CLEANING AND SURFACE PROPERTIES

M.Taborelli, CERN

Introduction

Methods of precision cleaning for UHV applications

Evaluation of cleanliness and quality control

How clean can we clean?

Packaging and storage

Introduction

The definition of cleanliness depends on the application

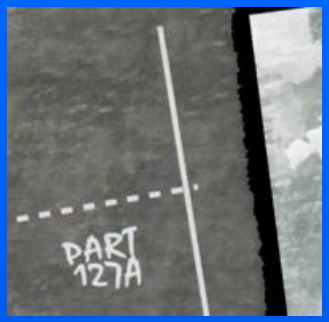
UHV, beams → avoid interaction of gas with particle beam
Thin films → ensure adhesion of coatings

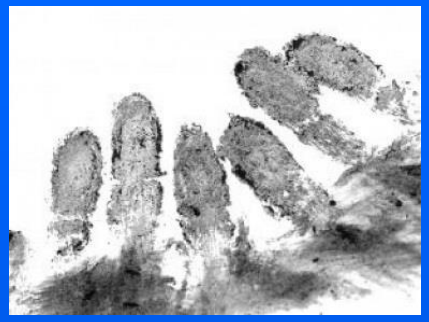
NB: Classical cleaning > 1 µg/cm^2 contamination
Precision cleaning <1 µg/cm^2 (< 3x10^{15} molec/cm^2 of $C_{12}H_{14}$)

Particle (dust) contamination:

- not considered in the following
- is relevant in some cases for accelerators:
  - -for UFOs (LHC) the relevant size is above 20-50 um (Z dependent)
  - -for RF accelerating cavities related to field emission: particles are removed by high pressure water rinsing and clean room handling is mandatory
  - (-particles down to small diameter, 100 nm, are relevant in semiconductor manufacturing)

Some of the relevant surface contaminations are:



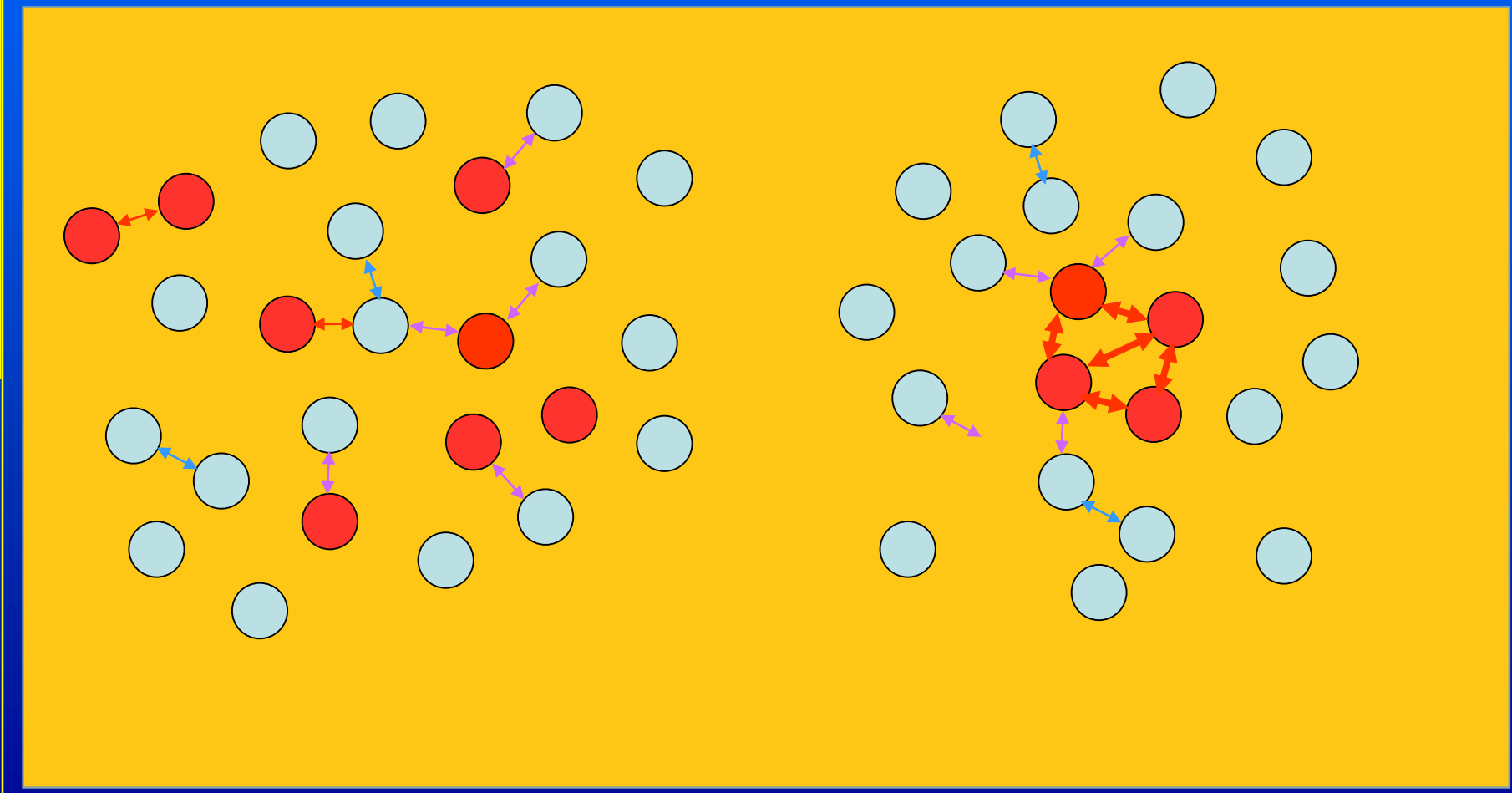


- Adsorbed heavy hydrocarbons (cutting oils, lubricants, markers inks, glue, fingerprints): induce static and dynamic outgassing, hinder coatings adhesion (have low surface energy)
- Adsorbed "intermediate vapour-pressure" compounds: provoke long lasting static outgassing (alcanes: C_{16} Pvap= 10^{-3} mbar, C_{21} 10^{-6} mbar, C_{26} 10^{-10} mbar)
- Other elements/compounds:
  - corrosion inducing elements and compounds (halogens, sulphur.....), metals with high pvap (Cd, Zn 10^{-7} and 10^{-9} mbar at 100C, in platings and brazings) , silicone oils and greases (outgassing, insulating layer of SiO_2 deposits on electrical contacts upon irradiation)

Cleaning by solvent:

Principle :

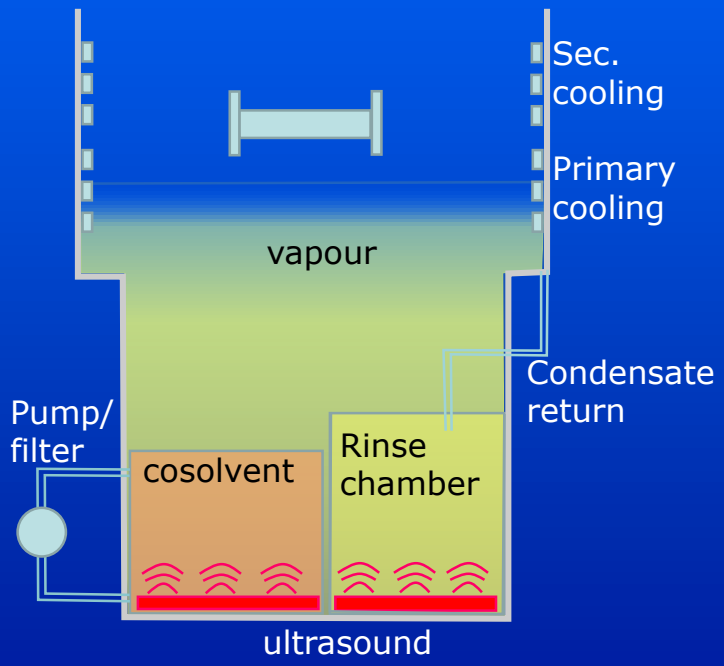
Solvation: balance of entropy (→diffusion) and molecular interaction strength for solute-solute (→precipitation), which must not be too strong compared to solute-solvent



Solvent degreasing procedures

By immersion: (as in ethanol…)
Dip the piece to be cleaned in the solvent bath (proper temperature and time) with ultrasonic agitation.
Final rinsing with pure solvent and drying by evaporation.

Without immersion (vapour degreasing):
-Heat the bath of solvent to get vapour
-Keep the cold workpiece above the bath to condense the solvent on it
-Collect the condensed liquid with dissolved contamination dropping from the workpiece in a continuously recycled bath



Combination with co-solvent
To extend the range of solvated materials

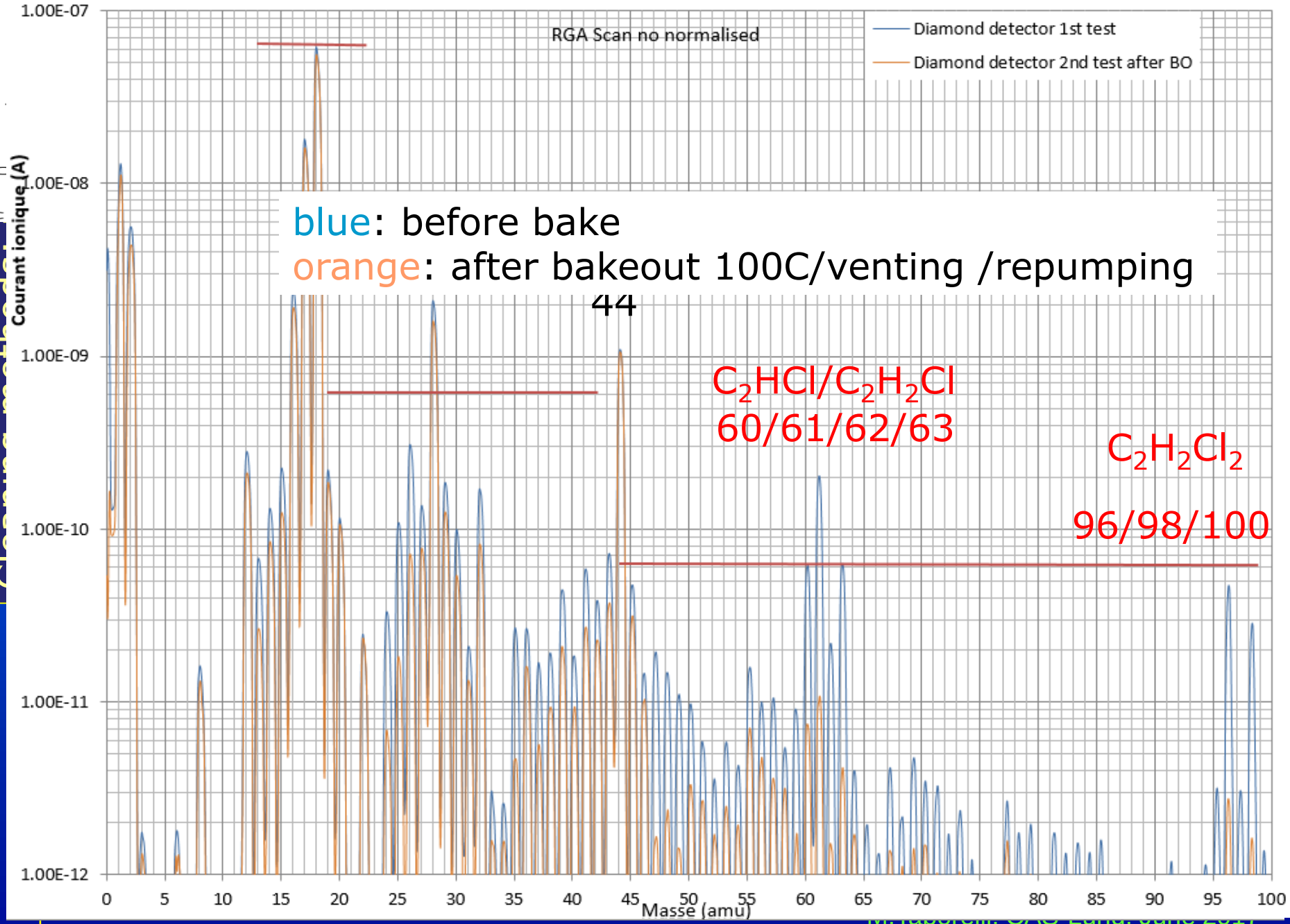
Vapour degreasing:

- ☺ the solvent is continuously distilled and purified
- ☺ often used as pre-cleaning
- ☹ needs adapted closed plant to avoid loss of solvent (safety and environment)

☺ Solvents are better for parts with complex shapes (bellows), porous materials (ceramics, composites…) which cannot be easily rinsed or dried, and cannot sustain aqueous cleaning….with some limitations…

