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# Cleaning and surface properties

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**Abstract**
Principles of precision cleaning for ultra high vacuum applications are reviewed together with the techniques for the evaluation of surface cleanliness. Methods to verify the effectiveness of cleaning procedures are discussed. Examples are presented to illustrate the influence of packaging and storage on the recontamination of the surface after cleaning. Finally, the effect of contamination on some relevant surface properties, like secondary electron emission and wettability is presented.

## 1 Introduction

In an ultra high vacuum (UHV) system a low residual gas density can be obtained and preserved only by using constituent materials having a sufficiently low vapour pressure at the working temperature [1]. For the same reason, namely to reduce residual gas pressure, the surfaces facing vacuum of all the constituent parts must be free of organic additives, oils, greases, packaging residues, which were used for instance during the manufacturing process.

In an accelerator the adverse influence of the residual gas manifests itself in the interaction with the particle beam and the related degradation of the beam quality [2]. The strength of such an interaction depends on the type of beam particles, but for most of them it increases faster than linearly as a function of the atomic number of the residual gas atoms and molecules. In general, carbon-containing molecules are more harmful than, for instance, hydrogen molecules which might be outgassed from the constituent metallic parts.

There are further possible reasons to apply cleaning procedures to the constituents of the accelerator. For instance, chlorine-based lubricants should be either avoided during manufacturing or completely removed from internal and external surfaces by cleaning in order to preserve a stainless steel vacuum system from corrosion during the entire lifetime of the machine. As a further example, the surface of the metal pipes delivering the working gas of gas ionization detectors (drift tubes, wire chambers, etc.) must be free of silicones to guarantee a constant high efficiency and gas purity. Cracking of silicone molecules present in the working gas generates an insulating silicon oxide coating on the electrodes and deteriorates the detector response [3].

Thus, different contaminations are relevant at different sites and the definition of cleanliness and contaminant is related to the application of the parts. It is, in other words, a specification which must be based on a method of control to be performed before assembly and operation.

The next section illustrates the basic concepts of cleaning and cleaning methods. In the following sections the methods of cleanliness control and packaging after cleaning will also be reviewed together with the effects of contamination on some of the surface properties related to accelerator physics. Previous reviews on cleaning for accelerator technology can be found in Refs. [4,5].

## 2 Methods of precision cleaning for UHV applications

This section presents an overview of the general principles of cleaning methods suitable for UHV components. Cleaning at this level of accuracy is often called precision cleaning. No universal recipe will be given since commercial cleaning products evolve quickly and the most appropriate solution must be selected by considering the particular application.

### 2.1 Cleaning with solvents

In a practical description a solution is a system where a solute, in our case the contaminant, is uniformly distributed at the molecular level in a solvent without formation of aggregates or precipitates. The interactions between the molecules of the solute (contaminant) and those of the solvent will determine whether solution or aggregation will occur. If the solute–solute interaction is particularly strong compared to the solvent–solute interaction, aggregation will dominate and the system will separate in two phases. Otherwise solution will occur.

The formal definition of the solubility in thermodynamics is related to the chemical potential of the solvated and aggregated state of a substance. The solubility $X_s$ (in mole fraction) of a contaminant in a solvent is expressed through the equilibrium condition:

$$\mu_0 = \mu_{\text{solution}} + k_B T \cdot \ln X_s \ .$$

$\mu_i$ is the chemical potential or Gibbs free energy per molecule, $G = \mu N$. $\mu_0$ is the value for a molecule in an aggregate (or bulk) of contaminant immersed in the solvent and $\mu_{\text{solution}}$ the respective value for a molecule in solution. The difference in free energy between the two states must be as small as possible to favour solubility:

$$X_s = e^{-\frac{(\mu_{\text{solution}} - \mu_0)}{k_B T}} \ .$$

The free energy per molecule includes the energy due to the interaction of the molecule with its environment. A strong attractive solute–solute interaction has the tendency to lower the chemical potential $\mu_0$ and induces aggregation. An attractive solute–solvent interaction has the tendency to lower $\mu_{\text{solution}}$, lowers the difference in chemical potentials and solubility becomes significant when the difference $(\mu_{\text{solution}} - \mu_0)$ becomes comparable to $k_B T$. In other words, solution is favoured if the interaction strength for solute–solute is similar to that for solute–solvent.

Molecular interactions depend on the chemical species of the solute and solvent and as a result a given solvent will be able to dissolve and remove only a certain type of contamination. A combination of various solvents can be applied in sequence, where each substance has a specific contaminant as target. A simplified view of the principles and interactions governing solubility is given in the following. The types of interactions are either ionic, Van der Waals, hydrogen bonds or based on the hydrophobic effect [6].

In a solvent the molecules held by ionic bonds, as salts, are dissociated when dissolved. The strength of the Coulomb interaction holding together cations and anions in an ionic solid decreases by a factor corresponding to the dielectric constant $\varepsilon$ of the surrounding solvent. Therefore in a solvent the anion–cation attraction is weaker than in air, $\mu_0$ is higher than in air, the difference $(\mu_{\text{solution}} - \mu_0)$ is low and the dissociated state of the molecule is favoured. For instance a salt like NaCl exhibiting a strong bond between anion and cation in the crystalline lattice can dissociate and therefore be dissolved in water ($\varepsilon = 78.5$). This occurs less effectively in a solvent having a much lower dielectric constant as propanol ($\varepsilon = 20.2$), where indeed the solubility is 100 times lower than in water [6]. Solvents with high dielectric constant are often polar solvents [7] (by definition a polar molecule is one carrying a permanent electric dipole moment). Thus, ionic species dissolve better in polar solvents than in non-polar ones and perfectly in water. In a more refined picture, hydrogen bonds, described below, should also be considered to show the entire mechanism governing solubility.

Molecules held by covalent bonds interact through Van der Waals forces. This interaction has three main components: orientation between permanent dipoles (polar molecules), polarization between permanent and induced dipoles (polar with non-polar molecules), and dispersion between instantaneous dipoles (in non-polar molecules). The dispersion interaction does not need the presence of any permanent dipoles. For sufficiently large molecules the dispersion term dominates and the polar groups on the molecules, are less important. The dispersion term always provokes attraction between the solute molecules, and its strength (in the approximation of a continuous medium) is governed by the difference in refractive indices $(n_{\mathrm{solvent}}^2 - n_{\mathrm{solute}}^2)^2$ [6]. Therefore solution is favoured with respect to aggregation when the refractive index of the contaminant is similar to that of the solvent and this attraction is weak. Instead, for small molecules carrying strong permanent dipoles, like water, dispersion is no longer dominating and other interactions occur. Water can dissolve effectively many substances thanks to the strong interaction with polar groups. In some cases it can also form hydrogen bonds with the solute molecules. Hydrogen bonds are particularly strong, directional dipole–dipole interactions and are formed between chemical groups carrying $O^{\delta-}–H^{\delta+}$, $N^{\delta-}–H^{\delta+}$ and $F^{\delta-}–H^{\delta+}$ bonds. These groups are strongly polarized and neighbouring molecules are oriented though Coulomb interaction between the dipoles.

The solubility in water of non-polar hydrocarbon molecules, such as typical oils and greases, is instead very low first because their Van de Waals interaction is weak with water: the orientation and polarization terms dominate in this case, but for molecules like alkanes and similar long aliphatic chains all three terms of the interaction are weak. Solution is hindered by the so-called hydrophobic effect [8]: non-polar molecules, which cannot participate in hydrogen bonds (hydrophobic), induce around them an arrangement of the water molecules which is unfavourable from the entropy point of view. In other words, the entropy in such a configuration is decreased. Since water does not interact strongly with such molecules the loss of entropy upon solution would not be balanced by any decrease in enthalpy and would result in an increase of $\mu_{\mathrm{solution}}$. The final result is segregation in two phases rather than solution. Therefore water as a solvent cannot clean greases and oils or other non-polar molecules.

