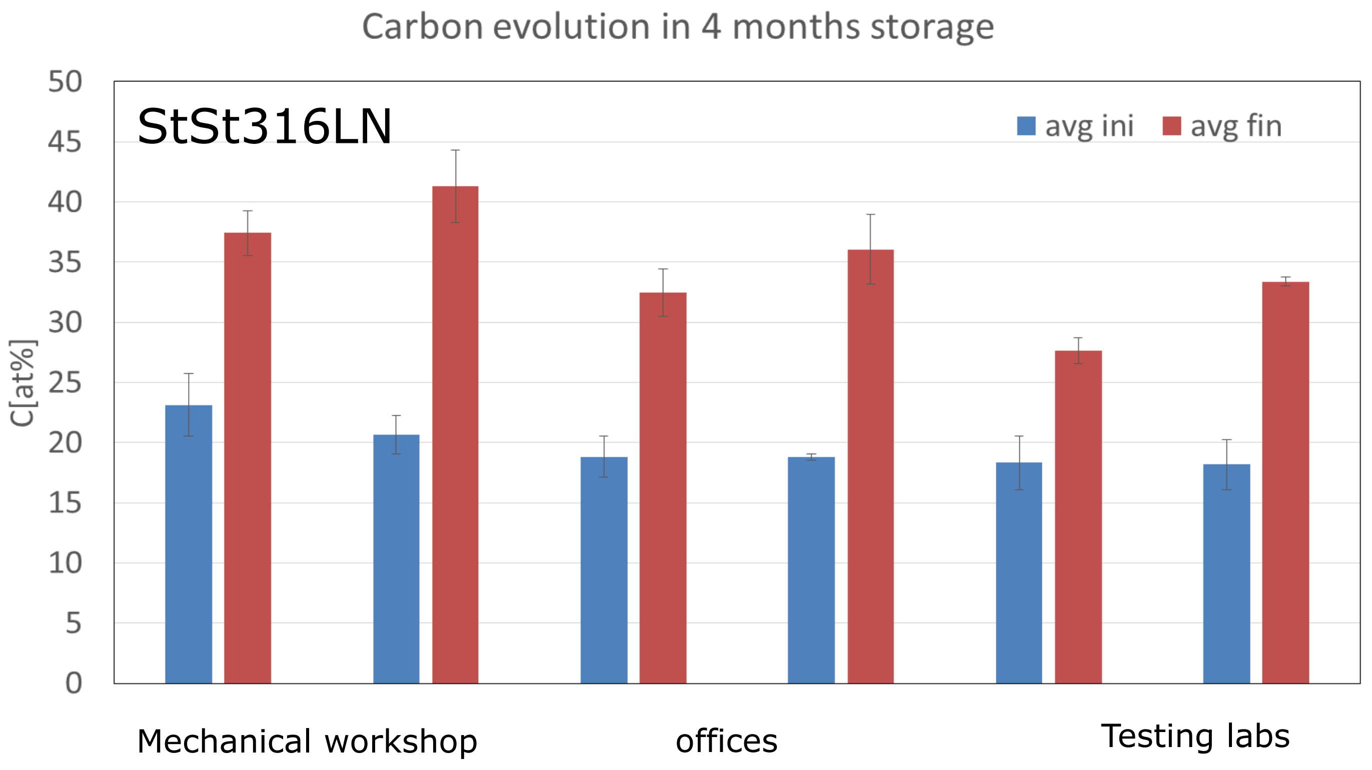


XPS principle



Storage place:

A chemically cleaned surface is prone to re-adsorb hydrocarbons: test of storage in air (vertically) without protection in various environments



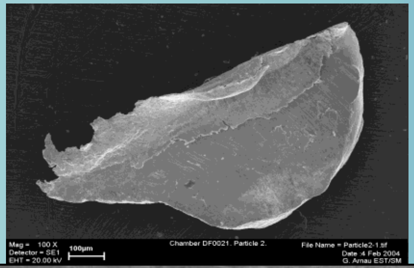
XPS analysis

NB: the quantification of surface contamination is made by surface analysis with electron spectroscopy (as XPS) or by FTIR

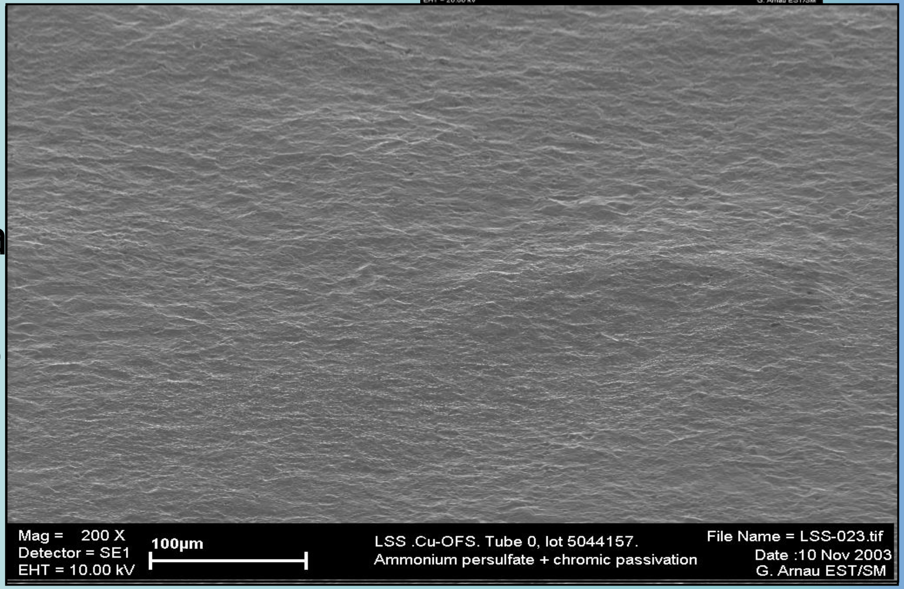
A difficult case: extruded copper pipes

Copper pipes for a UHV chamber designed to receive NEG surface coating showed peel off of the coating and metallic particle residues