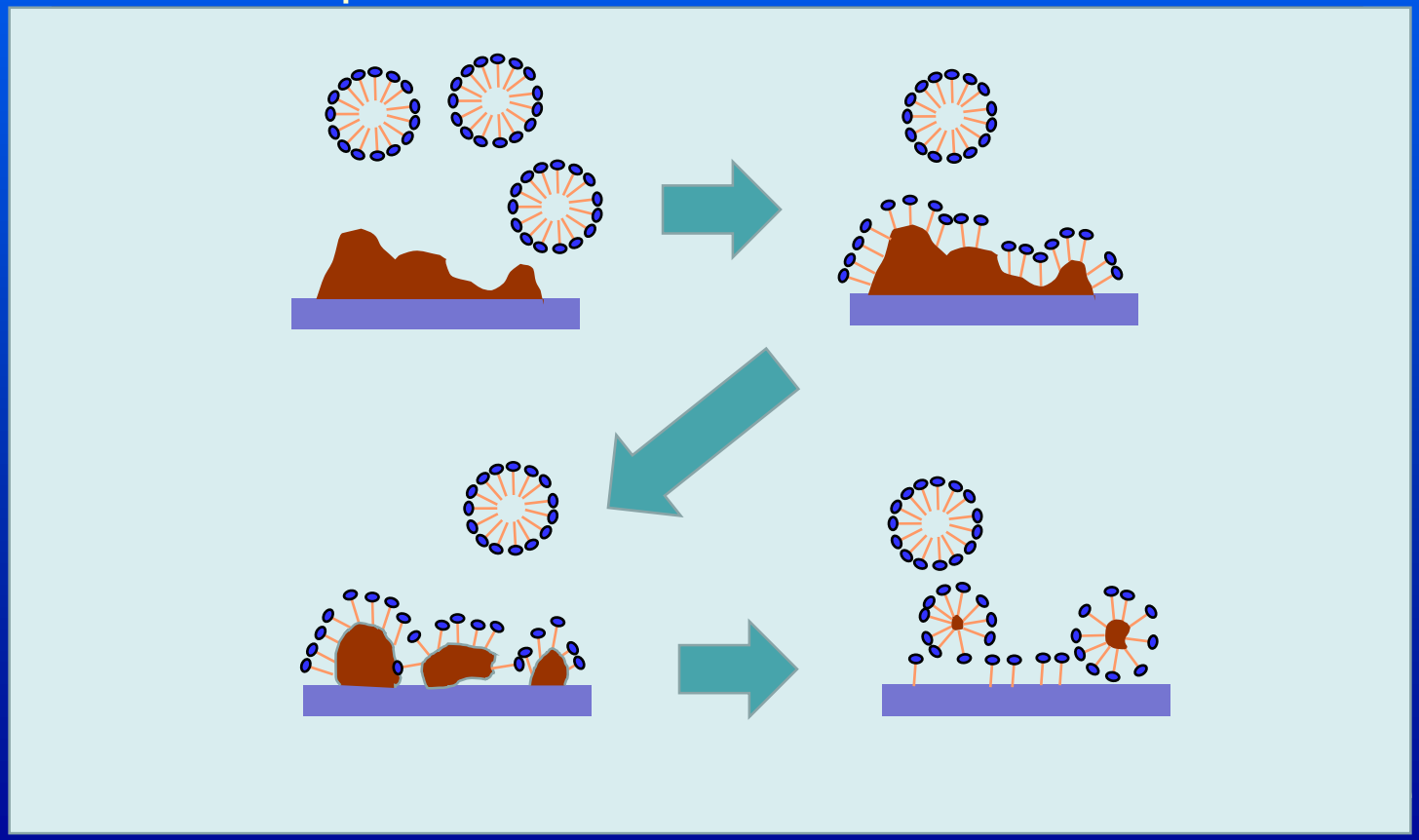
☹ solvent solubility and cleaning efficiency are contaminant dependent ("like with like")

Ex: CO_2 , hydrofluoroethers C_nF_{2n+1}-O-C_mH_{2m+1}, modified alcohols (having polar and non polar components R'-O-R''-OH), hydrofluoro/chloro carbons with zero ozone depletion potential, but GWP….


RGA Scan no normalised
Diamond detector 1st test
Diamond detector 2nd test after BO
Courant ionique (A)
1.00E-07
1.00E-08
1.00E-09
1.00E-10
1.00E-11
1.00E-12
0
5
10
15
20
25
30
35
40
45
50
55
60
65
70
75
80
85
90
95
100
Masse (amu)
blue: before bake
orange: after bakeout 100C/venting /repumping
44
C2HCl/C2H2Cl
60/61/62/63
C2H2Cl2
96/98/100

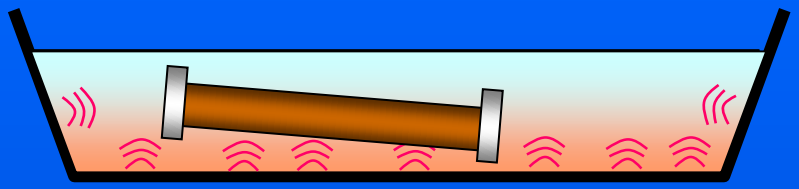
Water based cleaning: detergents

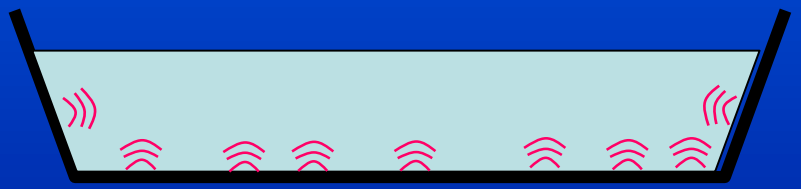
Principle: a detergent can wet any surface (surfactant: reduces the surface energy of the liquid): amphiphilic molecule with polar head and non-polar tail, soluble in water and organic solvents, can incorporate the non-polar hydrophobic material which can thus be dissolved (formation of micelles) and cannot be redeposited on the surface.



Detergent cleaning procedure

water and detergent bath
(surfactants, builders)
+
T (typically 50°-60°C)
ultrasonic agitation
(or turbulent flow for long pipes which cannot be immersed)
+
rinsing with demineralized or tap water stream or ultrasound
+
rinsing with demineralized water bath (conductivity <5 μS cm^{-1})





NB: the first effective control is a verification of wetting of the surface by the rinsing water

Drying in oven 80°-100°C (possible for small parts only and suitable materials) or dry nitrogen (filtered) or spreading ethanol

☺generally used for non-porous materials and parts of simple shape, which can be properly rinsed/dried

☹ pH is basic (~9.6 for the CERN bath), 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

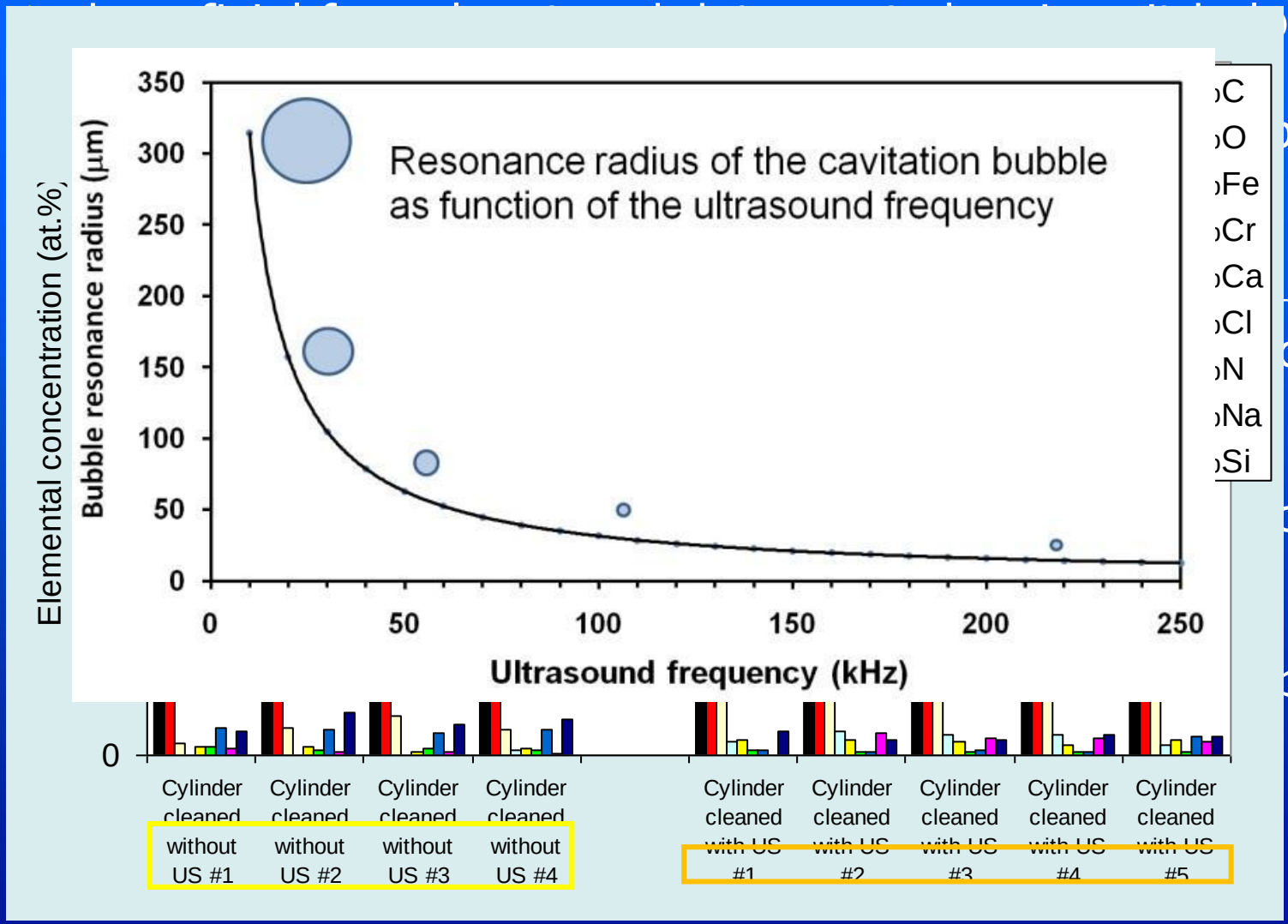
☹ it is difficult to eliminate silicones, since they float on the bath surface and are recollected by the workpiece

NB:

-Cleaning time is function of contamination amount, part shape, brittleness (ultrasound), surface roughness, vessel size

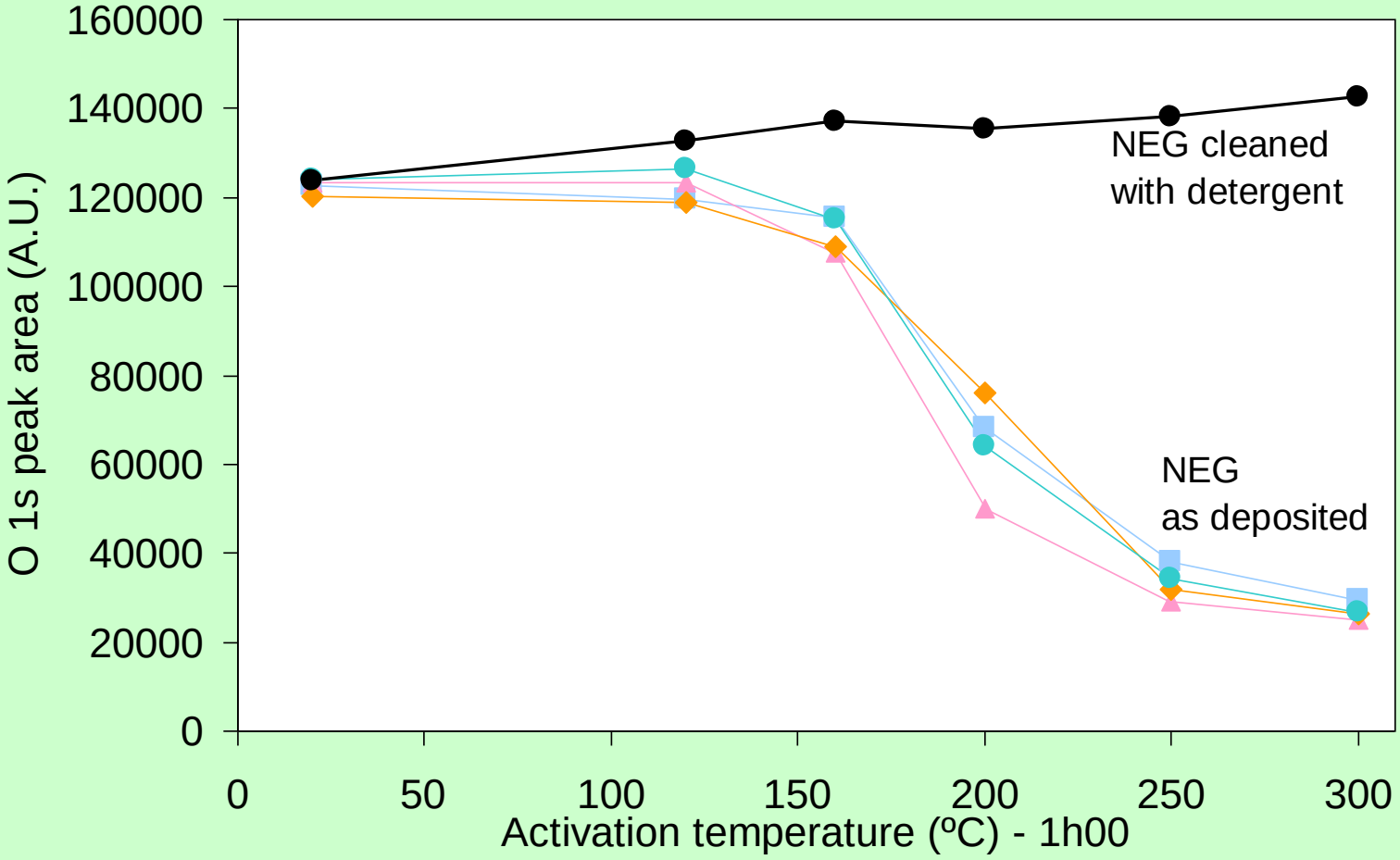
- bath quality must be monitored (conductivity, pH, concentration of detergent) as frequently as the use requires it; it is effective to filter and recycle

Ultrasonic agitation



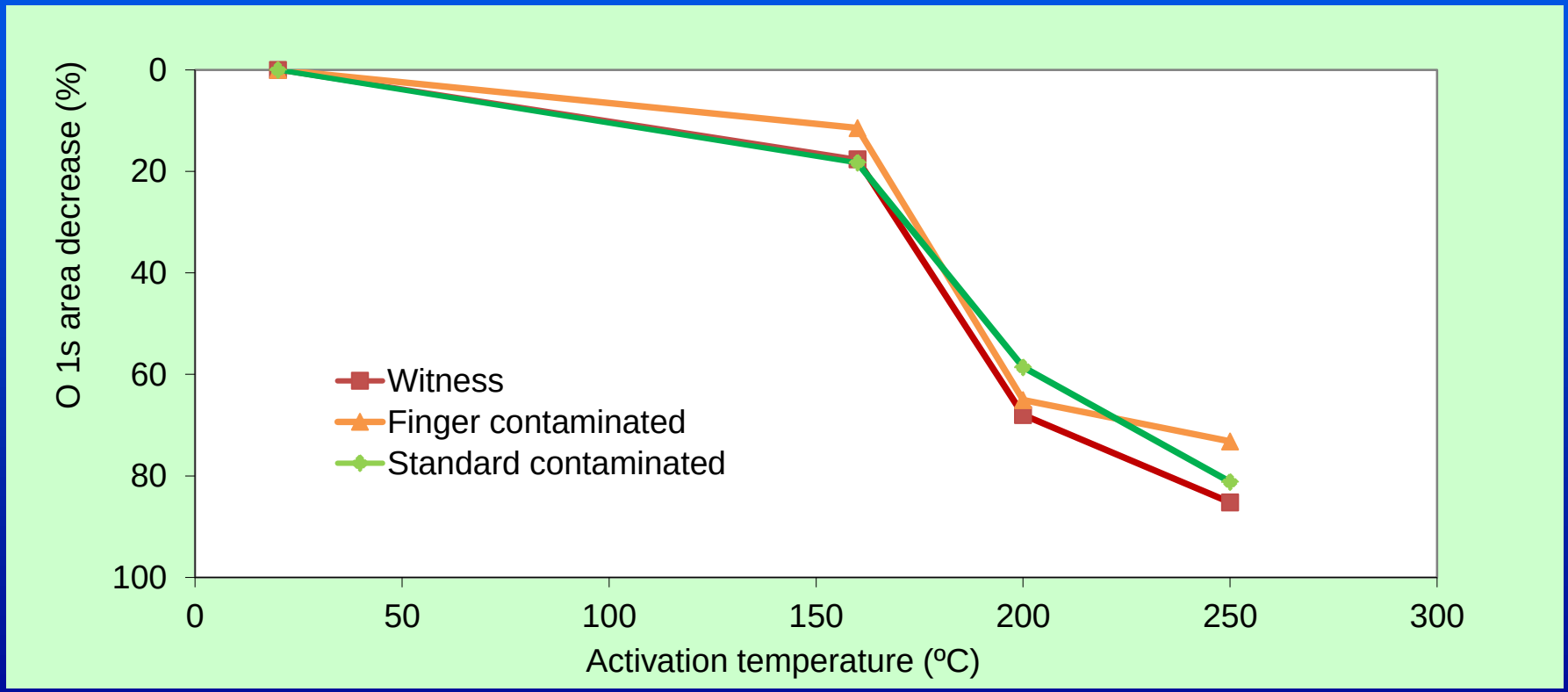
Test of cleaning TiZrV NEG with alkaline detergent:

