

# Measurement of composite surface contamination using the Agilent 4100 ExoScan FTIR with diffuse reflectance sampling interface

## Application note

### Materials testing

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### Introduction

Contamination of composite surfaces is a large problem in the composites industry. Contamination is obviously a problem for adhesive bonds used in manufacturing, but it can also cause problems with composite repairs. In most cases, composites are contaminated either by a hydrocarbon or silicone based contaminant. Detection of these materials on carbon epoxy composites has always been difficult. Strong background signals present in composites along with the desire to attain low levels of detection have typically presented problems with these measurements.

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Infrared spectroscopy provides a means of measuring contamination on composite surfaces. The unique infrared signature of both hydrocarbons and silicones allows them to be differentiated from the underlying epoxy substrate. One issue preventing the use of infrared, however, was the size of laboratory instruments. Until now, laboratory instruments were only practical for measuring small samples. The handheld Agilent 4100 ExoScan FTIR spectrometer allows direct measurement of components without bringing them to the lab. Advancements in the design and production of the 4100 ExoScan allow for a small instrument size without affecting the analytical performance. This allows one to take the instrument to the production part instead of taking the part to the instrument. FTIR can now be used as a true nondestructive technique for evaluation of composite parts.

The 4100 ExoScan FTIR provides the full performance and frequency range of a standard laboratory FTIR. Additionally, the diffuse reflectance sampling interface produces high signal-to-noise measurements of low reflectance surfaces, such as carbon composites. This interface brings the light normal to the sample surface and collects the scattered, diffusely reflected light. The design provides an easy to perform measurement, which can typically be made in 30 seconds.

## Silicone

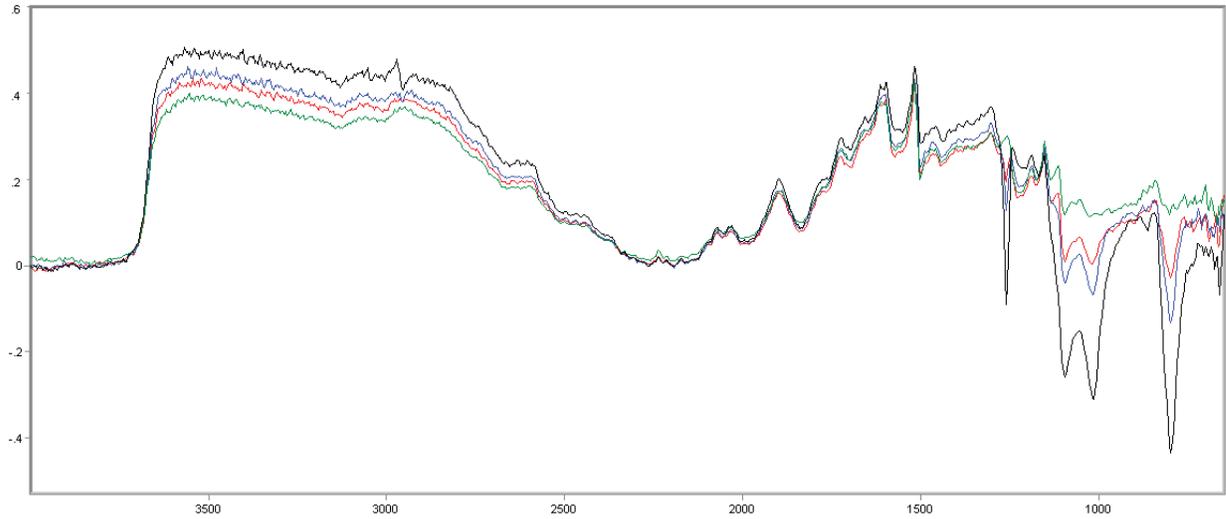
Silicone is pervasive in lubrication and mold release products. Contamination of bond surface by silicone can be difficult to detect; additionally, silicone is difficult to remove and can significantly reduce the effectiveness of a bond. Silicone has a distinctive infrared spectrum, making it easy to identify; it has a characteristic doublet at 1095 and 1018  $\text{cm}^{-1}$  accompanied by two sharp bands at 1260 and 800  $\text{cm}^{-1}$ .