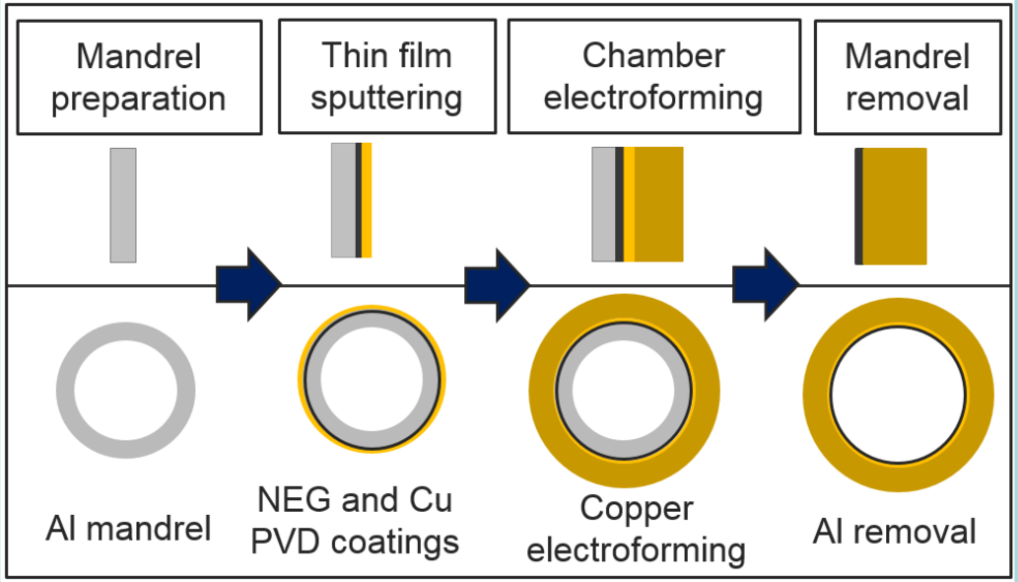
❖Amiss extrusion tool did not enable draining of the copper shavings, which remained instead incrusted on the tube's surface.



➔Mechanical removal of most of the Cu particles (Cloth and hot high pressure wa jet) and chemical etching of the internal surface with ammonium persulphate (abo 60µm) + chromic acid passivation and rinsing

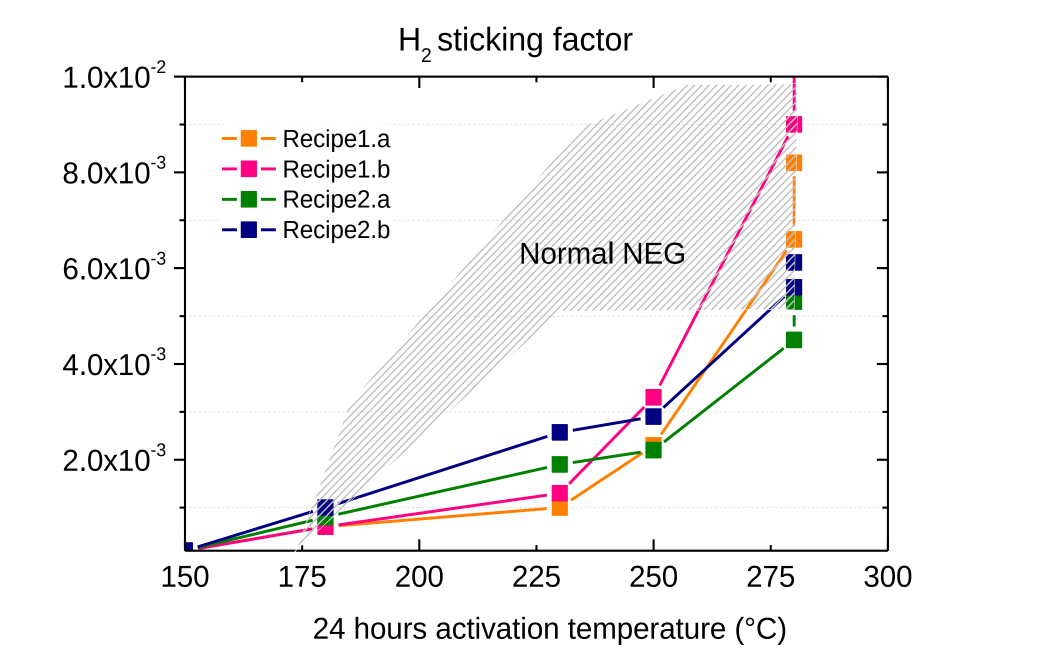


Alternative deposition scheme for small diameter chambers



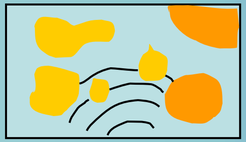
L. Amador et al
JVST A 36, 021601 (2018)

- Demonstrated down to 3 mm diameter and up to 2 m length with integrated flanges
- Activation temperature higher than with standard method (275 C)
- R&D in progress to include stiffeners, cooling lines and to reduce the wall thickness



Quality control and qualification of cleaning procedures

Significant number of samples contaminated in a standardized way with representative contaminants, oils, mixtures…..