Presence of large amounts of silicates (up to 10%at), likely depletion of V, deterioration of activation properties:

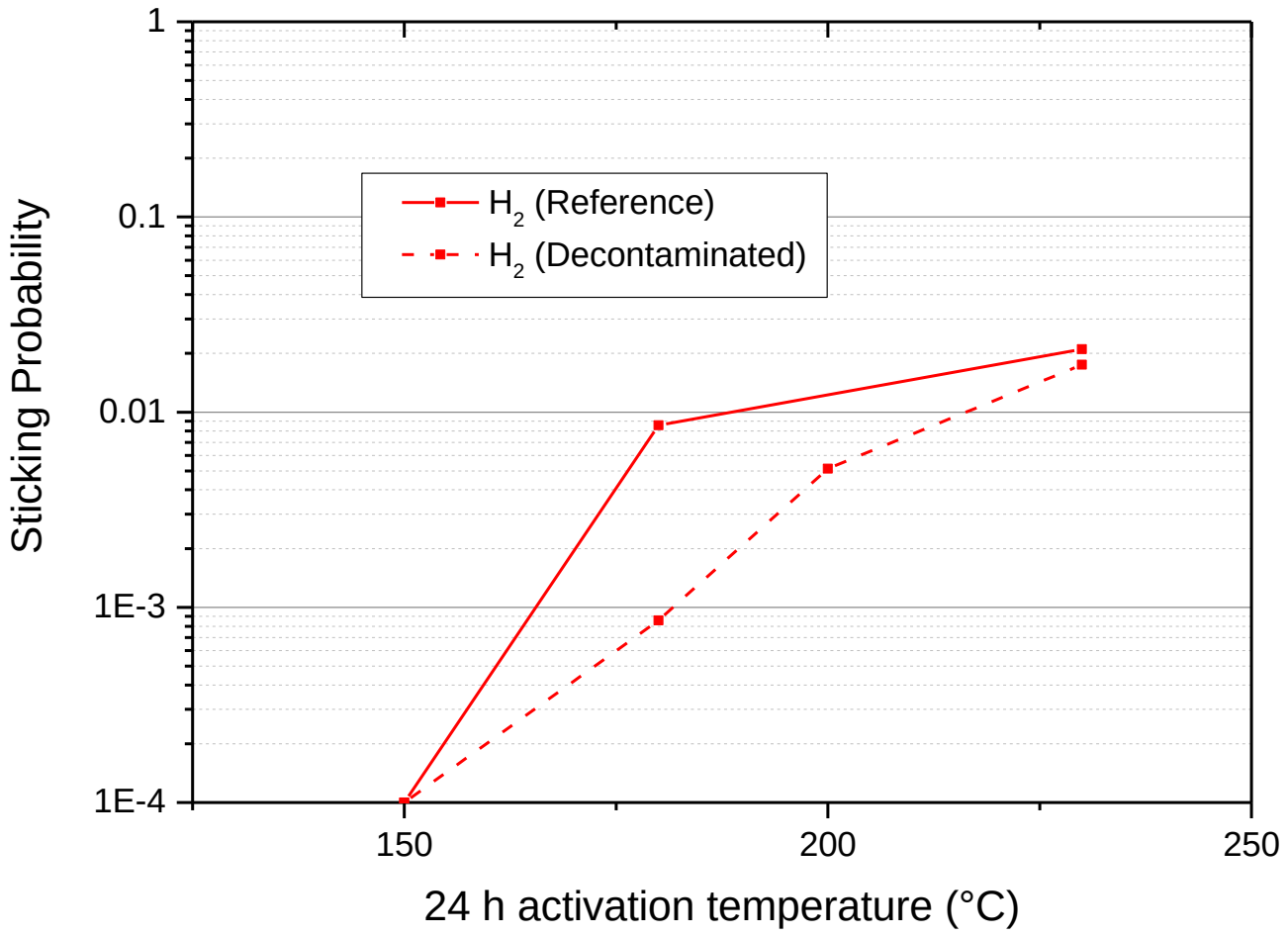


A further test with NEG:

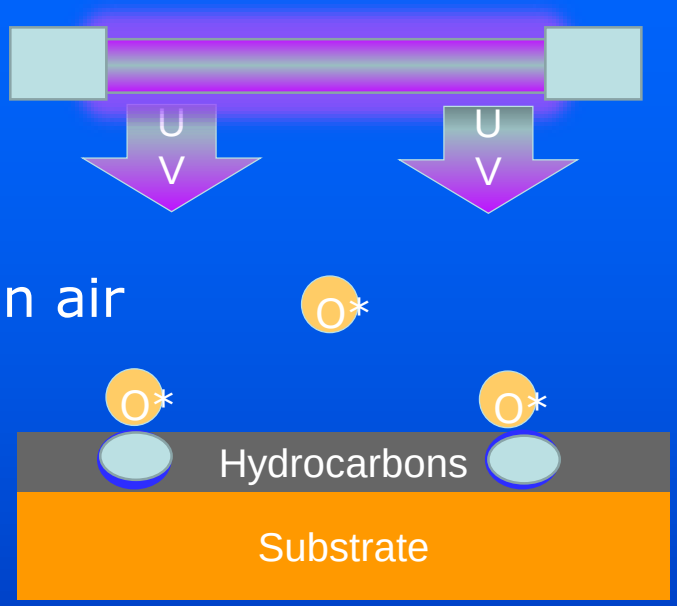
Clean NEG contaminated with figerprints and standard contamination (cutting oil, pump oil, bearing grease) and clean in NaOH 5M, 40C: small samples and chamber
Slight V depletion (26 at% to 22 at%), some 3-4at% of Na, but perfect activation in XPS



Pumping speed results



Ozone cleaning



Produced by UV-lamp
184.9 nm + 254 nm

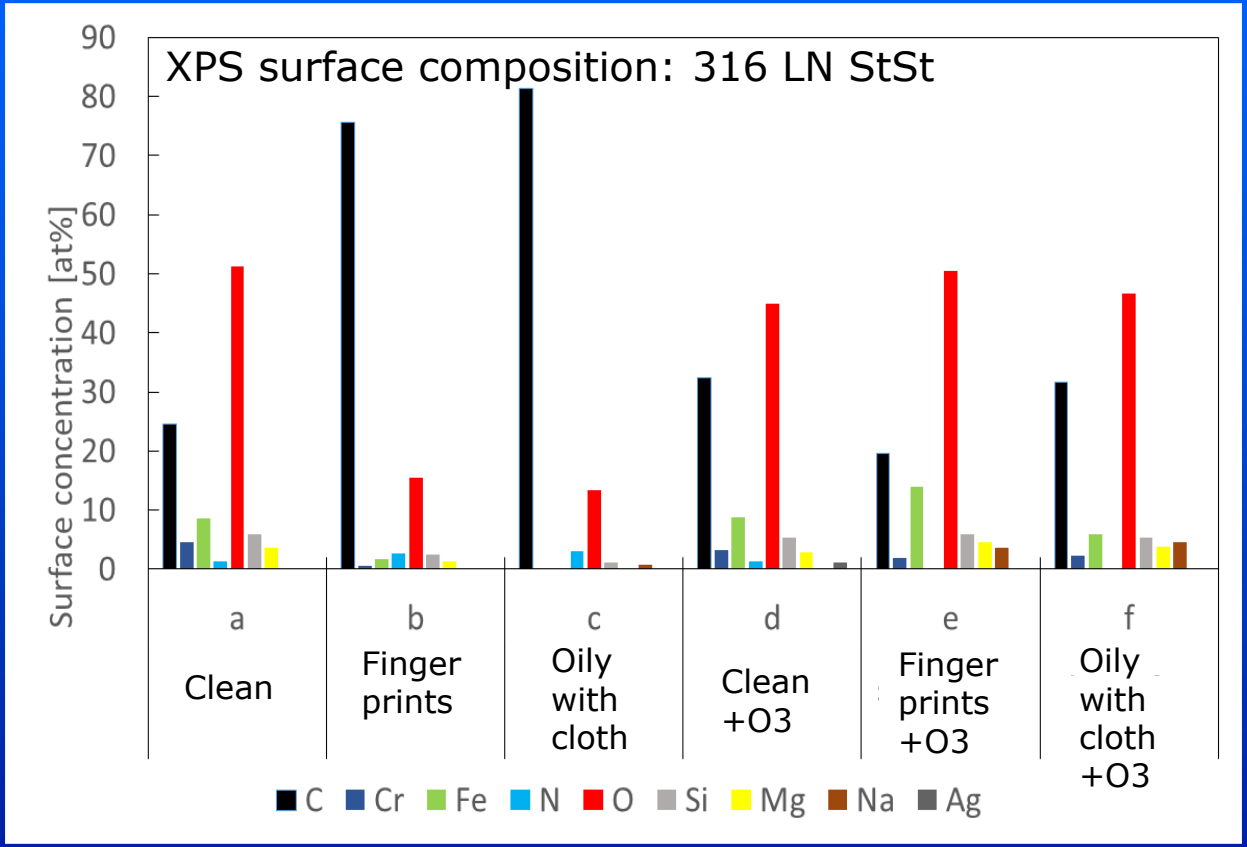
$O_2 \rightarrow O + O$
$O_2 + O \rightarrow O_3$
$O_3 \rightarrow O_2 + O^*$ (decomposition)
J.R.Vig JVST A3 , 1027 (1985)

- Photolysis of hydrocarbons by UV
- Oxydation by O* and production of volatile species

- For organic contaminants
- Not for gross contamination (thick polymer layer is cross-linked rather than decomposed), is more a finishing step
- UV alone is not sufficient
- High dose can oxidise the surface (for Cu, not StSt)
- Under study for «in situ» use

Ozone cleaning

Clear improvement of cleanliness in all samples:



1h UV irradiation

Only detergent and solvent cleaning was discussed here, but sometimes chemical etching, electropolishing, passivation …….must be used

The usual question

We are using this product, is it good for cleaning parts for UHV?

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

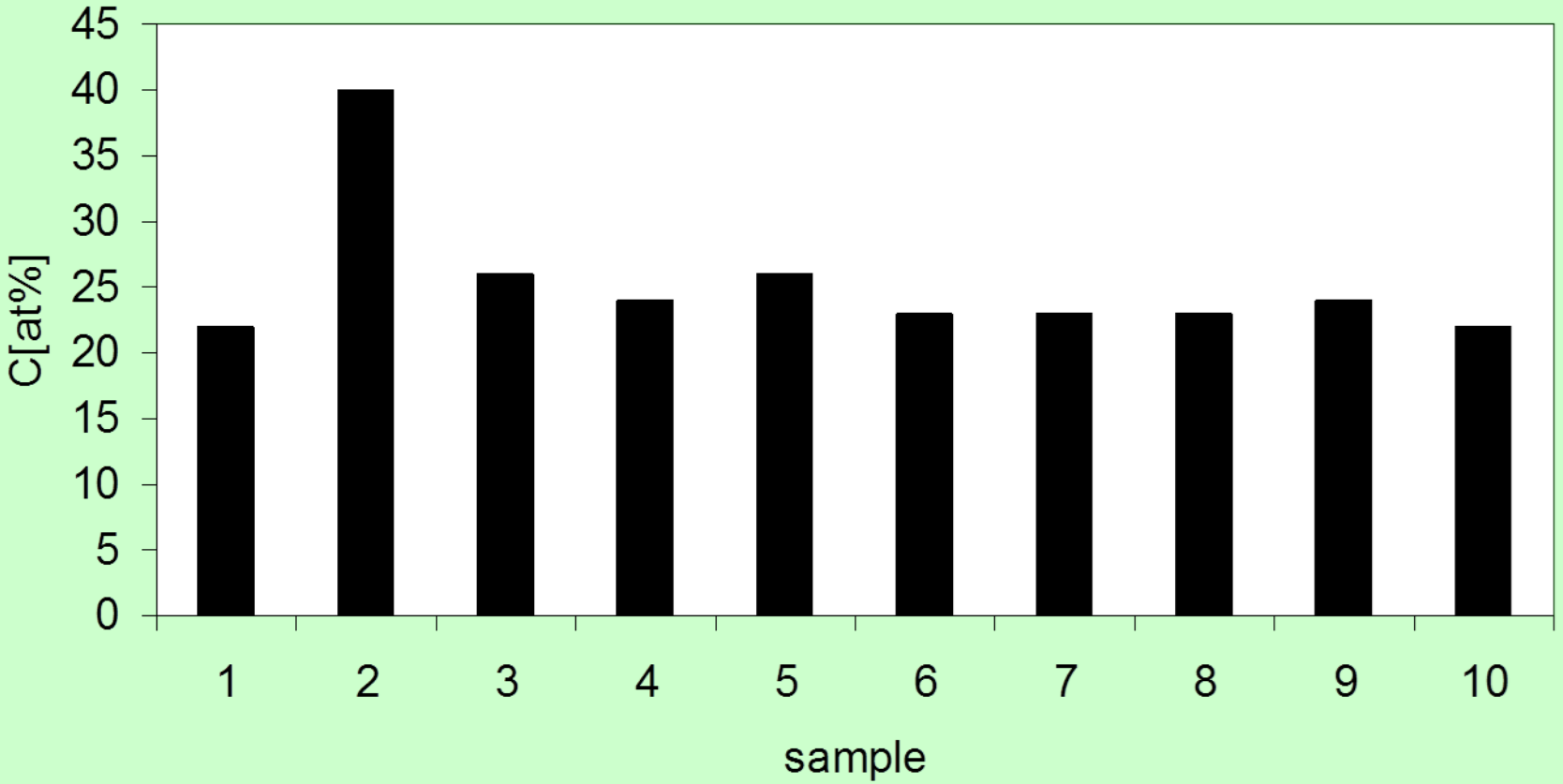
Compare to your application-dependent acceptance levels

