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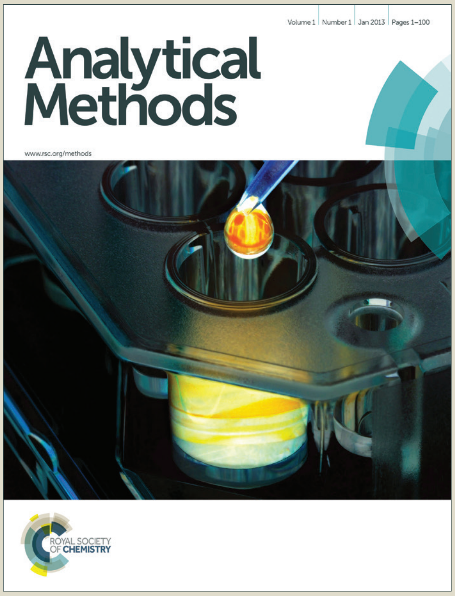

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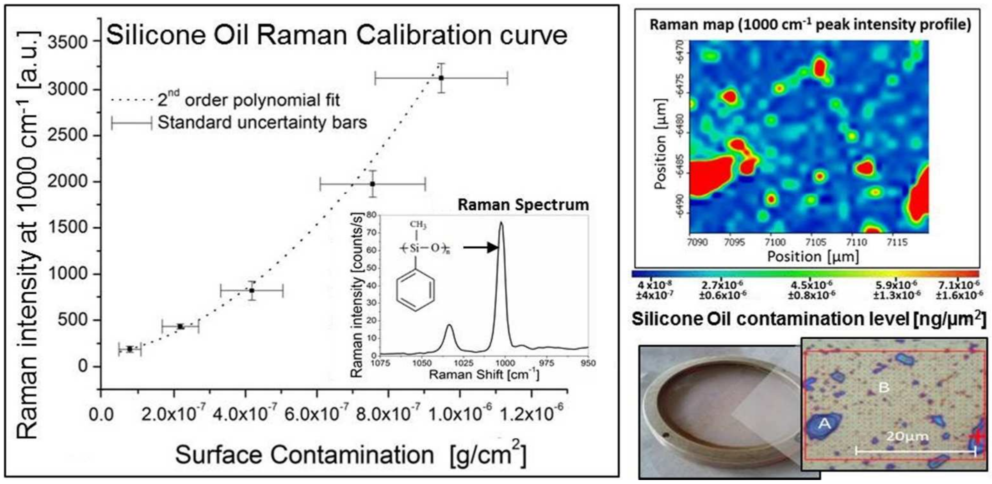

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ARTICLE

# Direct detection and quantification of molecular surface contaminants by Infrared and Raman spectroscopy

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Detection and identification of surface molecular contamination is important for improving process and product yields in a wide range of industrial applications. In particular, molecular compounds can easily deposit on the surface of hardware, optical components, semiconductor devices, medical devices, etc. with the risk of impairing their functionality. In this work, qualitative and quantitative metrological methodologies for surface molecular contamination detection based on Fourier Trasform Infrared Spectroscopy and micro-Raman Spectroscopy are presented. The specificity of detection of two ubiquitous industrial contaminants i.e. poly(methylphenylsiloxane) and paraffin oil by Infrared and Raman fingerprints is first demonstrated. Moreover, in order to obtain homogeneously contaminated surfaces that can be used as standard materials for Raman calibration, films of different thickness of contaminants were prepared on calcium fluoride windows, within a contamination range of 70-900 ng/cm$^2$, by a spin coating method. The amount of contaminants spread on the surface was quantified by applying a pre-set FT-IR calibration curve in accordance with the European Cooperation for Space Standardization procedure (ECSS-Q-ST-70-05C) and it was subsequently used to calibrate the Raman equipment which demonstrated a sensitivity up to $10^{-8}$ g/cm$^2$. A real case study of industrial contaminated surfaces i.e. a glass lens for laser cutting machine is also presented to assess the applicability of both techniques in molecular contamination monitoring. In the discussed case Raman analysis turned out to be particularly useful for punctual investigation of the surface, especially when the sample is not transparent to the infrared radiation.