Examples of simple solvents are alcohols (methanol, ethanol, propanol, etc.) and halogenated hydrocarbons. Alcohols can be easily used in laboratory application in small amounts. For UHV applications it is recommended to use high purity grades to avoid residues left on the surface. They can have Van der Waals interaction with polar as well as with non-polar molecules, the strength of which depends on the respective aliphatic chain length. In addition they can form hydrogen bonds. They are able to dissolve various chemical species, but are rather ineffective on some grease, like for instance Apiezon® vacuum grease. Their main disadvantages are flammability and toxicity, so that large amounts cannot be conveniently handled.

Halogen-based solvents (trichloro-ethylene, trichloro-ethane, chloroform, freon, perchlorethylene) are only slightly polar or non-polar and very effective in dissolving many types of greases, but some are highly toxic. Some of them are nowadays banned by security and health regulations and allowed emissions are strictly regulated. Perchlorethylene is tolerated in working areas when the concentration is below 20 mg/m$^3$ [9]. More refined solvents and blends are nowadays available on the market, based also on non-polluting halogen molecules as hydrofluoroethers (HFE), which can have remarkably low surface energies (as 14.5 mJ/m$^2$) and wet most of the surfaces. The result of a recent series of tests on the performance of solvents for UHV application including HFE can be found in Ref. [10].

After selection of the best solvent for the actual application and contamination, cleaning can consist in complete immersion of the work-piece to be cleaned in the solvent bath and agitation of the piece or of the bath (see later). After extraction the work-piece is dried by letting the solvent evaporate. Clearly the solvent must not leave on the surface any residues of itself or of dissolved contaminants and rinsing with pure solvent can be necessary. Drying must be performed through a

controlled and reproducible procedure. Evaporation of the solvent often cools the part due to the absorbed heat of evaporation and recontamination through adsorption and condensation from air can be avoided only by keeping the part warmer than the surrounding atmosphere, or by drying in an oven.

The alternative procedure, vapour degreasing, does not leave dry residues on the surface and can be applied to solvents having a sufficiently high vapour pressure slightly above room temperature. The bath of solvent is warmed up—for instance 120ºC for perchlorethylene—to obtain vapour above it and the colder work-piece is suspended in the vapour region. The vapour condenses on the surface of the part to be cleaned. The condensed solvent with the dissolved contaminants will fall into the underlying bath again. The interesting aspect of this method is that the solvent is continuously distilled and only pure solvent condenses on the work-piece, whereas contamination accumulates into the bath which can be filtered.

The same principle can be applied with $CO_2$, which is interesting for its non-toxic properties (the process does not produce $CO_2$, it just recycles it). This solvent is non-polar and is especially effective to dissolve aliphatic chains shorter than 20 methylene units and even silicones [11]. It is less effective for polar contaminants and residues of C = O and COOH groups which are not eliminated from the surface and can be detected for instance by X-ray Photoemission Spectroscopy (XPS). In a simple procedure $CO_2$ is used in the form of snow, where a jet of solid $CO_2$ forms a liquid layer upon impact on the surface to be cleaned [12]. During treatment the work-piece should be kept above room temperature to avoid re-contamination. In a more refined method, supercritical $CO_2$ ($SCCO_2$) is used. The gas is compressed (Fig. 1) and heated above the triple point (see dotted region in Fig. 2).

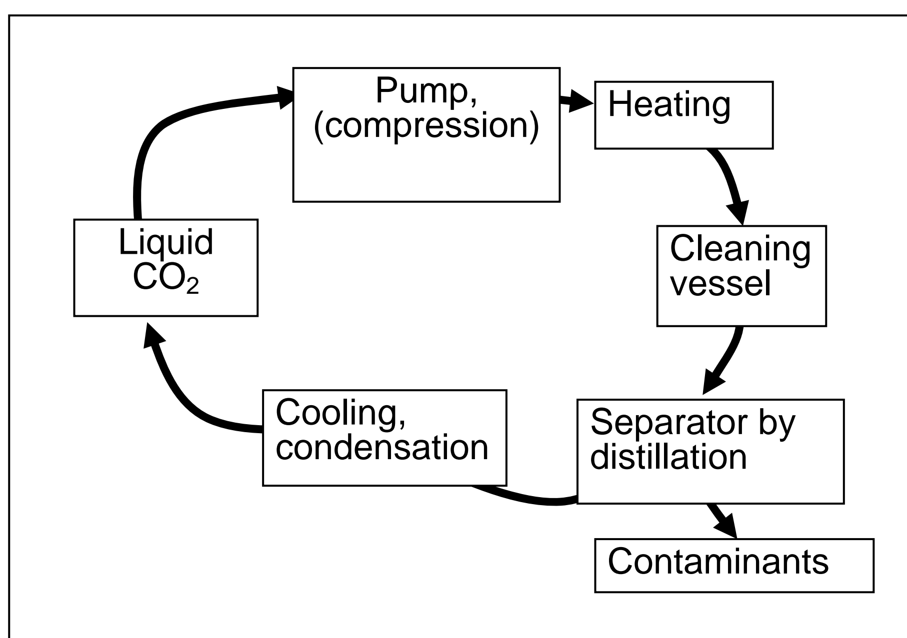


**Fig. 1:** Typical cycle for cleaning with $SCCO_2$. Note that the tank must be compatible with the high pressures used for the production of the supercritical phase.

The supercritical fluid can perfectly wet any surface, since it has an extremely low surface energy (1 mJ/m$^2$ for $CO_2$ to be compared to 32 mJ/m$^2$ for perchlorethylene and 72 mJ/m$^2$ for water) and a much lower viscosity than in its liquid phase. The solvation properties are similar to those for the liquid phase. To our knowledge this technique is not yet available on a commercial scale for the cleaning of parts for UHV and developments are still in progress. Suitable co-solvents and surfactants have been developed in order to improve its effectiveness in removing polar substances.

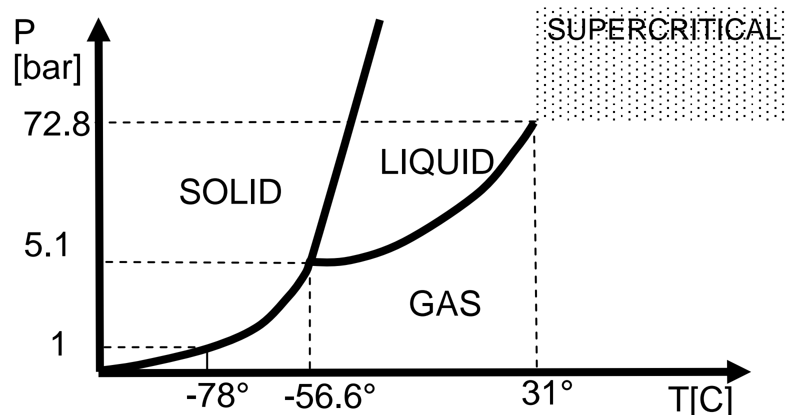


**Fig. 2:** Simplified phase diagram of $CO_2$. The supercritical region is marked with a dotted area above the critical point.

## 2.2 Cleaning with detergents

A detergent is a blend of substances designed for cleaning applications in combination with a solvent. In the following, only the most frequent case where the solvent is water will be considered. The main constituent is a surfactant (contraction of surface active agent), a substance which is able to wet virtually any surface. Such surfactant molecules are amphiphilic, i.e., are able to attract both hydrophilic (through H-bonds) and hydrophobic chemical groups. They consist of a polar or ionic hydrophilic head group and a long hydrophobic tail, as an aliphatic chain. The molecule can have attractive interaction with virtually any molecules, hydrophilic or hydrophobic, polar and non-polar with the most appropriate of its ends. Therefore such molecules like to sit at the interface between hydrophilic and hydrophobic media as water–air, water–oil. Above a critical concentration in the solvent—critical micelle concentration or CMC—a surfactant can build micelles (Fig. 3). Micelles are ordered aggregates of molecules which expose their heads to water. The hydrophobic effect is the driving force to form micelles and order the surfactant molecules. Inverse micelles can form in a hydrophobic liquid.

