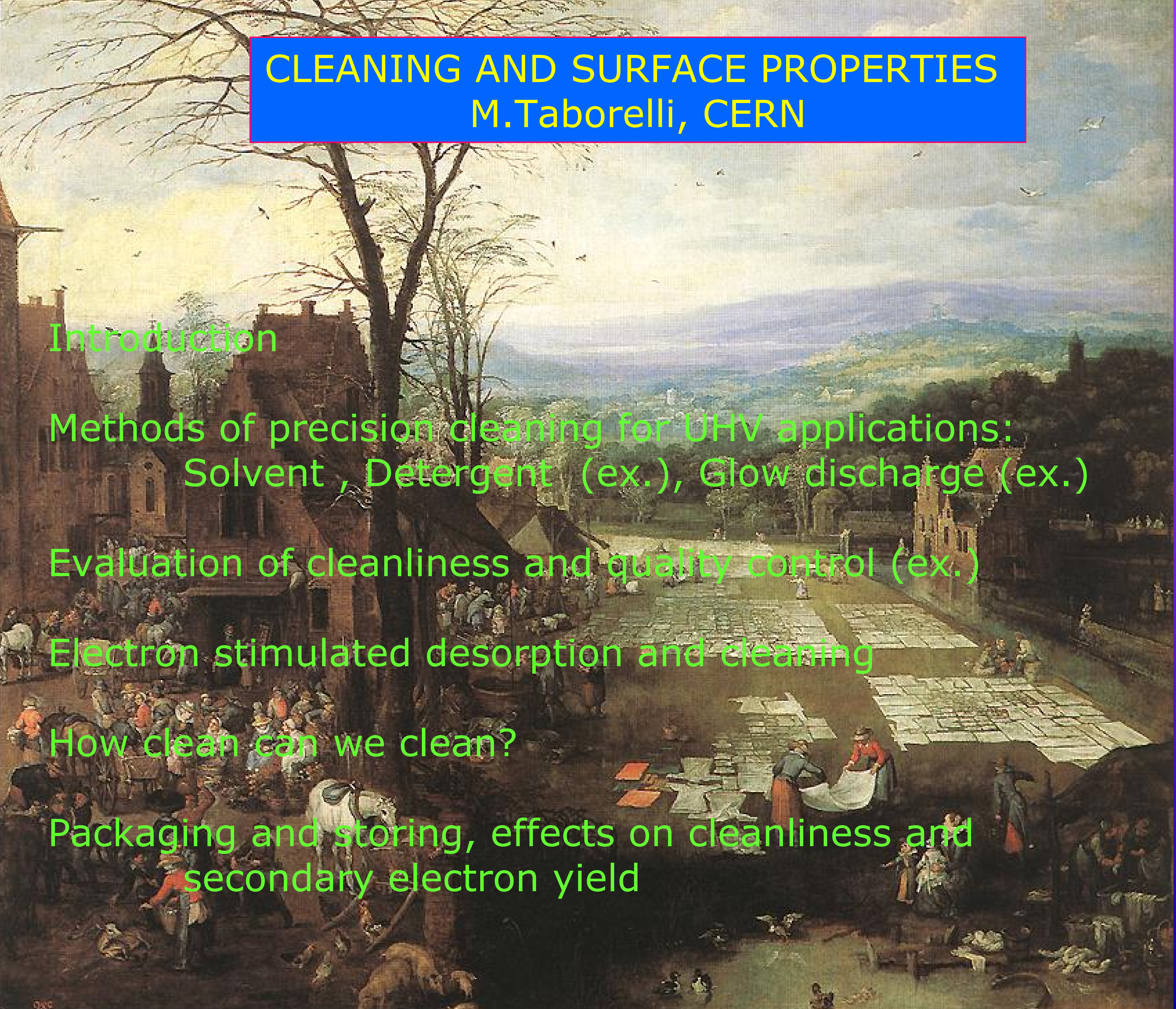
CLEANING AND SURFACE PROPERTIES

M.Taborelli, CERN



Introduction

Methods of precision cleaning for UHV applications:
Solvent , Detergent (ex.), Glow discharge (ex.)

Evaluation of cleanliness and quality control (ex.)

Electron stimulated desorption and cleaning

How clean can we clean?

Packaging and storing, effects on cleanliness and secondary electron yield

Introduction

The definition of cleanliness depends on the application

Some of the relevant contaminants for UHV systems are:

-In general “intermediate vapour-pressure” compounds adsorb and provoke long lasting static outgassing

-Various hydrocarbons (oils, lubricants and so on from fabrication process) are bad for static and also dynamic vacuum

-Corrosion inducing elements and compounds (halogens, sulphur.....)

-In some cases silicones (insulating layer of SiO_2 deposits on electrical contacts upon irradiation)

-Surface contaminants generally worsen wettability of the surface and adhesion of further coatings

NB: Classical cleaning > 1 $\mu g/cm^2$
Precision cleaning <1 $\mu g/cm^2$

Cleaning by solvent:

Principle :

Solvation of a solute by the solvent which is favoured by Gibbs free energy: entropy driven (diffusion) but controlled by the molecular interaction strength for solute-solute (precipitation) which must not be too strong compared to solute-solvent

Interactions:

- Ionic (ions in water)
- Hydrogen bonds ($H^{+\delta}\cdots O^{-\delta}$, $H^{+\delta}\cdots N^{-\delta}$, …)
- Hydrophilic/phobic: hydrophilic molecules have polar groups and can in general form hydrogen bonds with water molecules
- Hydrophobic effect: solvation of hydrophobic molecules is hindered by entropy since it requires an "ordered" arrangement of water around those molecules

All this was for water…but in most of the other solvents:

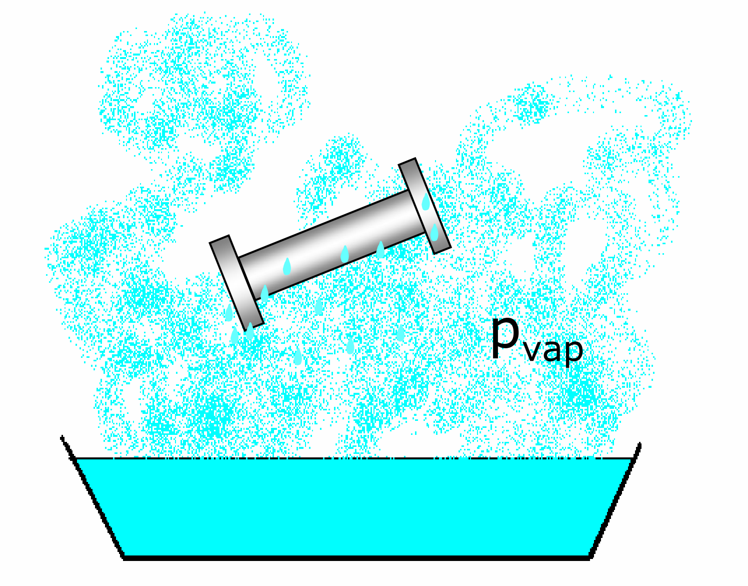
- Van der Waals: orientation (polar molecules), induction (polar vs non polar), dispersion (polar and non-polar).
  "like with like", interaction of A in medium B is $E_{AA} \sim (n_A^2 - n_B^2)^2$

Degreasing procedures

By immersion:
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:

- -Heat the bath of solvent to get sufficiently high vapour pressure
- -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 recycling bath



solvent

Without immersion:

- ☺ the solvent is continuously distilled and purified
- ☺ ideal for gross degreasing before further steps
- ☹ needs adapted plant to avoid loss of solvent (avoid species harmful for the environment)

☺ both procedures are suitable for parts with complex shape (bellows), porous materials (ceramics, composites…) which cannot be easily rinsed or dried, and cannot sustain aqueous cleaning

☹ "like with like" only, for a given solvent solubility and cleaning efficiency are contaminant dependent

Ex: CO_2 (see later), CCl_2=CCl_2 (not recommended), commercial brands (ex: aliphatic+alcohol+ additives, liquid at RT, Pvap= 6 mbar at 50C, 97%volatile)

CO_2 an environmental friendly solvent:

CO_2 snow:

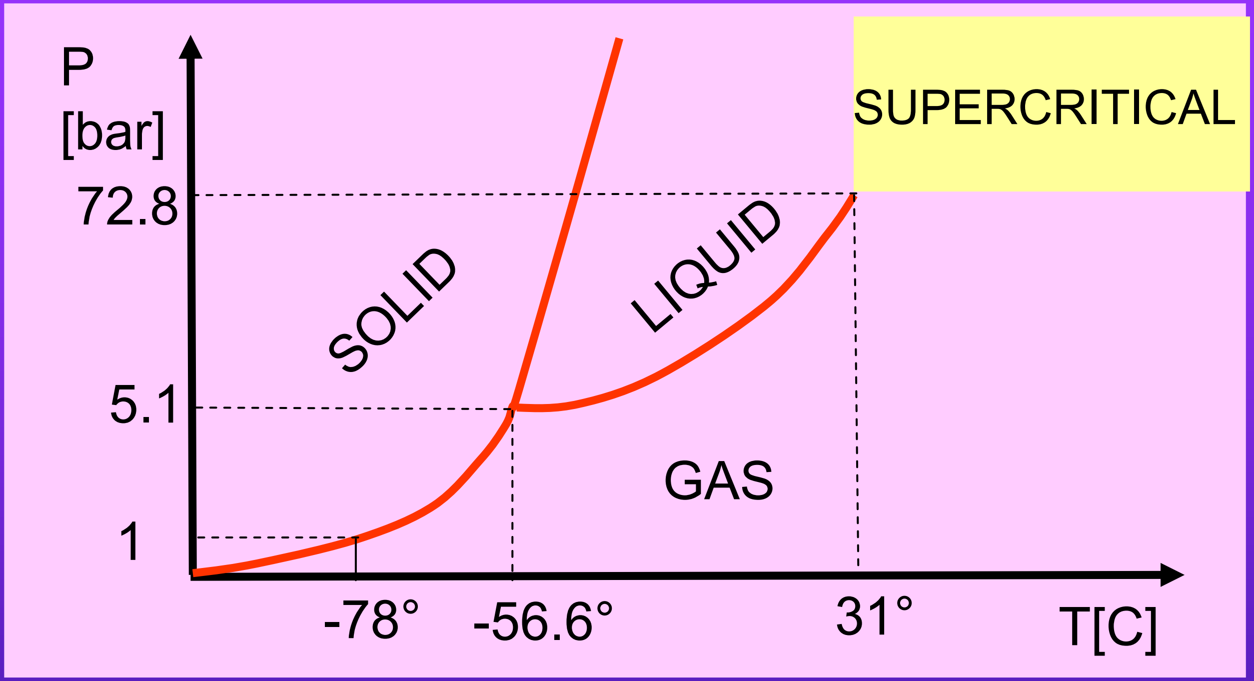
-jet spray of liquid CO_2 which condenses in solid clusters: mixture of gas and snow; by landing on the surface it builds a liquid film which dissolves contaminants

- 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)

