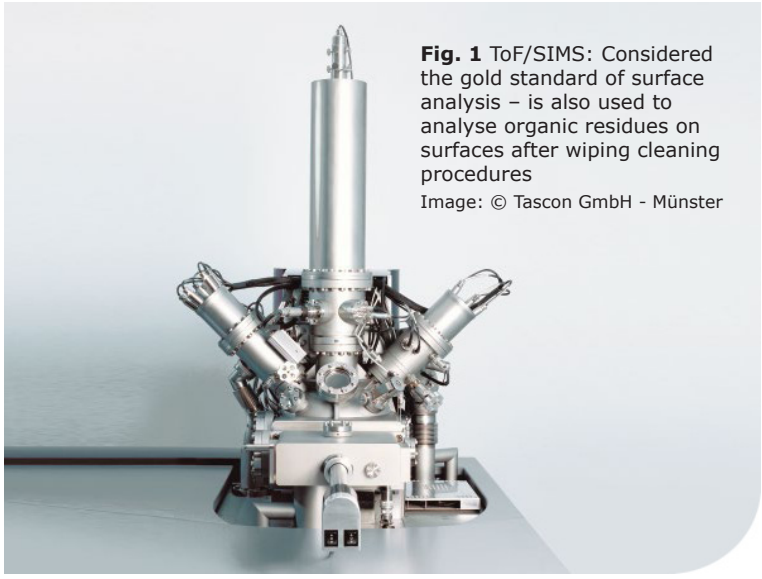

Fig. 1 ToF/SIMS: Considered the gold standard of surface analysis – is also used to analyse organic residues on surfaces after wiping cleaning procedures
Image: © Tascon GmbH - Münster

This paper is a summary of our findings on traces of contamination on object surfaces induced by cleaning procedures using cleanroom wipers. We discuss the unwanted side effects of such cleaning procedures and how to analyse and record them. Surface-related test methods are proposed and the results are discussed. Test methods that are related to the textile material are called into question. The analysis focuses only on the state of the object surface after the cleaning procedure.

Contamination of Functional Surfaces by HiTech Wipers: Surface Purity vs Wiper Purity

Win Labuda
Clear & Clean - Research Laboratory

In most cases, knitted wipers are used in clean work techniques for cleaning tasks with increased purity requirements. From these knitted wipers, relatively few particles are released into the environment during cleaning, and they have a high cleaning performance. However, from their manufacturing processes they contain traces of organic residues, such as surfactants, spinning lubricants, knitting oils and waxes. After cleaning with knitted wipers, thin residues of such chemicals remain on the object surfaces that are invisible to the eye - films and streaks that are even considered unacceptable in some manufacturing processes. This is especially true in the preparation for bonding production processes, the sustainability of varnish applications, the functionality of optical measuring devices, laser mirrors, prisms, for systems of oxygen production and last but not least and extremely important: for the final cleaning and packaging of hip and knee implants and pacemakers.

For such critical cleaning tasks, wiper production must be subjected to a strict quality control. This

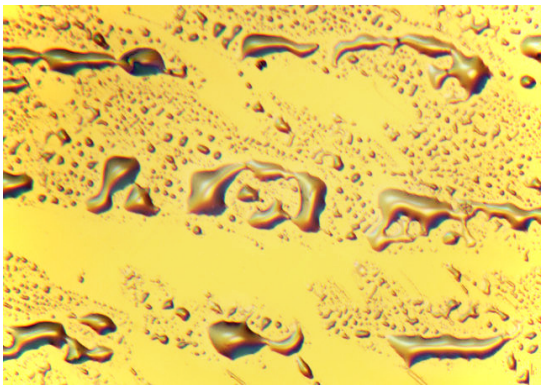

Fig. 2 Fingerprint - the classic surface contamination in the µg range. Differential Interference Contrast (crop, Zeiss - Photo Microscope - III)
photo: Win Labuda

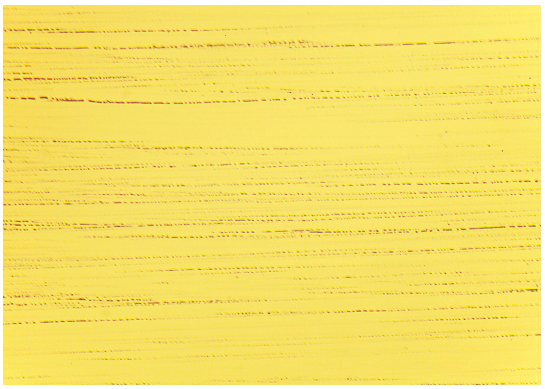

Fig. 3 After the wiping procedure only seemingly clean: In the DIC contrast, traces of contamination are still clearly visible.
photo: Win Labuda

requires accurate knowledge of the physics of cleaning by wiping, well-formulated test procedures and highly sensitive analytical instruments.