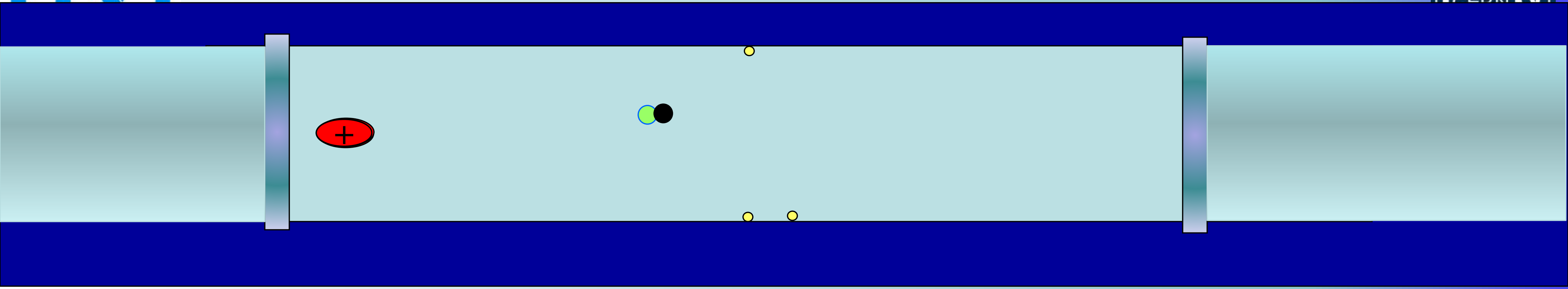
Clean the samples with the procedure under evaluation

Analysis of sample cleanliness → XPS/FTIR

Compare to your application-dependent acceptance levels

Reject or accept procedure

Electron cloud or why slow electrons matter in accelerators



Proton bunch (charge +)

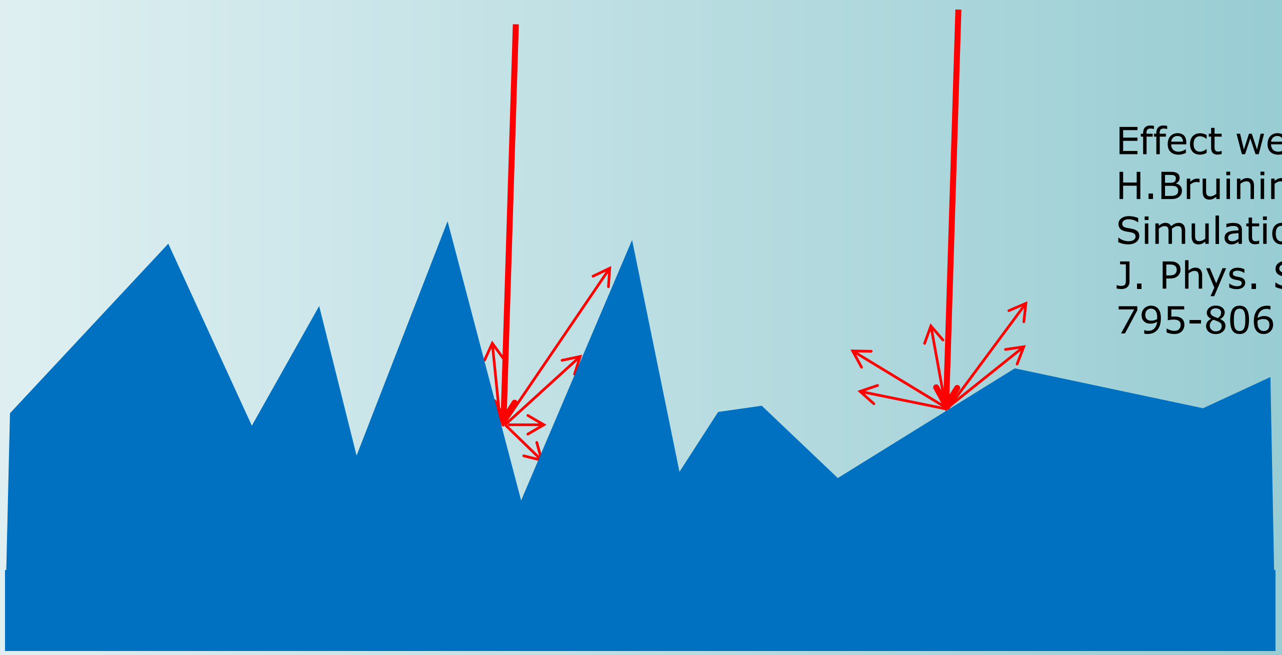
Gas molecule

Electron (charge -)

The beam is perturbed by the electron multiplication: emittance growth, beam instability
Cryogenic parts of the accelerator are submitted to heat load
The pressure rises due to electron stimulated desorption and provokes noise in the experiments

E-cloud is more pronounced for high beam currents and short bunch spacing
E-cloud is suppressed by a sufficiently low **secondary electron yield of the walls** (typically below 1.1-1.3)

Another approach: low SEY by roughness



Effect well known
H.Bruining 1938
Simulation J.Kawata et al
J. Phys. Soc. Jpn. 63, pp. 795-806 (1994)

- The secondary electrons cannot escape from high aspect ratio roughness
- The effect is purely geometric and is scale invariant (for a size above the mfp of electrons)