Reject or accept procedure

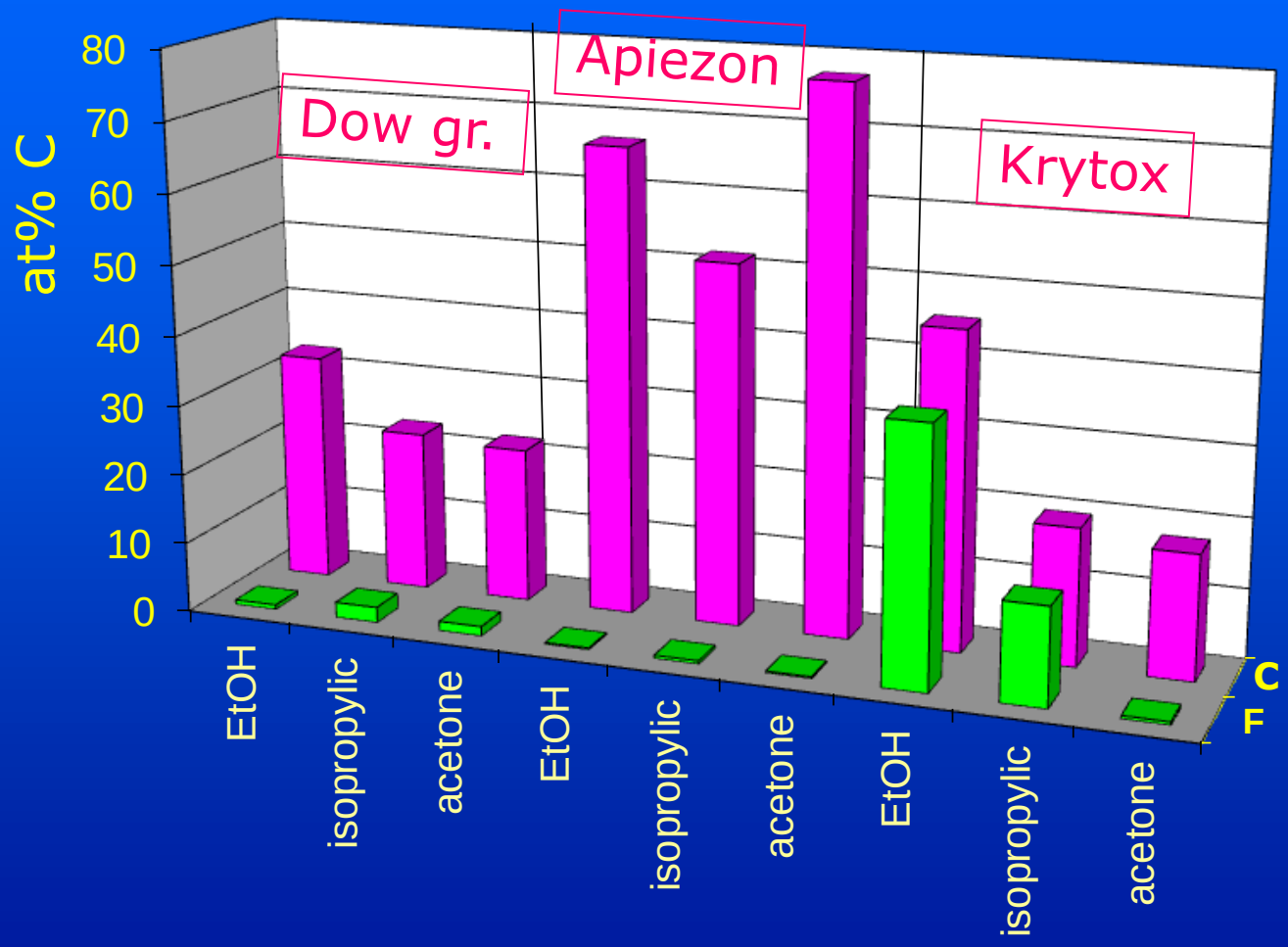
Qualification procedure in EDMS 1626970

Cleanliness analysis: XPS

Cleaning of standard contaminated copper samples: air exposure =< 30 minutes



Example of evaluation of solvent effectiveness on various greases , by XPS on StSt316LN

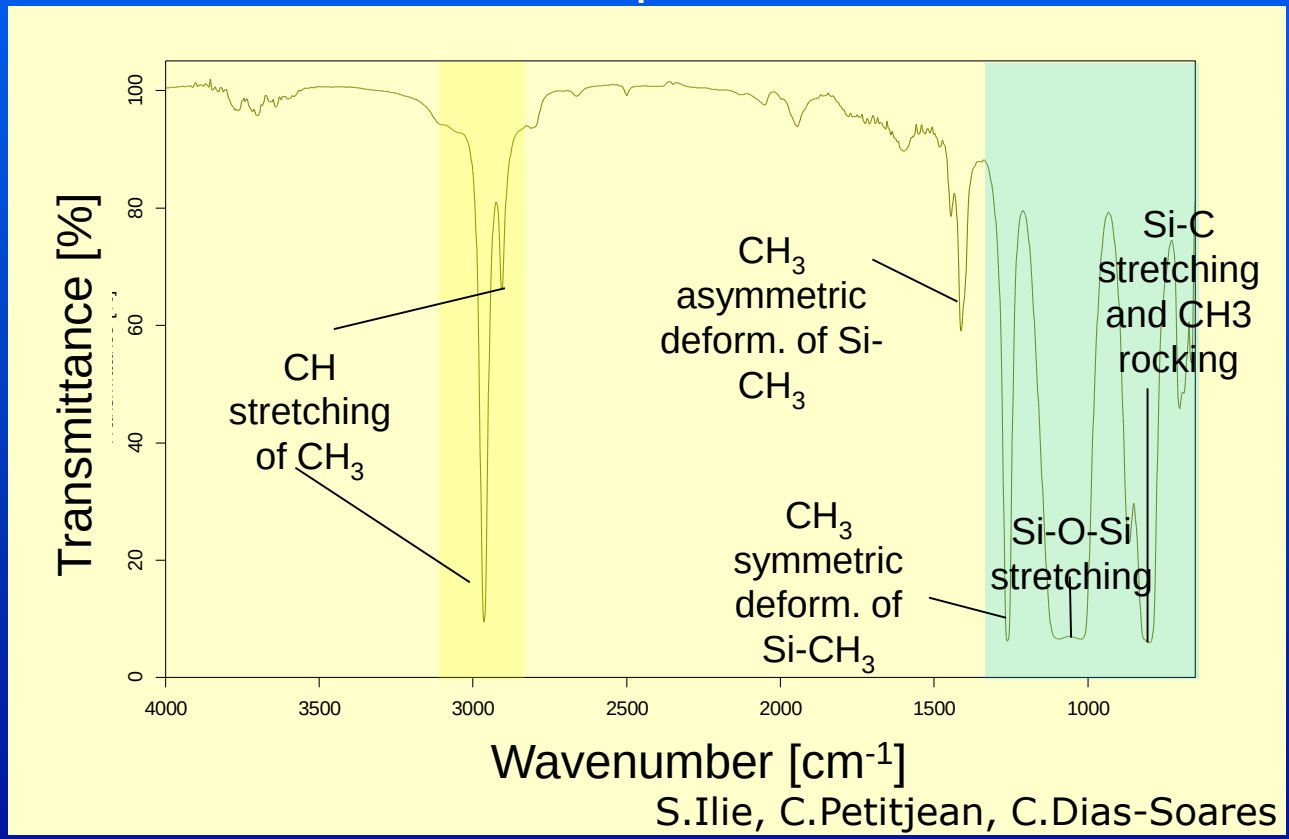


Cleanliness analysis: FTIR

- 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



Other techniques

Auger spectroscopy (AES)	On samples. Sensitive, but carbon partly modified by beam (dose eff.)
Static SIMS	On samples. Sensitive (silicones), but difficult to quantify in general, highly sensitive
Gravimetry	On samples. Low sensitivity (we need ~10^{-7} g/cm^2), no identification
Water contact angle	On parts, no identification, depends on surface roughness
UV fluorescence	On parts, no identification, needs calibration
UV-vis spectr, Ellipsometry	On samples through elution, hard to identify species
Optical stimulated Electron Emission, Surface potential difference	On parts, no identification of species, substrate dependent, needs calibration

ESD, PSD, ISD	On samples, sensitive, no identification (fragments)
Static outgassing rate	On parts, in acceptance tests, partial identification
TDS, TGA-MS	On samples (quartz balance for TGA, partial identification)
GC-MS, gas chromatography	On parts after elution, low sensitivity, powerful identification of large molecules
Total. Refl. X-Ray Fluoresc.	On samples, sensitive, needs mirror-like sample
Radioactive tracer	On samples, with selected contamination only

Cleaning and dynamic vacuum: Electron Stimulated Desorption test of detergents and solvents on 316LN

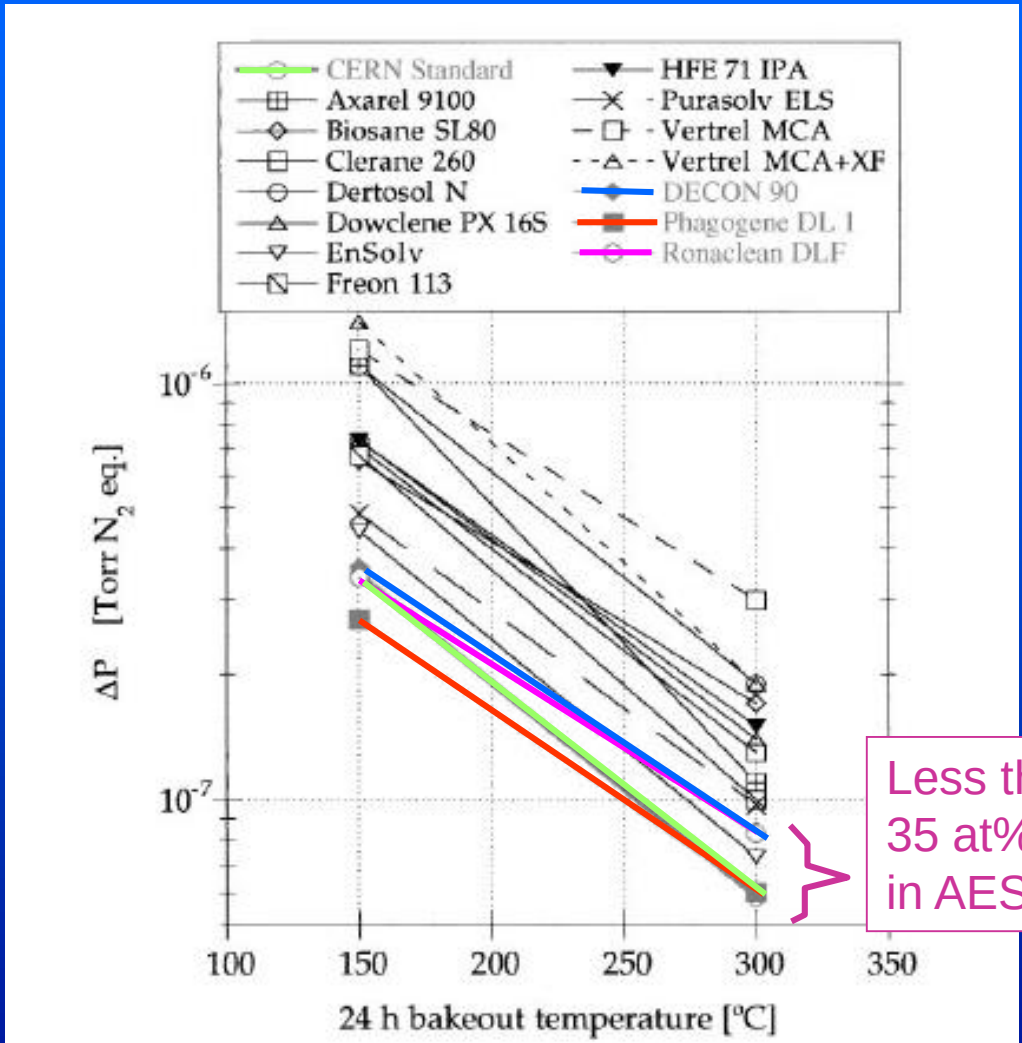
Desorption induced by 500eV electrons after 150°C bake and after 300°C bake

Memory even after 300°C bake!