In the reference literature, various test methods are described that determine the suitability for use of cleanroom wipers as well as other tools in clean technology. Until now they have mainly related to the material purity of the wipers. The aim of cleaning work, however, is to make the surface clean, not the wiper. This inconsistency between the application purpose and the evaluation parameters naturally leads to serious valuation errors. [2] The cause may be the test method IEST-RP-CC 4.3 "Evaluating wiping materials used in Cleanrooms and other Controlled Environments" and some of its sub-sections. This method originates from the U.S. "Institute for Environmental Science and Technology", and it was first formulated in the 1980s.
In the early phase of cleanroom technology, the measuring technique for traces of contamination on surfaces was still less developed. Moreover, data technology was in its infancy. In cleanroom technology during those years, the primary concern was to find a solution for the particle problem. Probably these were the reasons that prompted the American mentors of the first test methods for cleanroom wipers (IEST - working group 4.3) to make the material purity of the consumables and not the purity of the cleaned object surfaces the key parameters of the use suitability of cleanroom wipers. So still to this day it is up to the user to infer the achievable surface cleanliness from the textile purity of the respective cleanroom wiper.

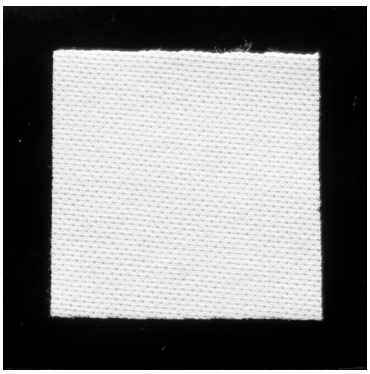

Fig. 4 Indicator plate with cloth section prior to acetone immersion.

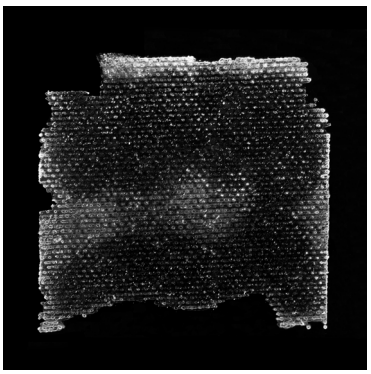

Fig. 5 Substantial organic compound residue from untreated cloth after acetone drying.

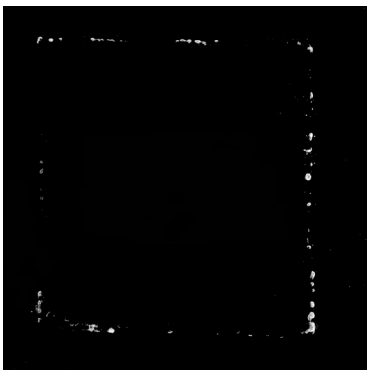

Fig. 6 In comparison to Fig. 5: Low residue from highly decontaminated cloth (soxhlet extraction).

The American technologist Steve Paley, former board member of the U.S. company Texwipe Inc. - still today the world's largest manufacturer of cleanroom wipers - wrote in an essay already back in 1996: [4]

"While most cleaning cloths are effective in absorbing liquids or drying wet surfaces, the essential difference between the various brands lies in the mass of contamination they leave behind on the surfacesduring the wiping process. Wipers that contain large masses of foreign substances will inevitably leave traces of them on the cleaned surfaces during the wiping process."

Approaches to surface analysis

The question is what are the reasons that almost twenty years after Paley's statement, hardly anything has changed in the dubious evaluation system for cleanroom wipers. It is clear that the cleanroom consumables industry itself has so far shown no appreciable ambition to remedy the sins of omission of the past. Rather, it has again created confusion by almost unanimously claiming that the industry's products could correspond to specific application-oriented cleanroom classes according to the ISO 14644-1 standard. That is of course questionable because ISO 14644-1 is a standard for particulate air quality, and cleanroom wipers do not affect the particle content of the cleanroom ambient air. at all. This also applies in principle to paper, gloves, swabs and other cleanroom consumables. Thus, this raises the question of what measures can be taken to support a paradigm shift from material analysis to surface analysis. Not until such a shift has taken place will we be able to explore the technological limits of cleaning procedures by wiping on a broad basis. More purity conversely means less contamination and therefore requires increasingly sensitive measuring systems.