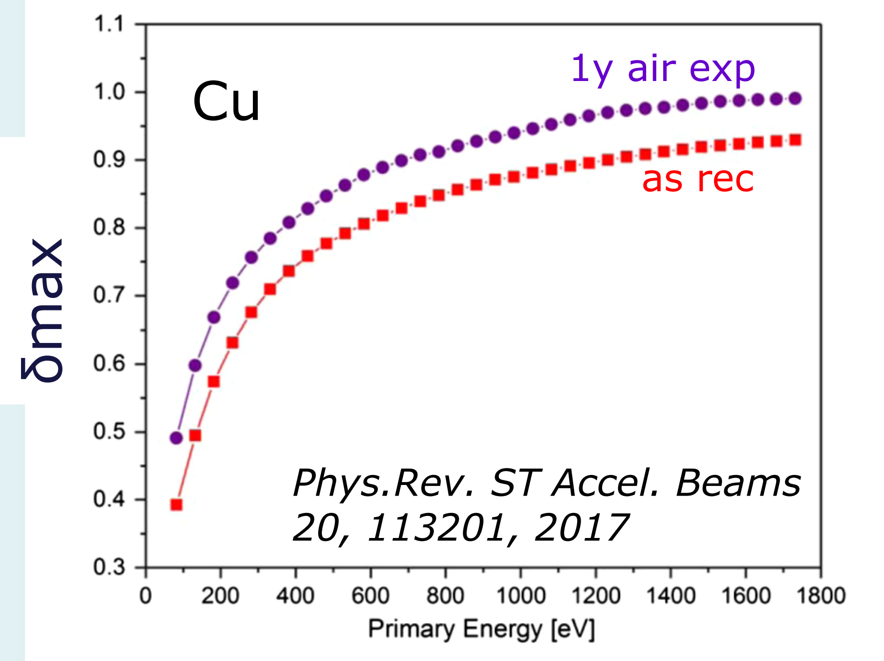
Implementation for in situ treatment

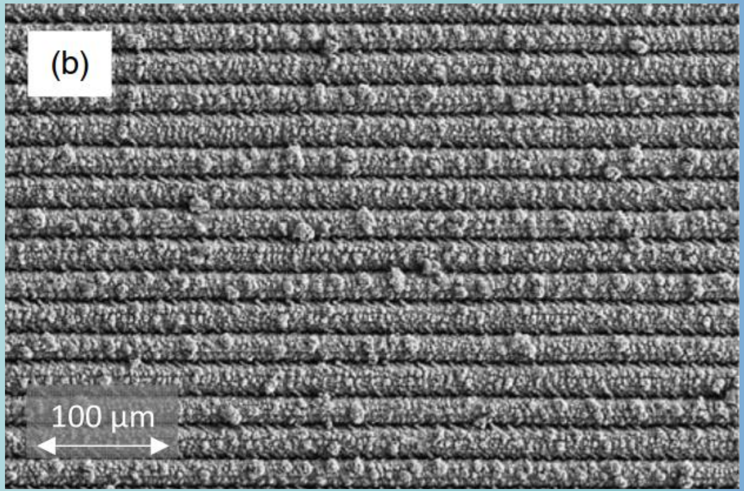
Electro-pneumatic robot and optical fibre

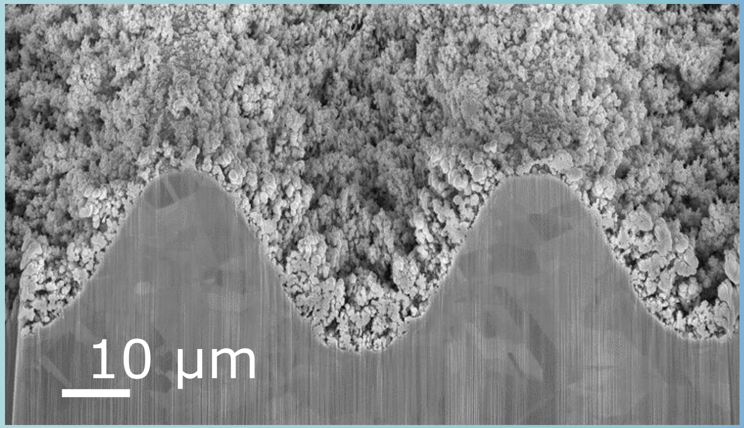
Laser treated surfaces, in collaboration with the Universtiy of Dundee (A.Abdolvand) and STFC Daresbury (R.Valizadeh)

Grooves and nano-roughness produced by **laser treatment** (Nd:YVO4, Nd:YAG etc)

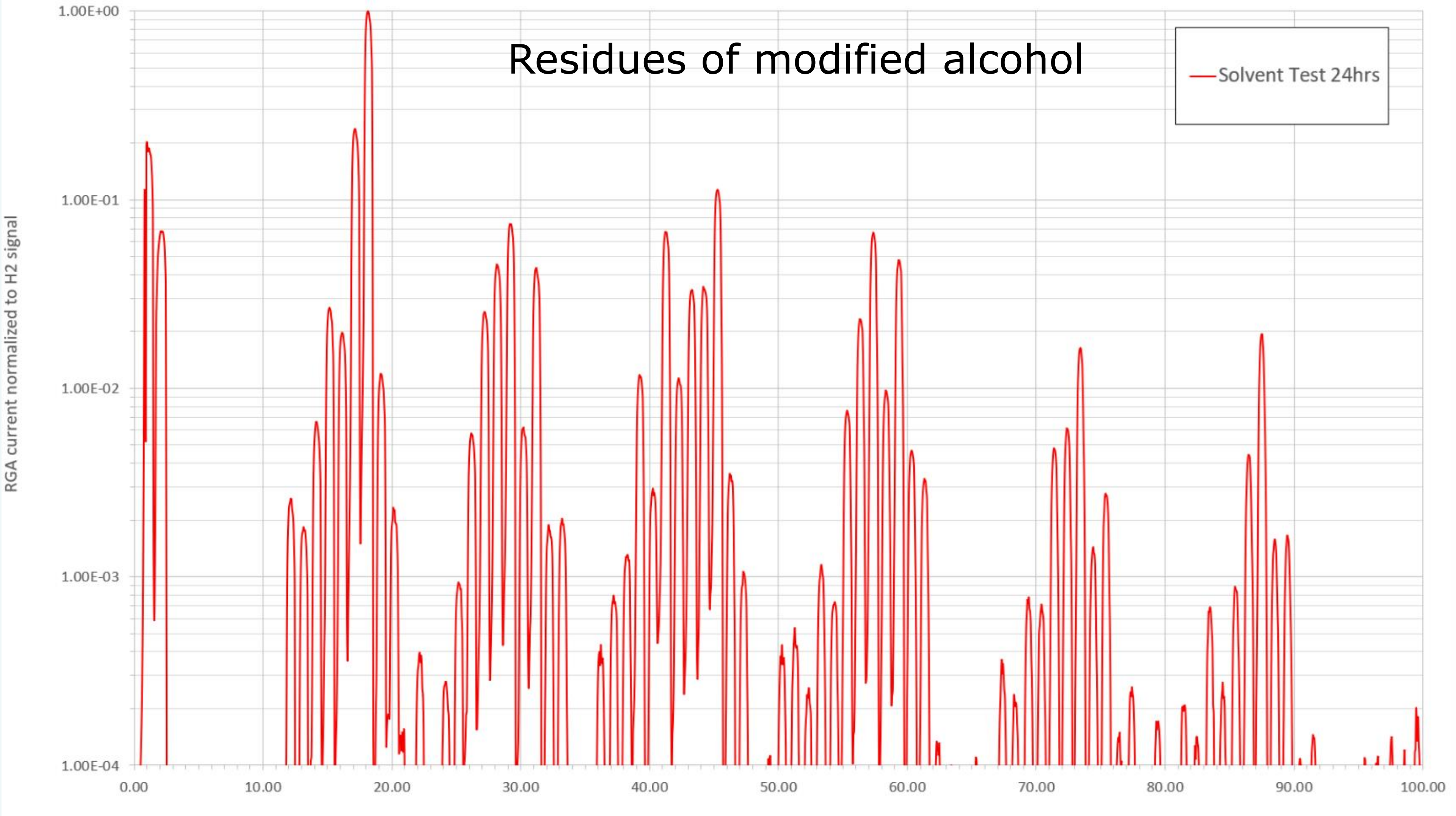
For in bakable or cryogenic surfaces (to cope with outgassing from large surface)