## Introduction

Detection and identification of contaminants or residual materials on cleaned surfaces represent a crucial topic in the industrial field in order to guarantee and to improve process and product yields in a wide range of applications. Examples include contamination in the production environment of pharmaceutical and food products such as the cleanliness of reaction vessels and sterility of biomedical devices and medical implants[1; 2], the neatness of slides and optical lenses for laser cutting machines, the adhesion performances of coatings such as paints and adhesives[3]. Molecular contamination is also a critical aspect in the fabrication of hardware and high tech vacuum components, for aeronautical and space industry devices[4] and miniaturization of Metal Oxide Semiconductor Field Effect Tansistors (MOSFET)[5]. The source of contamination usually comes from volatile condensable products of off-gassing materials or materials out-gassing under vacuum, back-streaming products from pumping systems, handling residues (e.g. human grease), residues of cleaning agents and creep of certain substances (e.g. silicones)[6]. In particular, hydrocarbon oil materials and siloxane compounds such as the poly-dimethylsiloxane (PDMS) can easily deposit on industrially relevant surfaces (hardware, optical components, semiconductor wafers etc.). For instance, plastic bags and boxes are known to be a source of PDMS[7]. Even the laboratory atmosphere might be the source of contamination, as reported in Leggett's study in ref[8]. Since the contamination can change the feature of a specific surface and might lead to impair the functionality of the instrumentations, reliable metrology tools able to measure surface layers, surface contaminants, defects and the 3-D distribution of chemical constituents in the near-surface region are required. Several methods were developed over the years for monitoring and identifying chemical species on surfaces and they usually involved analytical techniques such as gas chromatography, mass spectrometry following thermal desorption (TD-GC/ MS)[9],X-ray photoelectron spectroscopy (XPS)[10],time-of-flight secondary ion mass spectrometry (ToF-SIMS)[11] and infrared spectroscopy (IR). Although established surface analysis methods such as XPS and ToF-SIMS have demonstrated their value for the detection of surface contaminants, they are very poorly suited for routine monitoring of devices because they must be operated in ultra-high vacuum, they often require a special sample preparation, have a slow turn-around and, above all, are very expensive. In addition, it is not possible to perform rapid quantitative analysis with ultra-vacuum instrumentations because of the risk of contaminating the measurement chamber with the analyte, e.g. the molecular contaminant. It must be noticed that the most common contaminant observed in TOF-SIMS spectra is the PDMS[12]. Siloxane contaminants represent a ubiquitous problem in static SIMS analysis of polymers that is why this technique is not suitable for siloxane contaminant detection[7]. The appropriate choice of the analytical technique in each case is important for providing the expected answer to the contamination problem. Emerging ambient techniques that employ either vibrational spectroscopy (FTIR, Raman) or mass spectrometry (Desorption Electrospray Ionization DESI, Plasma Assisted Desorption Ionization PADI) are far better suited for the manufacturing environment but, up to now, these techniques lack of reproducibility, traceability and availability of standard materials needed for the characterization of surface contaminants. Recent advances in FTIR and micro Raman spectroscopy offer great promises to meet the industry needs for surface quality assessment[13]. Detailed chemical information can be provided by spectroscopies, which are non-contact and non-destructive analytical techniques, also well suited for in-line analysis. As far as the aerospace industry contamination is concerned, a metrological method based on Fourier transform infrared spectroscopy (FTIR) for the fast detection of the main categories of contaminants, including hydrocarbons and silicones, was already developed[14]. In this method, IR-transparent windows (e.g. $CaF_2$, ZnSe and Ge) are used as witness plates and placed for a certain time inside a vacuum facility, a clean-room or close to the spacecraft module. The surface of the witness plates is monthly analyzed (without further treatment) using a FTIR spectrophotometer. The quantification procedure is performed in accordance with the standard ECSS-q70-05a which is provided by the European Cooperation for Space Standardization and that represents the official method for contamination monitoring in cleanroom. However, some drawbacks dealing with the set-up of the quantification process and with the preparation of the calibration curves have emerged in the official methodology. In particular, the positioning of the standard solution onto the $CaF_2$ window, within a very small area covered by the IR beam, results to be quite difficult, and it might affect the validity of the quantification process. Even if well trained operators can perform the calibration procedure without misleads, the precision of the quantification method is strongly operator-dependent and the measurement uncertainty can vary from 10 to 20 % depending on the level of training. Moreover, the whole calibration procedure is time consuming and even a periodical control can represent a considerable waste of time, especially for a contamination monitoring in the manufacturing environment. In order to overcome the limitations of the official methodology and to propose a simpler quantification procedure that could be even used for a routine monitoring at the industry level, homogenous films of contaminants (paraffin oil and poly(methylphenylsiloxane)) with different thicknesses were prepared on calcium fluoride windows by spin coating, with the aim at using them as reference materials. The thickness of these films is at the nanometric scale, corresponding to an amount of contaminant on the surface within the concentration range useful for practical applications (70–1000 ng/cm$^2$). The resulting candidate reference materials were characterized by FT-IR and Raman mapping in order to check the homogeneity of the films over the whole surface of the windows. The amount of substance was quantified by the pre-set FT-IR calibration procedure in compliance with the standard ECSS-q70-05a, which provides information about the surface contamination, in terms of nanograms of contaminants per area unit. Quantitative contamination data were subsequently used to correlate the specific Raman peaks intensity to the amount of substance deposited on the surface, making also Raman spectroscopy calibrated for quantitative analysis and traceable to the International System of Units (SI).

A comparison analysis between FTIR and Raman spectroscopy based on a real case study i.e. a glass lens for laser cutting machine is also presented to assess the applicability of both techniques for molecular contamination monitoring. In the discussed application Raman analysis turned out to be particularly useful for punctual investigation of the surface, especially when the sample is not transparent to the IR radiation. In particular, the present work attests the possibility of implementing the established FT-IR method for the organic surface contamination detection with the more punctual and versatile Raman spectroscopy.

## Experimental

### 2.1 Reagents and materials

Paraffin Oil (suitable for IR spectroscopy), Poly(methylphenylsiloxane) (Silicone Oil) with purity at least 97 %, Chloroform (spectroscopic grade) and Acetone (spectroscopic grade) were purchased from Nova Chimica (Milan, Italy). Calcium Fluoride ($CaF_2$) infrared transparent windows (25 mm diameter and 2 mm thick) were provided by Crystran Ltd (UK). 10 µl glass micro syringe and stainless steel tweezers (145 mm, straight) were purchased from Appenlab srl (Italy). The representative test materials used for the calibration are of high purity. Solvents used to prepare calibration solutions are spectroscopic grade solvents, having a non-volatile residue (NVR) < 5 µg/g.

### 2.2 Preparation of standard solutions and spin coating procedure

Stock solutions for each representative test material (paraffin oil, and silicone Oil) with the appropriate concentration (*C*) in solvent were prepared. In order to cover the range of detection 5 $10^{-8}$– 1 $10^{-6}$ g/cm$^2$, five stock solutions at 0.1 g/l, 0.25 g/l, 0.5 g/l, 0.75 g/l and 1 g/l in chloroform were prepared for each representative test material. Standard solutions are conserved in a cool and dark area and the evaporation of the solvent is limited by sealing the measuring flask. Only glassware or components in PTFE are in order to minimize cross-contamination. Plastic bottles, lids and syringes are avoided because some mold release agent can be dissolved from the surface. Glassware are cleaned and rinsed several times with the spectroscopic grade solvent before use.

Homogenous films of different thickness of contaminant were prepared spreading different concentration solutions of paraffin oil or silicone oil on $CaF_2$ windows (Spin Coater WS-650MZ-23NPP/LITE by Laurell). 200 µl of each standard solution is deposited on calcium fluoride window using a metal needled glass syringe. The optimal spin coating method consists into two steps: (i) 10 s at 60 rpm (deposition during slow rotation); (ii) 60 s at 4000 rpm. Before starting the spin coating procedure, the IR transparent window are cleaned in an ultrasonic bath with acetone (5 min) and chloroform (5 min) to remove excessive contamination, rinsed with chloroform and dry with nitrogen.

