Application Note

Materials

Non-Destructive Analysis of Substrates and Contaminants by FTIR with Specular Reflectance Interface

Cleanliness-testing of materials using Agilent 4300 handheld FTIR spectrometer to prevent downstream issues

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Abstract

Verifying that substrates are clean before they are bonded to another material or coated with a protective layer is a critical application. Contaminants, such as trace oils, can compromise a substrate's surface by negatively affecting the stiction (static friction) properties of the material. Low stiction adversely affects the bond strength of glues and coating adhesion for paints, leading to premature wear and the potential failure of the material.

This study shows that the Agilent 4300 handheld FTIR spectrometer fitted with the specular reflectance interface can identify substrate materials, evaluate the presence of contaminants, and quantify contaminants. The instrumentation can also be used to determine the presence of chemicals and confirm the chemical condition of surface agents. As a fast, non-destructive technique, the 4300 FTIR enables large samples to be analyzed in-situ, without any damage to the substrate. Measurement times are typically less than 30 seconds per result and the results are displayed in a clear format on the screen of the 4300 handheld FTIR.

Introduction

In materials science, the condition and cleanliness of first produced substrates and materials is vitally important, especially if they are to be further bonded to another component or coated with a protective layer. Chemical adhesives are increasingly used to replace or supplement mechanical fixing methods as they can provide strong bonds, but only if the surfaces of the components are clean and free of contamination. Compared to mechanical fasteners, chemical glues reduce the weight of the assembled parts and ensure a more uniform distribution of stresses over the bonded area.

In many industrial and engineering processes, extensive cleaning procedures have been developed for critical bonding applications. It has been shown that even small deviations in these cleaning procedures can produce substandard bonds.[1, 2] To guarantee strong bonding, surfaces should be analytically tested and confirmed before the application of adhesives to confirm their cleanliness. A good testing technique should be non-destructive, identify and quantify contaminants, and ideally be field deployable. The technique must also have the sensitivity required to measure low levels of contamination that would adversely affect the bonding between surfaces.

Another application area that requires a high level of cleanliness includes the coated or uncoated surface of reaction vessels used in manufacturing processes. Contamination arising from surface coatings such as metals, alloys, treated metal, or glass lined metals can adversely affect the chemical reaction or yield of the product.

Infrared (IR) spectroscopy is a non-destructive method that can identify and quantify many substrates, materials, and contaminants. Virtually all organic chemicals and many inorganic chemicals can be measured by IR. When fitted with a specular reflectance interface, IR is sensitive enough to measure contaminants on reflective and non-reflective surfaces at low levels.

The Agilent 4300 handheld FTIR spectrometer fitted with the specular reflectance interface is capable of the nondestructive identification and quantification of many substrates and contaminants. Before coating or bonding of materials, the 4300 FTIR can be used to analyze components of virtually any size. The high sensitivity of the 4300 FTIR provides trace level detection of contaminants at pre-, mid-, and post-cleaning stages. The fast scan times of the instrument, typically less than 30 seconds per result, enable multiple positions on the substrate to be analyzed quickly. The instrument is also designed to be directionally ambivalent and robust, simplifying its use.

In this study, the 4300 handheld FTIR spectrometer with specular reflectance interface was used to detect a range of contaminants on the surface of a glass-lined vessel. A quantitative method was also developed to predict the concentration of a PTFE-based release agent formulation on aluminum.

Experimental

Selection of the sampling interface for the handheld FTIR

There are many ways to measure samples using a 4300 handheld FTIR spectrometer. In all cases, the IR light from the spectrometer must interact with the sample and then be directed to the detector. The IR beam interacts differently with the sample depending on which of the interchangeable sampling interfaces is used with the 4300 FTIR:

- Attenuated total (internal) reflectance (ATR)
  - Diamond
  - Germanium
- Transmission
- External reflectance
  - Specular 45° cone half-angle (CHA)
  - Diffuse
  - Grazing angle

The wide choice of interchangeable sampling interfaces available for the 4300 FTIR enables the handheld spectrometer to examine and measure samples nondestructively and *in situ*. The 4300 has been used to analyze samples that are atypical for FTIR, such as minerals, concrete, and coatings.[3]

For the analysis of glass and metal-based substrates, both the ATR internal reflectance and transmission techniques are unsuitable. For ATR, it is difficult to establish good contact between the ATR crystal and the surface of hard or brittle substrates, while for transmission, IR light cannot transmit through opaque materials. Also for ATR, the short penetration of the IR beam in the substrate results in a high limit of detection (LOD).