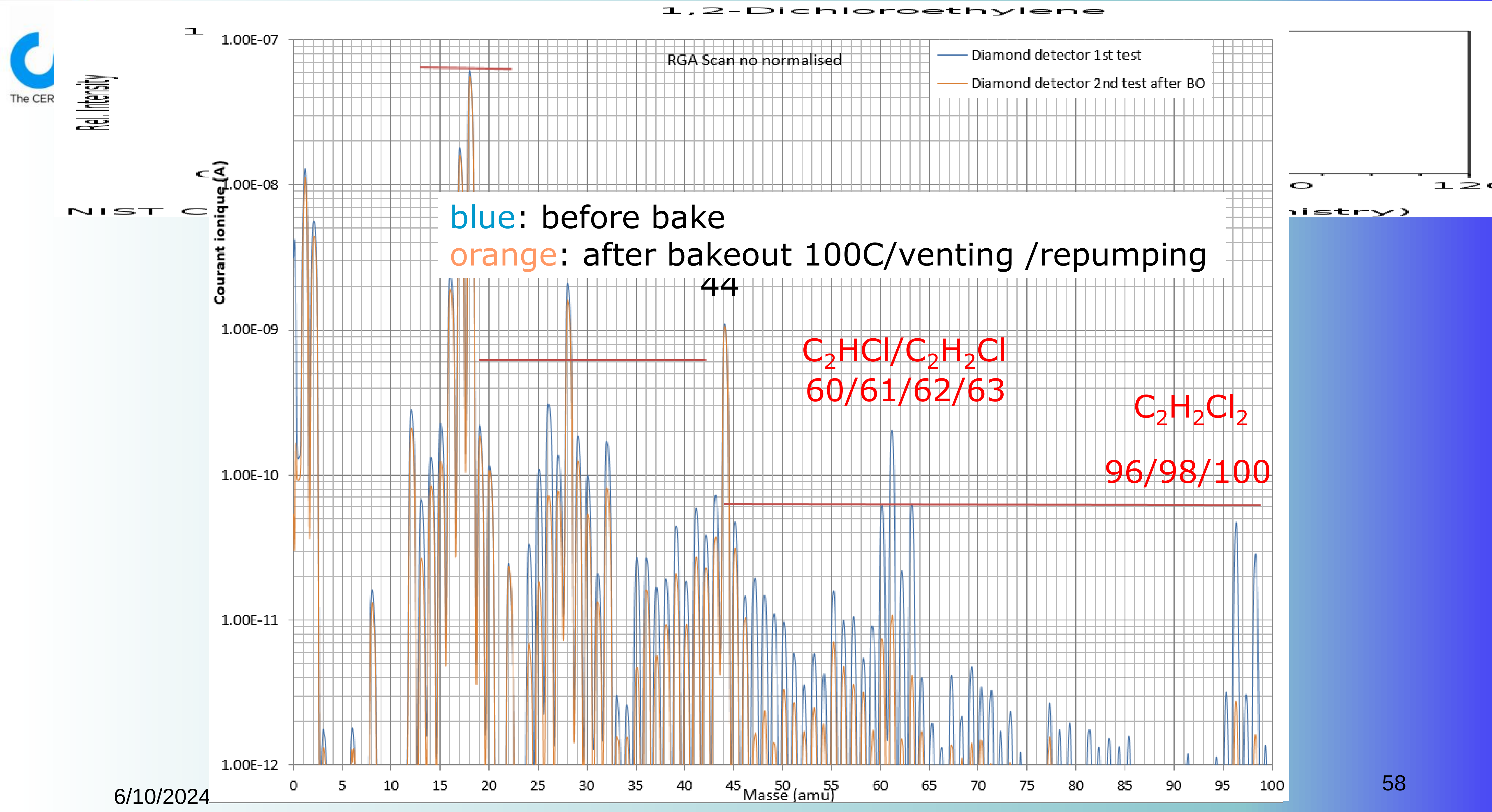




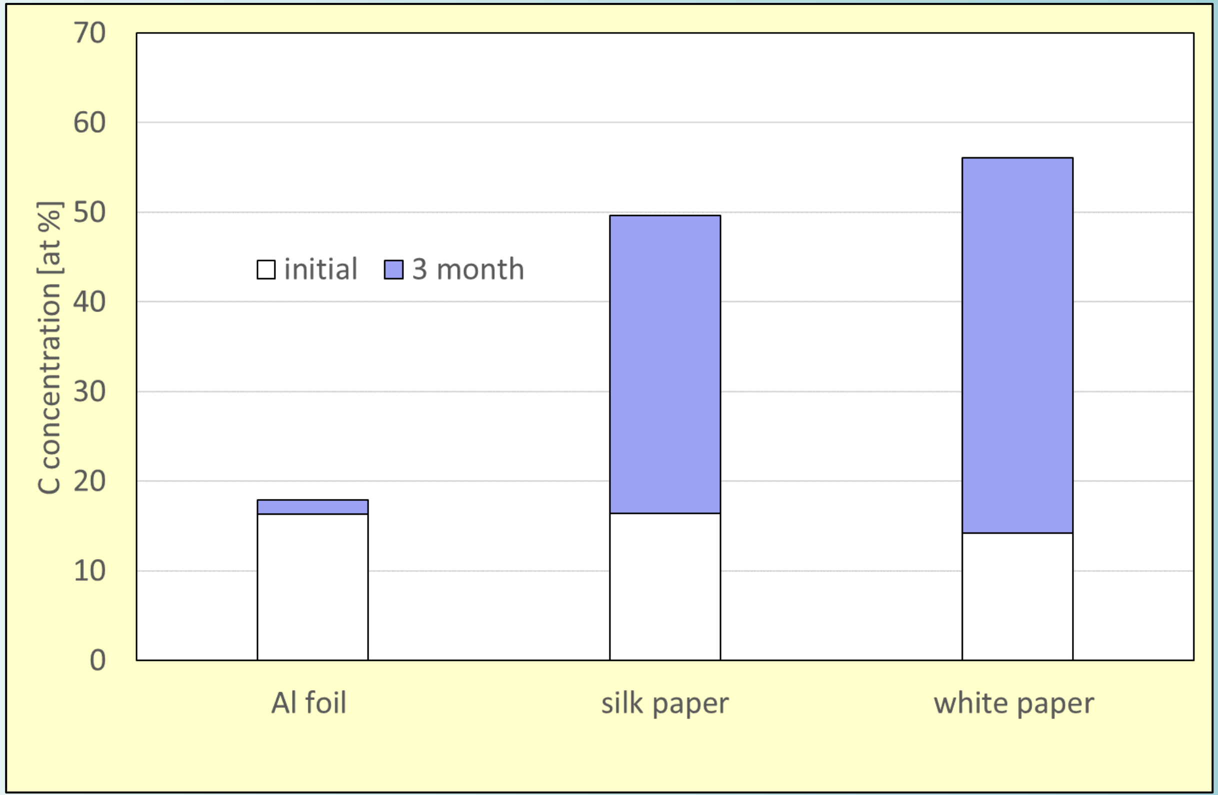


Successfully tested in SPS: PR ST Accel. Beams 20, 113201, 2017


Residues of modified alcohol
Solvent Test 24hrs
RGA current normalized to H2 signal
1.00E+00
1.00E-01
1.00E-02
1.00E-03
1.00E-04
0.00
10.00
20.00
30.00
40.00
50.00
60.00
70.00
80.00
90.00
100.00