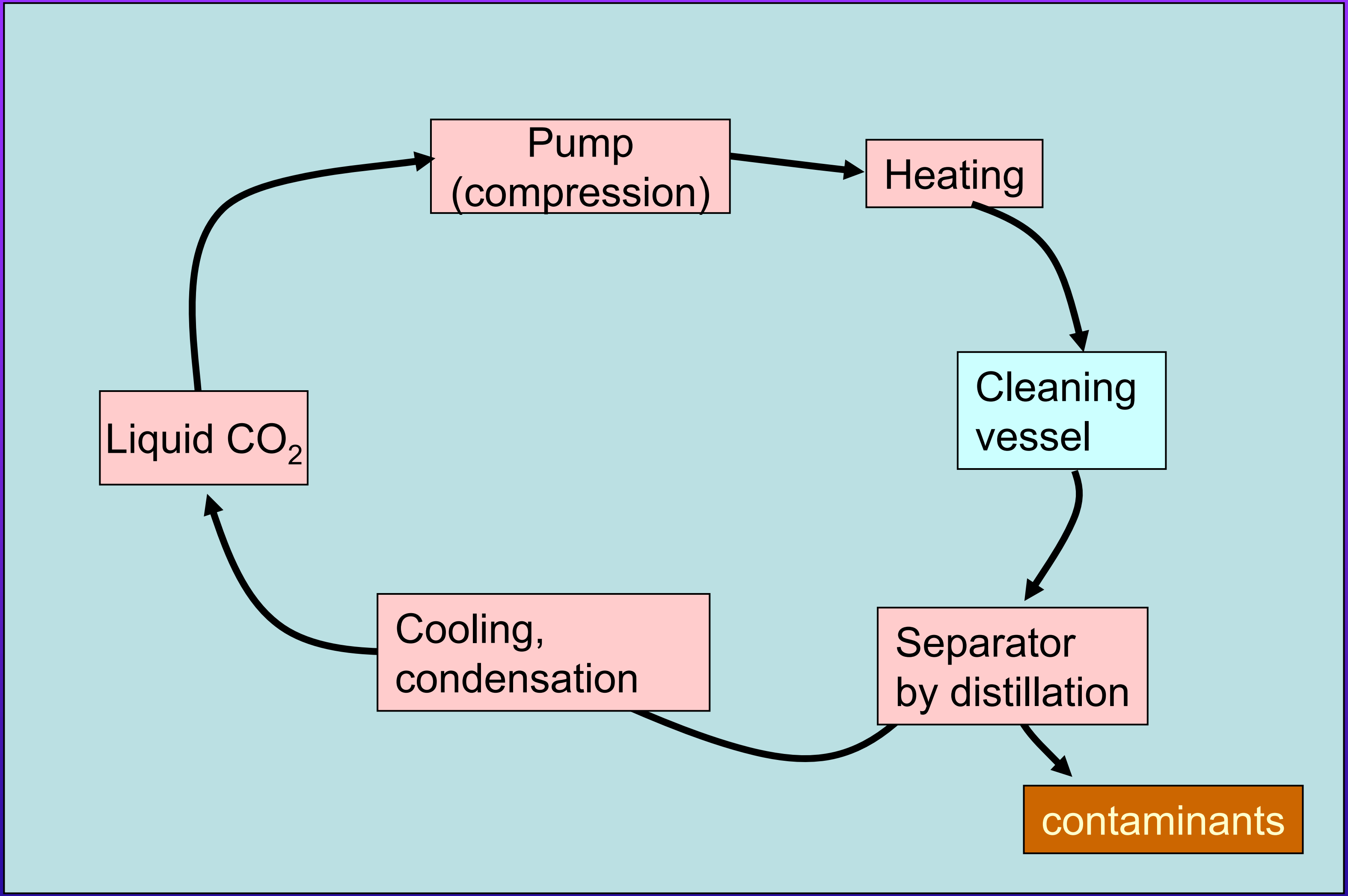
Supercritical CO_2 (SCCO2):

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



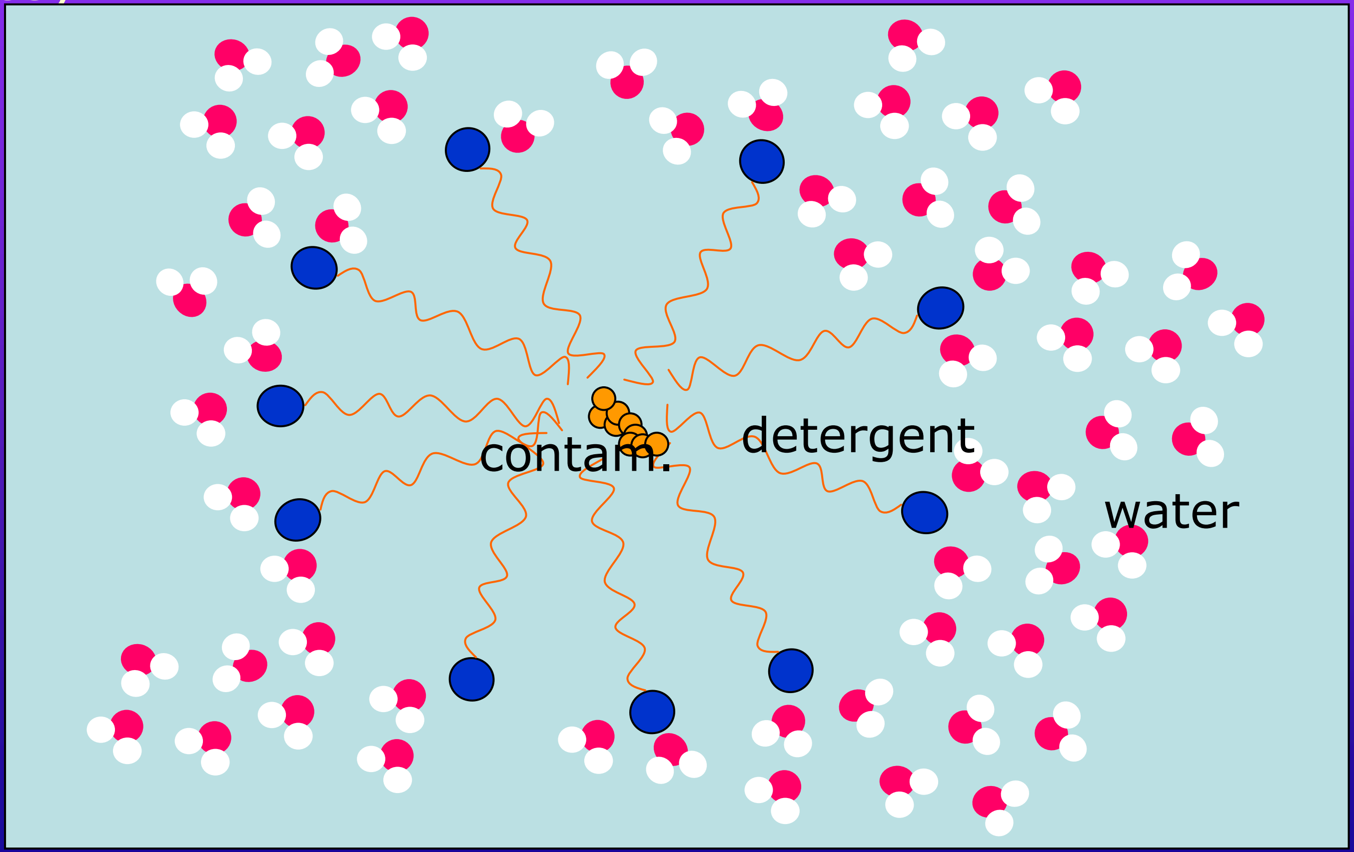
-Supercritical fluids wet a surface more easily than liquid phase: lower surface tension (1 mJ/m^2 for CO_2 compared to 32 mJ/m^2 for perchlorethylene and 72 mJ/m^2 for water) , 100 times lower viscosity and similar solubility as liquid phase (solubility increases with pressure)

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


Pump (compression)
Heating
Cleaning vessel
Separator by distillation
contaminants
Cooling, condensation
Liquid CO_2

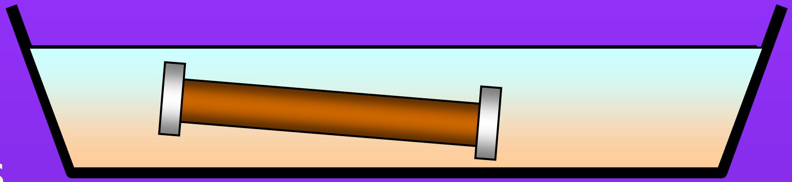
Cleaning with detergents in water

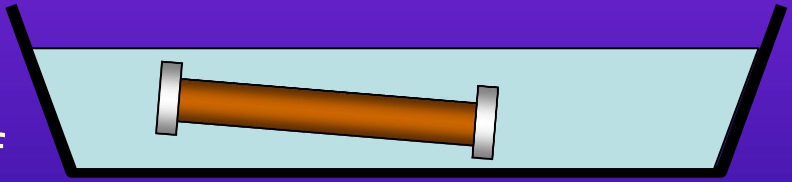
Principle: a detergent can wet any surface (is a surfactant): amphiphilic molecule with polar head and non-polar tail, soluble in water and organic solvents, can incorporate the hydrophobic material which can thus be dissolved (formation of micelles)

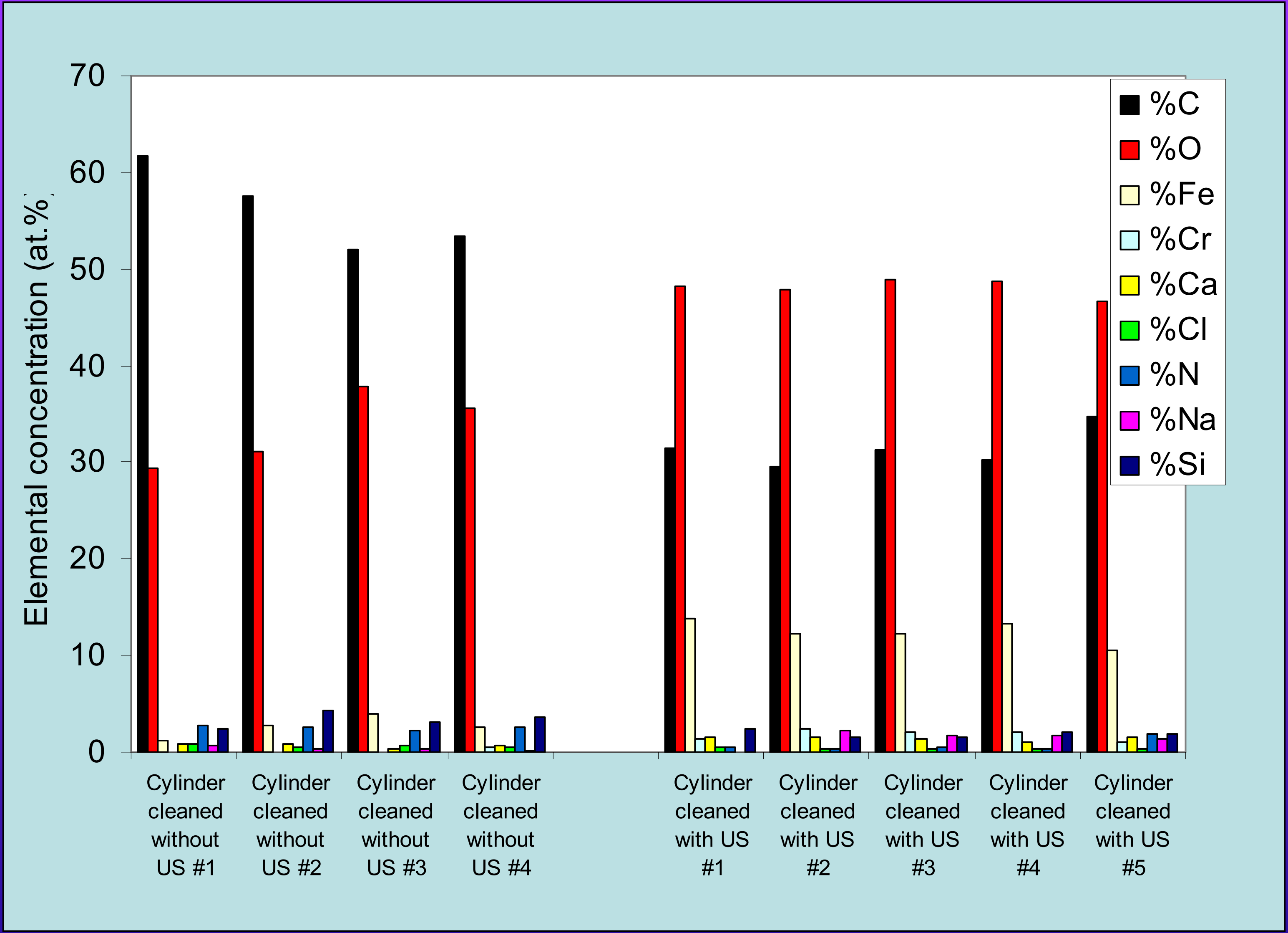


Detergent cleaning procedure

water and
detergent bath
+
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 verification of wetting of
the surface by the rinsing water is
a simple, but effective control
+
Drying in oven 80°-100°C (possible for small parts only
and suitable materials) or dry nitrogen (filtered)