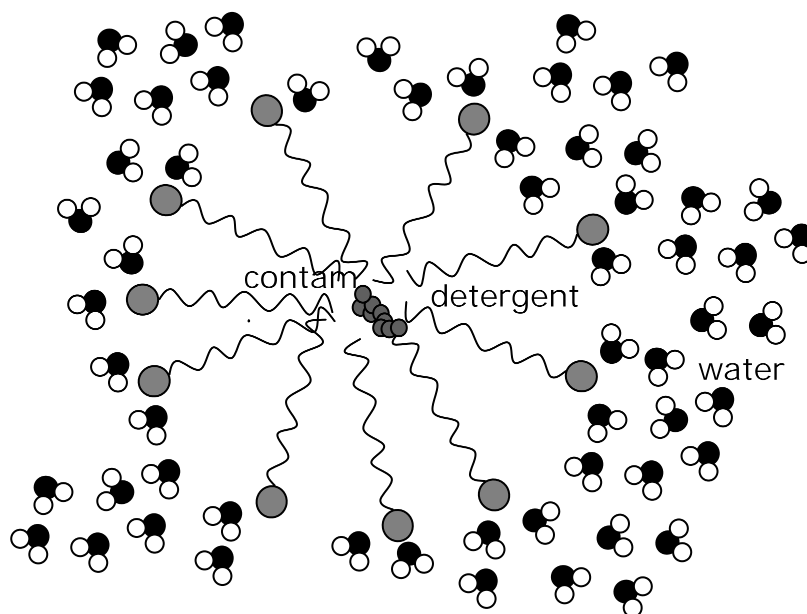


**Fig. 3:** Arrangement of surfactant molecules forming a micelle in water and encapsulating a hydrophobic contamination particle

The cleaning mechanism is twofold. First, the surfactant removes contamination from surfaces, since it can attract many types of chemical groups and wet both the surface and the contaminant. In this way it lowers the surface energy of the substrate avoiding re-adsorption of the contamination. The contact area of the contaminant with the surface decreases and removal through agitation is made easy. Second, the surfactant surrounds the contaminant, which could not otherwise be dissolved, and encapsulates it in a micelle. Recontamination is avoided and the micelle is then dispersed in the solvent. Continuous filtering of the bath removes the contamination. For instance, in water the surfactant molecules will surround an oil droplet, encapsulate it in a micelle (Fig. 3) exposing polar heads toward water.

The detergent can contain water 'softeners', like soluble silicates, which avoid calcium deposits. It often has a basic pH, an aspect which should be considered in view of the possible resulting surface damages. However, in general, slight etching eliminating the surface oxide is beneficial, since contaminants can be trapped inside. The performance of the detergent is generally optimized at a given concentration and temperature (50–60ºC), which should be compatible with the parts to be cleaned. At the end of the treatment in the detergent bath an extensive rinsing with tap water followed by demineralized water is necessary to eliminate residues of surfactant or additives, as the silicates, from the surface.

In order to guarantee a constant effectiveness of the cleaning bath over time, its quality must be periodically monitored, through pH, conductivity, concentration of detergent measurements, the latter being relevant for the formation of micelles. Another way of monitoring the cleaning effectiveness of the bath is to analyse the result on test specimen (see Section 3). If in a plant cleaning of one type of metal is frequent and some slight surface etching occurs during cleaning, it is safe to monitor the concentration of this metal in the bath to avoid transfer of such ions to other materials passing in the same cleaning station. Complicated cases in this respect are brazed joints, where one of the metals or one of the components of the brazing alloy can be spread on the entire surface of the work-piece.

As described above, the cleaning power of solvents is in principle improved by detergents, which operate always in combination with a solvent. A nice comparison between various solvents and detergents used for precision cleaning of UHV components is given in Ref. [13]. The main reason why solvents are still applied is the need to rinse the detergent cleaned parts with water in order to remove completely the traces of detergent from the surface. Such a rinsing can only be effective when the shape of the cleaned part does not trap water and residues through pockets, pores and meander-like shapes. Residues can provoke long-lasting outgassing or corrosion. For this reason vapour cleaning by solvents is necessary for bellows, porous materials such as ceramics, narrow curved pipes, valves and similar manifold components.

Moreover, since volatile solvents can be recycled by distillation during the cleaning process, they are particularly suitable for a gross cleaning phase of parts which are heavily contaminated by oils and greases after manufacturing. The gross cleaning can be used in combination with a subsequent treatment in a detergent bath. In this way the contamination of the generally expensive detergent bath can be limited and its lifetime prolonged.

In some cases detergents can provoke chemical deterioration of surfaces and alter their functional properties. A striking example is given by TiZrV non-evaporable getter (NEG) coatings used for pumping purposes in accelerator pipes. Figure 4 illustrates the effect on the surface composition of such a coating of cleaning by a detergent having a basic pH and commonly used in standard CERN cleaning procedures for vacuum chambers. The surface chemical composition is completely altered with a marked reduction of the vanadium content. As a consequence the functional behaviour of the getter is deteriorated and no activation occurs in the useful temperature range (Fig. 5).

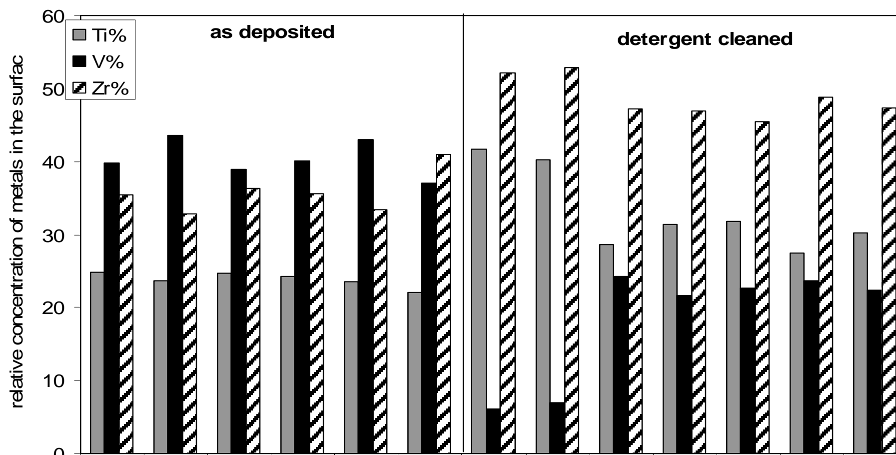


**Fig. 4:** Comparison of the surface chemical composition of several samples of TiZrV NEG coating in the as-deposited state (left side) and after treatment in a detergent bath (right side). The composition is measured by XPS.

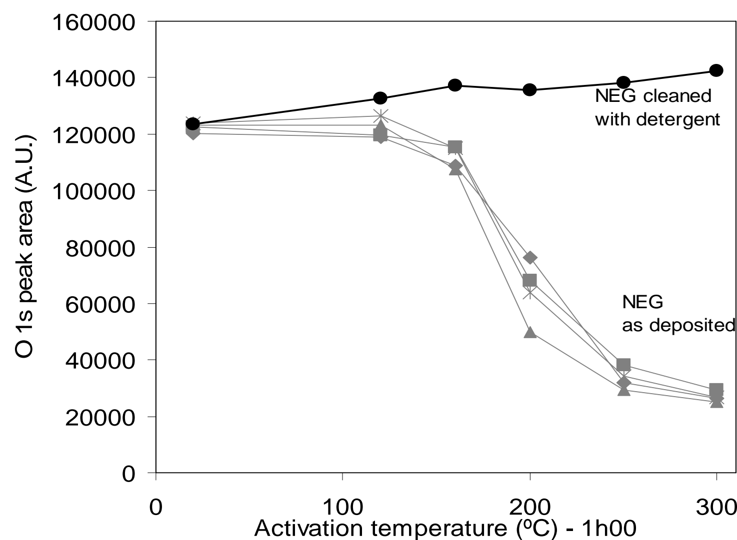


**Fig. 5:** Activation behaviour of TiZrV NEG coating illustrated by the decrease of the oxygen O 1s intensity in XPS. The sample cleaned in a detergent bath does not exhibit any activation.