Three contaminated samples were prepared by solvent evaporation onto a single composite coupon. The three contaminated locations were prepared at separate locations. A solution of silicone in chloroform was dried onto the coupon covering an area of approximately 10  $\text{cm}^2$ . The coupon was weighed to the nearest 0.1 mg before and after measurement to determine the surface

concentration of each application. Samples had the following approximate concentrations: 0  $\mu\text{g}/\text{cm}^2$ , 40  $\mu\text{g}/\text{cm}^2$ , 78  $\mu\text{g}/\text{cm}^2$ , and 300  $\mu\text{g}/\text{cm}^2$ . Each sample and a blank was measured by co-adding 128 scans at 8  $\text{cm}^{-1}$  resolution, producing a total measurement time of about 30 seconds per sample.

Figure 1 shows the spectra collected with the 4100 ExoScan FTIR on each of the samples and the blank. The silicone bands at 1260, 1095, 1018 and 800  $\text{cm}^{-1}$  are clearly present. Interestingly, the bands are negative on the absorbance scale. This often occurs in reflectance spectroscopy when the samples become strongly absorbing. The spectra shown in Figure 1 have been baseline corrected, but the true absorbance of the blank is near 1.2 absorbance units in the silicone region. The negative silicone bands still correlate with concentration; they just have a negative correlation.

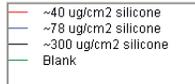
A band area was calculated using the 800  $\text{cm}^{-1}$  band of the silicone contaminant. This band is relatively free of baseline interferences. Figure 2 shows a calibration curve plotting the negative band area versus the approximate concentration. The concentration response becomes non-linear, fitting a second order curve; however, the low concentrations can be easily fit with a straight line. Although additional samples at low concentration are needed to accurately determine the limit of detection, this data indicates that a LOD near 10  $\mu\text{g}/\text{cm}^2$  could be obtained.



Absorbance / Wavenumber (cm-1)

File # 3 : CHLOROFORM DEPOSITION 304 UG P CM2\_2009-11

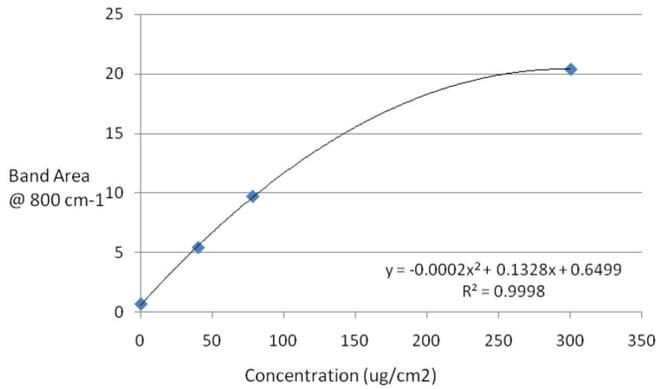
~300 ug/cm2 silicone



Overlay Y-Zoom CURSOR

Res=8 cm-1

**Figure 1.** FTIR spectra of three composite coupon samples contaminated with silicone, and a blank



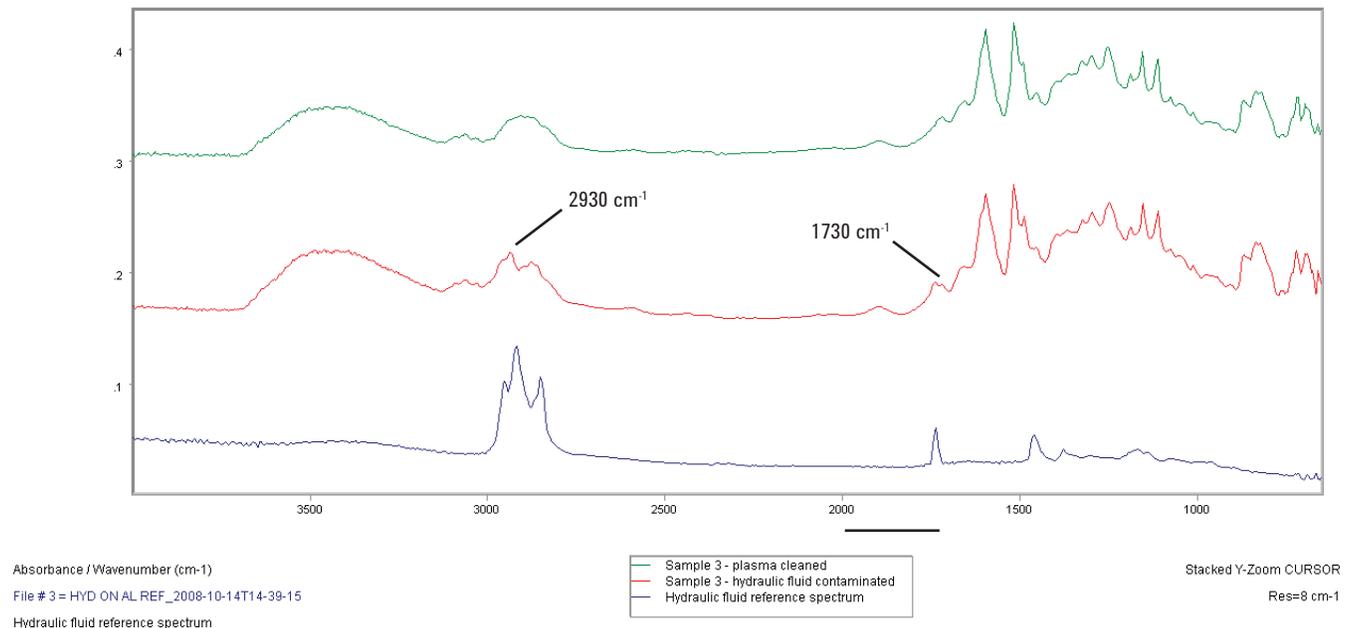
**Figure 2.** Calibration curve of negative band area versus approximate concentration of silicone