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detergent

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

☹ pH is not neutral, surface can be oxidized, surface oxides and some alloys (brazing, NEG) can be slightly etched; at best test for your workpiece material

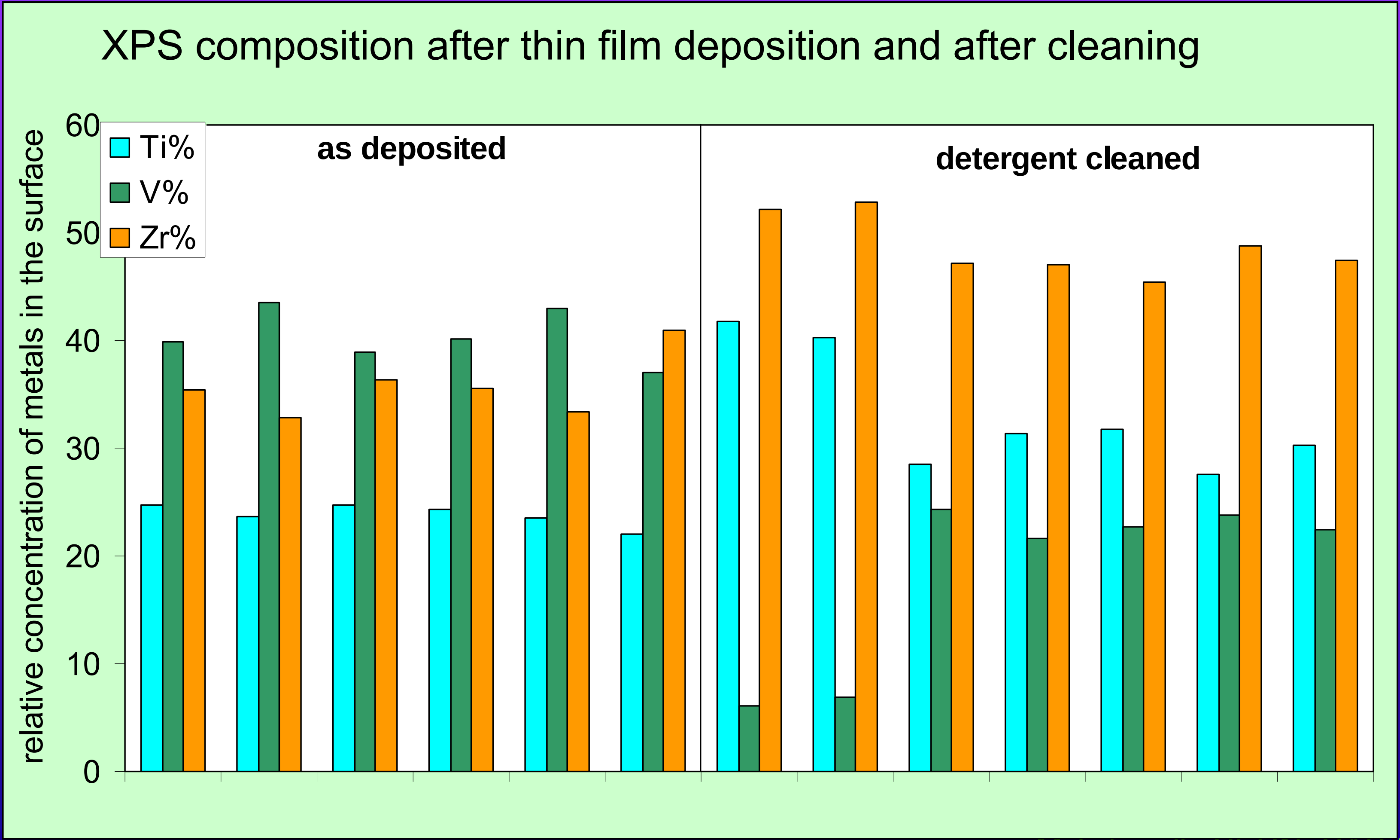
☹ it is difficult to eliminate silicones, since they float on the bath surface and are recollected by the workpiece

NB:
-time and ultrasound power is function of contamination amount, part shape, brittleness, surface roughness, vessel size
- bath quality must be monitored (conductivity, pH, concentration of detergent to be effective) as frequently as the use requires it; it is effective to filter and recycle

Ex.

Test of cleaning TiZrV NEG with alkaline detergent:

Depletion of vanadium at the surface, presence of silicates, deterioration of activation properties:



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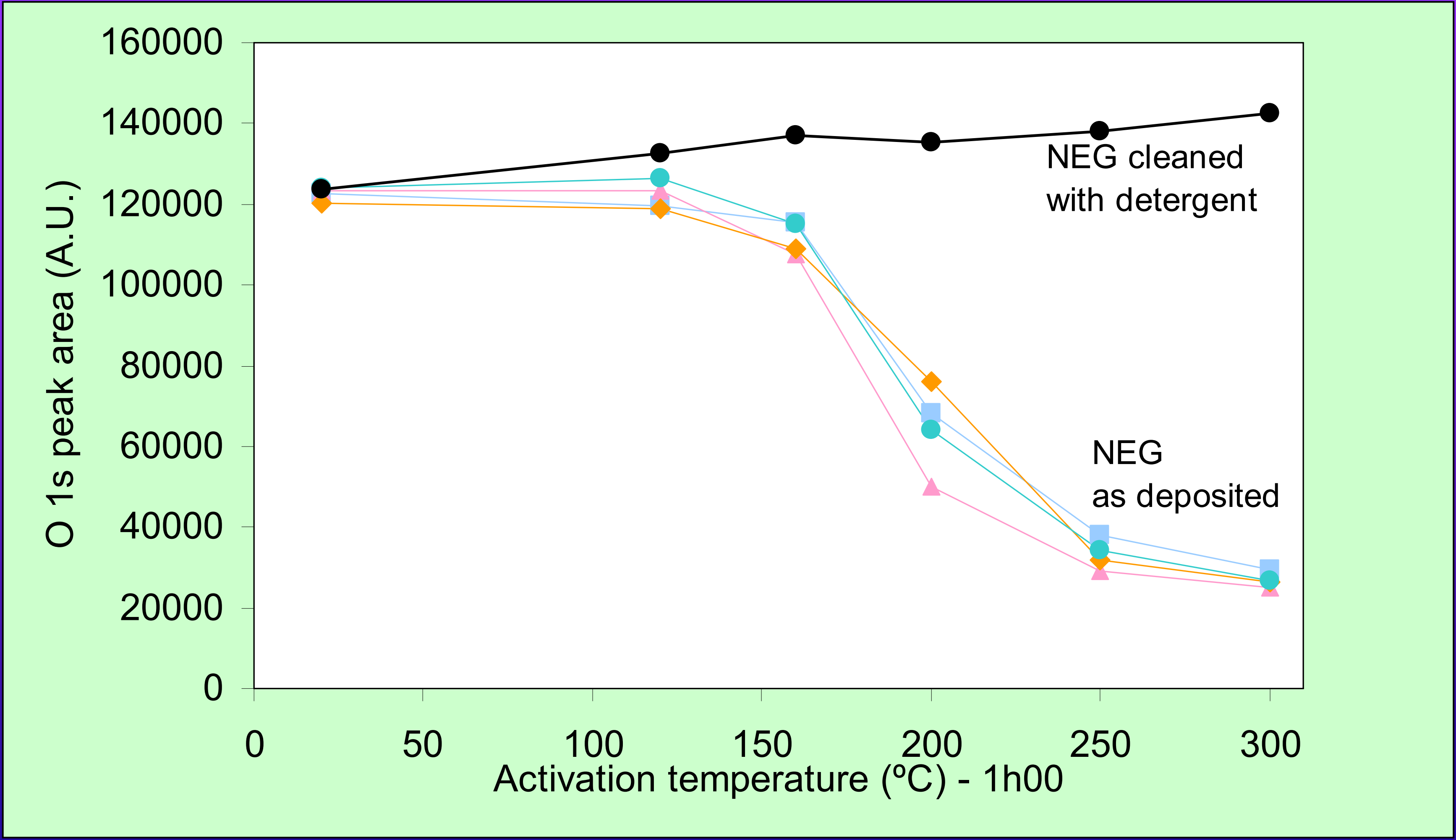

160000
140000
120000
100000
80000
60000
40000
20000
0
O 1s peak area (A.U.)
0
50
100
150
200
250
300
Activation temperature (ºC) - 1h00
NEG cleaned
with detergent
NEG
as deposited

Ex.

Uncleanable contaminant: BN

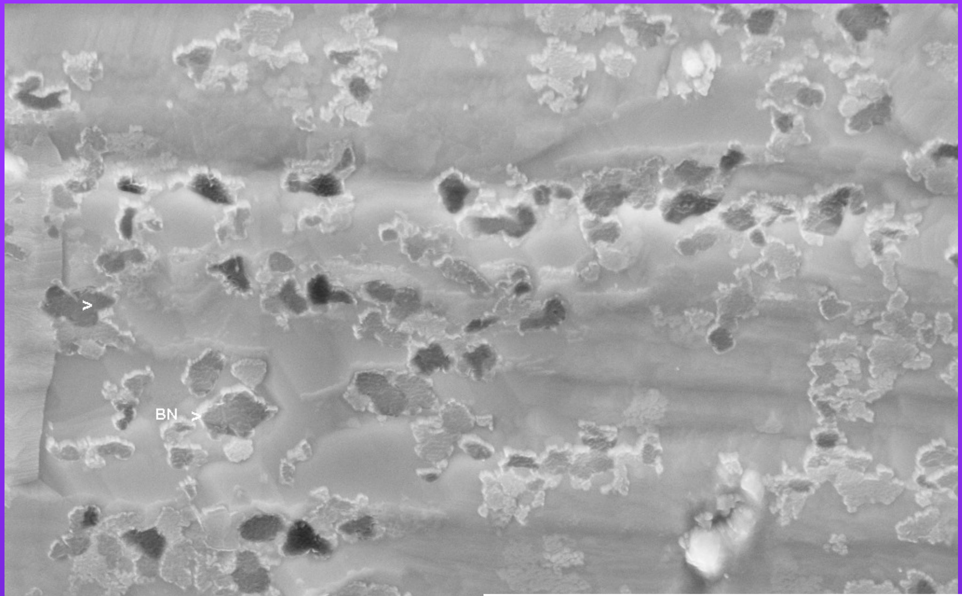
-B segregates to the surface from stainless steel 316LN upon vacuum firing (950°C) and BN precipitates upon cooling (it is introduced in steel to increase hot workability)