Need for information among manufacturers, users and sellers

Given the increasing hazard potential through the transfer of cloth-inherent contamination to critical object surfaces, cloth manufacturers and users have an increased need for information concerning specific risk scenarios, e.g. with respect to the biocompatibility of the wipers and especially the contamination released from these. This can be described as follows:

- How much contaminant mass is still acceptable on the object surface without endangering the production target?
- How high is the effective, particulate, microbial and/or chemical purity state of the object surface after a wiping cleaning procedure?
- How much time is necessary with a specific cleaning product to bring about the required state of purity?

According to the present state of technology there are different indicative, quantitative and qualitative measuring methods to solve the measurement task, which are briefly described below and are provided with explanatory diagrams and/orimages (see Table 1).

Indicator plate (pat.) [18]:

A piece of cloth with the dimensions of e. g. 35 x 35 mm is placed on a pure, dark-coloured glass plate that has been vapour-coated with an anti-reflective coating and that has a light reflexion of < 1.5 %. Using a glass pipette, several drops of an analytically pure solvent (acetone, isopropanol, nhexane etc.) are applied to the cloth specimen until it is fully soaked. The applied solvent quantity should be such that it does not spread over the edges of the cloth. After evaporation of the solvent a solid residue forms on the indicator plate, particularly in the marginal areas of the cloth section. When this residue is illuminated obliquely

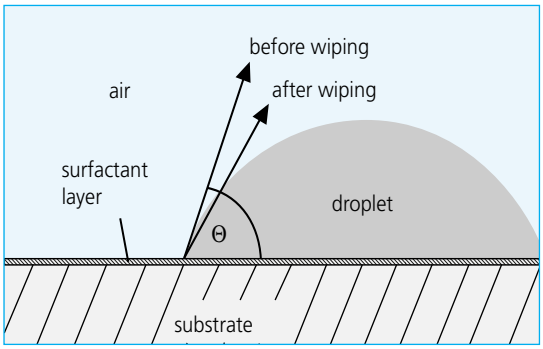

Fig. 7 Contact angle of a droplet as measure for the contamination of a surface by a surfactant layer.

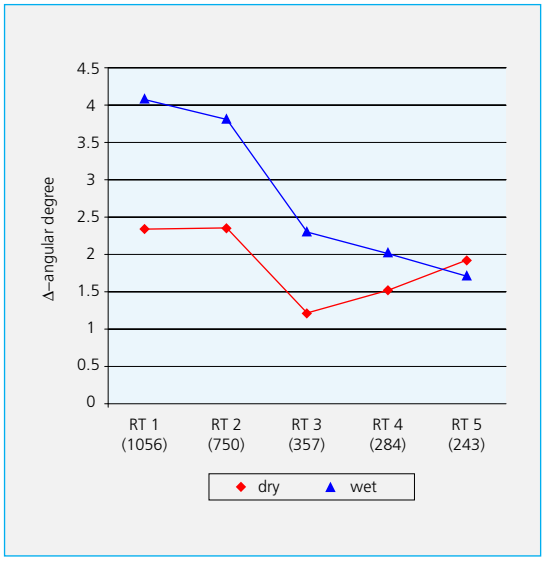

Fig. 8 Contact angle difference in degrees of wiped surfaces to wet surfaces for 5 selected cleanroom wipers (RT 1 to RT 5) in a dry and wet state

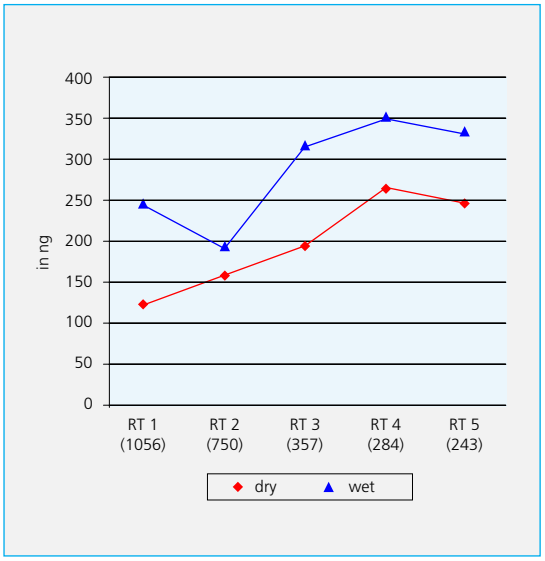

Fig. 9 Weight gain of a quartz crystal after dry / wet wiping procedure, 5 cleanroom wipers (value in parentheses = number of stitches/cm²).

it differs visually from the dark background of the plate. If the indicator plate is mounted on the boom of a suitable stereo microscope, the solid residue can be photographed. With some experience, a rough estimate of the amount of residue can be made.
The indicator plate is one of the most versatile, inexpensive and easy-to-use test devices for the visualisation of both particle deposits and organic surface coatings of porous fabric. In addition, it can be used for the rapid assessment of the purity of solvents as well as the cleaning efficiency of various cleaning agents.