Typical η (150°C)

H_2	0.1
CO	0.02
CO_2	0.03
CH_4	0.004

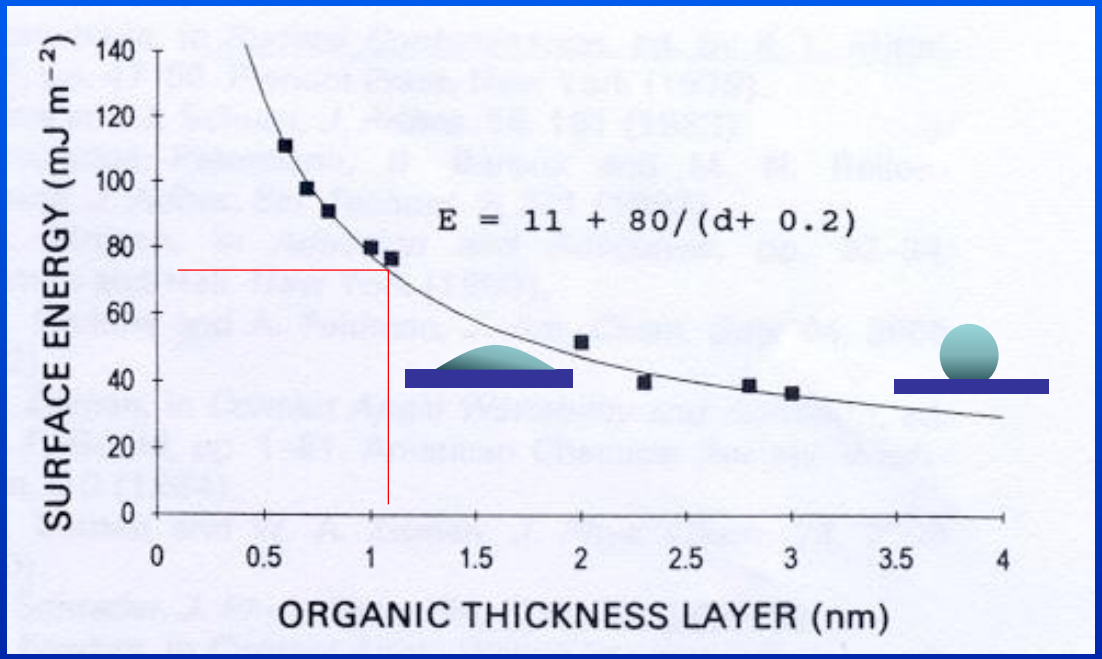
See also Middleman et al. Vacuum 81, (2007) 793



Chiggiato, Benvenuti et al, Vacuum 53, 317 (1999)

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



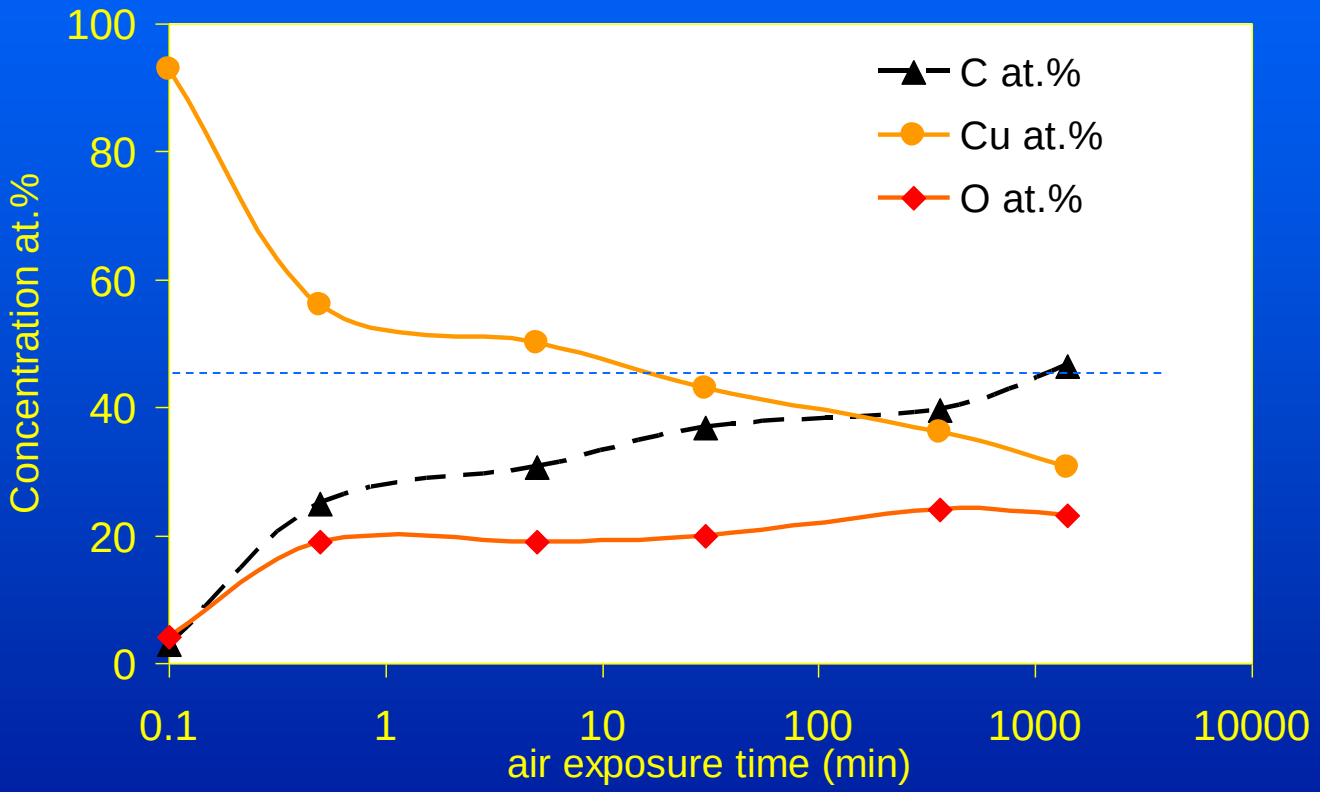
Hydrocarbons on stainless steel:
Mantel and Wightman Surf. Interf.An. 21, 595 (1994)

-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.

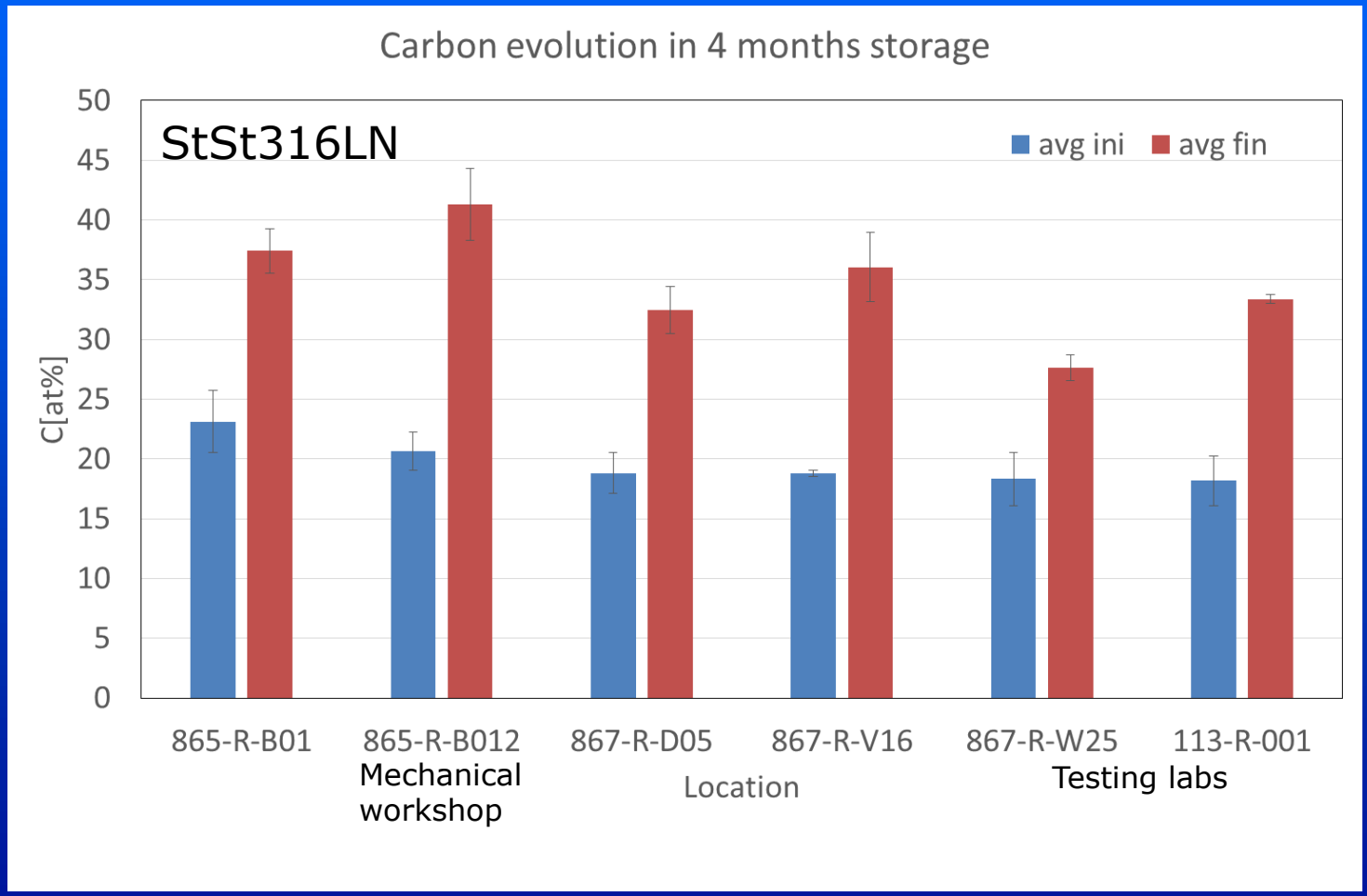
Hydrocarbon re-adsorption on sputter cleaned copper surface



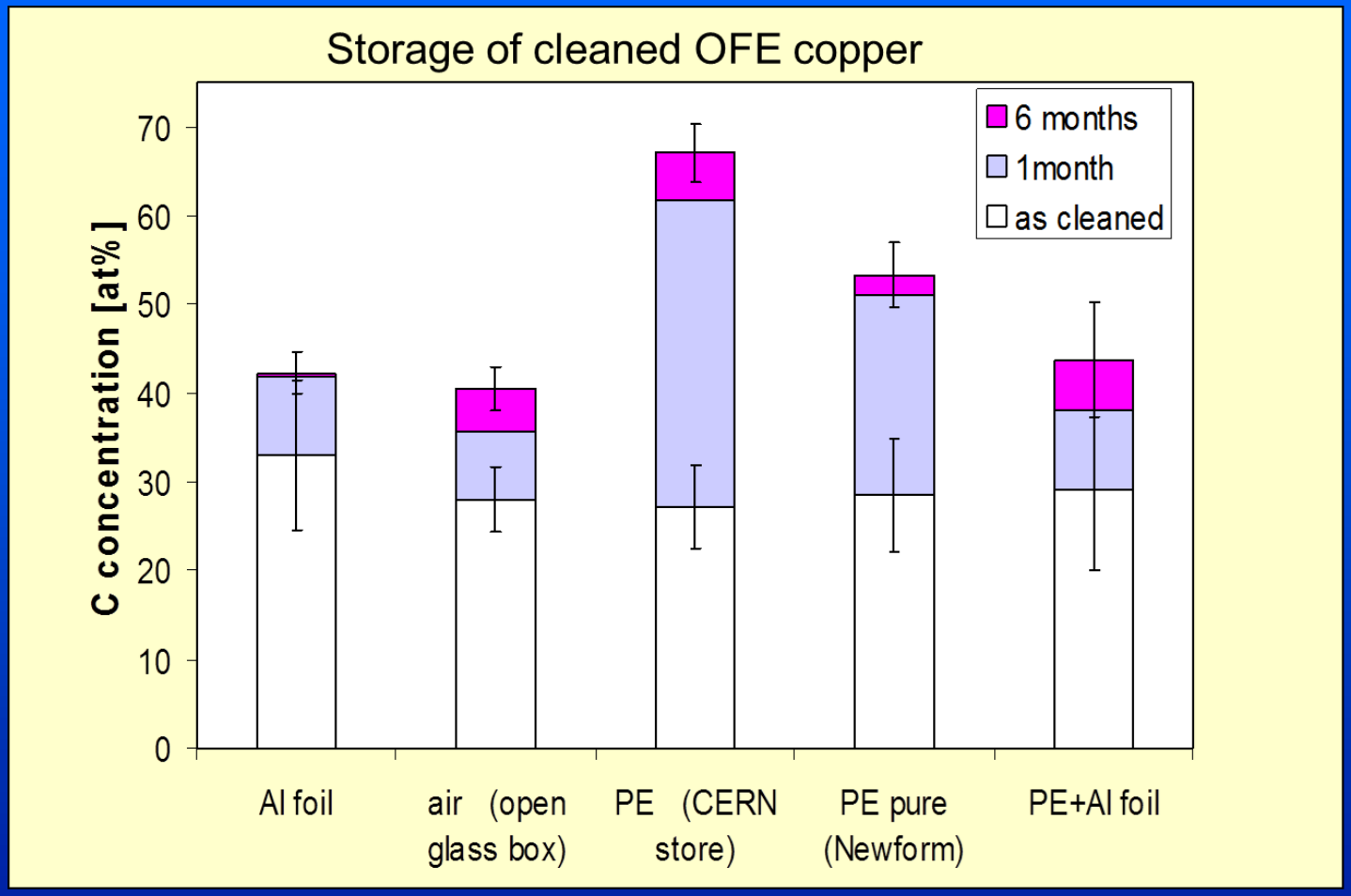
Trials of cleaning and keeping the sample in the rinsing water up to insertion in XPS does not improve the situation

Storage place:

Also a chemically cleaned surface is prone to re-adsorb hydrocarbons: storage in air (vertically) without protection gives similar values of carbon contamination after 4 months