## Hydraulic fluid

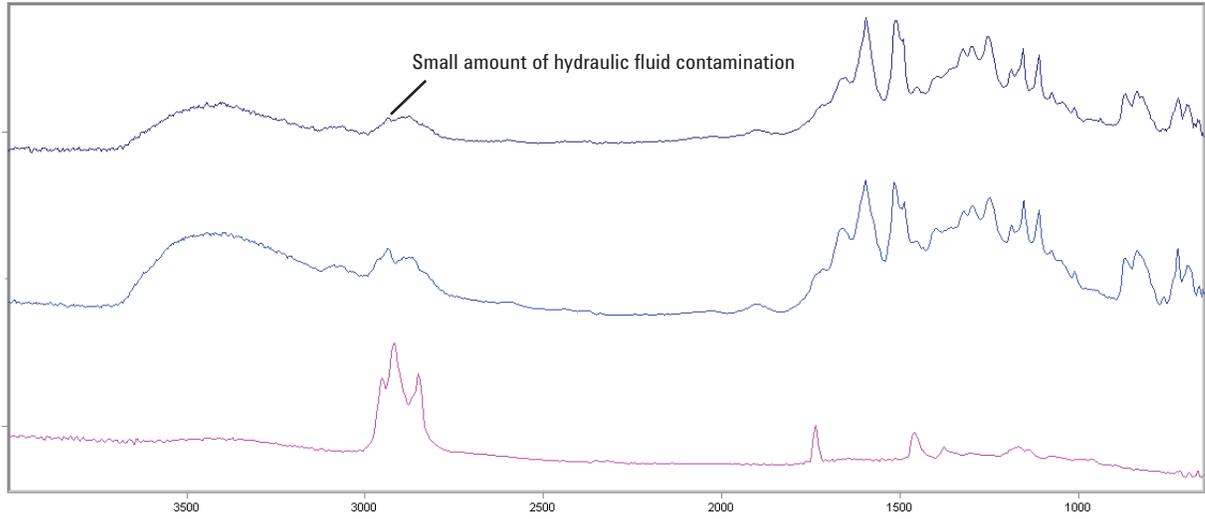
Contamination of composites by hydraulic fluid is a large concern for aircraft repair. Hydraulic leaks can cause the composite to be saturated. Although hydraulic fluid can be removed from the surface by a simple solvent wipe, fluid present in micro-cracks may be pulled into the bond layer by heat and vacuum used to effect the repair. Plasma cleaning can be used to remove residual hydraulic fluid from a saturated sample. Care must be taken, however, to ensure that the plasma is strong enough to remove the fluid, but not too strong as to damage the composite.

A set of three samples was saturated with a hydrocarbon based hydraulic fluid. The samples were cleaned with a standard acetone wipe. One half of each sample was then cleaned with a plasma cleaner. A different plasma cleaner was used on each sample, each imparting different amounts of energy to clean the surface. Figure 3 shows spectra collected on both the contaminated and clean side of one sample compared to a reference spectrum of the hydraulic fluid. The fluid in the contaminated sample can be clearly seen by the sharp CH stretching band at  $2930\text{ cm}^{-1}$  and the C=O shoulder at  $1730\text{ cm}^{-1}$ . These bands are clearly absent from the plasma cleaned sample.