The external reflectance interfaces are suitable for the measurement of various substrates. Figure 1 shows an overview of the range of materials that have been measured by the 4300 FTIR fitted with an external reflectance interface and includes a short list of typical applications of the technique.

Figure 1. Types of substrates that have been measured by Agilent 4300 FTIR fitted with an external reflectance interface and a summary list of typical applications of the technique.

Specular reflectance interface

In this study, the 4300 handheld FTIR was fitted with the 45° specular reflectance sampling interface (Figure 2). The technique is suited to the analysis of a wide range of surfaces with moderate-to-high reflectivity such as glass and metal, but also carbon fiber reinforced polymer (CFRP), which has low-to-moderate reflectivity. Figure 3 shows example spectra obtained using the instrumentation for CFRP, amorphous silicon on stainless steel, functionalized silicon oxide on stainless steel, stainless steel, and aluminum.

The specular reflectance interface is a "point and shoot" technique that does not require any force to be applied between the interface and sample during data acquisition. Spectral quality is not affected by poor contact with the sample, unlike ATR. The front clear-coated orange O-ring ensures the correct distance to the sample.

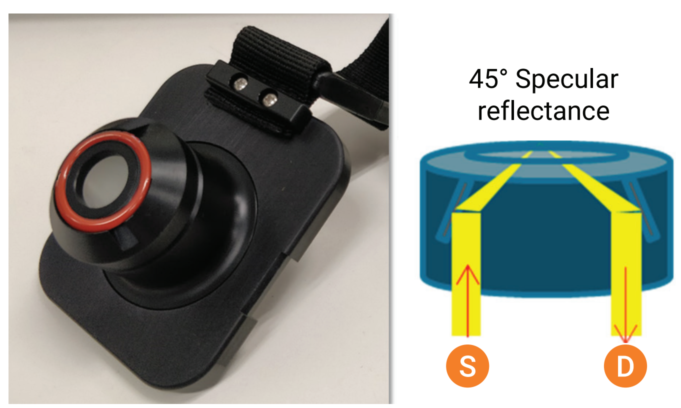

Figure 2. Left: the 45° specular reflectance interface with nonmarking clear fluorinated ethylene propylene (FEP) coated orange silicone O-ring. Right: schematic showing the principles of the technique, often referred to as infrared reflection-absorption spectroscopy (IRRAS); S=Source and D=Detector.

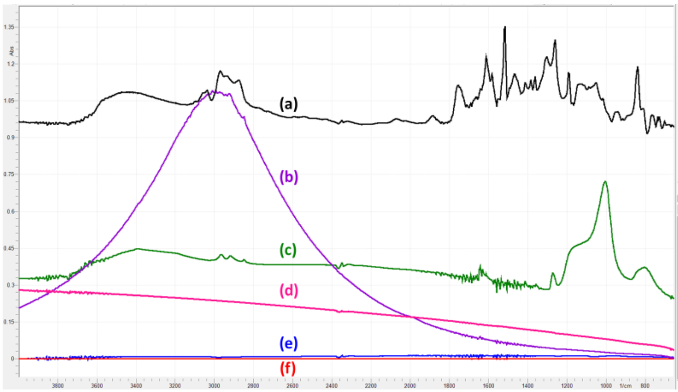

Figure 3. Spectra collected using an Agilent 4300 handheld FTIR spectrometer fitted with the 45° specular reflectance sampling interface shown in Figure 2. a) Carbon fiber reinforced polymer (CFRP), b) amorphous silicon on stainless steel, (c) functionalized silicon oxide on stainless steel, (d) stainless steel, (e) aluminum, and (f) mirror background cap for the 4300 handheld FTIR (part number G8180-67562).

When reflective surfaces are analyzed by IR, the typical measurement configuration is known as infrared reflection-absorption spectroscopy (IRRAS). Using IRRAS, the light from the spectrometer passes once through the sample, reflects off the reflective or semi-reflective surface, and then passes through the sample a second time, before being collected by the detector (Figure 2, right). Since the 4300 handheld FTIR is a Fourier transform instrument, scans can be co-added to both improve the signal-to-noise (SNR) and the LOD of the measurements. The penetration of IR light into the sample depends on the material being tested.