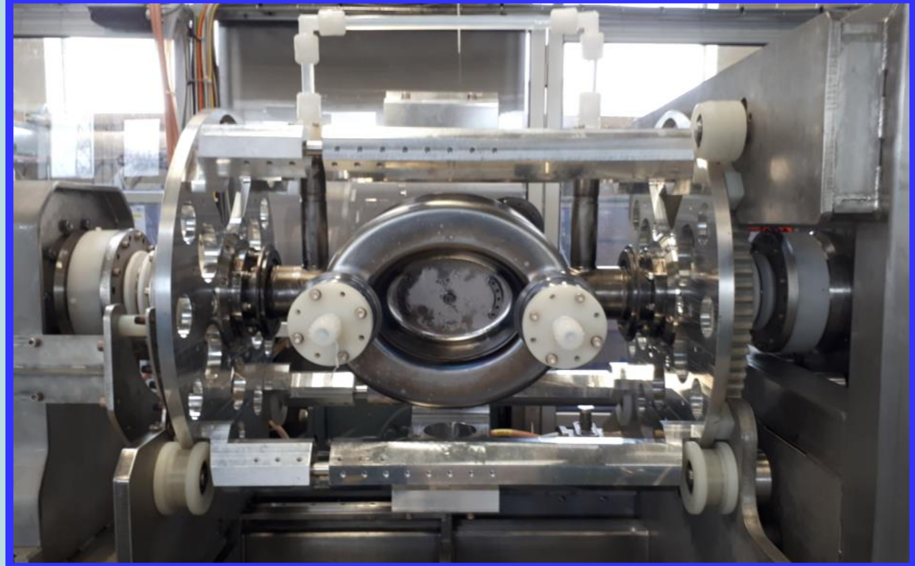
1,2-Dichloroethylene
RGA Scan no normalised
Diamond detector 1st test
Diamond detector 2nd test after BO
Courant ionique (A)
Masse (amu)
blue: before bake
orange: after bakeout 100C/venting /repumping
44
C_2HCl/C_2H_2Cl
60/61/62/63
$C_2H_2Cl_2$
96/98/100


C concentration [at %]
70
60
50
40
30
20
10
0
initial
3 month
Al foil
silk paper
white paper