DIC-microscopy

For the microscopy of organic layers, reflected light differential interference contrast microscopy (DIC) is a method that allows the three-dimensional imaging of the finest height differences in streaks of oil and surfactant layers on surfaces. With the method, the substrate and sample can be differentiated particularly well. Moreover, an elevated resolution is attributed to this method. (Fig. 2 and 3)

Drop shape analysis

Drop shape analysis is a well-known analytical method for determining the purity of object surfaces by comparative measurement of the contact angle on the recumbent DI water-drops. It was found that the contact angle of surfaces on which previously a dry wiping procedure with a knitted wiper had been performed was about 3° less than the contact angle of pure surfaces. This can serve as an indication of the transfer of e.g. traces of surfactant from the knitted cloth onto the test surfaces. In wet-wiped surfaces, the average contact angle difference even amounted to 4.6°.

Fig. 10 Quartz crystal microbalance QCM 200 (Stanford Research, USA)

Fig. 11 QCM 200 – Crystal absorption device of the quartz crystal microbalance

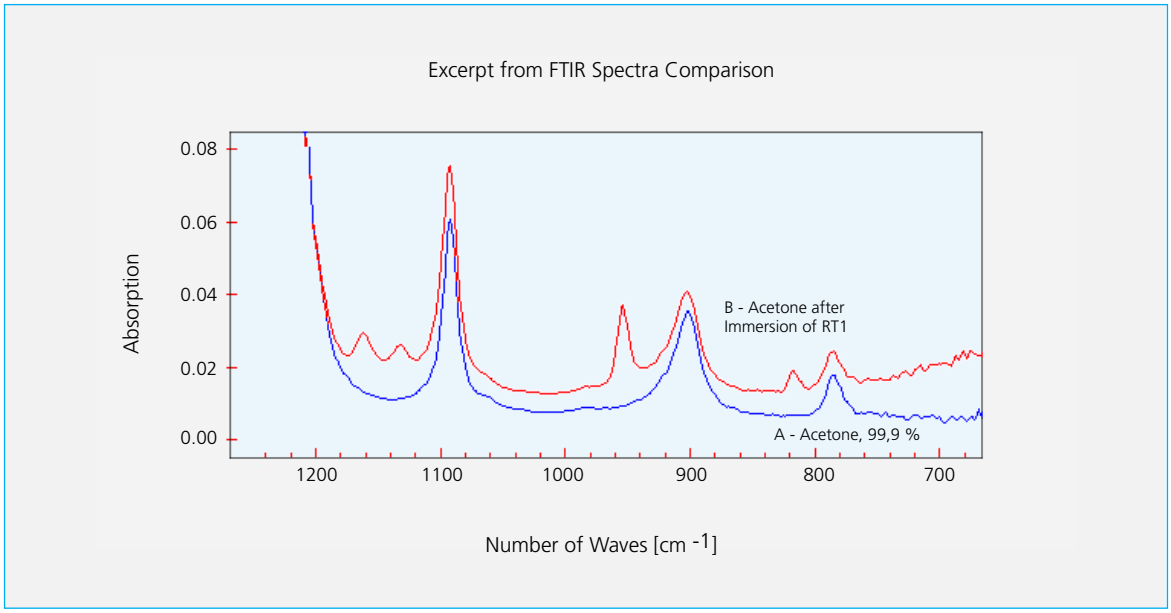

Fig. 12 FTIR spectrum of pure acetone (A - blue) vs. acetone after immersion of a cloth knit wiper (B - red): It is evident that a substance transfer from wiper RT1 has occurred into the pure acetone (see diagram B).

Laser fluorescence thickness measurement

Relative measuring method for the quantitative determination of the thicknessof fluorescent layers on surfaces.When they are illuminated with UV light of a certain wavelength, a fluorescence occurs whose intensity is dependent both on the beamed light intensity as well as the thickness of the layer. For this measurement method, values derived from previous experiments with fluorescent oil films are available. As a new finding, we have evidence that for cleanroom knits there is a product-specific, critical contaminant mass that cannot be reduced with the clothin question even if the wiping cleaning procedure is continued.