Samples

For the qualitative study (identification of the presence of contaminants), a clean glass lined vessel was lightly smeared with lubricant. A few milligrams of lubricant were spread thinly over an area of the vessel until it was no longer visible. To simulate potential contaminants, a range of different lubricants and release agents were added in turn to the clean vessel. The lubricants included an adhesive lubricant, a multipurpose lubricant, a PTFE aerosol mold-release agent, silicone oil, white mineral oil, and a 3-in-1 product.

For the quantitative contamination study, varying amounts of the PTFE aerosol mold-release agent, carefully weighed to 0.01 mg on a 5-digit balance, were applied to aluminum (Al) coupons, as detailed in Table 1. All coupons were 40.85 × 50.80 mm. A clean, blank Al coupon was also prepared. The clean coupon was cleaned using three wet wipes and an ethanol wash, and then dried with a lint free tissue.

Results and discussion

Identification of contaminants

The 4300 FTIR fitted with the specular reflectance sampling interface was used to analyze the surface of the clean glass-lined vessel and each of the lubricants added to the surface of the vessel. Each measurement (64 scans) took 16 seconds at 8 cm^{-1} resolution. Figure 4 shows the averaged spectra for the clean glass-lined vessel and for each of the six lubricants applied to the surface of the vessel. The spectra show that the method can easily detect the presence and type of contaminants (in this case, lubricant/release agent) on the surface of the glass-lined vessel.

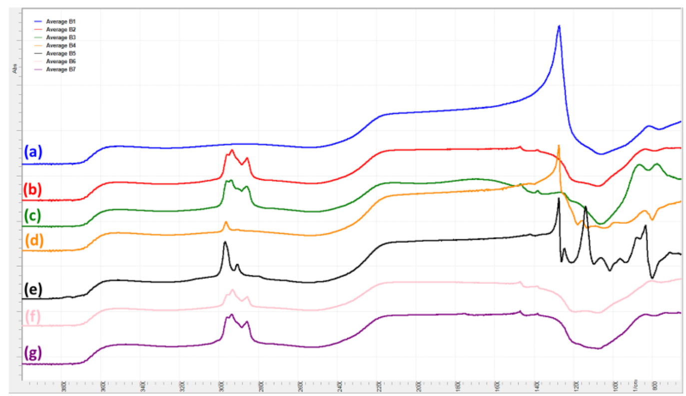

Figure 4. Agilent 4300 FTIR specular reflectance spectra for a) clean glass vessel, b) adhesive lubricant, c) multipurpose lubricant, d) PTFE aerosol, e) silicone oil, f) white mineral oil, and g) multipurpose 3-in-1 lubricant.

There are many differences in the spectra (Figure 4), especially in the CH stretching mode-region, around 3,000 to 2,800 cm^{-1}, as well as in the fingerprint region. If needed, it would be quick and simple to construct a library search of the spectra to identify the compounds or formulations. This would provide a qualitative answer for the presence or absence of contamination. For successful quantitative analysis of contaminants on substrates by FTIR, the instrument needs to provide sufficient sensitivity and selectivity, as required by industry. To demonstrate the quantitative capabilities of the 4300 FTIR, two quantitative models were created for the analysis of PTFE-contaminated Al coupons.

Quantitative measurements

The 4300 FTIR fitted with the specular reflectance sampling interface acquired multiple measurements (replicate number >10 for each sample) of the blank (clean) Al coupon (sample 7) and six PTFE-contaminated Al coupons (samples 1 to 6). The contamination levels of PTFE on the Al coupons were calculated as shown in Table 1.

Table 1. Reference samples of PTFE contaminated Al coupons.

ID	mg	mg/cm^2	ug/cm^2
1	10.28	0.495422	495.4217
2	3.40	0.163855	163.8554
3	1.92	0.09253	92.53012
4	0.69	0.033253	33.25301
5	0.18	0.008675	8.674699
6	0.08	0.003855	3.855422
7	0	0	0

The averaged spectra obtained by FTIR for each PTFE-concentration level are shown in Figure 5. Because stacking the spectra compresses the data's Y-axis, overlaid spectra of Al coupons 5, 6, and 7 are shown in the lower graph. The features present in the clean Al coupon (sample 7) are due to physisorbed (physical adsorption) water and the native aluminum oxide.