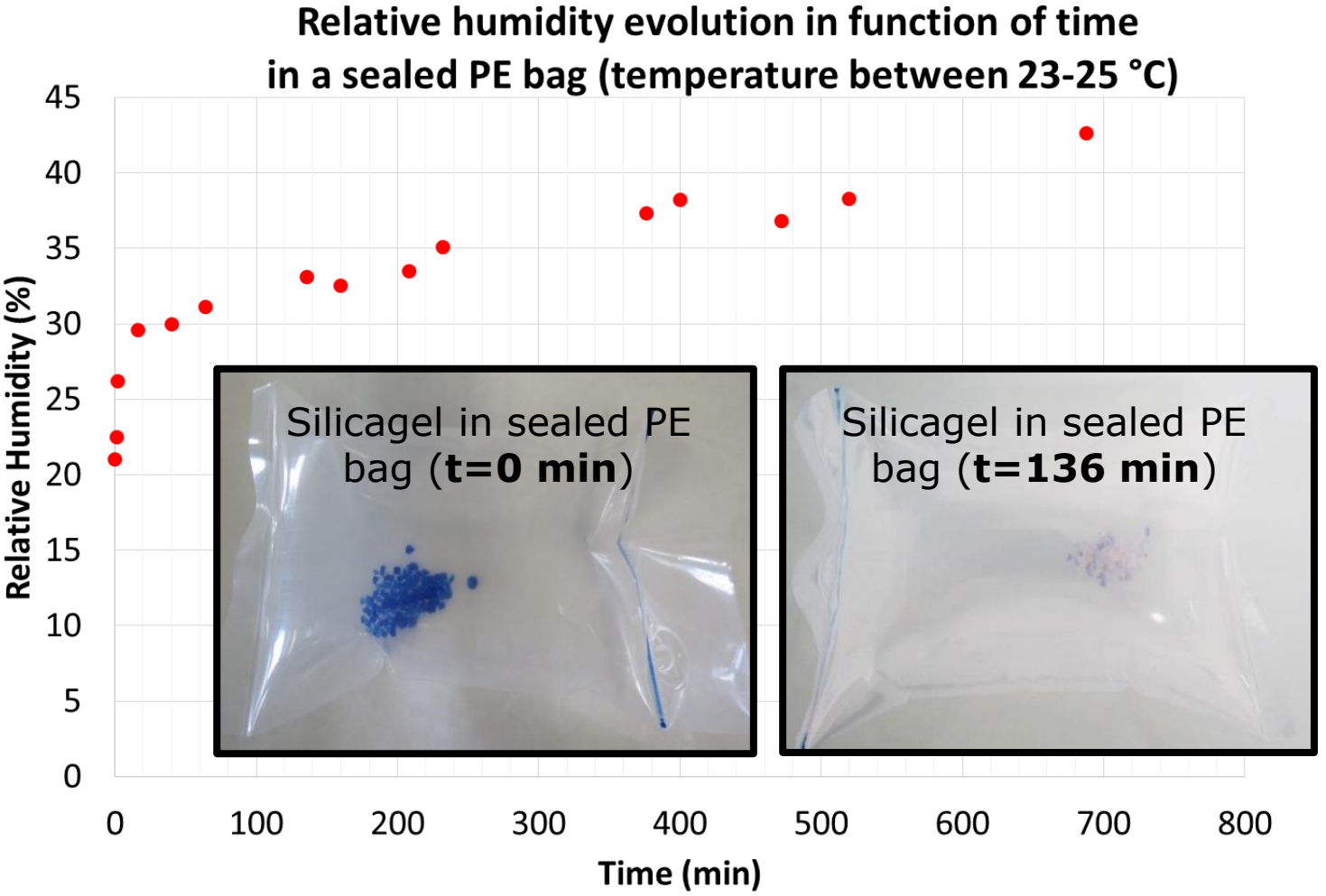


Cleanliness is not forever: Effect of storage in different packaging after cleaning



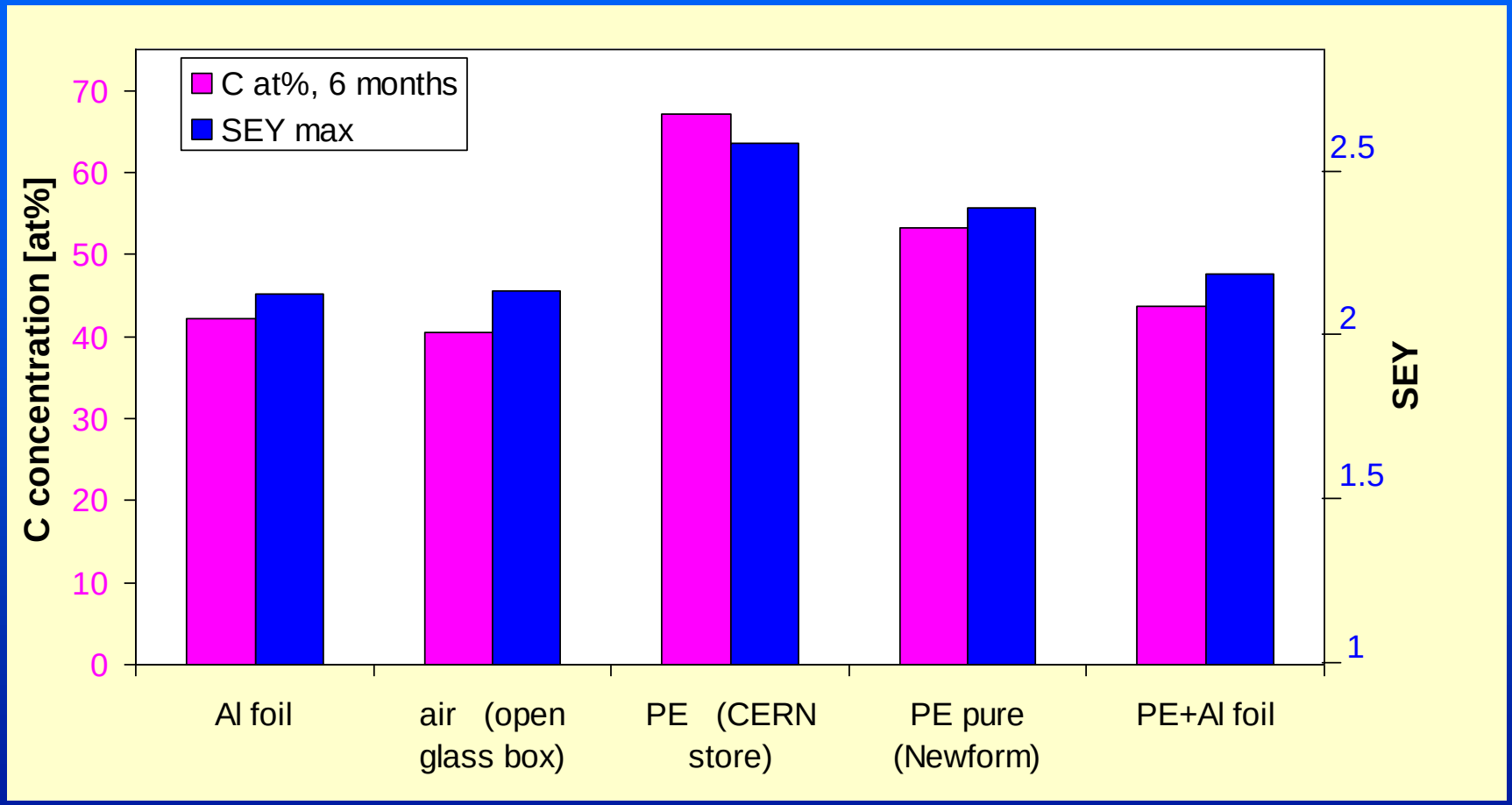
Aluminium foil is the best…but should not be used for copper parts , since it corrodes in presence of humidity

Storage and humidity: polyethylene bag



The PE bag is a good barrier against macroscopic contamination only

Influence of re-adsorbed contamination on SEY of copper



Check the cleaning procedure with your cleaning plant on your own materials
Design cleanable parts (shape, roughness,…)

Avoid undesirable compounds (halogens, silicones, Zn, Cd, BN…) in the fabrication process: even for the best cleaning procedure you will find them once at the end!

Avoid packaging in polymers in direct contact with the sample unless the polymer has been previously qualified.

All this will save time.


EVC -15
GENEVA AT WORK
CONVENTION BUREAU
European Vacuum Conference 15
In Geneva – Switzerland
from June 17 to June 22, 2018
THANK YOU AND…
SEE YOU IN GENEVA IN 2018

•References

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•Basic organic chemistry books as Atkins P., Physical Chemistry, or A. W. Adamson, Alice P. Gast , Physical chemistry of surfaces

•The effect of cleaning and other surface treatments on the vaccum properties of technological materials used in UHV, A.Mathewson, Il Vuoto vol XVII 1987, p102 and The surface cleanliness of 316 LN stainless steel studied by SIMS and XPS Vacuum 24, 0505 (1974) ; H.F.Dylla, Glow discharge techniques for conditioning high-vacuum systems, JVST A6, 1276, (1988)

•Influence of surface chemistry on the wettability of stainlesssteel, Mantel et al. Surf. Interf.An. 21, 595 (1994) : W.A.Zisman, Relation of the equilibrium contact angle to liquid and solid constitution, Contact angle, wettability and adhesion (Gould R. editor), Advances in chemistry series No43, American Chem.Soc.

•Surface cleaning efficiency measurements for UHV applications C.Benvenuti et al. Vacuum 53, 317 (1999)

•The assessment of metal surface cleanliness by XPS, C. Scheuerlein et al., Appl. Surf. Sci. *252,(2006),* 4279-4288 and references therein

•NEG experimental chamber coating procedure , S.Calatroni EDMS 607816

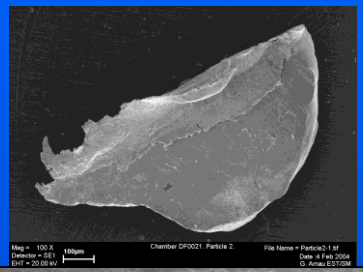
•R.J.Reid, Cleaning for vacuum service, CAS school on vacuum 1999, Snekkersteen

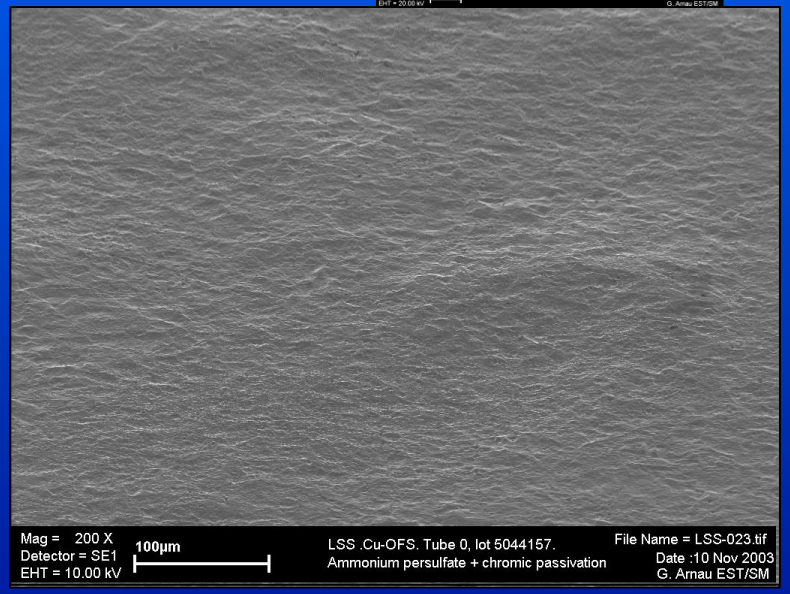
•M.Taborelli, CAS school on vacuum 2006, Platja d'Aro

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

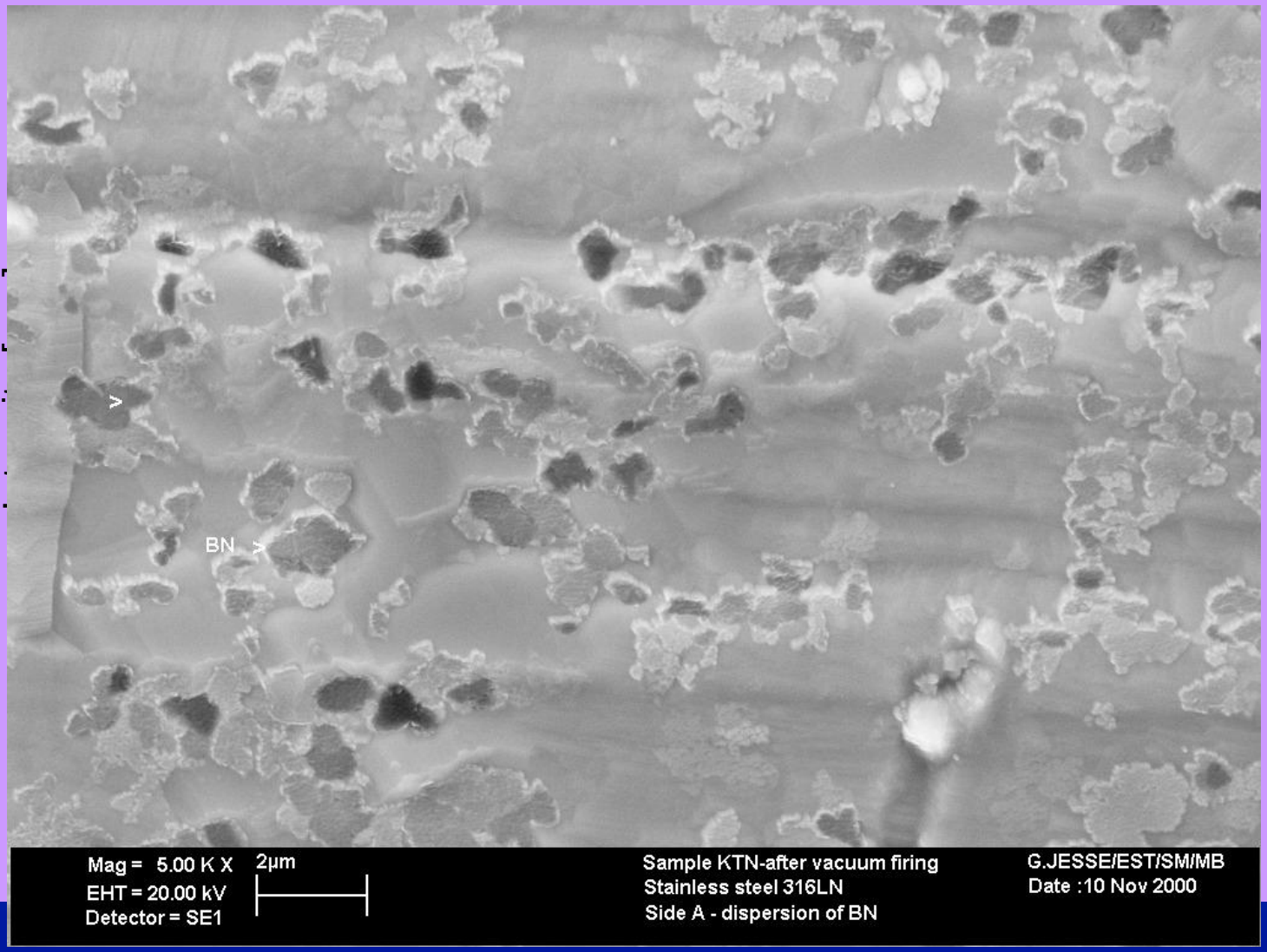
- Amiss extrusion tool did not enable draining of the copper shavings, which remained instead incrusted on the tube's surface.