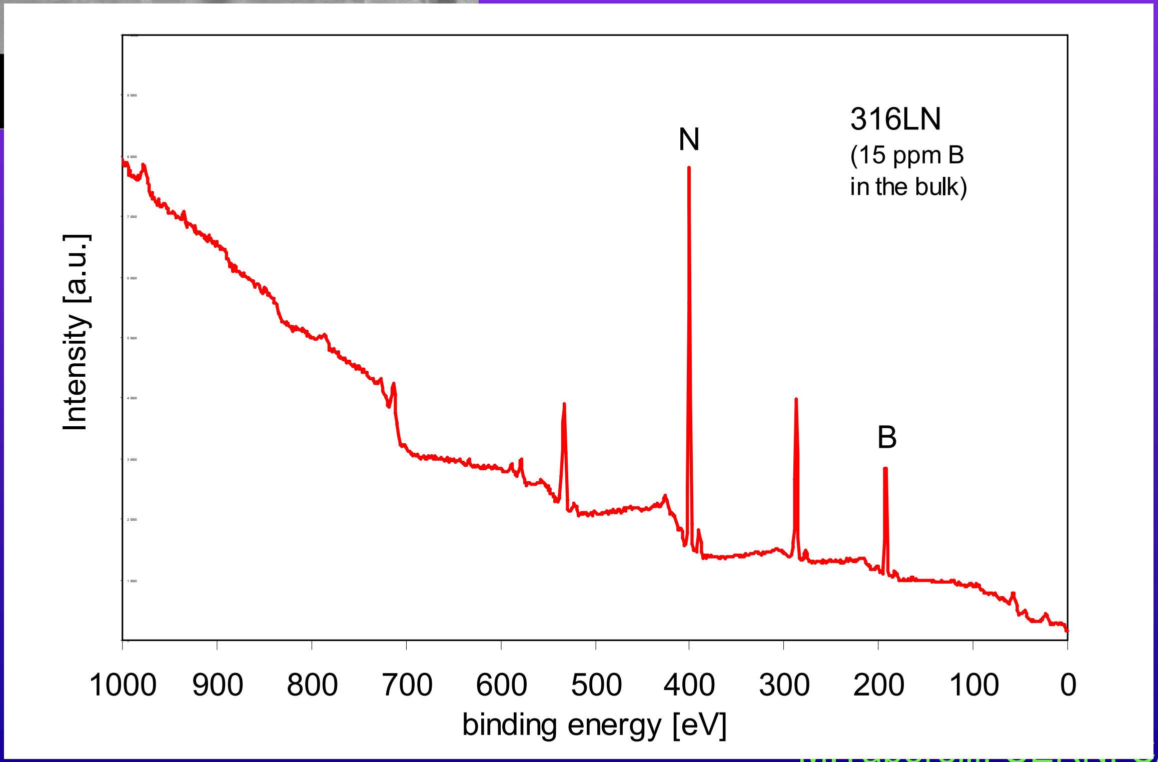
-Boron nitride is not removed by usual detergents

-It is not bad for vacuum, but it is insulating, hydrophobic, with low surface energy and adherence to the steel surface (any coating will not adhere and will readily delaminate)

- we found (S.Sgobba et al.) it only in in 316LN having sufficient B (≥ 9 ppm); MnS precipitates could act as possible nucleation sites

- is removed by electropolishing the surface


>
BN >
Mag = 5.00 K X
EHT = 20.00 kV
Detector = SE1
2µm

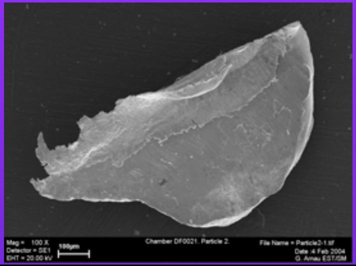

316LN
(15 ppm B
in the bulk)
N
B
Intensity [a.u.]
1000
900
800
700
600
500
400
300
200
100
0
binding energy [eV]

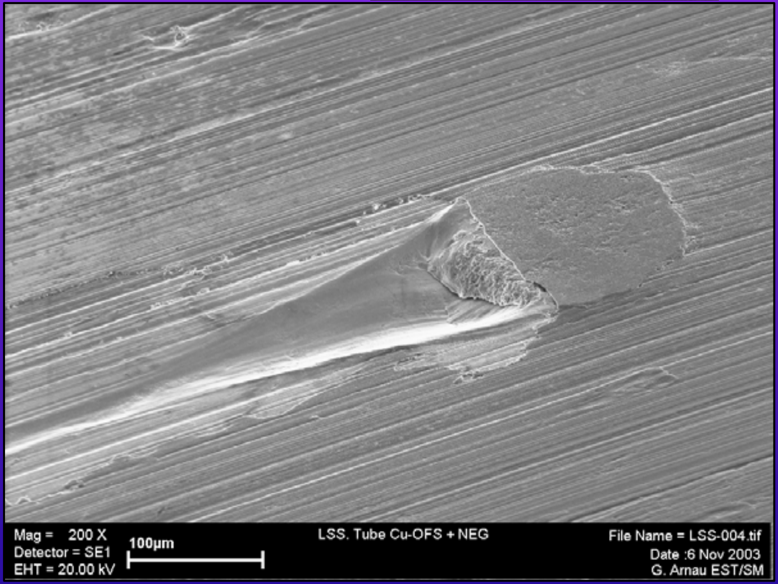
Only detergent and solvent cleaning was discussed here, but also chemical etching, electropolishing, passivation…….are widely used

A difficult case: extruded copper pipes

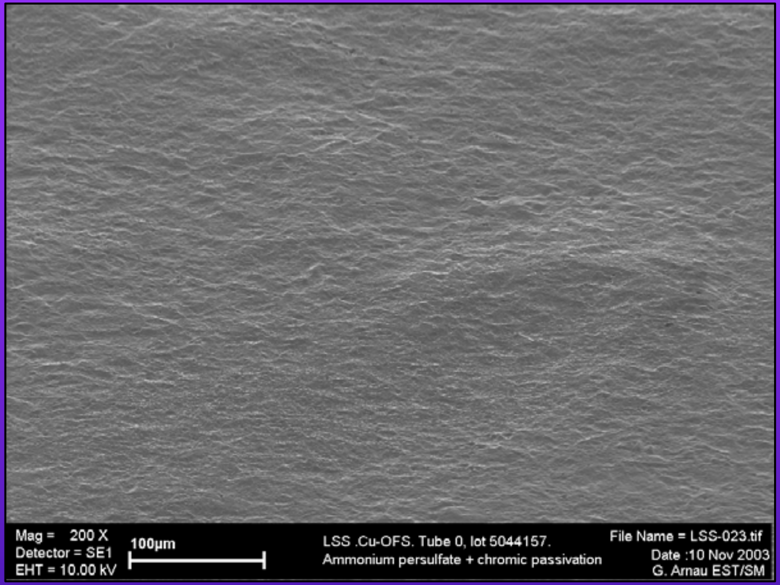
Copper pipes for a UHV chamber designed to receive NEG surface coating showed peel off of the coating and metallic particle residues

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



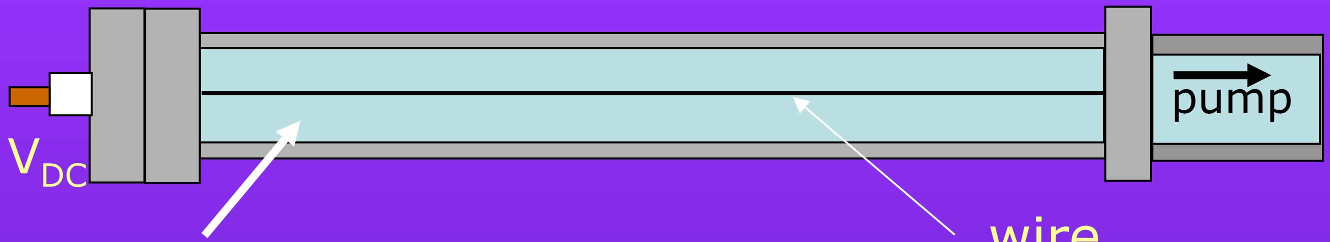


➔Mechanical removal of most of the Cu particles (Cloth and hot high pressure water jet) and chemical etching of the internal surface with ammonium persulphate (about 60µm) + chromic acid passivation and rinsing



After degreasing: Glow discharge cleaning

In DC or RF (requires more complex setup),see A.Mathewson and F.Dylla



Mechanism: sputter cleaning of the chamber walls

Gas: -Ar, some implantation of Ar in the wall (eliminate by baking at 350°C in StSt)

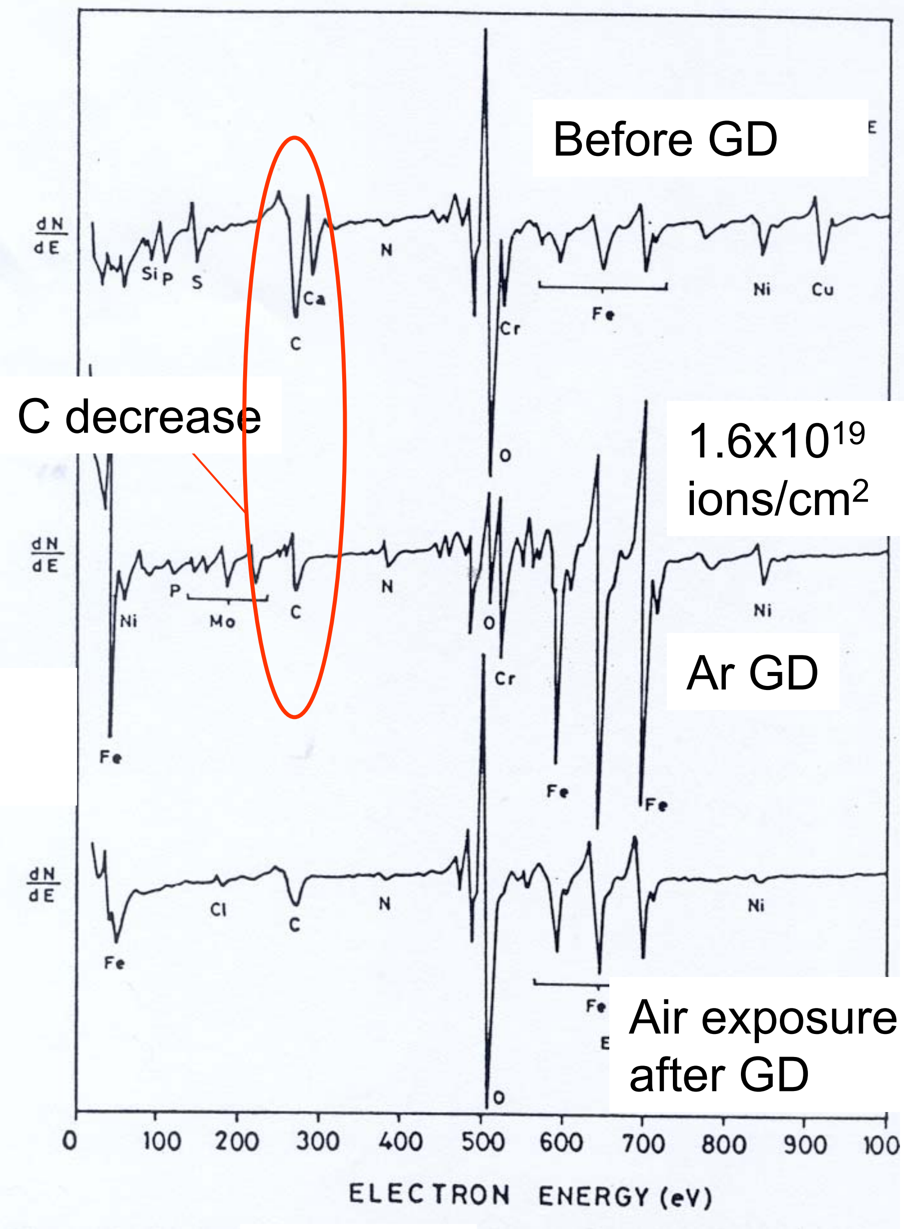
-Ar+5-10% O_2, more effective to eliminate carbon surface contamination by oxidation (forms volatile CO, CO_2 which are pumped)

- He, H_2, mainly for fusion reactor walls, not usual UHV systems

On StSt, Al, Cu, Ti and….Be.