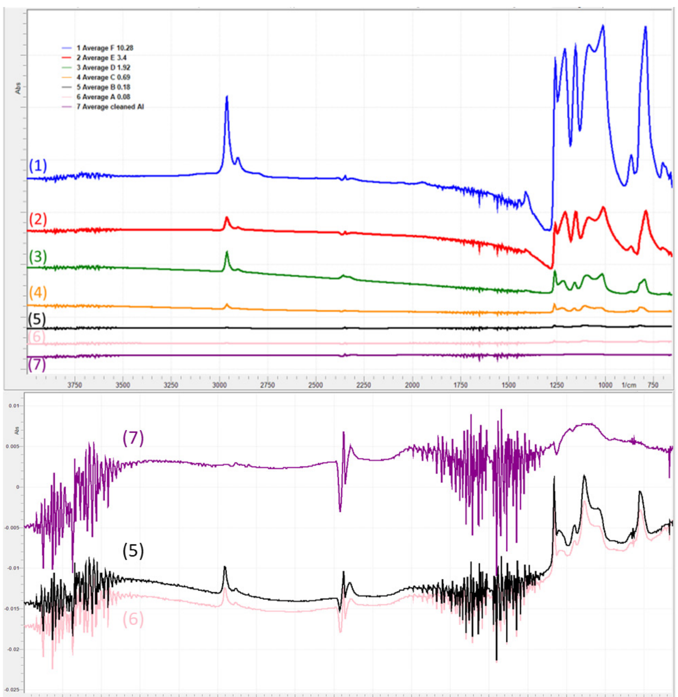

Figure 5. Agilent 4300 handheld FTIR spectra of varying concentrations of PTFE on aluminum. Top: Samples 1 to 7 stacked. Bottom: Samples 5, 6, and 7 overlaid. Sample 7 is the clean Al coupon.

The spectral features can be modeled univariately using the MicroLab PC software or by multivariate analysis (MVA) using Agilent MicroLab Expert software. MVA produces better LODs and the MicroLab Expert software provides a wider range of statistical testing options, so MVA was used in this study. (Results obtained using the univariate model diverged significantly from Beer-lambert assumptions and were not applicable to the IRRAS technique.)

Using the partial least squares (PLS1) MVA in MicroLab Expert with a 4:1 split in the training data for calibration and validation, two models were created: one global model (Figure 6) and a model for the lower concentration range of PTFE contamination (Figure 7).

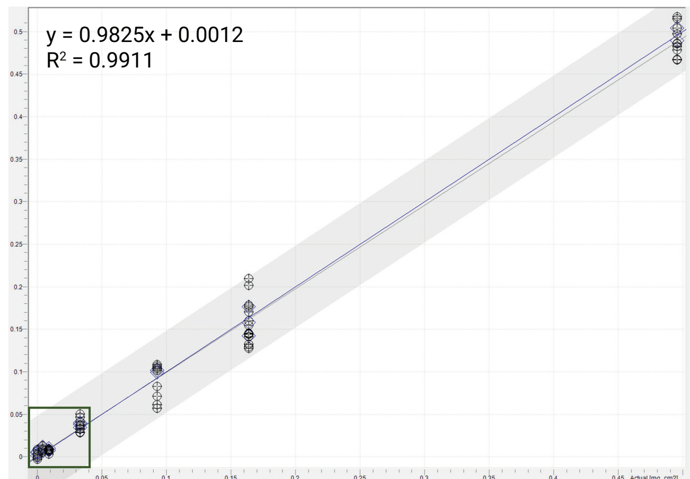

Figure 6. PLS1 MVA model based on samples 1 to 7 (low to high range model). The calibration data are shown by the black circles and validation spectra by the blue diamonds. The green square is the region of the lower range model.

When the analyte level spans a large range, a discrete low range model is often beneficial. Using all the spectra from samples 4, 5, 6, and 7, a second model was created using the MicroLab Expert software, as shown in Figure 7.