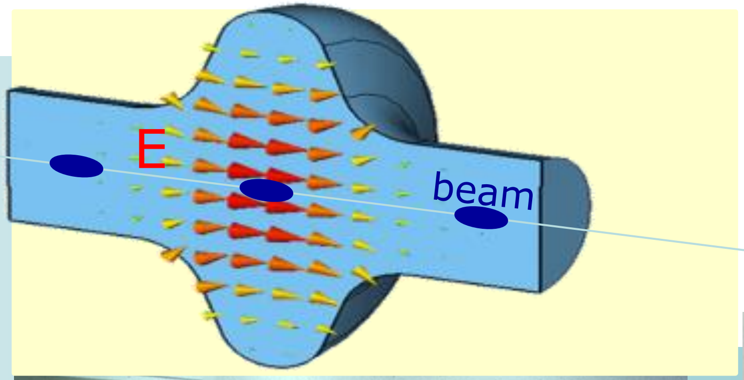
Wet surface treatments: SRF cavity surface preparation

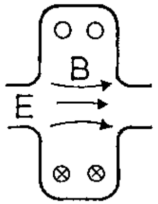
- surface chemical polishing of bulk Nb CRAB cavities
- chemical polishing/electropolishing of copper cavities before Nb coating

polishing before assembly



Application: Superconducting Nb thin films on RF cavities






LHC 400MHz (protons)

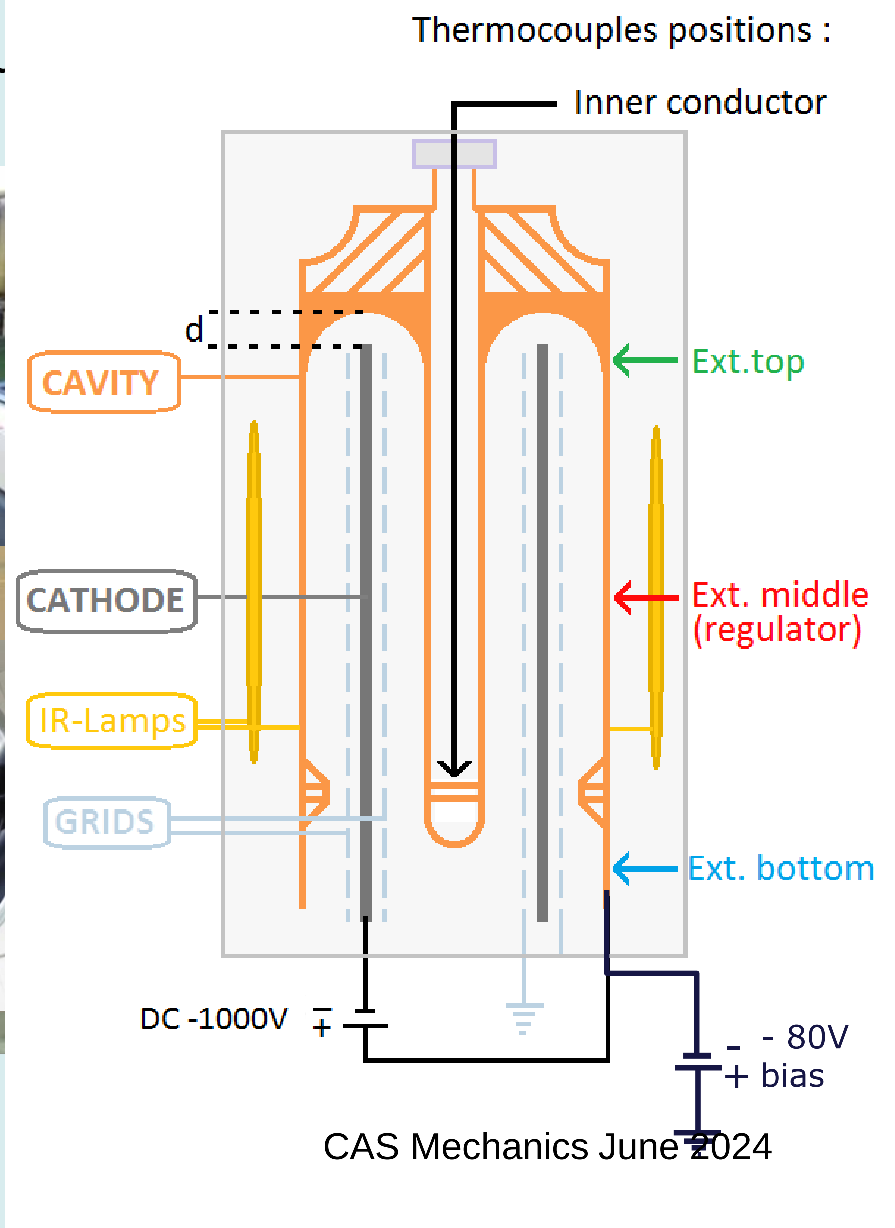

LEP 352MHz (leptons)

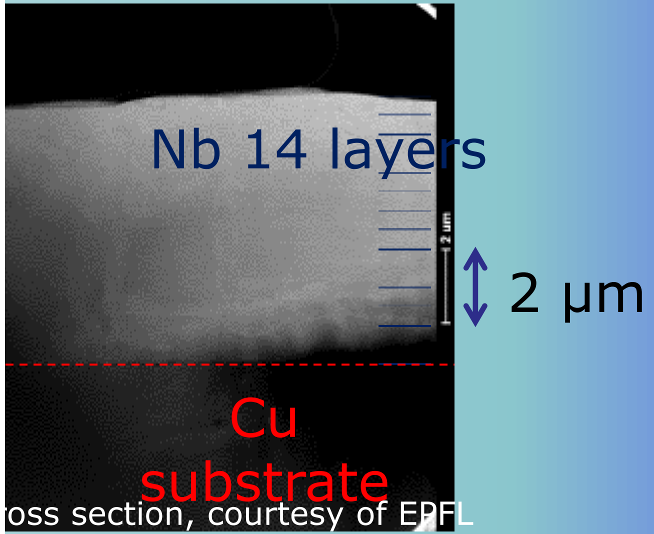

HIE ISOLDE 100MHz QWR (ions)