### 2.3 FTIR measurement

A FTIR-Nicolet (Thermofisher Scientific) IR spectrophotometer equipped with a DTGS detector and a KBr beamsplitter was used for the organic contamination measurements. 64 scans were done for background and sample spectra collection in the spectral range 4000-800 cm$^{-1}$ with spectral resolution of 8 cm$^{-1}$. An infrared beam spot of 0.5 cm$^2$ was aligned into the center of the window to optimize the signal. Nitrogen purging was continuously fluxed inside the main compartment in order to increase S/N ratio and to reduce the interferences from the environment such as water and carbon dioxide. A FTIR-Nicolet ContinuµM (ThermoFisher Scientific) microscope equipped with cooled MCT detector was used for contaminant thin film IR mapping. The infrared beam covers a 150x150 µm$^2$ square area; resolution of 8 cm$^{-1}$ was applied and 64 scans were collected for background and sample. Spectra were collected in the range 4000-800 cm$^{-1}$ in transmission mode.

### 2.4 Calibration procedure

The FTIR calibration procedure was previously reported in ref[14]. Briefly, proper volumes of stock solutions corresponding to specific mass values are applied on the IR transparent window by manual drop coating. It is fundamental to position the droplets on the window in an area corresponding to the beam shape of the IR equipment. This can be reached practically by fixing the glass micro syringe to a support and positioning it perpendicularly very close to the surface. The drop coating is performed on a 45 °C heated plate to facilitate the very fast solvent evaporation in order to obtain small and circular spots.

For the determination of the calibration curves, seven mass values of the standard were analyzed in the range $2{\cdot}10^{-8}/1{\cdot}10^{-6}$ g. Blank signal was registered on the neat IR window and used for the evaluation of the limit of detection (LOD), that was calculated to be equal to 3S/N ratio. The S/N ratio was calculated at the wavenumber of the characteristic peak of paraffin and silicone oil e.g. 2920 cm$^{-1}$ for the first and 1260 cm$^{-1}$ for the latter. According to Lambert-Beer's law, which relates the absorbance at a specific wavelength with the standard concentration, a regression curve was fitted to the intensities of main absorption peaks for each contaminant (a) Paraffin Oil, 3000-2800 cm$^{-1}$; b) Silicon Oil, 1300-1180cm$^{-1}$). The applied fitting procedure was a weighted total least square (WTLS) regression, and was implemented by means of a MATLAB®-based tool for calibration problems[15] that is able to deal with uncertainty (and correlation) in both the dependent (average intensities) and independent (mass values) variables. As reported in ref[14], the calibration curve obtained for each contaminant can therefore be used as the basis for subsequent quantitative analyses.

### 2.5 Raman measurement

Raman spectra were collected using a Thermo Scientific DXR Raman equipped with a microscope, a motorized microscope stage sample holder, and a charge-coupled device (CCD) detector. The excitation laser wavelength is 532 nm. Spectra of contaminated $CaF_2$ windows were collected using a 100x microscope objective (laser spot diameter ~ 0.7 µm corresponding to 0.4 µm$^2$ area) with a 7 mW laser power in a spectral range from 3500 to 100 cm$^{-1}$ with a grating resolution of 5 cm$^{-1}$. The acquisition time was of 8 scans with 46 s exposure time.

## Results and discussion

Contamination of organic materials on the surface represents a ubiquitous problem in the manufacturing processes of several industries. As soon as the performance of semiconductors, optoelectronic and photonic devices as well as medical and pharmaceutical products has improved, the tolerance for molecular contamination has decreased. Emerging ambient techniques such as FTIR and Raman spectroscopy are better suited for organic contamination monitoring in the manufacturing environment and offer great promise for surface quality assessment. As indicated by ECSS and stakeholder partners, some classes of contaminants such as long chain aliphatic hydrocarbons and siloxanes are frequently found on industrially critical surfaces. FTIR and Raman spectroscopy are able to monitor and identify these materials since hydrocarbons and siloxanes present typical vibrational peaks as molecular "fingerprints" in both infrared and Raman spectra. Fig. 1 shows FTIR and Raman spectra of paraffin oil and poly(methylphenylsiloxane) (silicone oil) which were selected as representative test materials for hydrocarbons and siloxanes categories, respectively.

Fig. 1

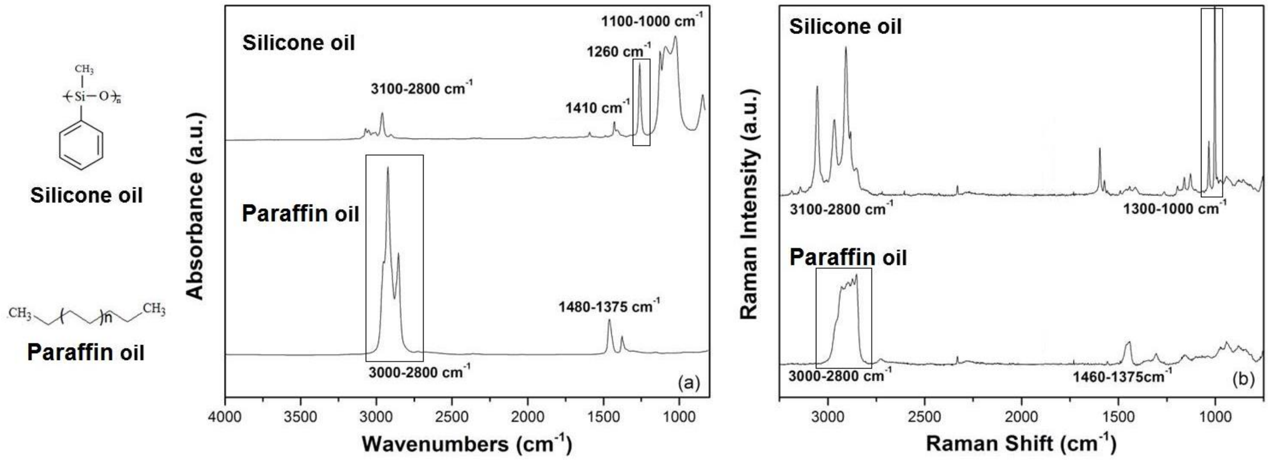

Figure 1: (a) FTIR spectra of paraffin oil and silicone oil; (b) Raman spectra of paraffin oil and silicone oil. The peaks used for the quantification are highlighted in the rectangular boxes.