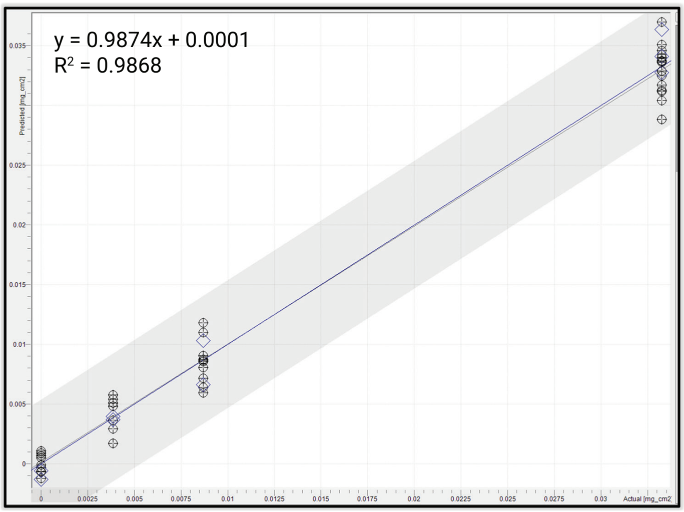

Figure 7. Lower range PLS1 model for PTFE on Al (based on spectra acquired for samples 4, 5, 6, and 7). The calibration data are shown by the black circles and validation spectra by the blue diamonds.

Both these models can be implemented into a single method to predict the level of PTFE lubricant on aluminum. There are three types of analytical methods that can be selected in the MicroLab PC software:

- **Spectral Collection:** data collection of spectra.
- **Qualitative Search:** where the spectral data are checked against a spectral library for identification of compounds or formulations.
- **Components:** an interrogation of the spectra by any one or combination of peak area, peak height, peak ratio, SNR, center of gravity, and also application of a wide range of mathematical models ranging from Beer-Lambert type basic models to PLS1-MVA modeling. A well-trained and validated model enables the software to predict the level of a measured quantity of the analyte, providing quantitative data. More than one trained model can be queried in a single method.

Once established, the method and its model or models can then be transferred to the MicroLab Mobile software of the 4300 handheld FTIR (and/or still be used from the MicroLab PC software with a laptop). Both MicroLab Mobile software or MicroLab PC software will both provide step-by-step graphical instructions, and can be tailored to:

- Check that the 4300 is fitted with the correct interface, as required by the method.
- Warn of poor alignment to the surface.
- Automatically apply the correct model (if there is more than one), and when several models are available, the software can be directed to show the most appropriate result.
- Display the results using a user definable traffic light system, enabling quick and easy interpretation of the data.

For a closer inspection of the predicted values of PTFE on Al, a table of all the spectra collected for PTFE samples 4 to 7 that have been reprocessed by the lower range PLS1 model (Table 2). Although the method was approaching the limits of the 5-digit balance, the model can clearly still predict the lowest standards. The boxplot in Figure 8, which displays each spectral result with the statistical boxplot, confirms the effectiveness of the method for the quantification of PTFE on aluminum.

Table 2. Predicted values for each spectra of PTFE on Al coupons 4, 5, 6, and 7.

	Coupon 7	Coupon 6	Coupon 5	Coupon 4
Actual	**0**	**0.003855**	**0.008675**	**0.033253**
Predicted	−0.00032	0.00395	0.00641	0.03460
	−0.00010	0.00369	0.00865	0.03699
	0.00048	0.00396	0.01180	0.03170
	−0.00121	0.00295	0.00596	0.03511
	−0.00058	0.00363	0.01099	0.03430
	−0.00131	0.00541	0.00663	0.03042
	0.00089	0.00511	0.01033	0.03250
	−0.00064	0.00169	0.00808	0.03374
	−0.00067	0.00510	0.00717	0.03275
	0.00107	0.00484	0.00872	0.03409
	0.00066	0.00575	0.00904	0.03634
	N/A	N/A	0.00854	0.03360
	N/A	N/A	N/A	0.03403
	N/A	N/A	N/A	0.03368
	N/A	N/A	N/A	0.03291
	N/A	N/A	N/A	0.03125
	N/A	N/A	N/A	0.02885
	N/A	N/A	N/A	0.03117
Average	−0.00016	0.00419	0.00853	0.03322
Standard Deviation	0.00079	0.00115	0.00176	0.00198