## 2.3 Agitation

In the case of precision cleaning by immersion in a bath for both solvents and detergents, ultrasonic agitation [14] of the bath is applied. In this way removal of soils is much more effective, as illustrated in Fig. 6. Ultrasonic waves (20–120 KHz) are mechanical pressure waves generated by piezoelectric transducers placed in the cleaning tank. The waves create bubbles of some 10–100 microns in the liquid medium. Bubbles grow up to implosion and energy is then released. In such a way adsorbed contaminants and particles can be removed even from crevices and blind holes. Agitation is mandatory for all samples having a complex shape. The power of the ultrasonic actuators must be correctly dimensioned and depends on the bath volume, their position and orientation, and on the shape of the bath tank. For long pipes which cannot be easily immersed the ultrasonic agitation can be replaced by turbulent flow. The cleaning fluid is forced to stream through the pipe in a turbulent flow regime.

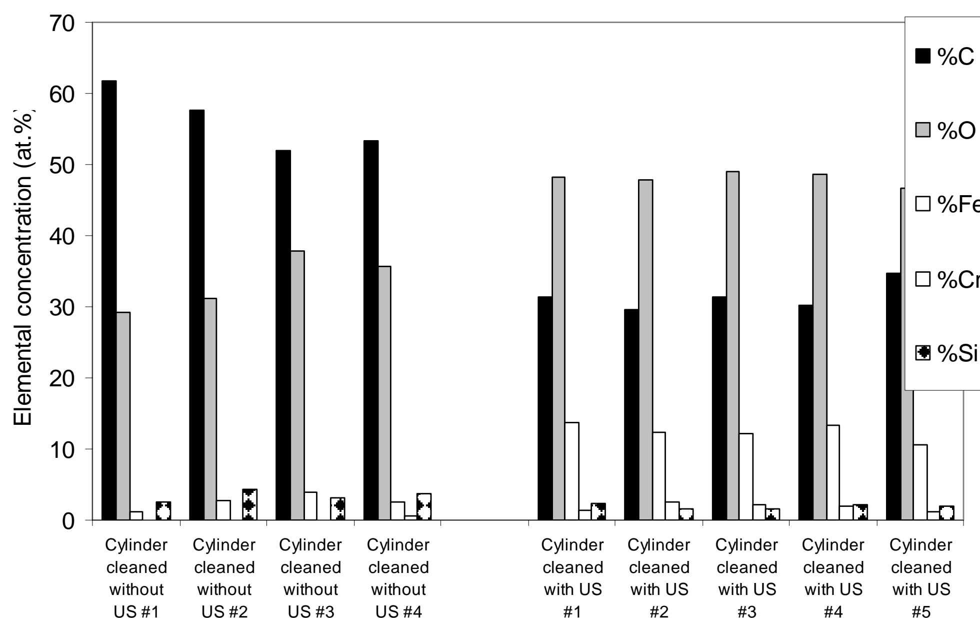


**Fig. 6:** Example of samples cleaned in the same detergent, with and without ultrasonic agitation, respectively. The XPS composition reflects the higher efficiency of cleaning with ultrasonic agitation.

Examples of cleaning procedures including some optional steps are illustrated in the schemata in Fig. 7. The application of the various optional steps depends on the level of contamination of the parts to be cleaned, on their shape, material, application, and so on. For instance, pre-cleaning in a solvent is applied on heavily contaminated parts. High-pressure water rinsing has been found successful for improving the performance of superconducting radiofrequency cavities [15].

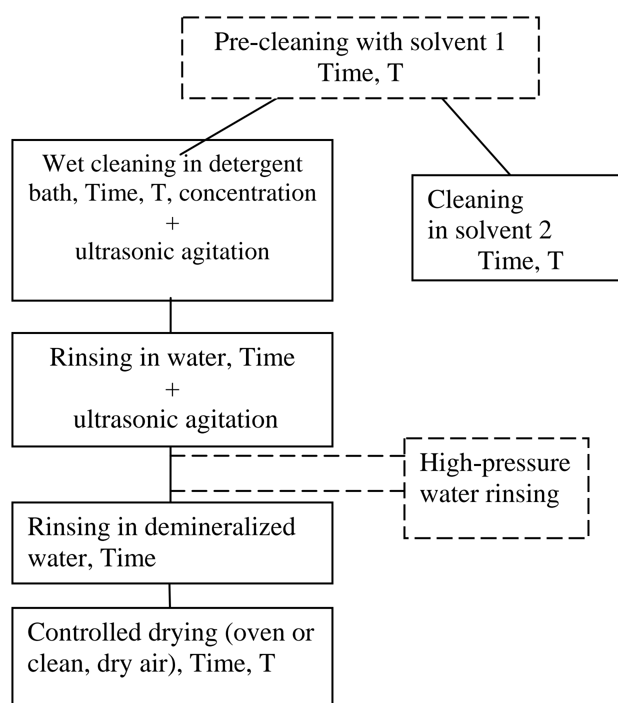


**Fig. 7:** Typical sequence for cleaning of UHV parts with solvents or detergents and typical parameters to be controlled. Dashed lines represent optional steps depending on the particular application.

### 2.4 Special cases

It is worth mentioning an example where cleaning seems to be impossible. Stainless steel such as 316LN is often used for UHV applications and is vacuum fired at 950ºC in vacuum for degassing purposes. If the amount of boron concentration in such steel is higher than some 9–10 ppm [16], boron nitride (hexagonal) can form at the surface during the vacuum firing treatment (Fig. 8). Boron nitride itself is not harmful for UHV, however, such a layer prevents the adhesion of a further coating made by evaporation, sputter deposition, or electroplating. Adhesion of the coating will be hindered by the fragile lamellar structure of boron nitride and its low surface energy. Water cannot wet such a surface and the usual detergents are not able to remove such a layer. Only etching or electropolishing of the surface is possible in order to enable further coating.

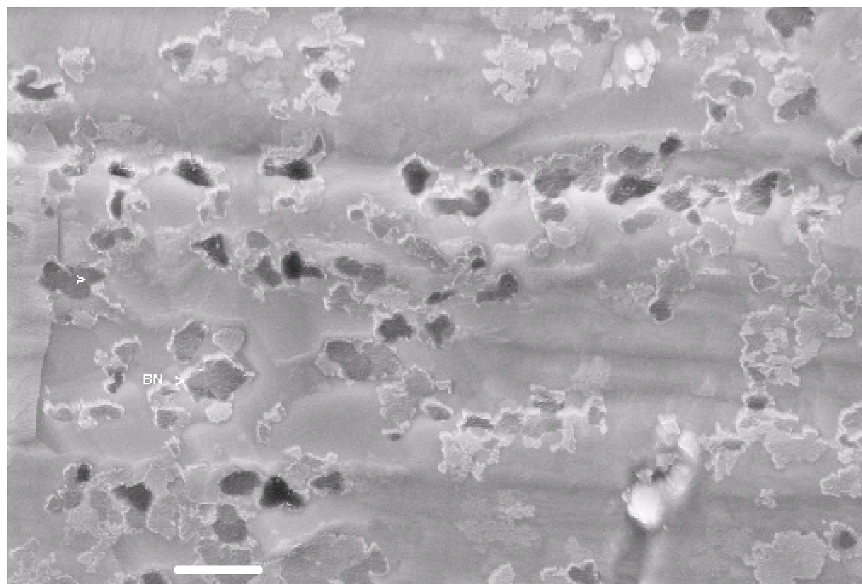


**Fig. 8:** Scanning electron microscope image of stainless steel 316LN after vacuum firing (scale bar is 2 microns). The leaflets visible on the surface are boron nitride crystals formed through surface segregation and reaction of boron (15 ppm in the volume) with the nitrogen of the steel.