Of the three plasma cleaning techniques, Sample 3 (shown in Figure 3) clearly provides the best cleaning without damaging the surface. The plasma cleaned side of Sample 1 still shows a small amount of hydraulic fluid as is shown in Figure 4. On the other extreme, the plasma used on Sample 2 used too much power. Figure 5 shows the hydraulic fluid contaminated sample and the plasma cleaned sample; no epoxy signature is evident in the plasma cleaned sample, indicating that it has been damaged by the plasma.



**Figure 3.** FTIR spectra of composite 'Sample 3' contaminated with hydraulic fluid, and cleaned composite, compared to a hydraulic fluid reference spectrum

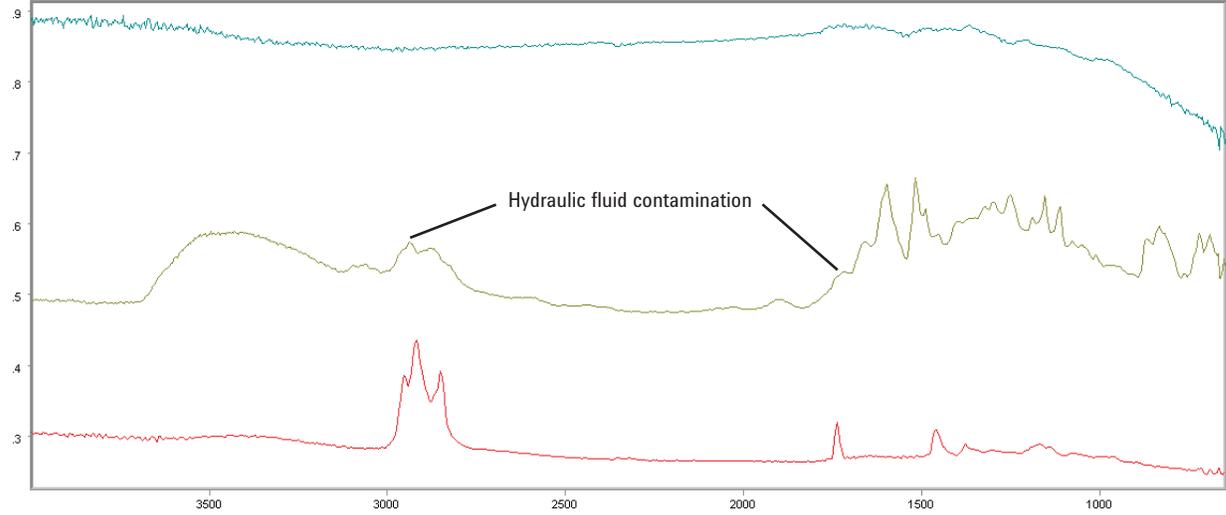


Absorbance / Wavenumber (cm-1)  
 File # 1 = HYD NCSU 1 HF EXPOSED\_2008-10-14T14-50-57  
 Sample 1 - plasma cleaned

— Sample 1 - plasma cleaned  
 — Sample 1 - hydraulic fluid contamination  
 — Hydraulic fluid reference

Stacked Y-Zoom CURSOR  
 Res=8 cm-1

**Figure 4.** FTIR spectra of composite 'Sample 1' contaminated with hydraulic fluid, and cleaned composite, compared to a hydraulic fluid reference spectrum. It is evident that the cleaned sample still contains a small amount of hydraulic fluid.



Absorbance / Wavenumber (cm-1)  
 File # 1 = HYD NCSU 2 HF EXPOSED\_2008-10-14T14-48-27  
 Sample 2 - plasma cleaned

— Sample 2 - plasma cleaned  
 — Sample 2 - hydraulic fluid contaminated  
 — Hydraulic fluid reference

Stacked Y-Zoom CURSOR  
 Res=8 cm-1

**Figure 5.** FTIR spectra of composite 'Sample 2' contaminated with hydraulic fluid, and cleaned composite, compared to a hydraulic fluid reference spectrum. It is evident that the cleaned sample was damaged by the plasma.

## Conclusion

The Agilent 4100 ExoScan FTIR with diffuse reflectance sampling interface can measure contaminants on composite surfaces. Both silicone and hydraulic fluid were measured on epoxy carbon composites. Hydraulic fluid could still be detected on composite surfaces even after they were cleaned with solvent. Additionally, the 4100 ExoScan was used to determine the efficacy of plasma cleaning on composites; cases were displayed of cleaning, over-cleaning and under-cleaning the surface.

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Published November 23, 2015

Publication number: 5991-0007EN



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