Hydrocarbon chain have a characteristic bands just below 3000 $cm^{-1}$ and at 1460–1375 $cm^{-1}$ in both Infrared and Raman spectra (Fig. 1a,b); these bands are related to the C–H asymmetric and symmetric stretching vibration (3000-2800 $cm^{-1}$) and to methyl groups asymmetric and symmetric deformation (1460 $cm^{-1}$and 1380 $cm^{-1}$respectively); the methyl deformation band overlaps with $–CH_2–$ scissoring band (1480-1460 $cm^{-1}$). Silicone oil fingerprint is quite different from the paraffin oil and it can be easily identified both in the infrared and Raman spectrum. The main IR absorption peaks of silicone oil are shown in Fig. 1a,b. They are referred to the stretching vibration of the alkyl and aryl $CH_x$ at 3100-2800 $cm^{-1}$, the characteristic sharp band at 1260 $cm^{-1}$ is due to the symmetric deformation of methyl groups attached to Silicon atoms; the asymmetric deformation vibration of the $CH_3$ group results in a week band at 1410 $cm^{-1}$. Phenyl-silicon compounds have several characteristic sharp bands at about 1100 $cm^{-1}$ 1130 $cm^{-1}$ corresponding to Si–O–Ar group and more precisely to to Si–O–C stretching. The bands just above 1000 $cm^{-1}$ are attributed to Si–O–Si stretching, the intensity of two bands depends on the Si–O chain length. Raman spectrum of silicone oil (Fig. 1b) also exhibits the same vibrational peaks with a slight difference in mutual intensities ratio: 1260 $cm^{-1}$ and 1410$cm^{-1}$ (deformation of $CH_3$ attached to Si atom) are very low intensity signals compared to Si-O-Si and Si-O-Aryl stretching vibration just above 1000 $cm^{-1}$. This is reasonable due to the fact that Raman spectroscopy is not as sensitive for heteropolar $CH_x$ vibrations (which provoke a strong IR absorption instead) as it is for C-C and C=C symmetric vibrations of the aromatic rings which have a strong change of polarizzability of their electronic cloud inducing a strong Raman effect.

As Fig. 1 shows, specific absorption peaks and peaks ratio can be assigned to each representative test contaminant and exploited for the quantification. In FTIR spectroscopy the quantification procedure is based on the Lambert-Beer's law which relates the absorbance at a specific wavelength with the recommended concentration, as already reported in ref[14] and in section 2.4 of material and methods. For paraffin oil, the peak area in the range 3000-2800 $cm^{-1}$, assigned to the stretching vibration of $CH_2$ and $CH_3$ groups, is the most intense signal and it was considered for the calibration. For the silicone oil, the absorption band in the range 1300-1180 $cm^{-1}$ (the deformation of $CH_3$ group connected to Si atom) was used for calibration (Fig. 1a)[16]. The calibration curves of paraffin oil and silicone oil are shown in Fig. 1S a,b in supplementary information section.

In the present calibration method proposed by the ECSS, the drop coating procedure used for the standards preparation does not guarantee a uniform distribution of the material on the surface and it is poorly reproducible. Hence, a rapid and simple way to produce standards with a homogeneous distribution of the contaminant on the surface is highly required in order to introduce this practice at industrial manufacturing level. Moreover, homogeneous films of contaminants are strongly needed as reference material when a metrological comparison with other quantitative techniques has to be performed. Most of the surface analysis techniques, such as XPS, ToF-Sims, DESI, PADI, ATR-FTIR and even Raman spectroscopy, are punctual analysis techniques which require standard materials with a uniform distribution of the contaminant on the surface as a basic condition to provide quantitative and traceable results.

A reproducible spin coating procedure was developed for preparing homogeneously contaminated reference materials.

First of all, the choice of the IR and Raman window is fundamental for the contaminant to be analyzed. Calcium Fluoride ($CaF_2$) window was chosen for our purpose because it is transparent in the infrared range 4000-800 $cm^{-1}$,no interfering signals are present in the Raman spectrum (one single Raman peak only at 321$cm^{-1}$ specific to $CaF_2$ is present), minimal fluorescence is guaranteed and it provides efficient stability to humidity and chemical compounds (only incompatible with ammonium salts and concentrated acids).

The best spin coating conditions to spread tens of ng/$cm^2$ on the hydrophobic $CaF_2$ surface were set by the standardization of a two steps method: the first slow rotating step (10 s at 60 rpm) allows a gentle spreading of the solution over the entire surface of the window, while the second step provides a gradual acceleration (reaching 4000 rpm at 200 rpm/s, 60 s in total) to permit the complete evaporation of the solvent. It is important to note that part of solution is thrown away from the round plate during the fast rotation step, this is why it is not possible to know exactly the amount of contaminant deposited on the surface. The accurate quantification of contaminant deposited on the candidate reference material is performed exploiting a FTIR calibration curve previously set.

The homogeneity of the deposited thin film was studied by FTIR and Raman spectroscopy coupled with microscope equipment. For each contaminant (paraffin oil and silicone oil) five different standard solutions at increasing concentration (0.1 g/l, 0.25 g/l, 0.5 g/l, 0.75 g/l and 1 g/l) were deposited as a thin film on a 2 cm diameter round $CaF_2$ window in order to obtain progressively thicker films corresponding to an higher amount of contaminant on the surface. FTIR and Raman spectra were collected in the center and in the four cardinal points of the round substrate to check the homogeneity of the contaminant layer over the entire surface of the window (Fig. 3). An example is reported in Fig. 2 where a homogenous film of paraffin oil is obtained by spinning a 0.5 g/l solution. FTIR spectra were collected with a microscope spot dimension of 150x150 μm in the selected regions. The integrated area of the $CH_x$ absorption band (3000-2800 $cm^{-1}$) was taken into consideration to prove the homogeneous distribution of the contaminant on the surface. As Fig. 2 shows, the intensity of the bands is exactly the same in each region of the sample. Seen that the peaks' intensity depends on the amount of substance, the perfect superimposition of the displayed characteristic bands attests that the amount of contaminant is the same on the entire surface. The same mapping was performed for all films of different thickness, revealing a difference in the integrated area of the infrared signal lower than 13 % for each analyzed film. A detailed statistical analysis is reported in Tab 1S available in supplementary information.