Another interesting case is represented by silicones as contaminants. Vacuum greases often contain silicones which are difficult to eliminate from the surface. Indeed, silicones can float on a cleaning bath, and during extraction of the work-piece from the bath the contamination wets the surface again. As mentioned previously, some silicone species have non-negligible solubility in $SCCO_2$, but no commercial system exists yet to apply this technique for cleaning of large UHV parts. An excellent solvent for many silicone greases and compounds is hexane [17]. Its effectiveness has been verified for instance by analysing by XPS a copper surface previously contaminated with silicone grease and cleaned with hexane. The silicon signal was below detection limit. Unfortunately hexane is highly volatile. It must be used in low amounts in well vented rooms, so that the average concentration remains below 200 mg/m$^3$ [18]. Therefore this treatment can be applied to small parts or extraction for analytical purposes (see below).

This review considers only the cleaning methods. In addition, etching to eliminate damaged layers or treatments to induce surface passivation and avoid for instance re-oxidation can be performed if necessary. Some treatments are described in Ref. [4]. They are not suitable for parts which need to preserve accurate dimensions and precise surface finishing. Moreover, it is worth noting that the surface in operational conditions is often not the same as after cleaning since bake-out is frequently used for UHV systems.

### 2.5 Cleaning with ions: glow discharge

After cleaning with the methods described in Sections 2.2 and 2.3, a further processing step can be applied in order to remove oxides or contaminants adsorbed upon air exposure. Glow discharge treatment can be applied to vacuum pipes after evacuation and filling with a suitable gas at low pressure ($10^{-1}$–$10^{-3}$ mbar). Parts with other shapes can be inserted in a vacuum chamber designed for this purpose and in this case the geometry of the electrodes should be studied carefully. Glow discharge can be applied with DC, AC or rf voltages and by using various gases. The principle consists in accelerating ions toward the surface so that the surface is sputter cleaned. In addition, especially in the cases of AC and rf discharges, also ultraviolet light is emitted by the plasma and can help contamination cracking through photochemical reactions. In the DC case the typical voltages used are 300–1000 V. For long pipes, such as accelerator beam chambers, the anode is a wire placed along the chamber axis and the chamber is kept at ground potential. In general, the wire is removed after the treatment by venting and opening the chamber. Such a technique was applied on the Intersecting Storage Rings (ISR) vacuum chambers at CERN. If the air exposure time to remove the electrode is minimized, the beneficial effect is partly preserved [19]. Venting must be carefully performed with clean (or at least dry) gases, like pure $N_2$. Depending on the dose of ions, the treatment can remove the topmost hydrocarbon contamination or even the native oxide layer on the surface. This configuration is exploited also if additional cleaning or oxide removal is necessary prior to magnetron sputter deposition of coatings on long pipes; the anode is already in place and acts then as a cathode during the deposition process.

Sputter cleaning with a noble gas such as argon does not induce chemical reactions with the surface to be cleaned, but some implantation occurs. In stainless steel implanted argon can be removed by baking at 350ºC [20]. A mixture of gases can be used to remove more effectively a specific contaminant so that the total ion dose can be reduced. For instance mixtures containing oxygen (Ar with 5–10% $O_2$) are very effective in the elimination of carbon from the surface [20, 21]. A 100 times lower dose of ions is sufficient to remove surface contamination of carbon from stainless steel when 10% $O_2$ is added to Ar, compared with the case where pure Ar is used. This is due to chemical reactions forming volatile species like CO and $CO_2$, which are evacuated together with the working gas. Hydrogen and helium are used as working gas for glow discharge treatment especially in fusion reactor walls [22] where such gases are not harmful and are less frequently used for UHV systems. A special use of helium is the so-called helium processing performed to condition radio-frequency niobium superconducting cavities. The process is again a sputter cleaning and helium is used just for convenience, since pure gas is available for the cryogenic circuit [23].

The main disadvantage of glow discharge treatment is the possible coating of insulating parts or windows with the sputtered material. The treatment can be applied on various metals such as stainless steel, aluminium, copper, titanium and beryllium. Glow discharge on beryllium is attractive, since this material cannot be easily handled in a wet cleaning facility owing to the toxicity of its oxide. In the case of beryllium [24] it is of great advantage that at sufficiently low energy (below ~300 eV) the sputtering coefficient of $O_2^+$ on C is higher than on beryllium thanks to a chemical reaction producing CO and $CO_2$. The effect is even more marked for beryllium oxide. Tests made at CERN with glow discharge in pure oxygen on small samples showed a strong decrease of carbon levels on the beryllium surface and no detectable (XPS) amount of beryllium on the mounting used to hold the sample.

In other domains glow discharge treatment is used to increase wettability and reactivity of polymer surfaces, since the plasma or sputtering breaks surface bonds.

# 3 Cleanliness and cleaning effectiveness

## 3.1 Methods for assessing cleanliness

Cleanliness must be evaluated with respect to the application for which the surface is intended. Often it is not possible to verify directly the functional performance without assembling an entire device and therefore a control technique is chosen providing sufficient sensitivity to the known crucial contaminants. The control procedure measures the amount of contaminant still present on the surface or a quantity related to it and compares it with the preset limit for acceptance. This limit defines cleanliness. More generally if contamination can be quantitatively monitored, one can define cleanliness classes, which are specifications for each application.

In accelerator technology various contaminants present on the vacuum chamber surface can deteriorate vacuum (hydrocarbons, intermediate vapour pressure compounds), propagate through the system (low vapour pressure metals like Cd and Zn), promote corrosion (halogens), transform into insulating layers upon irradiation (silicones). For the assessment of surface cleanliness many techniques and procedures have been used (Table 1) [25,26]. Most of them reveal the presence of the contaminants, without verifying directly the functional performance of the surface. Many of them require special sample size or shape and cannot be applied on the cleaned part itself, but only on a test specimen, which has followed the same treatment. The techniques can be divided into two types. Analytical techniques can identify and more or less quantify the contamination. Other methods measure a quantity, which is related in a complex and sometimes obscure way to surface cleanliness, but can indicate at least whether excessive contamination is present and enable one to reject the part before insertion in UHV.

The advantage of the analytical techniques is that by identifying the contamination they often enable one to understand its origin. Common surface analyses, such as XPS, Auger Electron Spectroscopy (AES) and Secondary Ion Mass Spectroscopy (SIMS) are well adapted to detect and identify a broad range of organic and inorganic contaminants and obtain a high surface sensitivity. XPS enables easy and fast identification of the elements present on the surface and has a detection limit close to 1 at% in the probed depth of 1–3 nm for most elements. With a monochromatized X-ray source, even distinction between organic species is possible. AES is as good as XPS from the point of view of sensitivity, but Auger lines are wider in the energy spectrum and overlap is frequent. Moreover, care should be taken by using AES to limit the current density of the electron beam, otherwise it can induce surface modifications through Electron Stimulated Desorption (ESD) and also influence the local carbon coverage through stimulated diffusion [27]. ESD measurements indicate that desorption yields on air-exposed surfaces decrease by about a factor 10 for $10^{16}$ electrons/cm$^2$. The typical primary beam currents used in Auger analysis (for instance $10^{-8}$–$10^{-7}$ A on an area of $10 \times 10\ \mu m^2$ up to $100 \times 100\ \mu m^2$) result in some $6 \times 10^{15}$–$6 \times 10^{18}$ electrons/cm$^2$ in 10 seconds, which can be a typical time to acquire a full spectrum. There is experimental evidence that the carbon concentration measured by AES depends on the impinging beam current density [27] and decreases with irradiation. Therefore, the current density and the dose should be well controlled, when comparing data of surface cleanliness. Using XPS, without high spatial resolution options, the amount of surface damage is reduced by a factor 10 to 100 [28]. SIMS, especially in its static version (SSIMS) and high mass resolution, is superior from the point of view of identification of the chemical species of contaminants and has a better sensitivity. The information is, in principle, more detailed; at the same time the interpretation and quantification, which is affected by matrix effects, is not straightforward.