Problem: possible coating of insulators with sputtered metal

Auger spectra before/after GD on 316LN



Before GD

C decrease

$1.6x10^{19}$ ions/cm^2

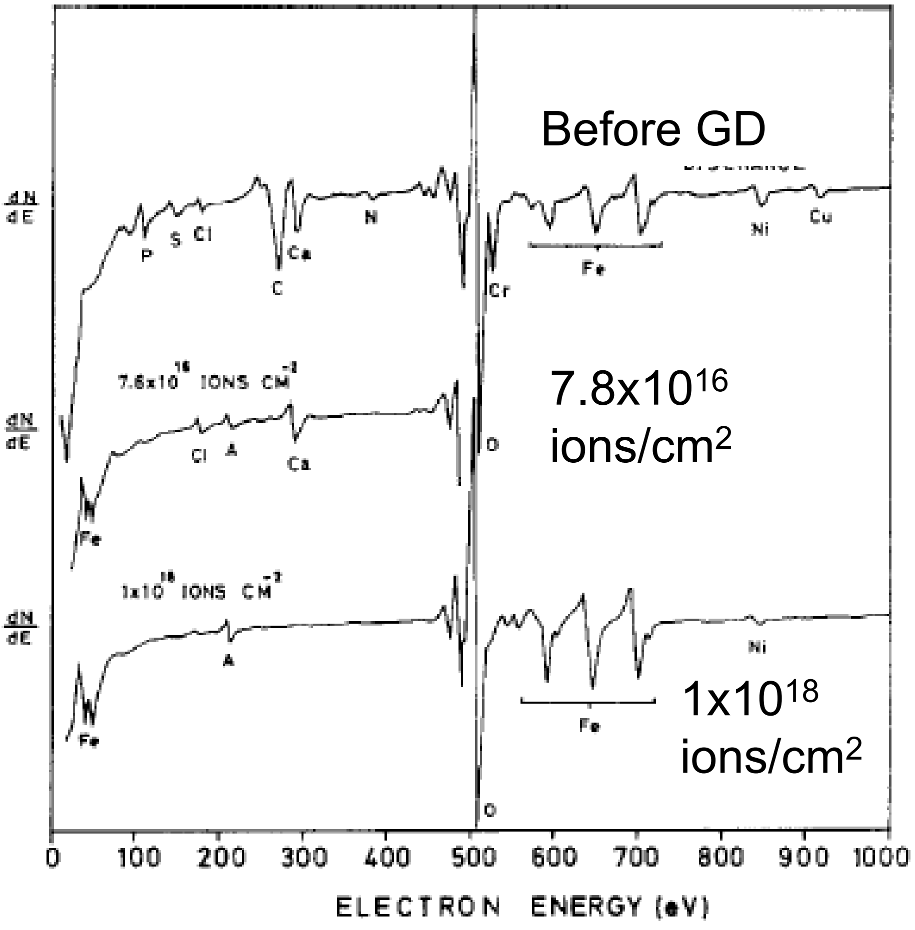
Ar GD

Air exposure after GD

Pure Ar

A.Mathewson,Vacuum 24, 505, 1974

Ar+10%O$_2$ GD

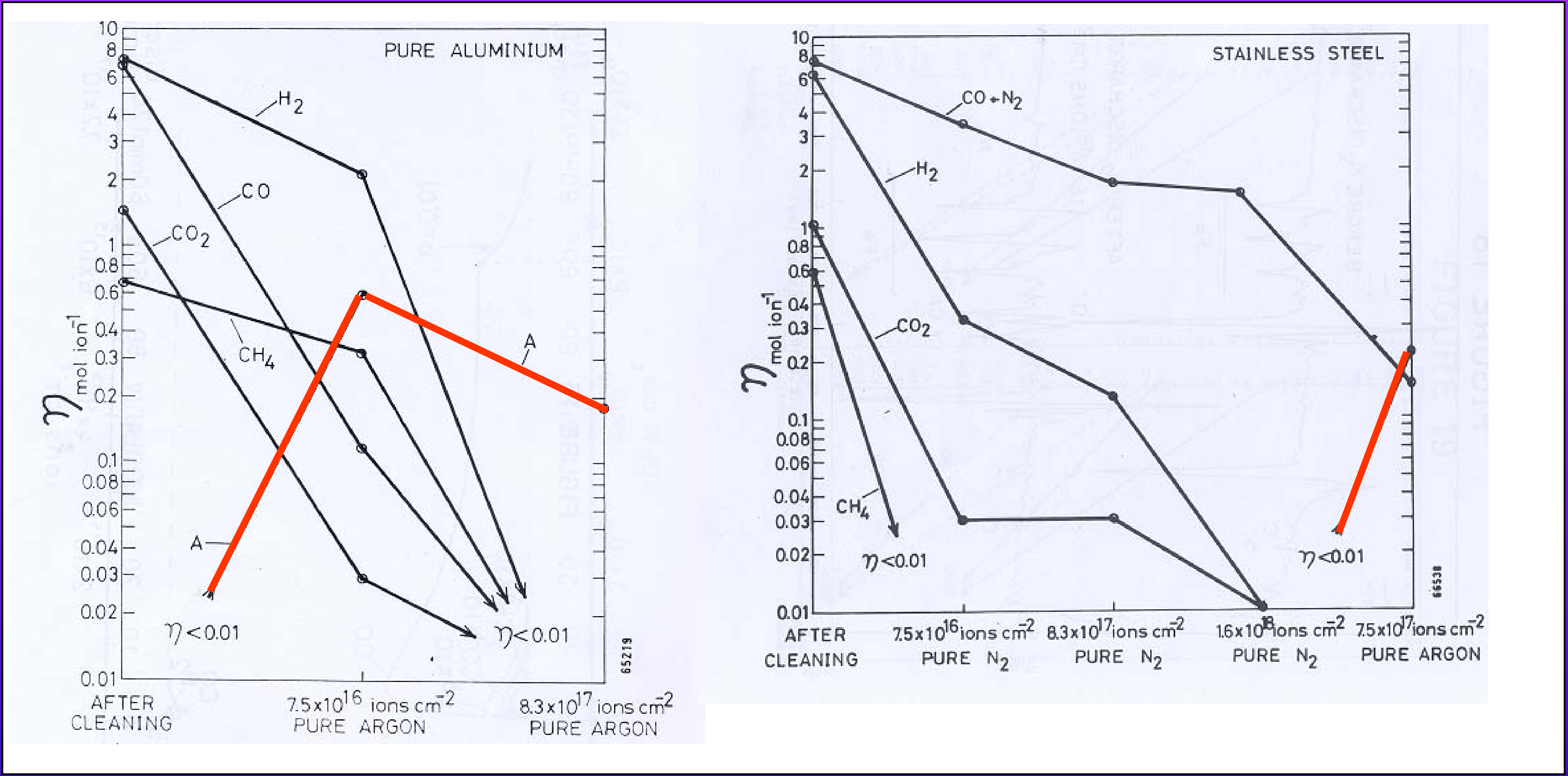


Before GD

$7.8x10^{16}$ ions/cm^2

$1x10^{18}$ ions/cm^2

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

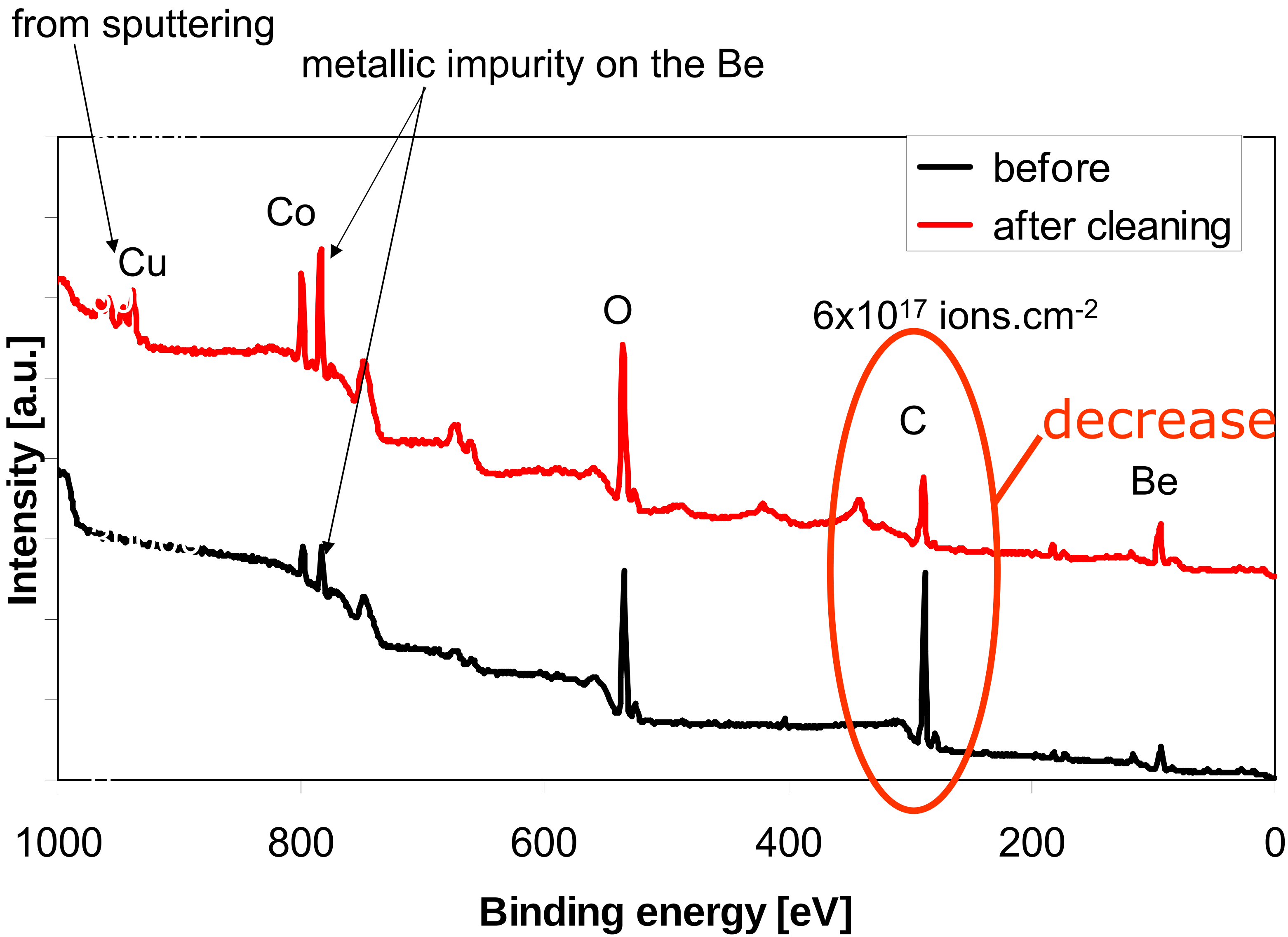
Special case: Be cleaning with O_2 glow discharge

(S.Calatroni, CERN)

Beryllium is difficult to handle because of toxicity of its oxide (not safe to put it in a detergent cleaning bath!).

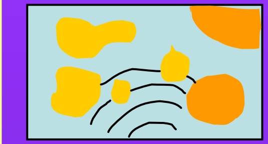
At sufficiently low kinetic energy (below ~400eV) the sputtering coefficient of O on C is higher than on Be due to chemical reaction; even better ratio for BeO

Test made on small sample: The amount of C on the surface decreases after plasma cleaning. no Be is found on the stainless steel strip used to hold the sample in place.