- Massive Nb (T_C=9.3K) with the required purity is very expensive
- 1-2 µm Nb thin film are sufficient (skin depth) for 5-7 MV/m fields at 100MHz-6GHz frequency range, operate at 4.2K
- successfully developed in the 80’s, recent development for HIE-ISOLDE project

Complex shape Nb thin film coating:
HIE Isolde quarter wave accelerating cavities

Purity (vacuu ... hemical &
mechanical) ... ctor
High T bake





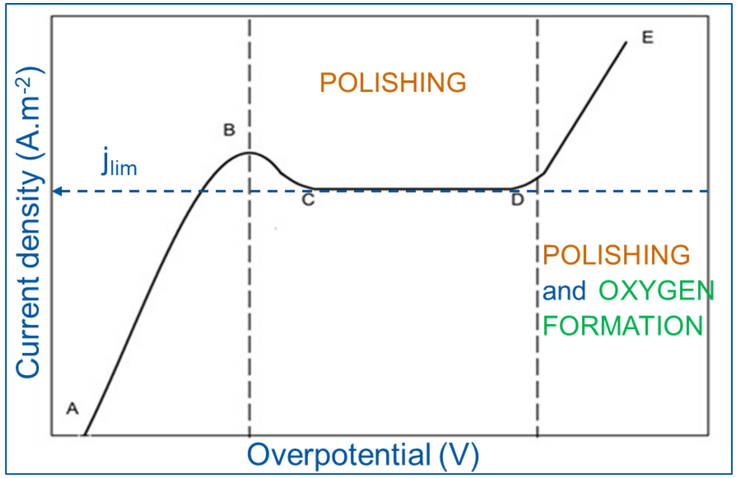
...ing in 14 steps (5 days)

Wet surface treatments: copper plating on 3D printed polymers

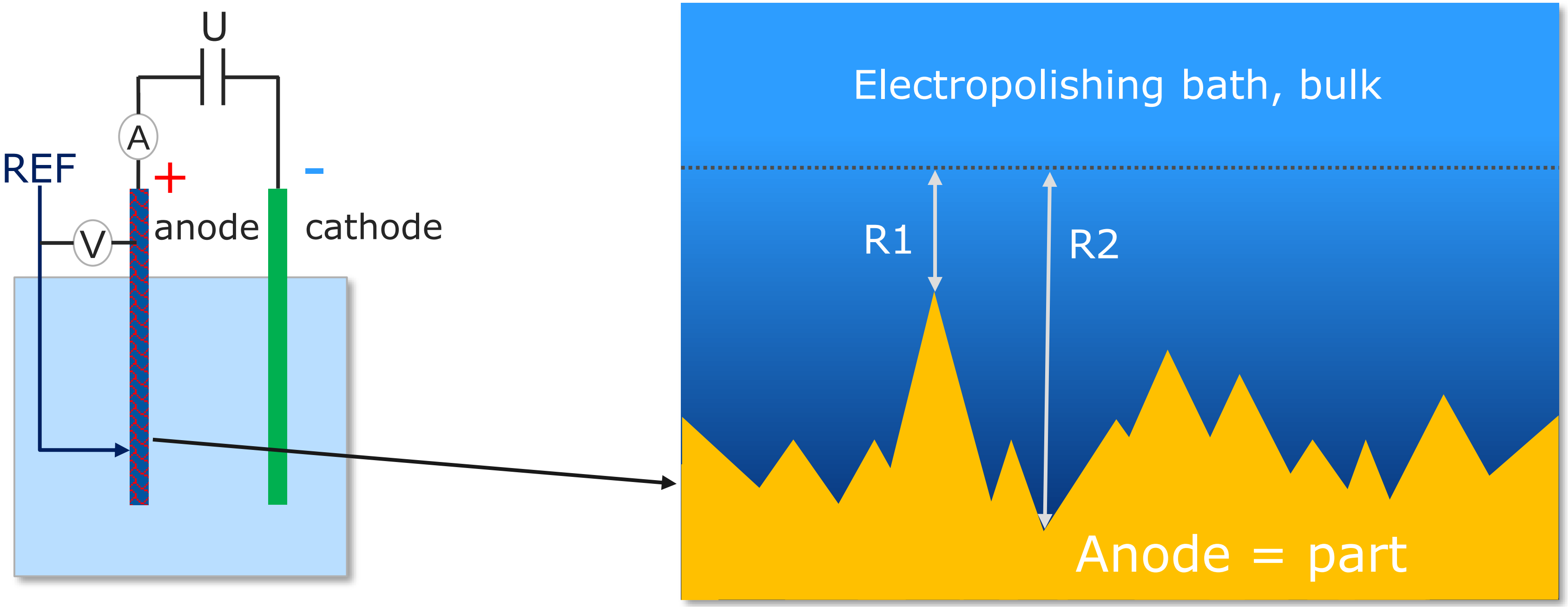
-in collaboration with EN-MME, TE-MSC polymer lab, EP-DT
-Mock-ups for low power RF testing and design validation
-3D printing in Accura polymer + 30 um copper plating on a pre-layer of chemical carbon based conductor
-complex configuration of electrodes to get a good thickness distribution

Electropolishing

Electropolishing (EP) is an anodic dissolution process that reduces the roughness of a metal surface.



Example of an anodic polarisation curve



convection domain

diffusion domain:

- higher density
- Higher viscosity resistance

R1 < R2