A five point map was also collected on the same samples by Raman spectroscopy coupled with microscope equipment in order to demonstrate the homogeneity of the films. The laser spot on the sample using a 100x objective covers a 0.4 $\mu m^2$ area, allowing a more punctual mapping compared with the FTIR analysis. In Fig. 2b Raman peaks of paraffin oil at 3000-2800 $cm^{-1}$ are compared. They result to be perfectly superimposed confirming the uniform distribution of the contaminant on the entire surface. A relative standard uncertainty less than 11 % was obtained for the integrated area of the selected Raman peaks for all paraffin oil films tested as shown in Tab 1S (supplementary information). The inlet figure 2b shows a Raman map corresponding to an area of 100x100μm which attests the homogeneity of the contaminant distribution at a micrometric scale. The map step size is 2 μm and the intensity of the 2920 $cm^{-1}$ peak associated to every map point is reported in the color scale bar below. The same FTIR and Raman mapping procedures were performed on silicone oil films and they showed a high homogeneity of the contaminant distribution on the surface as well.

Fig. 2

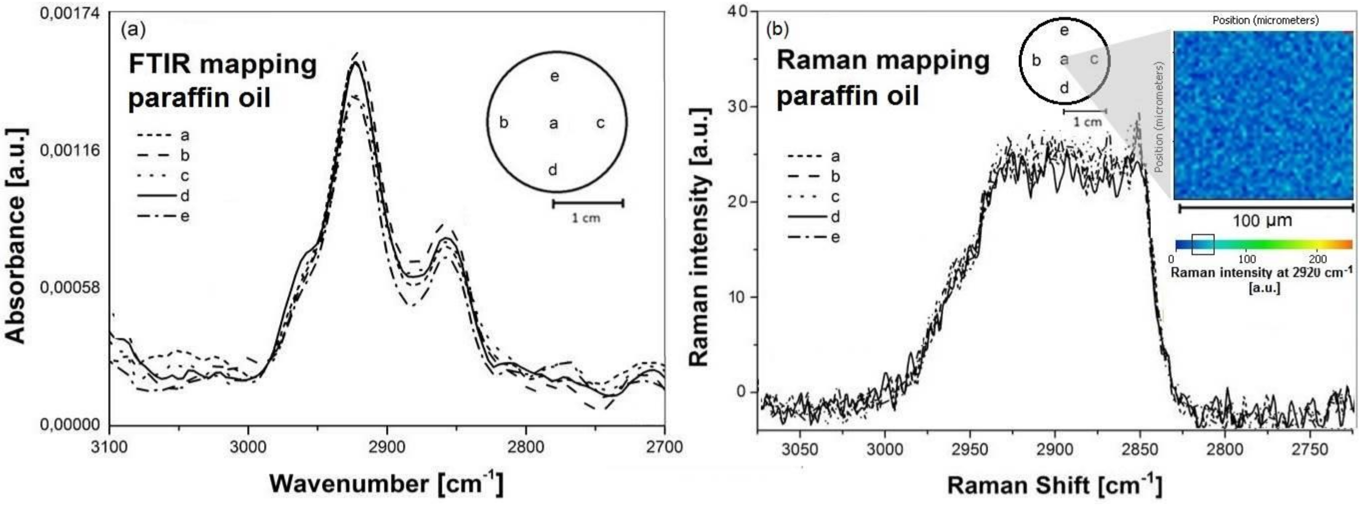

Figure 2: FTIR (a) and Raman (b) spectra of a paraffin oil film in positions a, b, c, d, e of the coated $CaF_2$ round window. Raman map of 100x100 μm area with step size 2 μm in the inlet figure.

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Quantification of the amount of substance on the $CaF_2$ surface was then performed for all the spread films by the FTIR calibration curves of Fig. 1S a,b for both paraffin oil and silicone oil films in order to obtain surface contamination values as described in ref.[14] Since a second order polynomial fit $y = a + bx + cx^2$ was used for the FTIR calibration curves, the uncertainty of the corresponding analysis curve $x = \left(b - \sqrt{b^2 + 4c(-a + y)}\right)/(-2c)$ can be obtained by propagation of the probability distributions characterizing the calibration parameters $a$, $b$, $c$, and the reading $y$, corresponding to the unknown mass amount, by applying a Monte Carlo simulation according to international guidelines[18]. Infrared analysis on the films obtained from different concentration solutions (0.1 g/l, 0.25 g/l, 0.5 g/l, 0.75 g/l and 1 g/l) was performed in the main compartment of the FTIR instrumentation in transmission mode with a spot of 0.5 $cm^2$ in the middle of the window. As Fig. 3a,b shows, as soon as a higher concentration of contaminant solution is spread on the surface, an increased amount of contaminant is deposited, this results in a higher absorbance of the specific paraffin oil (3000-2800 $cm^{-1}$) and silicone oil (1268 $cm^{-1}$) peaks in both FTIR and Raman spectra. The spectroscopic analysis revealed a linear relationship between the concentration of the solution used for spin coating and the mass of contaminant deposited on the $CaF_2$ windows, showing very high determination coefficients, i.e. $R^2 = 0.999$ for paraffin oil and $R^2 = 0.996$ for silicone oil. The plot shown in Fig. 3c,d is aimed at demonstrating that the spin coating procedure provokes a mass amount deposition linearly related to the concentration of the spread solution. The (relative) spin coating reproducibility (vertical bars in Fig. 3c,d are the corresponding absolute standard uncertainties) was evaluated as equal to 14 % on the basis of repeated experiments as reported in Table 2S in supplementary information.