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

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

Sample analysis: XPS

- ➔ surface analysis technique for surface sensitivity XPS is simple for interpretation, sensitive and able to identify most contaminants (does not distinguish silicones and silicates)

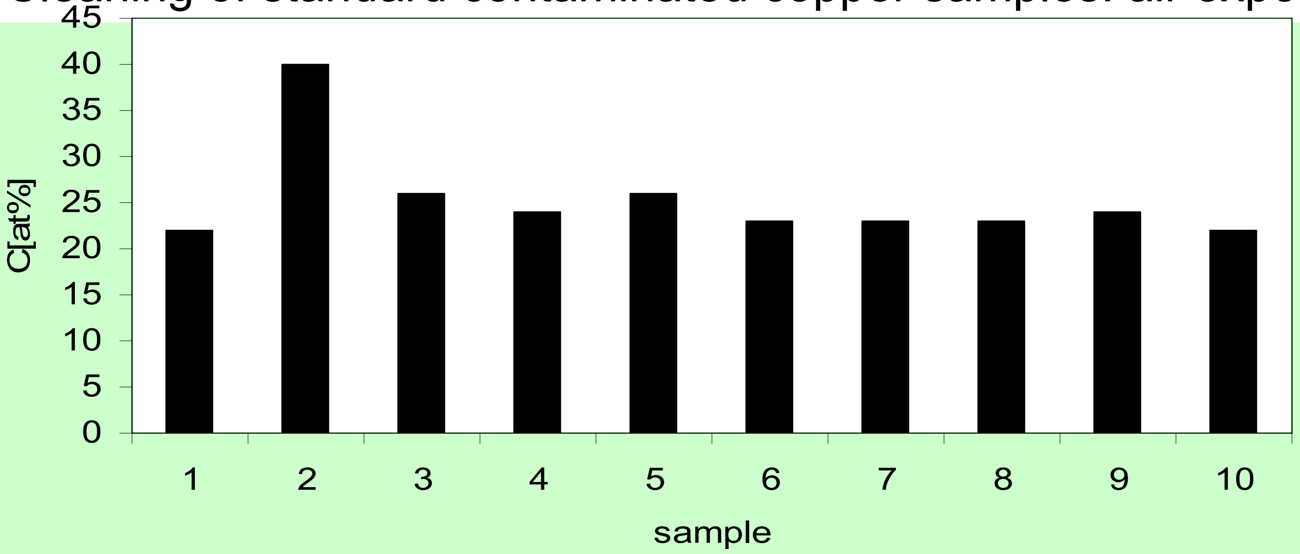
- ➔ at CERN the acceptance level for contamination is set to 40 at% of C on StSt (45° emission, XPS parameters must be kept constant for comparisons); based on experience of performance (and also realistically achievable results); corresponds to 0.5-0.8 nm coverage

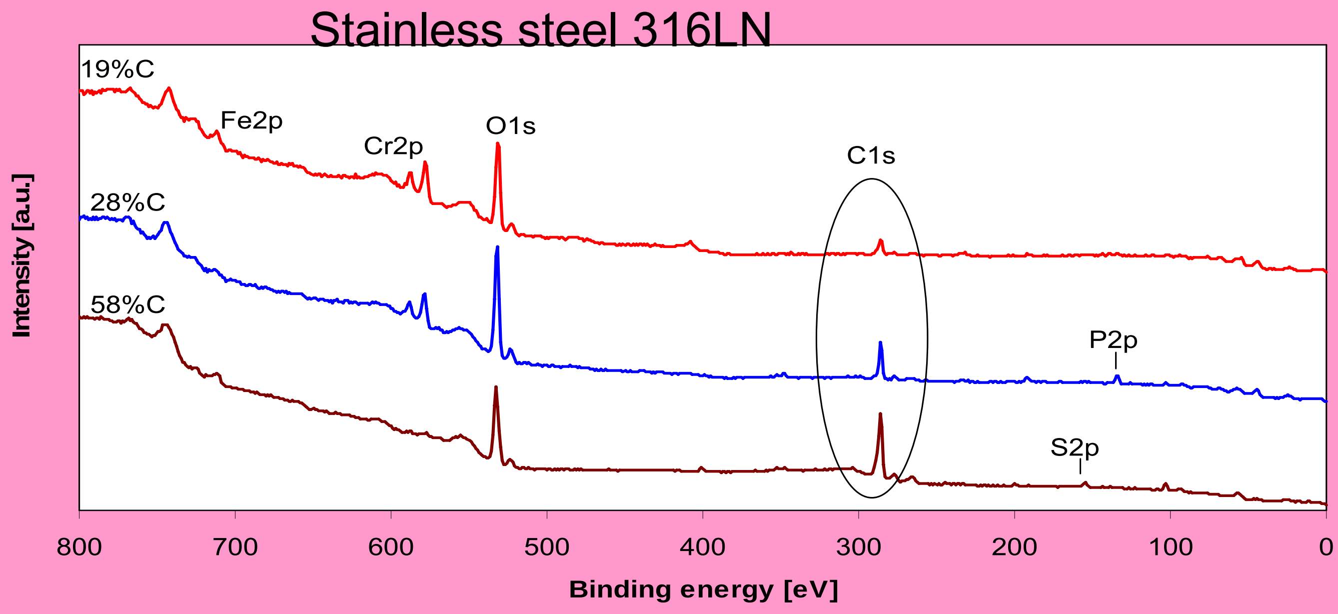
- ➔ criteria from static/dynamic outgassing can be equally valid

- ➔ for equal absolute amount of C on the surface, the measured at%C is material dependent as the probing depth (ex, 44% on copper, 29 at%C on Al, 30 at%C on Be, 36 at%C on Ti)

- ➔ CERN standard cleaning procedure gives 25 ±5 at% C on 10 copper samples cleaned nominally in the same way in the same run; scattering is larger between different runs

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





Other techniques

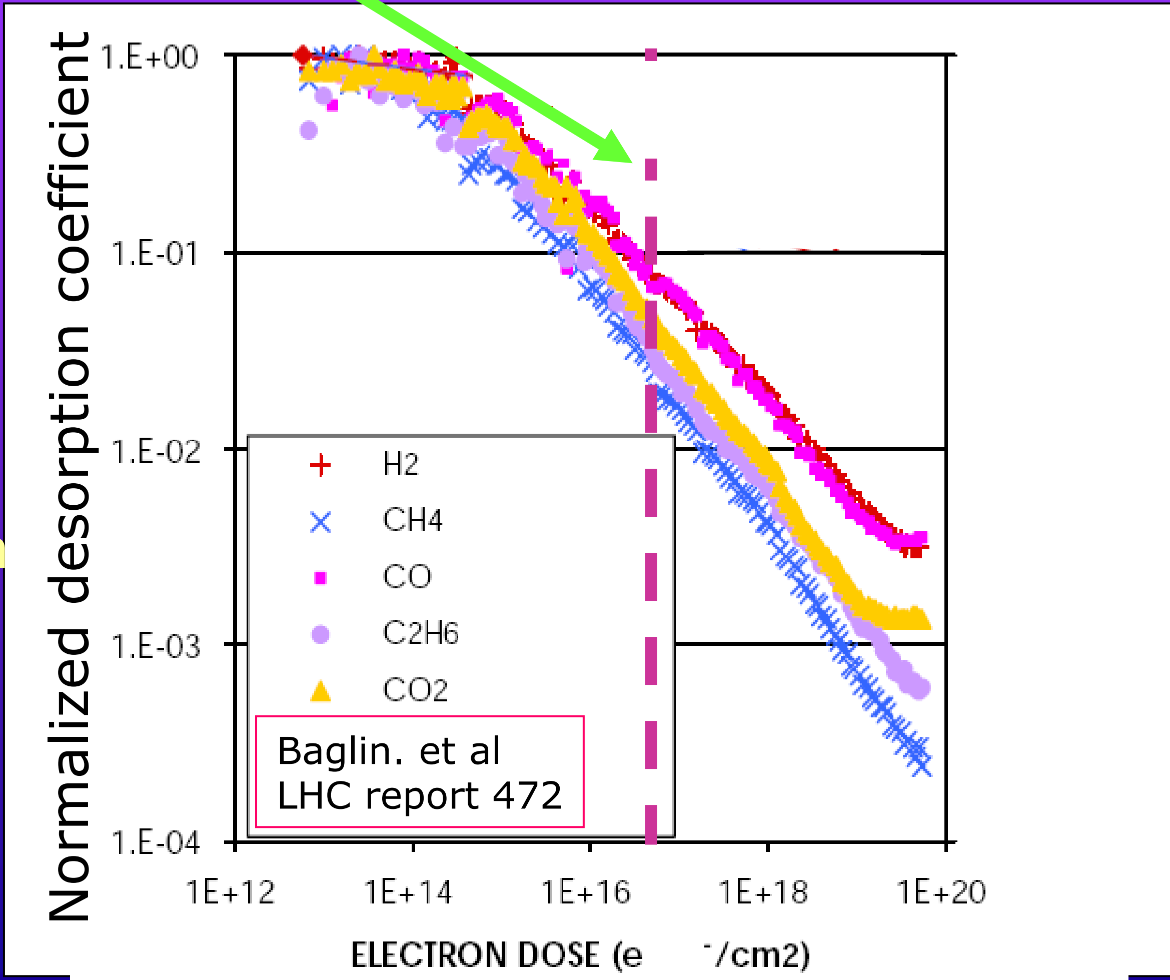
Auger spectroscopy (AES)	modifies C content, see later
Static SIMS	good (silicones), but difficult to quantify in general, highly sensitive
FTIR	good (silicones) through elution
ESD	see later
Total. Refl. X-Ray Fluoresc.	needs mirror-like sample
UV-vis spectr, Ellipsometry	through elution, hard to identify species
OSEE, Surface potential diff.	no identification of species, substrate dependent
Gravimetry	low sensitivity (we need ~10^{-7} g/cm^2)
Outgassing rate	only partial identification of contaminants, special sample shape
Water contact angle	no identification
Radioactive tracer	on selected contamination only

Why should we pay attention with electron beams (as AES) for cleanliness characterization?

Typical density for the e-beam: 10^{-7}A on $100\times100\,\mu m^2$ gives in 10 s a dose of 6×10^{16} electrons/cm^2

Important electron stimulated desorption of C related species !