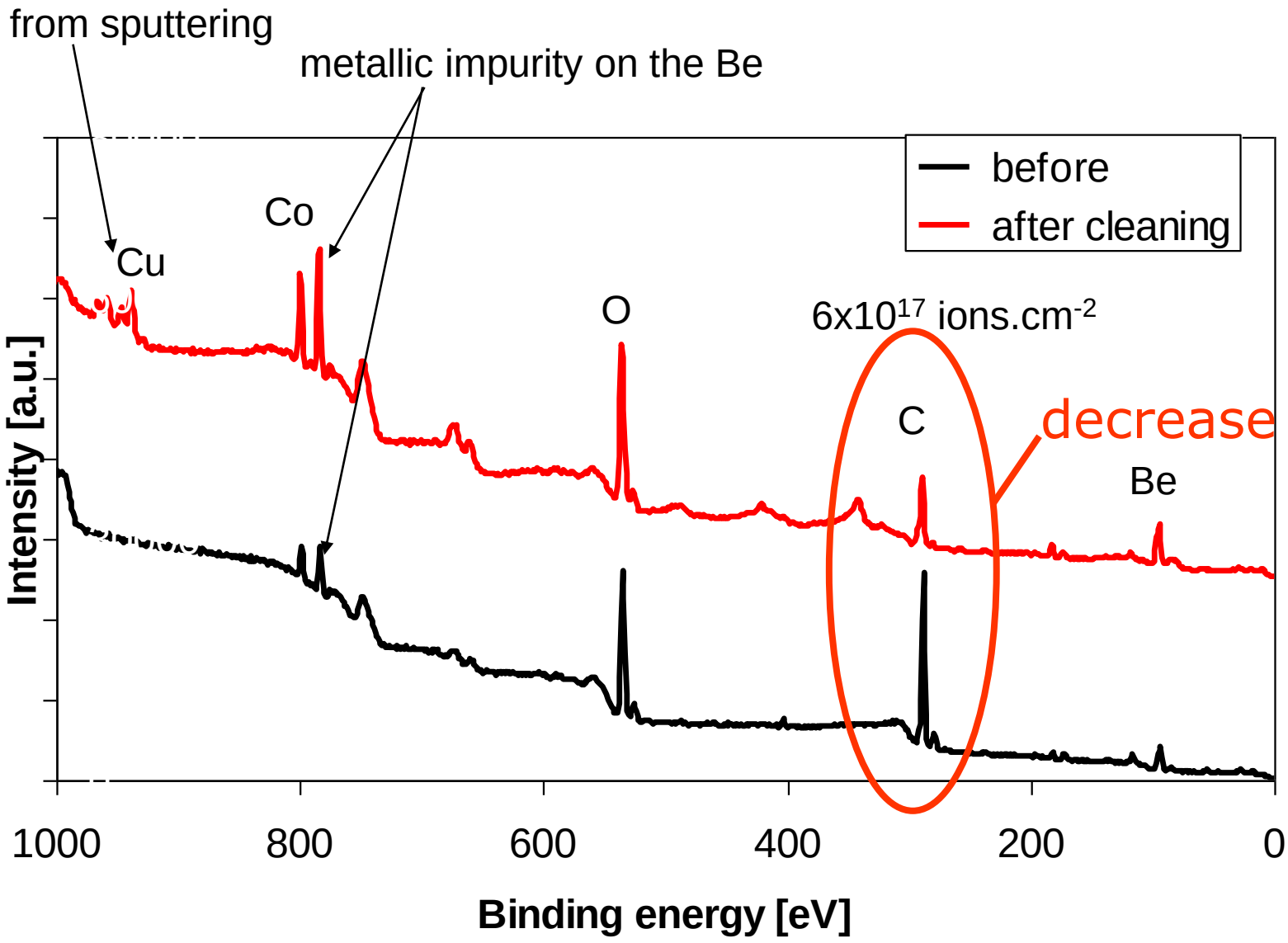




➔Mechanical removal of most of the Cu particles (Cloth and hot high pressure water jet) and chemical etching of the internal surface with ammonium persulphate (about 60µm) + chromic acid passivation and rinsing

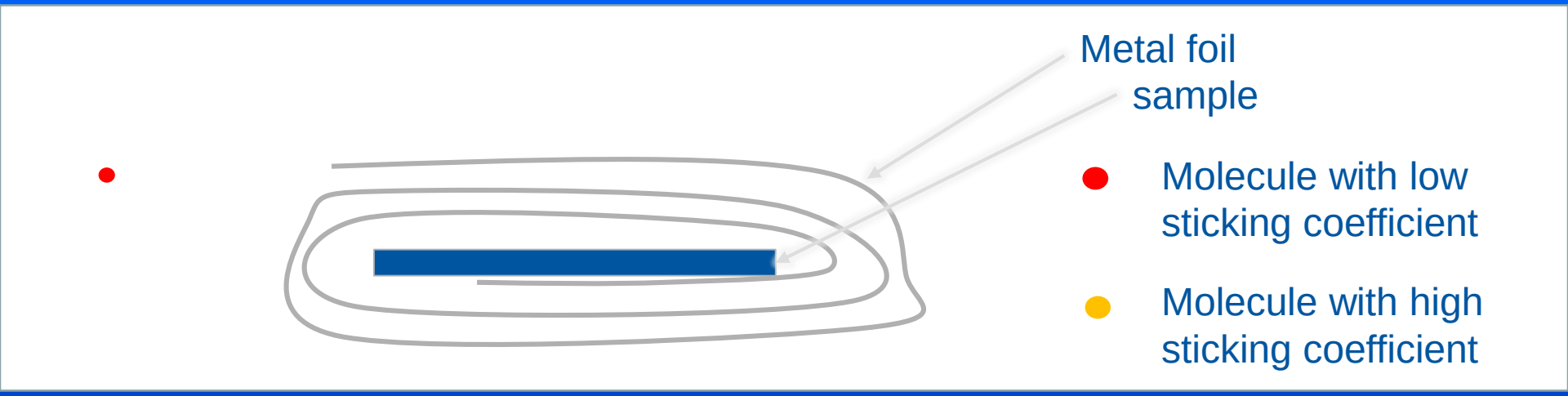
Uncleanable contaminant: BN




from sputtering
metallic impurity on the Be
Cu
Co
O
C
Be
6x10^17 ions.cm^-2
decrease
before
after cleaning
Intensity [a.u.]
1000
800
600
400
200
0
Binding energy [eV]

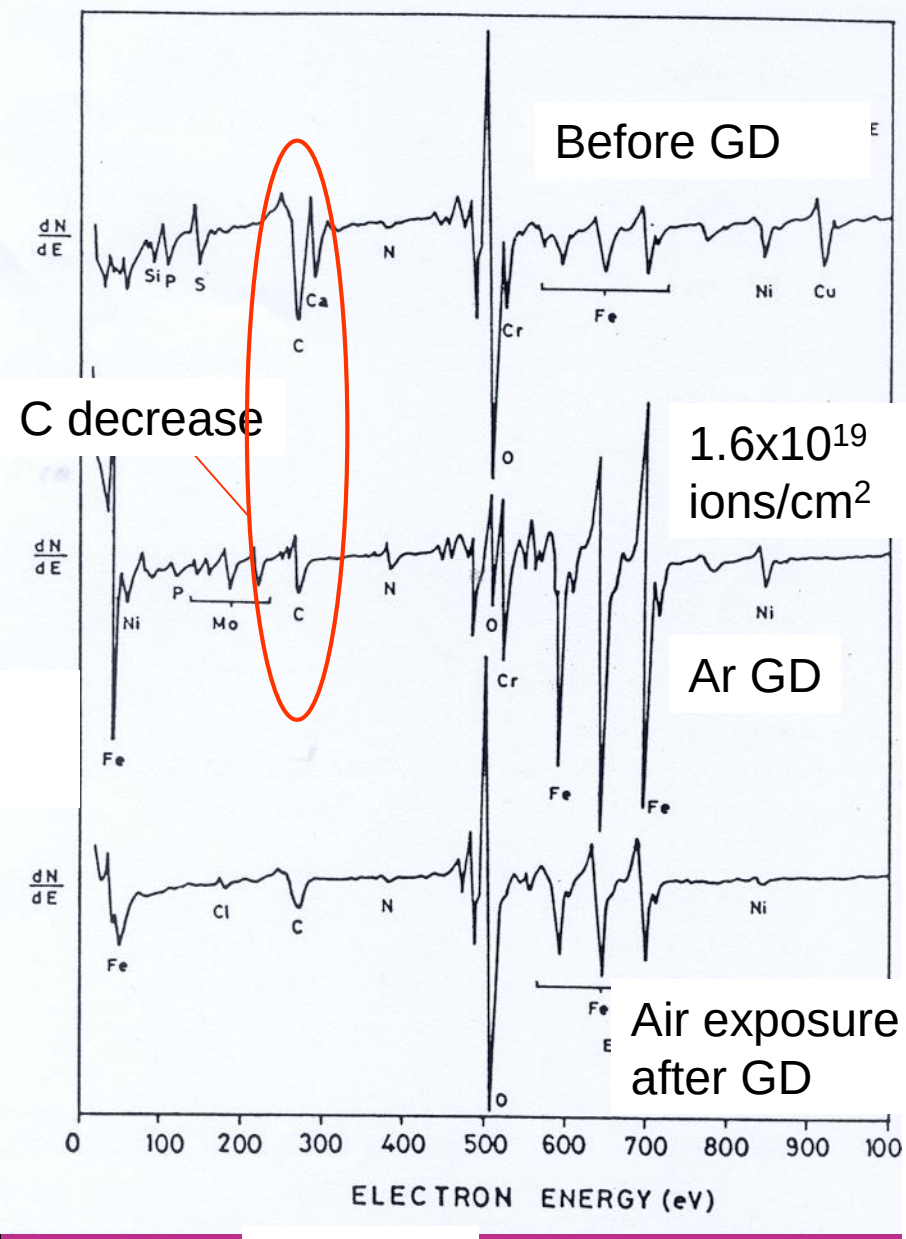
Why is contamination stopped by aluminium foil ?

Aging is strongly retarded by packaging in metal foil (aluminium or stainless steel), which is not tight to gas

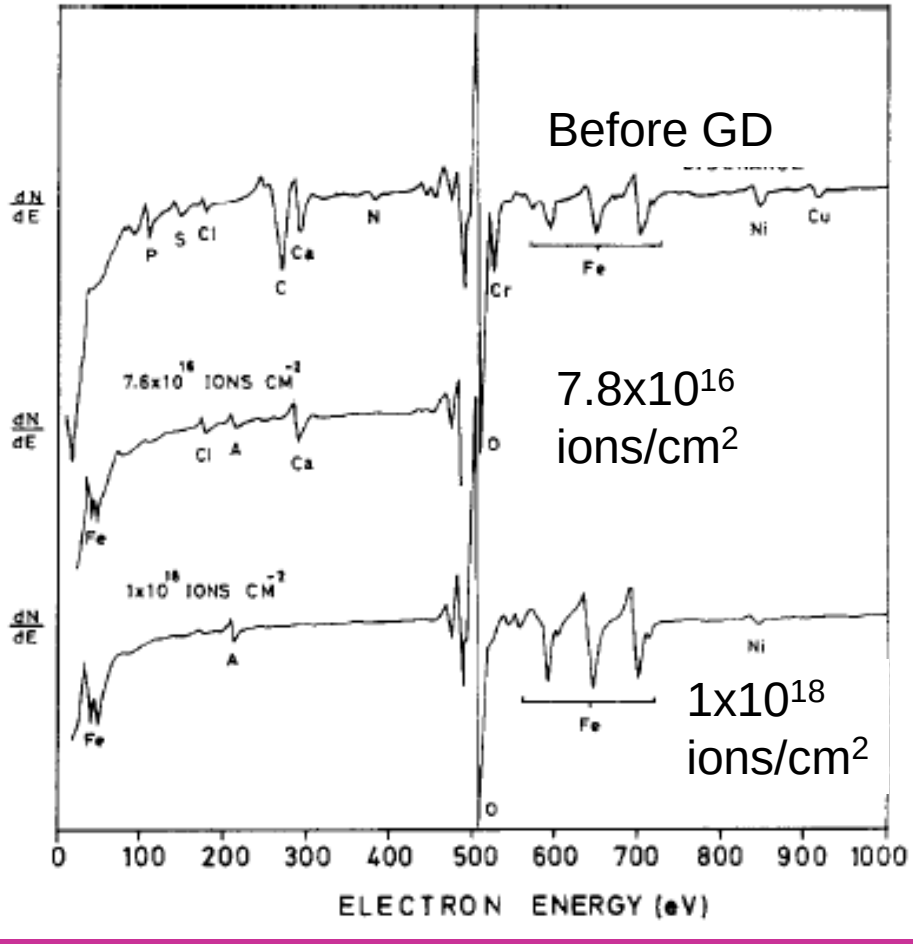


A molecule with low sticking coefficient can go very far in a small conductance. A molecule with high sticking coefficient will adsorb immediately and never reach the sample surface.
The metal foil protects from molecules with high sticking coefficient, like heavy hydrocarbons.
NB: This is strictly valid only in molecular regime, but also in viscous flow in the absence of drag (if the collisions with the gas can be "mimicked" by a reduced sticking coefficient)