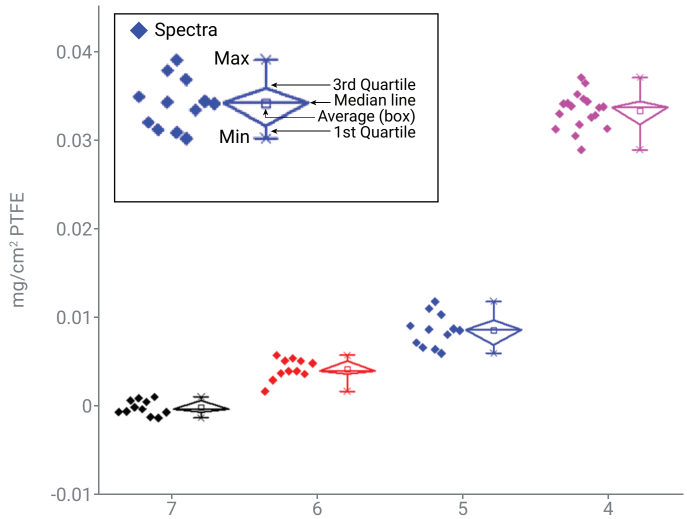

Figure 8. The boxplot and values of PTFE on Al coupons 4, 5, 6, and 7.

A previous study was done on the quantification of a silicone-based release agent on the surface of a CFRP substrate, where the substrate was a cured epoxy-based carbon composite.[2] That study required more intense pre-processing of the data to enable model compensation of variances in the resin:fiber ratio. The same level of pre-processing was not required for the PFTE on Al data.

Both the full range and the low range PTFE on Al models required minimal pre-processing of the model training data to provide excellent model statistics. Industrial uses of metals bonded to glass fiber reinforced polymer (GFRP) or CFRP are increasing, as they provide a good balance of strength and weight. For these applications, the cleanliness of the metal (typically Al because of its lightweight properties) before application of the GFRP or CFRP layer is critical.

Conclusion

The Agilent 4300 handheld FTIR spectrometer fitted with a specular reflectance sampling interface was used for the qualitative study of a variety of substrates and common lubricant and aerosol release agents. Spectra were all collected from the samples at multiple sites and orientations and all samples were shown to be spectrally distinct.

A quantitative method was also developed using the PTFE-based aerosol release agent deposited on aluminum coupons. By analyzing accurately weighed amounts of PTFE by FTIR, the Agilent MicroLab Expert software and a PLS1 multivariate analysis (MVA) modeling technique was used to create a quantitative method. Two MVA models were developed based on spitting the model training set spectra into roughly three-quarters calibration and one-quarter validation. Both models were implemented and incorporated into a single method for the handheld 4300 FTIR.

This method could be used to directly measure PTFE release agent on a coupon in a force-free and non-destructive manner. Each measured position would lead to a discrete predicted value that can be color-coded to suit the user's requirements for cleanliness. The method could also be used to check the presence and chemical condition of PTFE in a mold.

The efficacy of cleaning procedures can now be performed at-site or on-site using the sensitive 4300 FTIR spectrometer. The handheld 4300 weighs ~2 kg with batteries, so is portable and easy to handle, and a simplified graphical user interface ensures its ease-of-use by nonexpert operators.

The study has shown that the 4300 FTIR coupled with the specular reflectance interface provides a highly tailorable and flexible solution for on-site cleanliness testing of a wide variety of substrates. The system can be used for qualitative testing of contaminants or models can be trained to quantify for a specific contaminant or multiple contaminants, providing quality assurance for critical bonding applications.

References

1. Extended Non-Destructive Testing of Composite Bonds (ENCOMB), FP7, CORDIS, European Commission (europa.eu), accessed April 2023, https://cordis.europa.eu/project/id/266226/reporting
2. Tang, P. L.; Rein, A. Quantification of Release Agent on a Carbon-Fiber-Reinforced Polymer using a Handheld FTIR, *Agilent Technologies application note,* publication number 5991-5595EN, **2018**.
3. Tang, P. L., Comparison of Portable FTIR Interface Technologies for the Analysis of Paints, Minerals & Concrete, *Agilent Technologies application note*, publication number 5991-8359EN, **2017**.

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