Use unfocused technique as XPS (about 10-100 times less damages) with higher signal-to-backg.
or scan the beam
(J.Cazeau, Appl.Surf.Sci. 20, 1985, 457)



Baglin. et al
LHC report 472

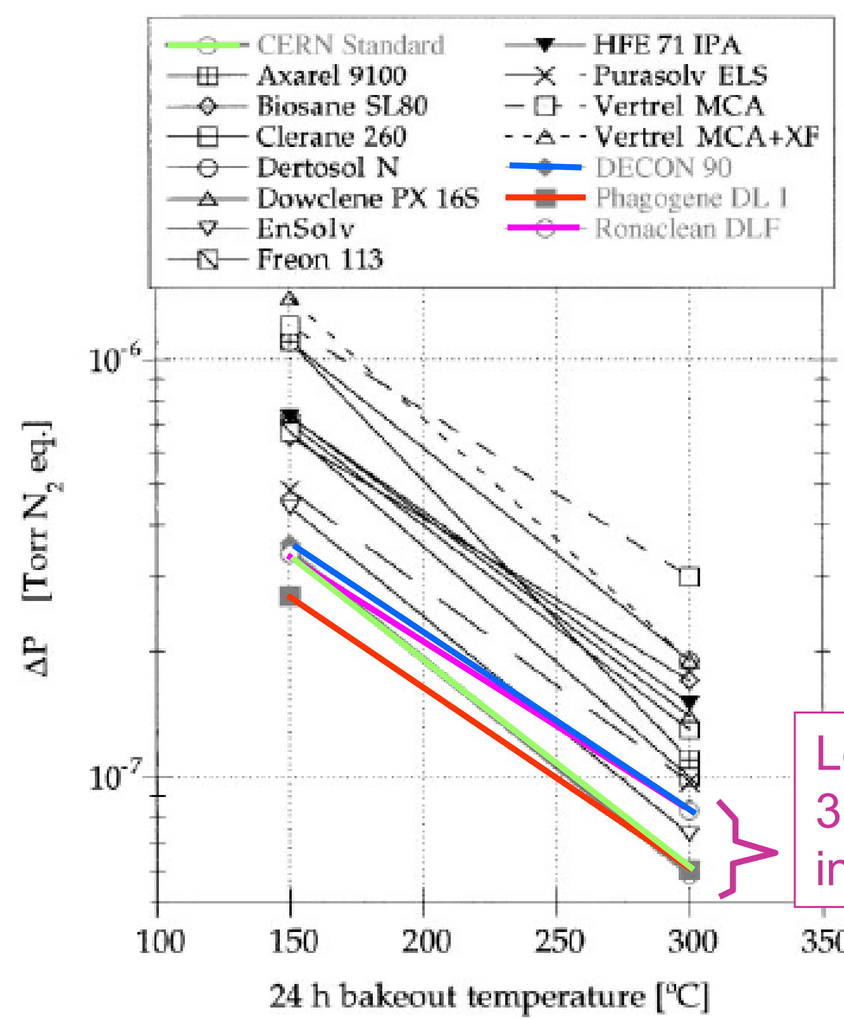
Cleaning and dynamic vacuum: Electron Stimulated Desorption test of detergents and solvents on 316LN

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

All the detergents (colour lines)tested so far are better than the solvents (possible residues left….)

Typical η (150°C)

H_2	0.1
CO	0.02
CO_2	0.03
CH_4	0.004



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

Less than 35 at% C in AES

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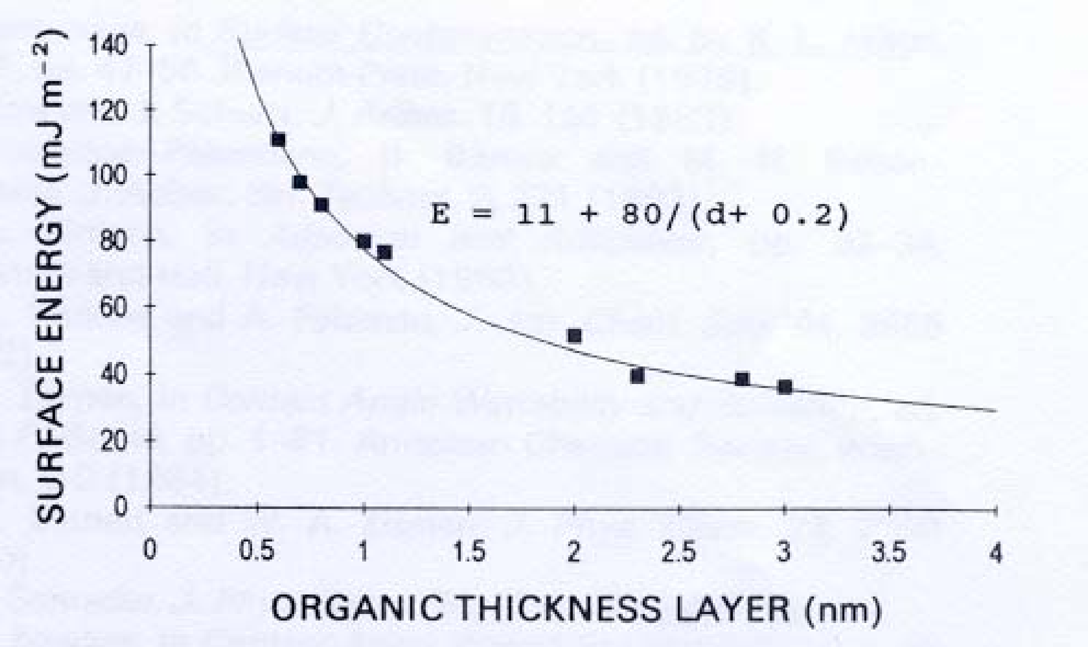
Wetting and cleanliness

-Contaminating hydrocarbons have low surface energy (~25 mJ/m^2 for alkanes , 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



Stainless steel:
Mantel and Wightman Surf. Interf.An. 21, 595 (1994)

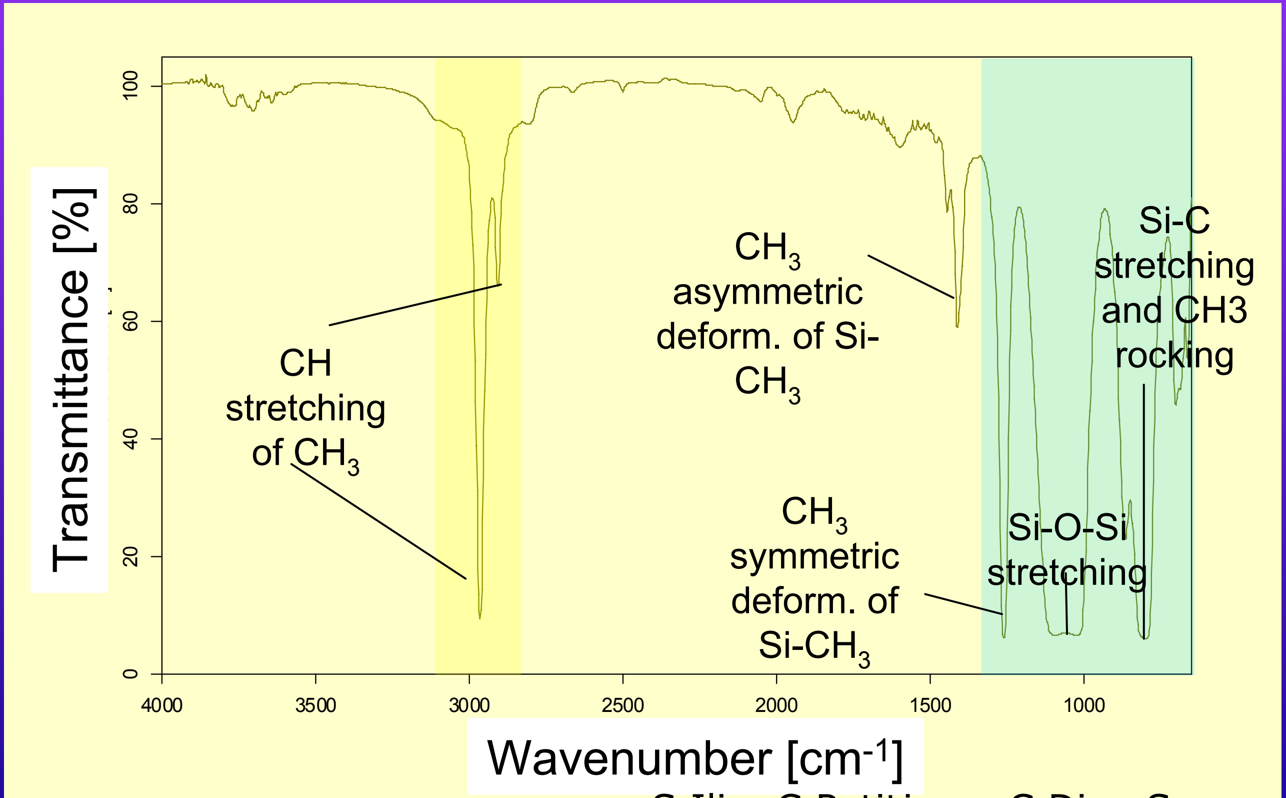
-In general they do not react chemically with the substrate (at RT) and therefore form a loosely bound layer preventing good adhesion of thin film coatings

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

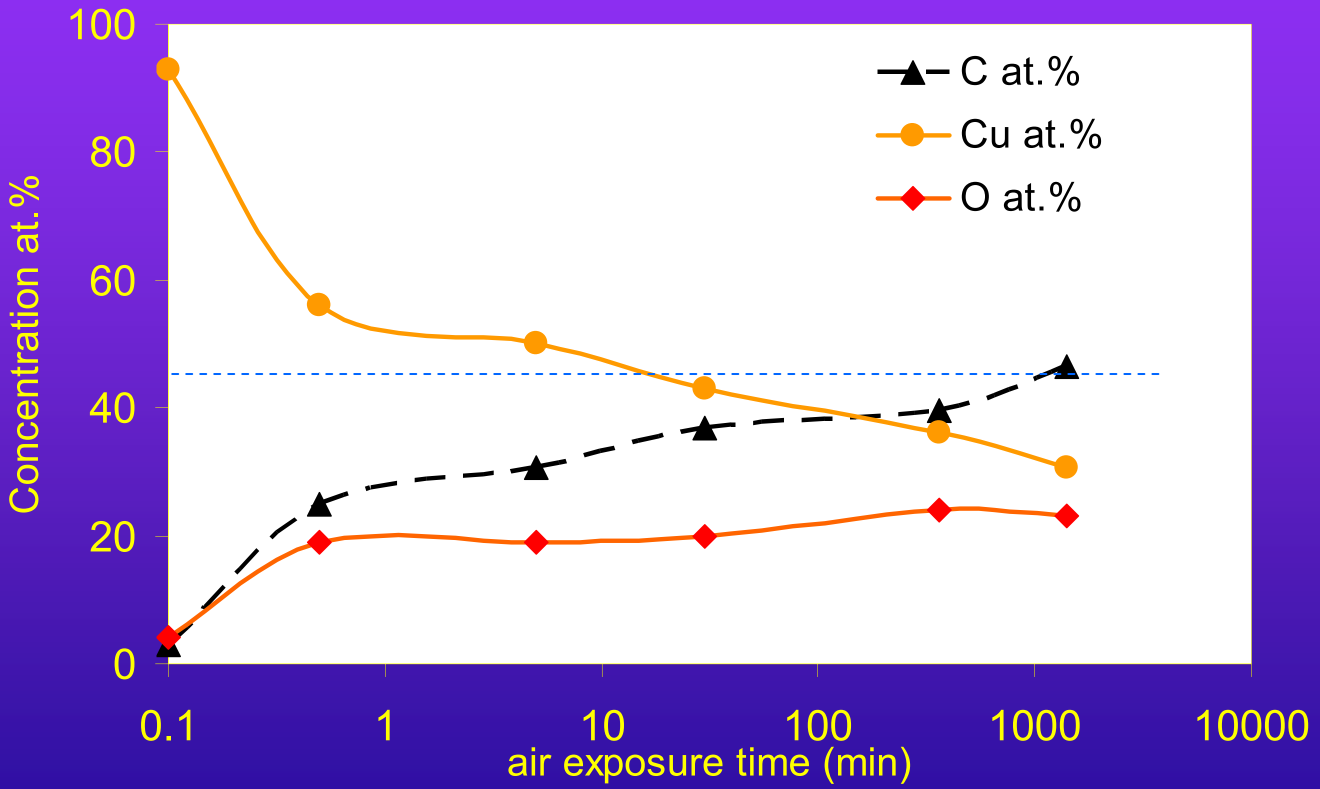


S.Ilie, C.Petitjean, C.Dias-Soares

Storage

How clean can we clean?