Fig. 3

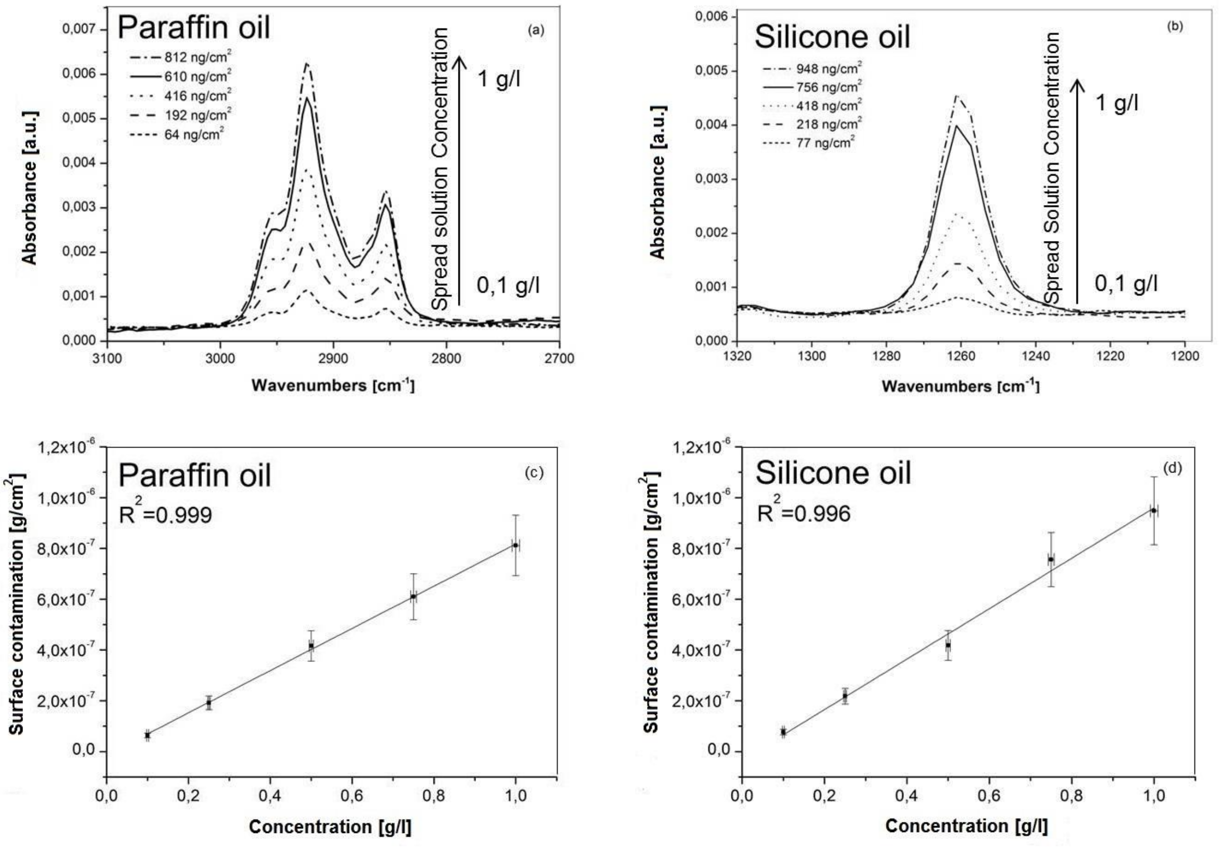

Figure 3: FTIR spectra of paraffin oil (a) and silicone oil (b) films obtained by spreading solutions in a concentration range from 0.1 g/l to 1 g/l. Plot of the surface contamination versus the concentration of the spread solution of paraffin oil (c) and silicone oil (d)

The quantitative results of FTIR analysis of the new candidate reference materials are summarized in Table 3S (supplementary information).

The spin coated candidate reference materials were subsequently exploited to correlate the intensity of Raman signals to the surface contamination level making also Raman spectroscopy a quantitative calibrated technique. By correlating the Raman intensity to the surface contamination level obtained by FTIR it is possible to obtain a calibration curve able to provide quantitative information from Raman spectra. Raman punctual characterization also reveals an increased intensity of the specific Raman peaks at 3000-2800 cm$^{1}$ and at 1100-1000 cm$^{-1}$ for paraffin oil and silicone oil respectively, together with an increased mass amount deposited on the reference surface (Fig. 4).

Fig. 4

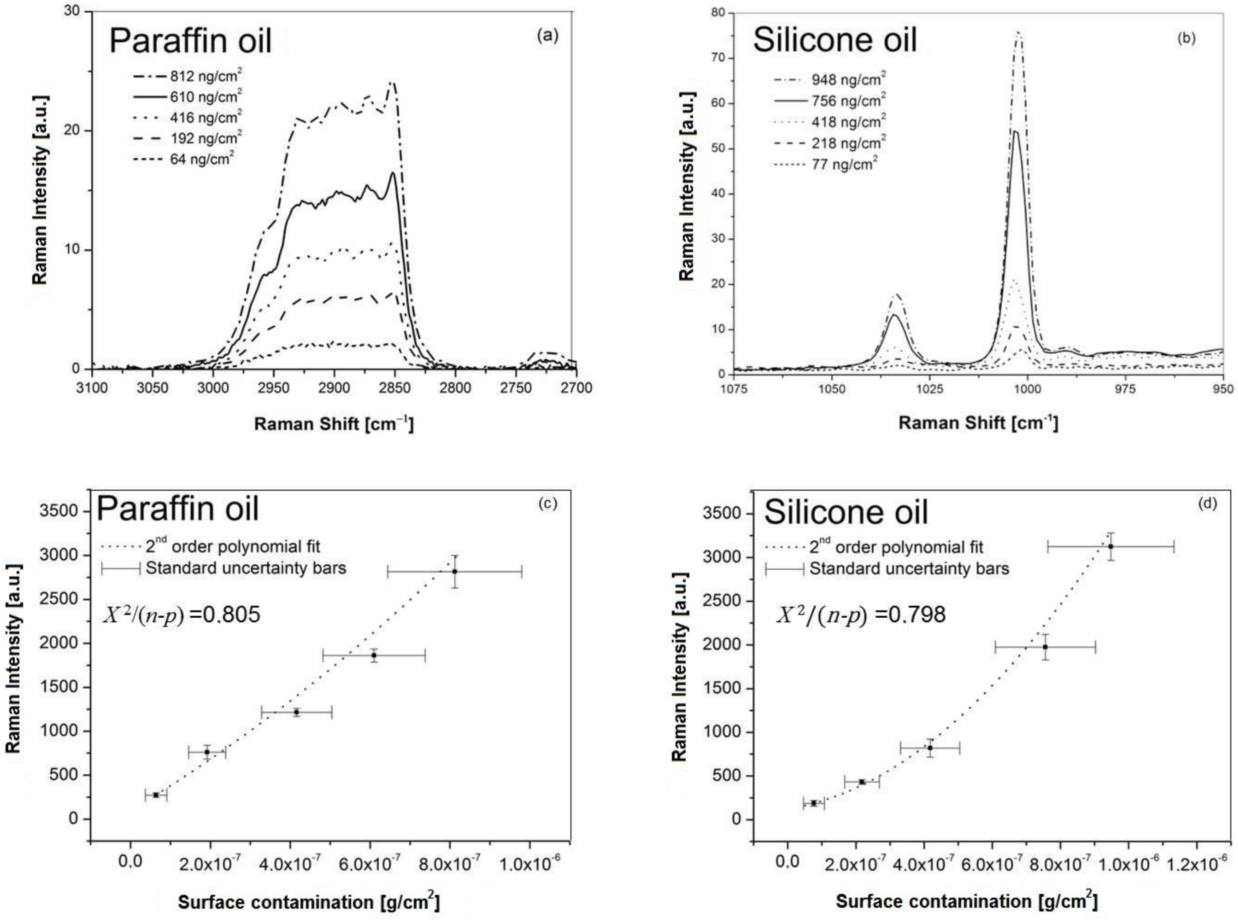

Figure 4: Raman spectra of paraffin oil (a) and silicone oil (b) films obtained by spreading solutions in a concentration range from 0.1 g/l to 1 g/l. Plot of the Raman intensity versus the amount of paraffin oil (c) and silicon oil (d) deposited on the surface.