**Table 1:** Techniques for evaluation of surface cleanliness. Sensitivities should be taken as estimated orders of magnitude.

| **Technique** | **On site, on cleaned pieces** | **Limitations (Analytical or not)** | **Cost** | **Time** | **Principle of measurement (detection limit for carbon species, when known)** |
|---|---|---|---|---|---|
| XPS, ESCA (X-ray Photoemission Spectr.) | No | UHV, small sample size (analytical) | High | Slow | Electron photoemission (3% at. in the probed depth, corresponding to ~$10^{14}$ atoms/cm$^2$) |
| AES (Auger Electron Spectr.) | No | UHV, small sample size (analytical) | High | Slow | Electron-induced electron emission (~$10^{14}$ atoms/cm$^2$) |
| SSIMS (Static Secondary Ion Mass Spectr.) | No | UHV, small sample size, interpretation (analytical) | High | Slow | Ion erosion coupled to mass spectroscopy ($10^{12}$ atoms/cm$^2$ [29]) |
| ESD (Electron Stimulated Desorption) | No | Needs suitable sample shape and size (partly analytical) | High | Slow | Electron-induced desorption of adsorbates detected by mass spectroscopy (sensitivity depends on irradiated sample size) |
| Outgassing rate | Yes | Sample shape, (partly analytical) | High | Slow | Thermal desorption monitored by mass spectroscopy (depends on accumulation time) |
| FTIR (Fourier Transform Infrared) | No | Needs rather smooth surface to get high surface sensitivity, partly overlapping peaks (analytical) | High | Slow | Infrared absorption ($10^{12}$ atoms/cm$^2$ in multiple-internal-reflection mode, MIR-FTIR on flat Si wafer [29]) or grazing incidence reflection or based on extraction |
| UV-vis | No | Needs extraction through solvent, overlap of absorption lines (analytical) | High | Slow | UV absorption, extraction method |
| TRXRF (Total Reflection X-ray Fluorescence) | No | Needs smooth flat surface (analytical) | High | Slow | X-ray fluorescence |
| Ellipsometry | No | Needs smooth flat surface | High | Slow | Rotation of light polarization upon reflection ($10^{12}$ molec/cm$^2$) [29] |
| OSEE (Optically Stimulated Electron Emission) | Yes | UV light modifies (cleans) the surface. Does not distinguish between oxides and contaminants | Low | Fast | Photoelectron emission in air ($10^{15}$ molec/cm$^2$ [26]) |
| Wettability by water | Yes | Depends on experience of the operator | Low | Fast | Wettability of the surface by water |
| Water contact angle | Yes, for portable instruments | One model tested and found unreliable | Medium | Fast for portable system | Wettability of the surface by water |
| SPD (Surface Potential Difference) | Yes | Instability of reference surface | Low | Fast | Measure changes of work function due to oxidation and adsorbates (~ $10^{14}$–$10^{15}$ molec/cm$^2$) |
| Gravimetry | No | Insufficient sensitivity | Low | Slow | Measure weight loss of the sample due to cleaning |
| Surface tension markers | Yes | Insufficient sensitivity, pieces must be re-cleaned | Low | Fast | Wetting by inks of various surface energy (surf. en. < 44 mJ/m$^2$) |
| Radiactive tracer | No | Only on test sample contaminated on purpose | High | Slow | Measure decrease after cleaning of radioactivity of a sample contaminated with a tracer [13] |

In the following the application of XPS is discussed more in detail. In general the result of an XPS analysis is not the absolute concentration, as molecules per $cm^2$ for instance. A so-called surface concentration or relative atomic concentration (at%) in the probed depth is obtained. This quantity is calculated from the measured intensities for each element, as peak areas, and the corresponding elemental calibration factors. In fact this quantity corresponds to the true relative atomic concentration only for the case where the distribution of the considered elements is uniform in the probed depth. For contamination this is rarely the case, since it is by definition on top of the surface. However, such a quantity can be used safely for the quantitative characterization of cleanliness and the comparison of results obtained with the same excitation source, the same analyser parameters and geometry (source-sample-analyser) [30]. The case of carbon, which is one of the most common contaminants, is considered more in detail as an example. It is present as hydrocarbons left by lubricants, cutting oils, rotary vane pump oils, residues of packaging materials, fingerprints, and finally airborne hydrocarbons from storage in unprotected environment. An upper limit for the amount of carbon on the surface is therefore often adopted as criterion for surface cleanliness, possibly accompanied by an upper limit for the total amount of other minor impurities. The validity of the so-called surface concentration, at%C, to assess cleanliness has been discussed in detail in Ref. [30]. At CERN for UHV applications a level of 40% at of C on stainless steel is defined as upper acceptable limit (non-monochromatic MgKα, PHI-ESCA 5400 analyser, slit 4, 45° escape angle, 35eV pass energy). This value is chosen based on the accumulated experience on UHV applications, showing that such a surface will have an acceptable degassing rate and will enable one to achieve UHV conditions for static vacuum. Moreover, recontamination kinetics justifies such a limit (see Section 3.5). The thickness of such a layer is estimated around 0.5 nm, assuming the common electron attenuation length values [31] and assuming a homogeneous layer of pure carbon to simulate the contaminant. Care should be taken when comparing cleanliness of different materials. The attenuation of the XPS signal from deeper layers provoked by the attenuation length of the photoelectrons is energy dependent. As a result the same absolute amount of hydrocarbons on two different metals will give a different relative atomic concentration as measured by XPS. Conversion factors can be established, based on the experimental data, to compare the values measured on different materials, as described in Ref. [30]. For instance the same amount of carbon contamination on stainless steel and copper will result in 40% at C and 44% at C, respectively.

A weakness of XPS, at least when used with a non-monochromatized X-ray source is its incapacity to distinguish between silicones and silicates. The chemical shift of the silicon line Si $2p^{3/2}$ is similar in both cases and distinctions based on the detected amount of oxygen are unreliable due to variations in silicone species and adsorbates. The problem is not only academic, since silicates are not so harmful as silicones and are sometimes left on the surface after detergent cleaning (silicates are often included in the cleaning agent). Two techniques can help, SIMS and FTIR. Even in low-sensitivity SIMS fragments like $Si(CH_3)_3^+$ at 73 m/e can be detected and do not overlap in the spectrum with other intense hydrocarbon fragments. For FTIR the sample can be rinsed with hexane, which is a good solvent for silicone oils and greases as mentioned before. The resulting solution is deposited directly on the window used for the IR reflection or transmission measurements and the data acquisition is carried out after evaporation of hexane. The typical absorption features are in the 800–1300 $cm^{-1}$ region. The sensitivity of this elution method is potentially high and depends on the size of the rinsed surface.

Thermal outgassing is another method of testing surface cleanliness which probes the functional performance in static vacuum conditions. The sensitivity of the method depends on the surface which is heated compared to the surrounding surface of the vacuum vessel, and generally samples of the suitable shape must be prepared. Comparison of cleaning methods by this technique has been carried for instance in Refs. [10, 32].

### 3.2 Tests for dynamic vacuum performance

In the particular case of surfaces, which are designed to be exposed to a particle beam, as in the case of an accelerator beam-pipe, the actual pressure or dynamic vacuum is determined by particle-induced desorption. For such cases it is safe to verify the cleanliness levels also by ESD. For the most common cleaning procedures used at CERN this has been done, as described in Ref. [13]. Often ESD is applied to tube-shaped samples measured after baking at 150°C to reduce the level of water in the residual gas, which would mask other fragments. The typical irradiation dose where the ESD yield decreases by a factor of 10 is about $10^{16}$ electrons/cm$^2$ ($10^{-3}$ Clb/cm$^2$) due to a progressive cleaning of the surface. This means that the dose must be limited in order to acquire relevant data for the characterization of the surface in an unconditioned state.

A similar technique is based on ion-stimulated desorption [33]. The ion source in the keV range can be obtained from usual SIMS or sputtering ion guns, where defocusing or scanning should be applied, since one should keep in mind that the sensitivity for constant dose is proportional to the irradiated surface. The main tendencies of ion-stimulated desorption, as desorbed species and intensities, correlate well with ESD [20]. A special case of ion-stimulated desorption is represented by high-energy (MeV/nucleon), highly ionized heavy ions [34]. This phenomenon is particularly important for ion storage rings where the impact of lost ions can induce pressure bursts. The lifetime of such particles is extremely sensitive to residual gas pressure and has a positive feedback mechanism, since ions with a modified charge will diverge from the beam, impinge on the chamber wall, and desorb more gas. It has been shown that desorption coefficients are some orders of magnitude higher for such ions than for instance for electrons. The phenomenon is not completely understood yet, but the usual relation between surface contamination level and desorption yield is confirmed. For instance coatings of the surface as getters or noble metals, which can be easily cleaned by baking in situ, exhibit lower yields than bare stainless steel-surfaces.