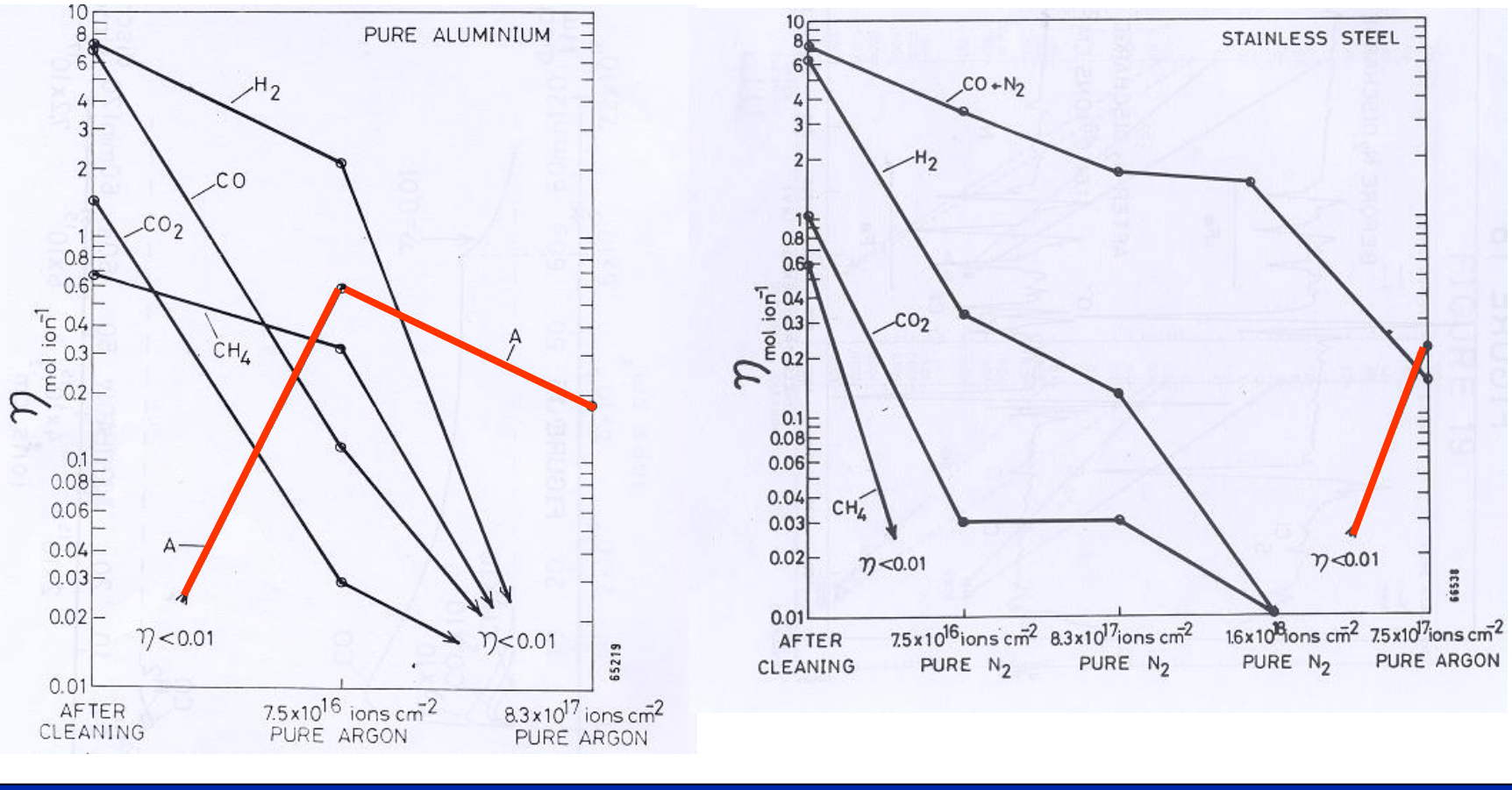
Auger spectra before/after GD on 316LN



A.Mathewson,Vacuum 24, 505, 1974



Ion stimulated desorption (by N_2^+, 2KeV): Ar desorption after Ar GD



A.Mathewson, CERN-ISR-VA/76-41 and il Vuoto vol XVII 1987, p102

CO_2 as environmental friendly solvent:

CO_2 snow:

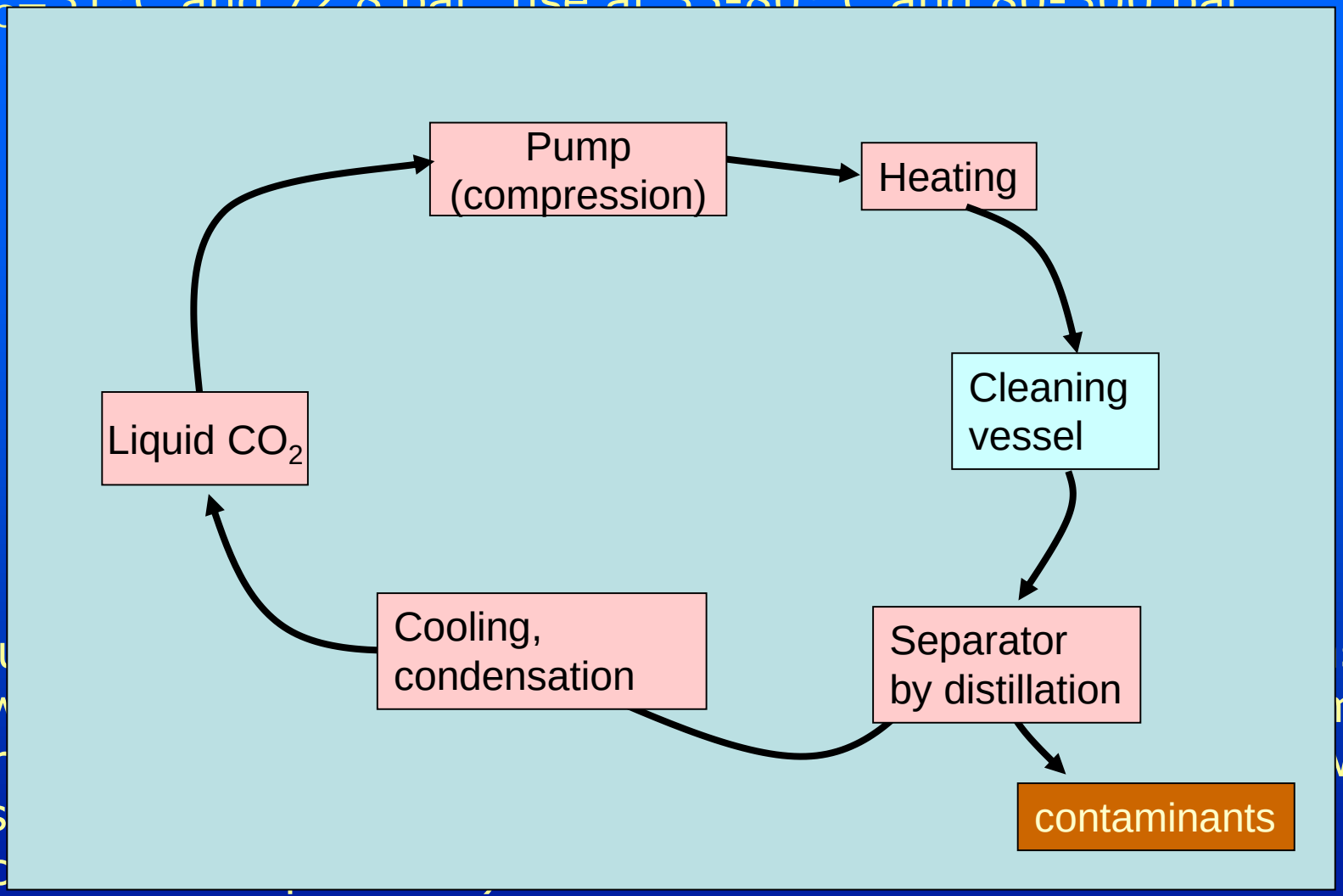
-jet spray of liquid CO_2 which condenses in solid clusters: mixture of gas and snow; by landing on the surface it builds a liquid film which dissolves contaminants

- CO_2 is non-polar, dissolves alkanes (but less effective for long chains >20) and silicones; not very effective for molecules with C=O, COOH polar groups, bad for contaminants forming drops on the surface

-to be used by keeping the workpiece warm to avoid condensation of contaminants on its surface (from environment atmosphere)

Supercritical CO_2 (SCCO2):

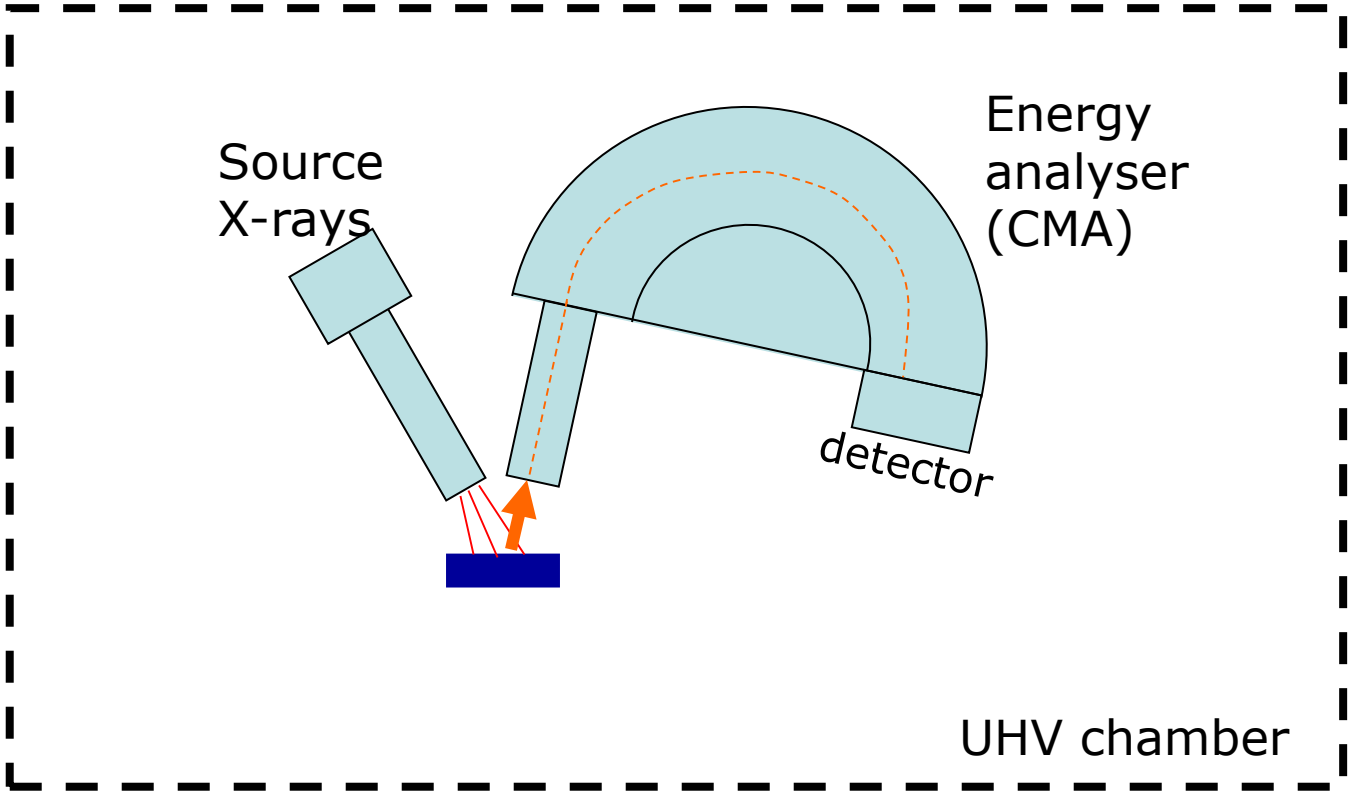
-T_c=31°C and 72.8 bar; use at 35-80° C and 80-300 bar



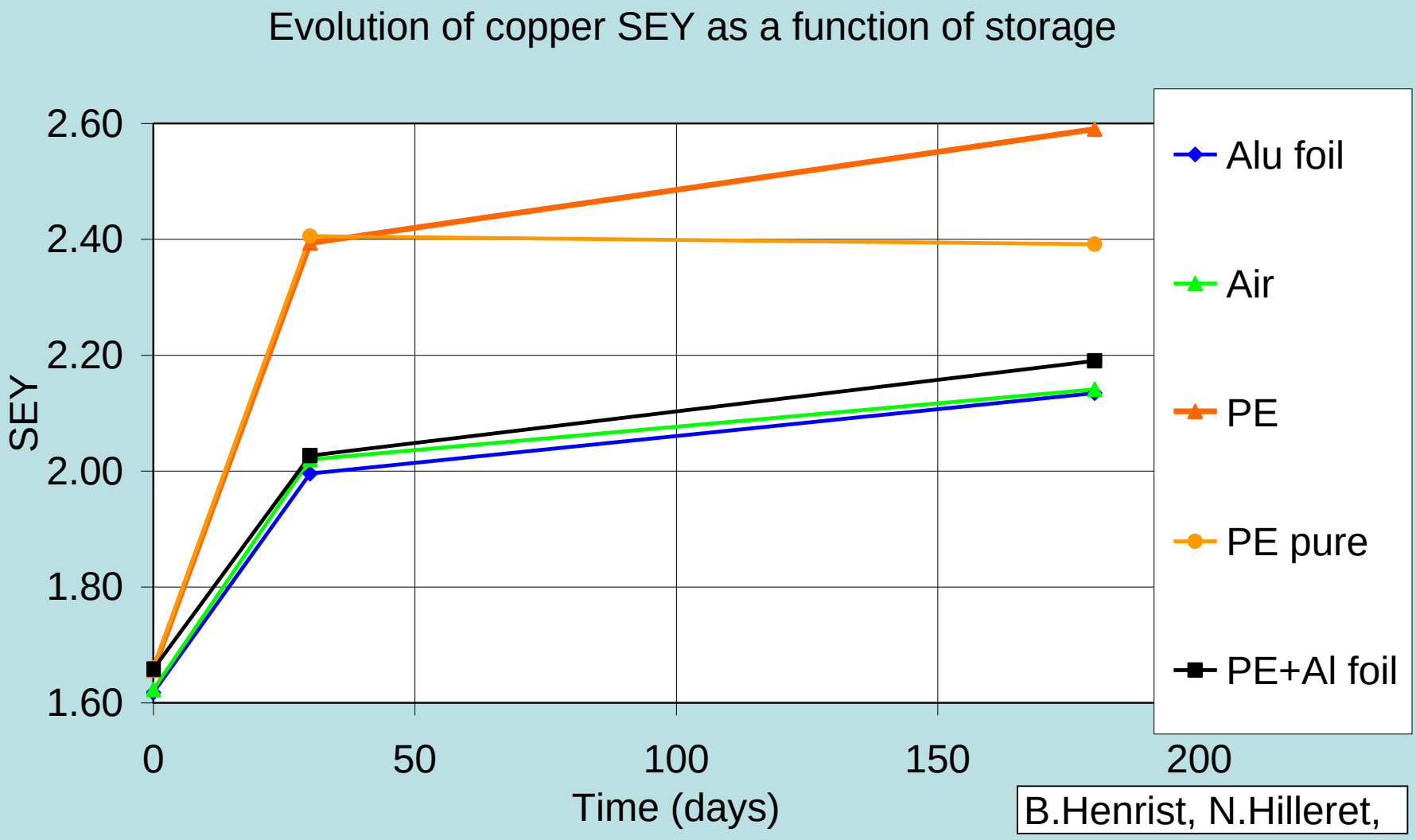
-Su… …se:
low… …m^2
for… …ver
vis…
inc…

- can be used with co-solvents or soluble surfactants to dissolve polar molecules and ionic species

XPS principle



Effect on secondary electron yield



Pumping speed results