Since both the contamination level values and the Raman intensities are affected by uncertainty, a WTLS regression was used for fitting the data. The uncertainty associated with the *x* values was calculated by combining together, according to the law of uncertainty propagation[17], the different sources of uncertainties due to the FTIR measurement, the spin coating reproducibility and the solution concentration (B-type contributions due to the purity of the oils, the weighting procedure and the volume measurement). The obtained uncertainties are shown, for each point in Fig. 4c, d, as standard uncertainty bars (with coverage factor $k = 1$) parallel to the *x* axis. The standard uncertainty associated with the intensities (reported as *y* error bars in Fig. 4 c,d) were calculated on the basis of the standard deviation of repeated Raman measurements performed in one week. In this way, the day to day repeatability was also taken into account in the calibration procedure. A second order polynomial fit was used for both paraffin and silicone oil since the chi-squared value (i.e. the sum of the weighted squared residuals normalized by the number of degrees of freedom) showed a high goodness of fit for both the representative test materials, being lower than the expected unit value (see Fig. 4 c,d). As already done for the FTIR method, the analysis curves were obtained by inverting the calibration curves, and the uncertainty to be associated to the results of the Raman analysis was calculated by applying a Monte Carlo simulation analogous to that performed for the FTIR analysis curves.

The experimental results show that the sensitivity of the technique increases with the progressive accumulation of contaminant which results in a second order polynomial growth of the Raman signal as soon as the film of contaminant gets thicker. Although the sensitivity is a little impaired at very thin films of paraffin and silicone oil, Raman analysis is still able to detect low values of surface contamination.

The main difference between IR and Raman spectroscopy arises in the spatial resolution and in the sensitivity related to the area of analysis. It should be noticed that IR beam invests a 0.5 $cm^2$ round area, while the Raman laser spot has a section of 0.4 $\mu m^2$ ($\lambda$ = 532 nm, 100x objective). It is possible to infer that, while IR analysis can be more suitable for a routine monitoring the contamination of transparent surfaces on a wider area of analysis, micro-Raman spectroscopy allows the characterization of a wide range of surfaces, guarantying a spatial resolution even close to the sub-micrometric scale.

A comparison analysis between FTIR and Raman spectroscopy based on a real case study is here presented to assess the applicability of both techniques in molecular contamination monitoring. The study was conducted on a glass slide from a laser cutting machine shown in the inlet figure 5. The analyzed slide was subjected to contamination in the manufacturing environment due to the presence of lubricants in the mechanical parts. According to the customer needs, the contamination analysis was devoted to determine the source of the contamination (lubricants or other organics such as algaecides contained in the refrigerant water system) with the aim at improving the manufacturing process as well as the useful life of the lens. In this particular case infrared spectroscopy analysis can be only performed in reflectance mode or with the ATR configuration because the lens is not transparent to the infrared radiation. Both methods can provide a qualitative characterization of the contaminated surface but no quantification is possible. As Fig. 5 shows, micro-FTIR spectrum collected on the contaminated region of the lens presents a broad and intense peak in the range 800 $cm^{-1}$ - 1350 $cm^{-1}$ due to Si-O stretching vibration of the glass. In order to reveal the fingerprint of the contaminant on the surface, a subtraction with a spectrum collected in the clean area of the lens needs to be performed. After the spectra manipulation it is possible to identify the specific peak of silicone oil at 1260 $cm^{-1}$ but it cannot be excluded that the mathematical treatment of data brought to a loss of information, because the cleanliness of the area in which the blank spectrum was acquired is just supposed. What is more, a mathematical artifact at 1400 $cm^{-1}$ is generated during the subtraction that could impair the possibility to correctly interpret the resulting spectrum. Therefore, it is clear that the direct FTIR analysis of the surface contamination for a real industrial application is insidious because a reference clean material is often required and a mathematical procession of data is needed.

Fig. 5

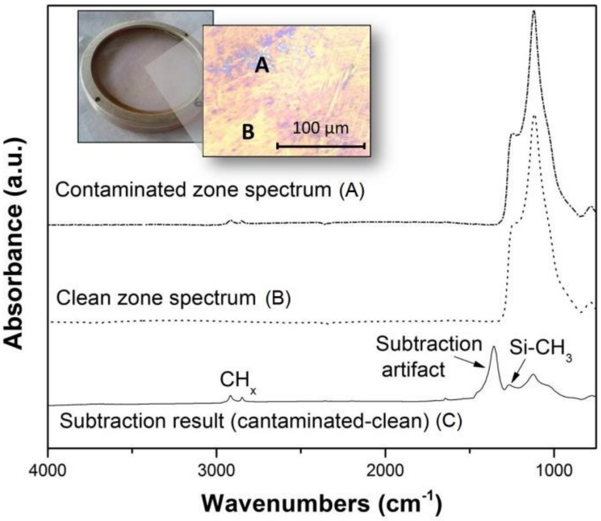

Figure 5: FTIR spectra collected on different regions of the lens: (A) contaminated zone spectrum (region A of the optical image in the inlet); (B) clean zone spectrum (region B of the optical image in the inlet); (C) FTIR spectrum obtained by the subtraction of the spectrum B from A.

A FTIR quantitative analysis of the contaminated surface could be done following the indirect method provided by the ECSS[6]. However, this procedure consists of several steps: wiping the contaminated surface with a neat wipe, extract the contaminant from the wipe with an organic solvent, concentrate the extracted contaminant solution and transfer it on a $CaF_2$ standard surface for the FTIR analysis in transmission mode. Each step of this method is inevitably affected by an error, the entire procedure results to be time consuming and well trained operators are required.