To measure Photon Stimulated Desorption (PSD), which is relevant in all the cases where synchrotron radiation impinges on the beam chamber walls, the only suitable source is generally obtained from synchrotron radiation itself at the necessary critical energy. Experiments along this line have been performed [20] by operating a large machine rather than a small set-up for laboratory-size experiments.

### 3.3 On-line and off-line quality control

The ideal quality control for a cleaning plant consists in the real-time monitoring of the surface cleanliness immediately after processing. This would enable one to provide the necessary bath maintenance in time and avoid delivery of parts which are not perfectly satisfactory. Some of the methods considered in the literature for the characterization of surface cleanliness are listed in Table 1. Unfortunately, none of these techniques can be applied as a fast selection test on-line on a series of cleaned objects having different base material, shape, size as in the case of parts cleaned in a facility for an accelerator. It is worth noting that the simplest fast monitoring for the cleanliness of treated parts is the observation of the wetting behaviour of the piece immediately after rinsing. The piece is considered clean if it remains covered by a uniform layer of water when it is lifted out from the rinsing bath or after spraying some water on it. This type of control relies on the experience of the operator of the cleaning station. Available commercial portable instruments for water contact angle measurement in situ have shown low reliability.

### 3.4 Evaluation of the effectiveness of a cleaning procedure

The evaluation of the effectiveness of a cleaning method is verified by contaminating a sample with a well-known blend, cleaning and analysing the surface for instance by XPS. A sufficiently large area and number of samples (4–5) should be measured, in order to average over statistical variations within the same cleaning run. A similar rationale is recommended also by international standards [35]. The

mixture should be chosen to contain chemicals which are representative of a real contamination supposed to occur on the parts arriving at the cleaning plant. For instance, a mixture of oils and greases used during machining at the local workshop or vacuum pump oil which might be present on previously used parts can be a reasonable choice [32]. At CERN such a method has been adopted also to assess the quality of cleaning procedures used by external manufacturers of parts to be inserted in UHV.

An especially elegant way of measuring the amount of residues left on the surface from a previous well-defined contamination is the method of the radioactive tracer [13]. The contamination molecules carry radioactive isotopes and the level of radioactivity after cleaning measures directly how effectively such a contamination has been removed over the whole sample surface.

### 3.5 Packaging and storing cleaned parts

Recontamination occurs through adsorption of contaminants from air or through incorrect packaging methods. Upon air exposure a clean metallic surface, for instance a sputter-cleaned copper surface, forms a layer of oxide, then possibly part of it converts to hydroxide or can be covered by adsorbed water. This occurs because the surface energy of an atomically clean metal or an oxide is some 10–100 times higher than that of water or hydrocarbons (1850 $mJ/m^2$ for clean metallic copper, 72 $mJ/m^2$ for water and 25 $mJ/m^2$ for alkanes). Hydrocarbons have the lowest surface energy and can cover such a surface in a dynamic process, which possibly results in a contamination layer including water and hydrocarbon molecules, the latter with the non-polar regions pointing toward air. Such a process results in the growth of carbon contamination illustrated in Fig. 9. Similar curves were measured by ellipsometry [29] on precision-cleaned silicon wafers. Two further conclusions should be drawn from Fig. 9. First, large parts which will inevitably be exposed to air before packaging or tight closure will always exhibit non-vanishing hydrocarbon coverage on the surface. Second, comparison of effectiveness of cleaning procedures is meaningful only when air exposure time and the storage method (see below) have been correctly defined in advance.

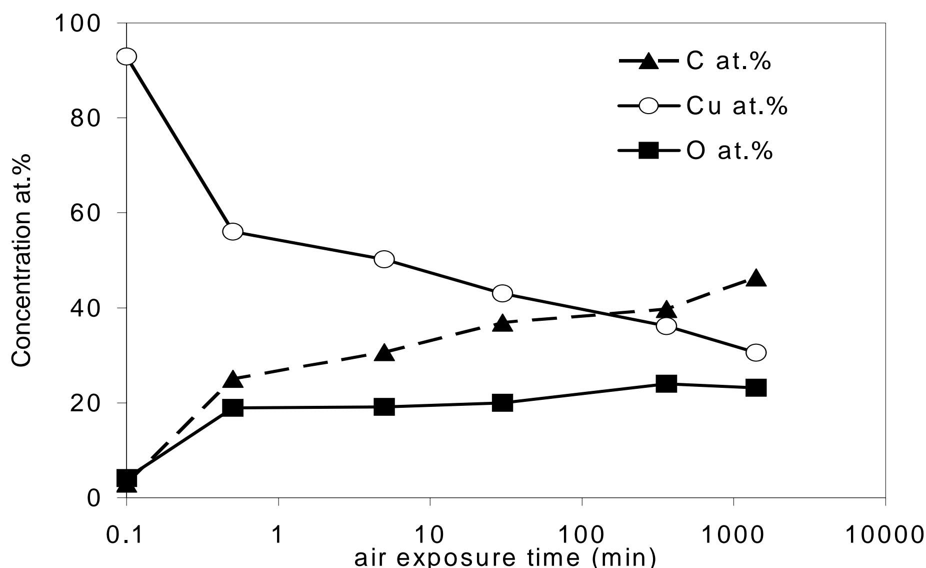


**Fig. 9:** Evolution for the composition, measured by XPS, of a sputter-cleaned copper surface as a function of the air exposure time in the laboratory

In order to avoid recontamination, parts should be used as soon as possible after cleaning. This is not always possible in case of construction of large plants where large series are cleaned, transported, and installed. A proper packaging to protect the part from contamination during storage is suitable. In Fig. 10 [30] a comparison of simple storage and packaging methods is shown. All the

samples were cleaned in the same run in a detergent bath, measured in XPS, and stored wrapped in aluminium foil, in air (protected from dust in a Petri dish), in a polyethylene bag, in a pure-polyethylene bag, and inserted in a polyethylene bag after wrapping in aluminium foil, respectively. It is clear that inserting the samples in a polyethylene foil can have dramatic effects and moreover the result depends on the polyethylene quality. However, packaging in a polymer bag has obvious advantages of protection from macroscopic contamination during transport. Wrapping the parts in clean aluminium foil (in this case common grade used for food packaging) before packaging them in the polyethylene bag removes completely the effect of the surrounding polymer bag. The sample remains as clean when as wrapped in aluminium foil alone. Such a method is obviously not suitable in cases where aluminium traces can provoke adverse effects on the parts.

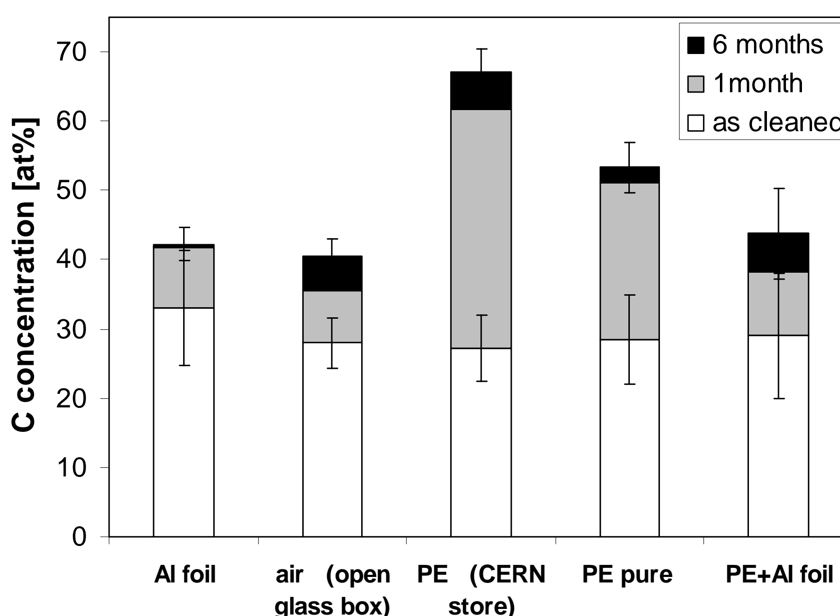


**Fig. 10:** Effect of recontamination of copper samples cleaned in a detergent bath and stored in different ways (average over four samples in each case)

It is worth noting that contamination increases during the first month of storage, but its amount saturates and the further increase measured after six months exposure is moderate. This translates the fact that initial adsorption on the high-energy surface is much more favoured than on the contaminated low-energy surface.