Air exposure provokes hydrocarbons re-adsorption on sputter cleaned copper surface (C_xH_y have low surface energy)



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

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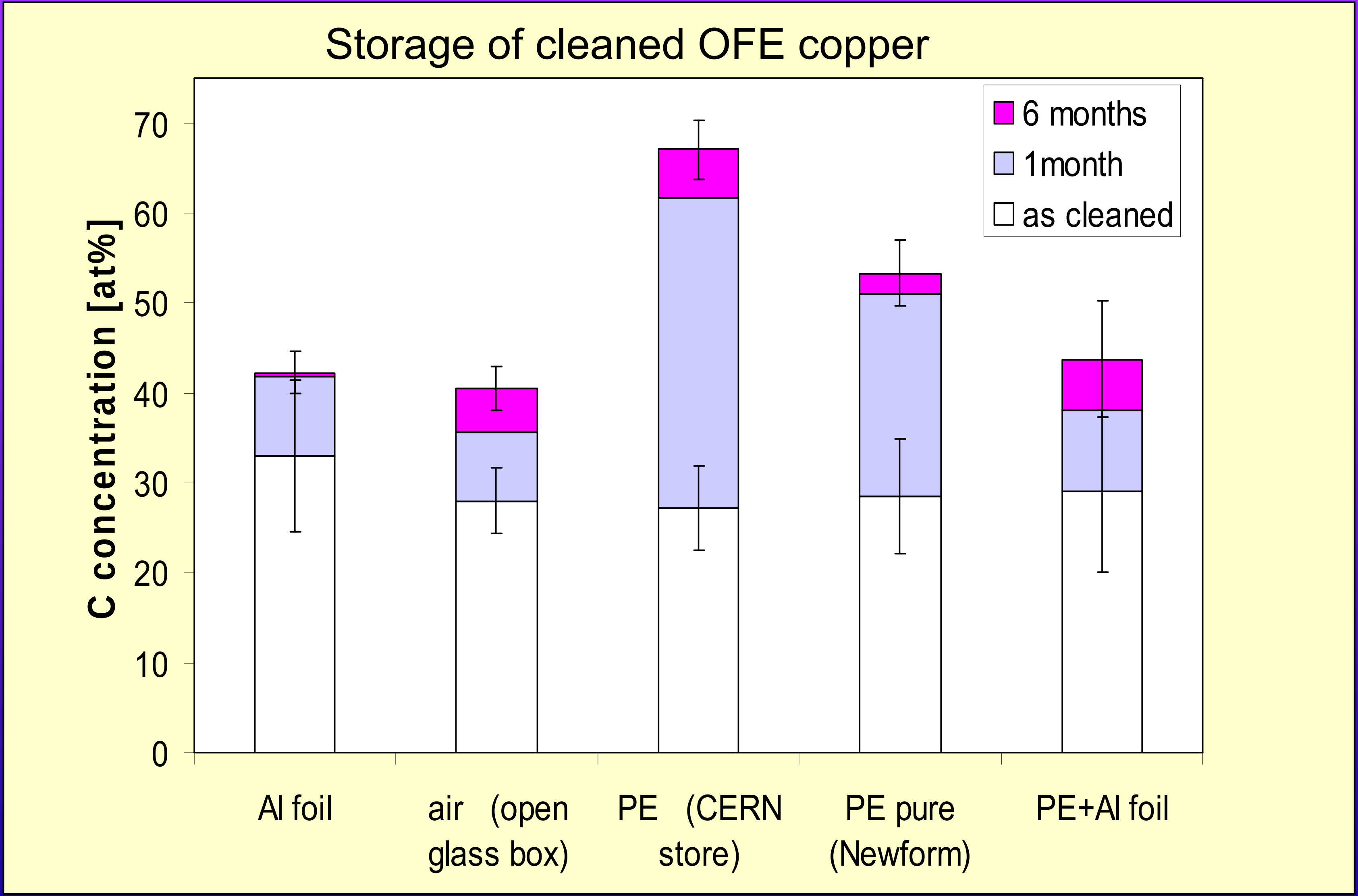
storage

Effect of storage in different packaging after cleaning



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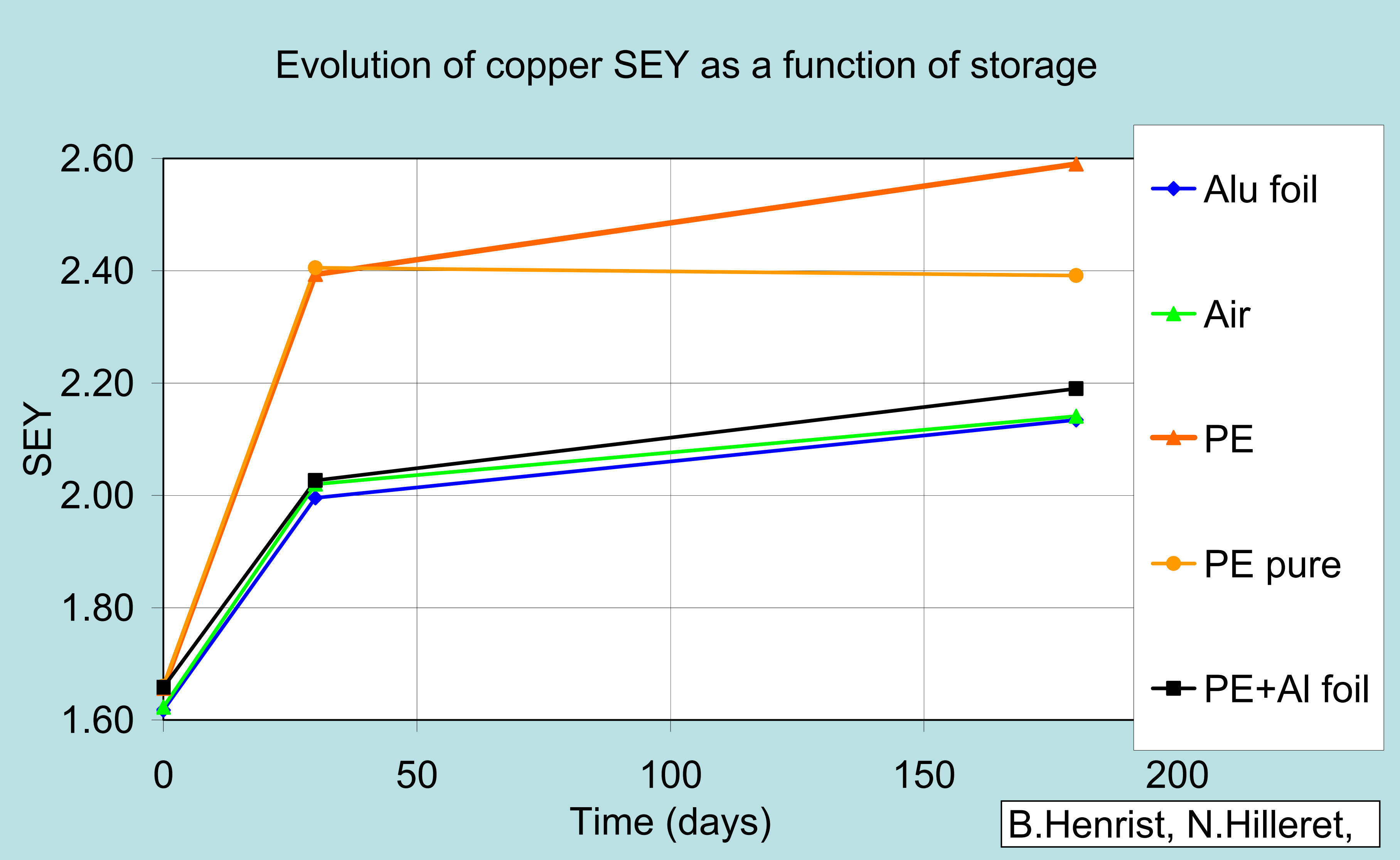
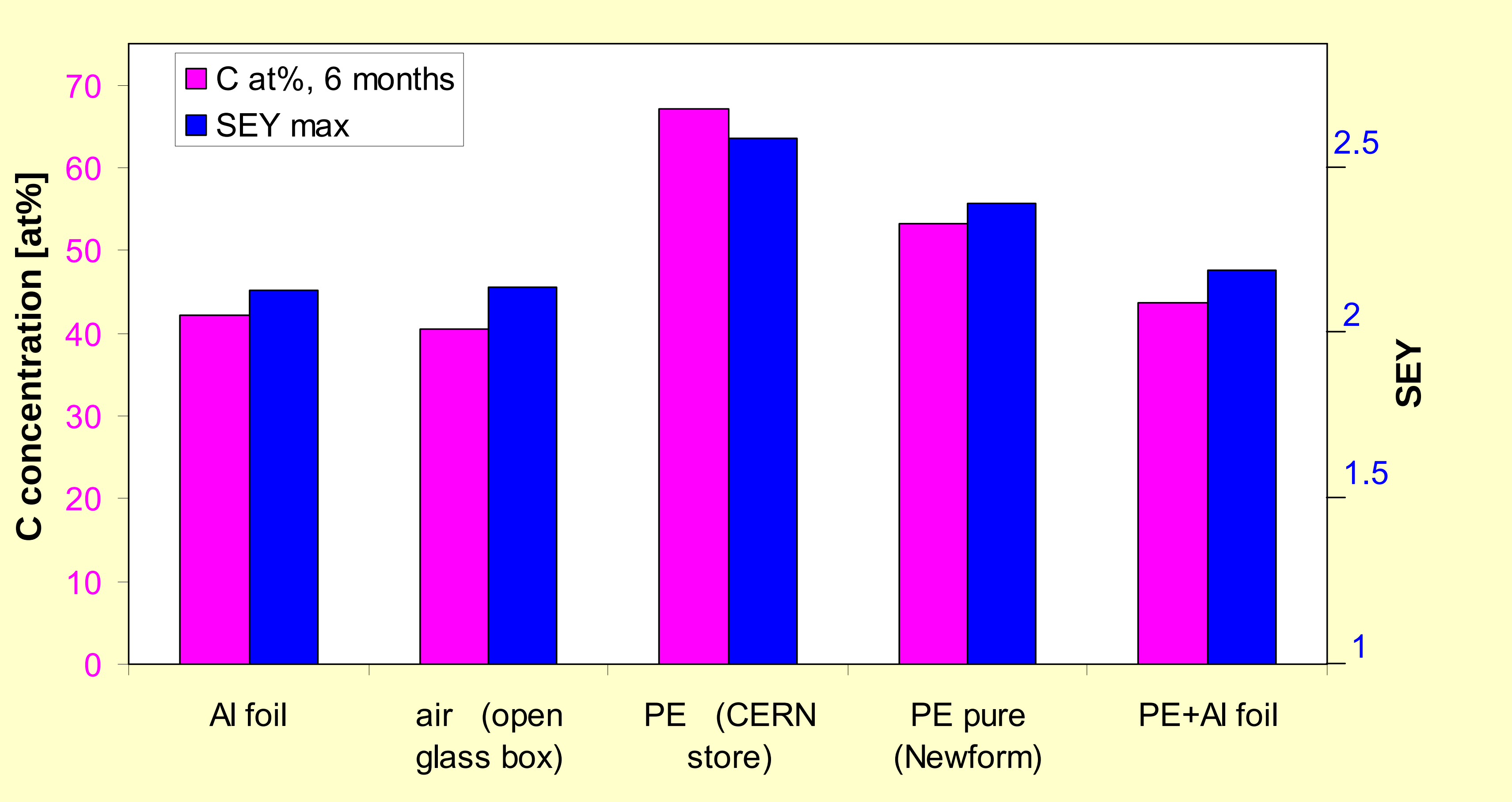
Effect on secondary electron yield



storage

Influence of re-adsorbed contamination on SEY of copper



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Check on your cleaning procedure with the own 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 contact with the sample unless the polymer has been previously qualified.

All this will save time.

- References

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

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