Since Raman Spectroscopy represents a more punctual, and direct approach for the characterization of the surface, it was also employed to identify the molecular contaminant on the lens. Using a 100x microscope objective it was possible to analyze either clean or contaminated zones on the lens with a micrometric spatial resolution and to compare spectra collected in the different regions of the surface. As Fig. 6a shows, Raman analysis was initially performed on the region A, which represents a micrometric stain of contaminant on the lens, and on the region B, which was chosen as an area supposed to be clean. In Fig. 6a Raman spectrum A clearly reveals the typical fingerprint of silicone oil with the $CH_x$ stretching band at 3100-

2800 cm$^{-1}$ and the characteristic siloxane stretching vibration at 1000 cm$^{-1}$. Raman spectrum B, instead, only shows peaks in the range 1200-300 cm$^{-1}$ related probably to a polymeric coating of the lens and to the glass substrate and no silicone oil signals are revealed in this region. Unlike FTIR analysis, qualitative Raman measurement resulted to be simpler and more straightforward because no background subtraction or spectra manipulation were performed to reveal the siloxane on the lens. Moreover, in order to perform a quantitative analysis, a Raman mapping of the lens on a contaminated area of 25x30 µm (Inlet of Fig. 6a with step size of 1µm was performed. As Fig. 6b shows, a 2D chemical imaging based on the peak intensity profile of the silicon oil band at 1000 cm$^{-1}$ was obtained, providing information about the spatial distribution of the contaminant on the surface. Correlating the intensity of the peak at 1000 cm$^{-1}$ at each point of the map with the amount of silicone oil per surface area unit (ng/µm$^2$), in accordance with the calibration curve in Fig. 4d, a punctual quantitative analysis was done. Surface contamination values are expressed through the color scale bar (Fig. 6b) which allows to visualize and measure the amount of silicone oil in each point of the map at the micrometric level. Raman Spectroscopy turned out to be particularly useful in this analysis because provides a micrometric chemical map of the lens to which contains both a spatial distribution of the contaminant on the surface and quantitative contamination values (with the associated uncertainties) for each analyzed point as reported in the color scale bar in Fig. 6b.

Fig. 6

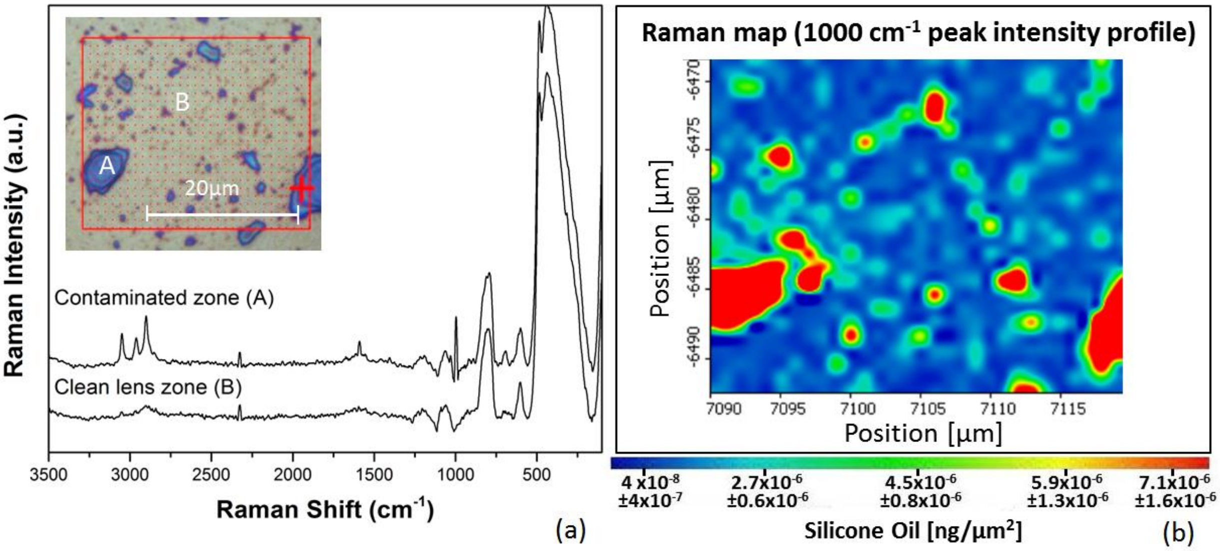

Figure 6: (a) Raman spectra of the contaminated (A) and clean (B) regions of the lens (Region A and B of the optical image in the inlet, respectively). (b) 2D Raman map (25x30 µm) of the glass lens (red square area in the inlet of Fig. 6a) showing spatial distribution of silicone oil on the surface and quantitative contamination values provided by the color scale bar.

## Conclusions

In this work a reproducible method to produce new candidate reference materials homogeneously contaminated for Raman calibration was developed. Films of different thickness of two of the main classes of contaminants i.e. long chain aliphatic hydrocarbons and siloxane compounds, within a contamination range of 70-900 ng/cm$^2$, were prepared by a spin coating method. The uniform distribution of a known amount of substance on standard surfaces represents a very relevant matter when punctual analytical techniques (for example XPS, ToF-Sims, DESI, PADI as well as Raman spectroscopy) that perform punctual characterizations of surfaces want to be quantitatively calibrated. Indeed, only if the analyte is homogeneously distributed on the whole standard surface the signal intensity provided by whatever punctual technique can be associated to a certain mass per area unit. This is worth even when Raman spectroscopy is concerned as punctual technique. Quantitative analysis of the films performed by FTIR spectroscopy, in accordance to the ECSS standard procedure, was used to correlate the intensity of the Raman signals to the amount of substance on the surface, making Raman spectroscopy traceable to the International System of Units. Comparing qualitative and quantitative ability of both techniques in surface contamination detection on real samples, some positive aspects in implementing the IR consolidated method with the dispersive micro-Raman technique have emerged. Even if both techniques can provide specific qualitative analysis on the contaminated surface due to the molecular fingerprint in the FTIR and Raman spectra, Raman analysis turned out to be particularly interesting for its simplicity and versatility. No background collection is needed, mathematical manipulation of the spectra is reduced and most of the surfaces are suitable for direct analysis. Moreover, Raman spectroscopy allows punctual investigation of the surface at a micrometric scale and new emerging portable systems could be successfully applied for molecular contamination monitoring in situ.

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## Notes and references

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