# 4 Surface properties and contamination

## 4.1 Wetting and surface energy

In addition to static and dynamic vacuum, other properties which are relevant for UHV application can be influenced by surface cleanliness. During air exposure, adsorbates like hydrocarbon and water cover easily any clean surface and lower its surface energy. This prevents the adhesion of further coatings, for instance deposited by magnetron sputtering or evaporation. In principle a single monolayer of tightly packed organic molecules covering the surface, like a deposited self-assembled monolayer or a Langmuir Blodgett film, is sufficient to reduce drastically the surface energy [36]. In the case of hydrocarbons adsorbed in a disordered layer during air exposure this occurs more gradually and a larger total thickness is needed. It has been shown [37] that the surface energy decreases down to the level of bulk hydrocarbons when the overlayer reaches a thickness of 2–3 nm. The behaviour

found as a function of thickness is summarized in Fig. 11. A similar set of data illustrates [29] the increase of water contact angle, proving the decrease in wettability, as a function of air exposure time.

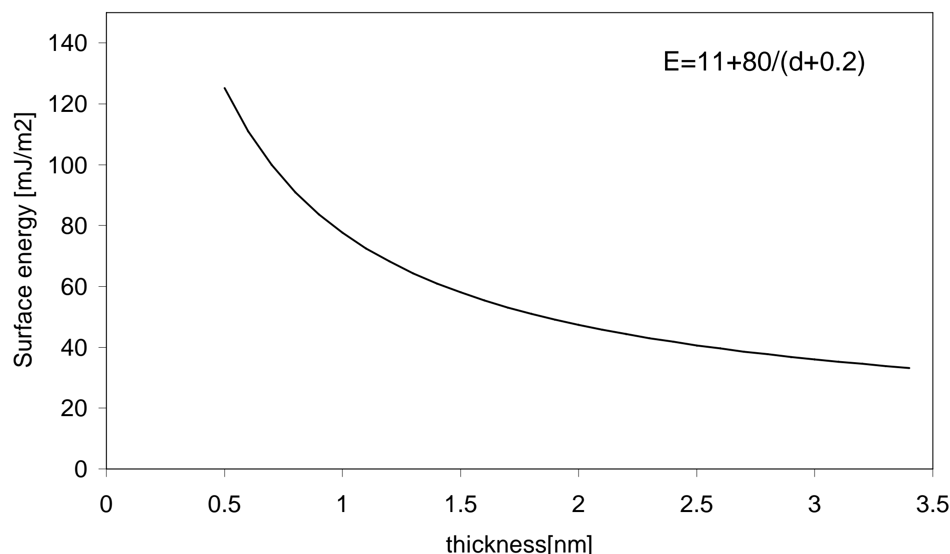


**Fig. 11**: Behaviour of the surface energy of stainless steel as a function of the thickness of the adsorbed contamination. The equation on the top gives the energy in mJ/m2 as a function of the thickness in nm [37]

### 4.2 Secondary electron yield

The secondary electron yield (SEY) of the surfaces exposed to the particle beam is a further quantity which is relevant for particle accelerators. This quantity influences the beam stability and in the worst case can maintain the so-called multipacting or resonant electron multiplication or electron cloud effect [38]. For common technological materials like stainless steel, aluminium, and copper the SEY of the air-exposed surface is much higher than for the clean metal or the corresponding oxide. As can be concluded from the shift of the maximum yield toward lower primary energies [39], the SEY increase is mainly due to the coverage with a layer of contaminant, which has itself a high SEY. Since thin layers of water have been shown to be ineffective to justify such an increase, the origin of the effect must be in the adsorbed airborne hydrocarbons.

For getter materials the activation process removes the surface contamination by transforming the hydrocarbons in carbides and by letting the oxygen of the oxide diffuse into the bulk; simultaneously the SEY is reduced [40]. For the more common metals used for accelerator vacuum chambers SEY can be progressively reduced by irradiation by electrons or photons (synchrotron radiation). This process is usually called conditioning and consists in surface cleaning through particle stimulated desorption and de-hydrogenation of the adsorbed hydrocarbons [27].

As already presented in Section 3.5, cleaned surfaces can be recontaminated due to improper storage materials or even by storage in air. The effect of such a recontamination on the SEY is shown in Fig. 12. SEY always increases with storage time for all methods used for packaging. Therefore parts which are cleaned and inserted in the accelerator after longer storage time will need a longer conditioning phase. In addition, the curves show that the adverse effect can be limited by selecting suitable storage conditions. For instance wrapping the parts in aluminium foil before inserting them in a polymer bag improves the situation in comparison with packaging in the polymer bag alone. The results of the SEY behaviour (Fig. 12) correlate well with those found for the carbon contamination increase as a function of storage time (Fig. 10). This fact proves that the high SEY of air-exposed surfaces is related to contamination from airborne hydrocarbons.

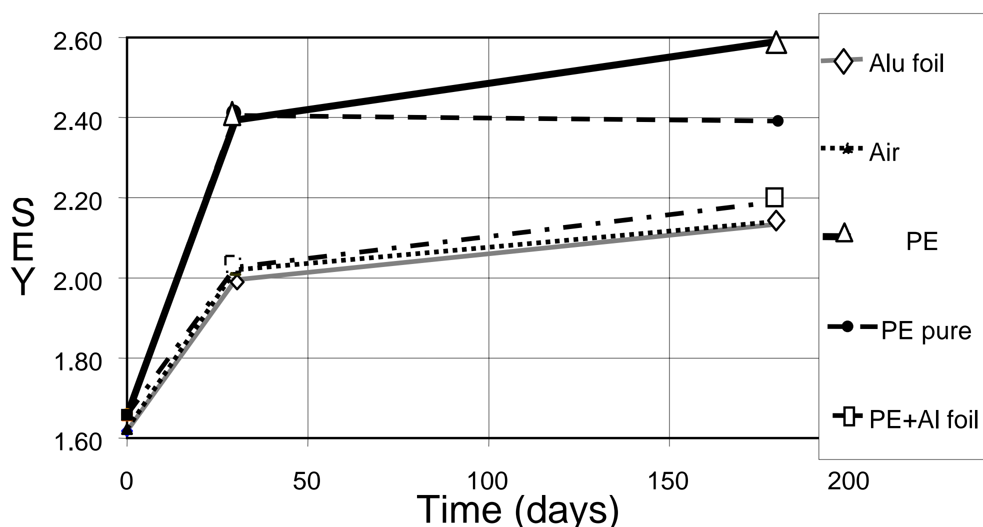


**Fig. 12:** Secondary electron yield of copper as a function of packaging method and storage time (B. Henrist, N. Hilleret, C. Scheuerlein, M. Taborelli, unpublished)

## 5 Conclusions

The various methods of cleaning presented above are not a complete and universal recipe, but give some guidelines in order to optimize a cleaning method for a particular application. Even the most accurately selected procedure should be tested on the real parts to be cleaned or on a specimen which is representative of them for shape, size, contamination, and surface composition. The possibility to clean the parts effectively should be considered, and implemented from the initial stage of development, design, manufacturing and assembly process, in order to build ‘cleanable’ parts. A good rule is always to remember that cleaning is only necessary because at some stage there is contamination added to the parts. Typically this occurs during the manufacturing process. Therefore, the safest way of proceeding is not to rely on cleaning, but to conceive a fabrication process which avoids the use of the most relevant contaminants.

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