Piezoelectric gravimetry

The comparative weight of the surface residues left by wiping procedures is measured here by means of a piezoelectric resonator whose resonance frequency varies as a function of the residue mass and thus permits a weight determination down to the Nanogram-range. We limited our task to measuring the transfer of contamination of organic substances - in particular oils, surfactants and waxes onto the object surfaces from the wipers.

Infrared spectroscopy (FT-IR)

The method makes it possible - even for specimens of low mass, e.g. for contaminations - to qualitatively identify the molecular structure of organic compounds in the mg range down to several molecule layers. This is done by the data technology-based comparison with reference substances. The measurement time is short. Using the Agilent DialPath spectrometer 630, it is possible within a few seconds to

Fig. 13 Agilent FTIR – Spectrometer 630 with ATR sampling interface

analyse a liquid droplet that has been extracted from a tissue section. The FTIR analysis of the organic soxhlet extract from knitted wipers by means of soxhlet extraction with acetone resulted in the same spectrum, in principle, with the same components as in the TOF / SIMS analysis. However, with this method we could not determine the transfer of erucamide from the packaging film to the fabric surface. In Fig. 13 the change of a pure solvent after immersion of a cleanroom wiper is shown as a comparative spectrum diagram.

ToF/SIMS secondary ion mass spectrometry

The time of flight secondary ion mass spectrometry is an analytical method for high-resolution chemical characterisation of solid surfaces. The method enables the analysis of the three upper molecule layers and thus serves, inter alia, the identification of surface contamination. The wiping cleaning procedure was done over a pure aluminium surface of low roughness with cleanroom wipers (RT) with the names RT 1, RT 3 and RT 4 in the following states: dry, acetone-wet and 2-propanol-wet. Thereafter, on all nine analysed substrates residues from the polyester matrix could be detected. In those wipers that had come into direct contact with the polyethylene packaging material, there were in addition Erucamidetraces (13-docosenamide) on the respective aluminium substrate after the wiping procedure on the aluminium surface. The substance belongs to the group of waxes which are often used as lubricants in the film production. In addition, on the cloth RT 1 sulfate traces such as dodecyl benzene sulfonate were found. Traces of oil, however, could not be found. A quantitative assessment of contamination is possible yet restricted with this method. Table 2 shows the results of the ToF/SIMS analysis in an overview.

Surface analysis to control wiping cleaning procedures	indicative	quantitative	qualitative
Indicatorplate	•		
Microscope, DIC Contrast	•		
Drop Shape Analysis	•		
Laser Fluorescence		•	
Piezoelectric Gravimetry		•	
FT-IR after Extraction			•
ToF/SIMS-Mass spectrometry			•

Table 1 Different types of surface analysis to evaluate wiping cleaning procedures

Summary and outlook

- The purity of functional surfaces is gaining significance in the life science and HiTech-industries. Wiping procedures for cleaning are part of a modern manufacturing culture. For many tasks, especially mobile cleaning tasks, they are indispensable.

Cleanroom wiper number	wiper RT 1	wiper RT 3	wiper RT 4
Mesh / cm²	1056	357	284
Polymer	PET / PA	PET	PET
Immersion none	Polyethylene terephthalate	Polyethylene terephthalate Erucamide	Polyethylene terephthalate Erucamide
2-Propanol (f. Chromatog.)	Sulfates Polyethylene terephthalate Dodecylbenzenesulfonate	Polyethylene terephthalate	Polyethylene terephthalate
Aceton p. A.	Sulfates Polyethylene terephthalate Dodecylbenzenesulfonate	Polyethylene terephthalate	Polyethylene terephthalate

- Today a sufficient range of analytical instruments and methods exists to determine the transfer of chemical substances from cleaning wipers onto the object surfaces both qualitatively and quantitatively. The same applies to particulate and bioactive contamination.

- Analytical methods that are related to the conditon of the textile wiper are unsuitable for determining the functional purity of object surfaces that can be achieved by cleanroom wipers. However, they are occasionally a welcome supplementary information to the results of the surface analysis.

- Demands are being made to industry to introduce low-cost instruments and devices to determine the purity of surfaces. One example for this is the C&C indicator plate. (18)

- This paper is devoted exclusively to the transfer of chemical constituents from wiping agents onto the object surfaces. Other essays concerning the transfer of particulate and bioactive contamination from cleanroom wipers shall supplement this writing at a later date.

Acknowledgments

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Translation: Carol Oberschmidt

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