# Detection of trace contamination on metal surfaces using the handheld Agilent 4100 ExoScan FTIR

## Ensuring ultimate cleanliness for maximum adhesion

### Application Note


### Author

John Seelenbinder

Agilent Technologies,
Connecticut, USA



### Abstract

Efficient adhesive bonding of metal surfaces requires a high level of cleanliness of the surfaces. The 4100 ExoScan FTIR with a grazing angle sample interface enables identification and quantification of metal surface cleanliness in the field. After the metal has been cleaned, the analyzer can be used to detect the presence of organic and some inorganic contaminants. Even very low amounts of contamination can severely decrease the ultimate bond strength; the highly sensitive 4100 ExoScan can detect trace levels of contaminants.


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## Introduction

Adhesive bonding provides strong, reliable attachment between similar and dissimilar materials. Often, adhesive bonds can provide greater breaking strength than the materials which are being bonded together. Additionally, the use of bonding can produce stronger, lighter components through the elimination of heavy mechanical fasteners and the holes which are required to use such fasteners.

Although adhesives can produce a very strong bond, the ultimate strength is often determined by the cleanliness of the two surfaces that are being bonded. Adhesives applied to a contaminated surface will only bond to the contaminant, leaving only a weak bond between the two substrates. For some applications, even trace amounts of contaminants can severely decrease the ultimate bond strength.

In order to ensure that bonding surfaces are free of contaminants, 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. To guarantee strong bonding, surfaces should be analytically tested to confirm their cleanliness before application of adhesives. A good testing technique should be non-destructive, identify and quantify contamination, and ideally be field deployable. The technique must also have the sensitivity required to see low levels of contamination on bonding surfaces.

Infrared (IR) spectroscopy is a non-destructive method, which can both quantify and identify many contaminants on metal surfaces. All organic chemicals and many inorganic chemicals can be measured by IR. Using a grazing angle sample interface, IR is sensitive enough to measure contaminants at very low levels. These are all positive properties; however, grazing angle IR reflectance has typically been measured on small test samples using traditional benchtop FTIR spectrometers in laboratory environments. The Agilent 4100 ExoScan FTIR overcomes this limitation by offering a sensitive, handheld IR spectrometer that can be applied to the analysis of components of virtually any size in manufacturing or maintenance facilities. This application demonstrates the use of the 4100 ExoScan with a grazing angle sample interface to measure small amounts of contaminants on metal surfaces.

## Grazing angle infrared reflectance

There are many ways to measure samples using IR spectroscopy. In all cases, the IR light from the spectrometer must interact with the sample, and then be directed to the detector. The simplest example of this is a transmission measurement, where the light passes straight through the sample. For samples on reflective surfaces, 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 metallic surfaces, and then passes through the sample a second time before being collected on the detector. A diagram describing the sample IRRAS is shown in Figure 1.

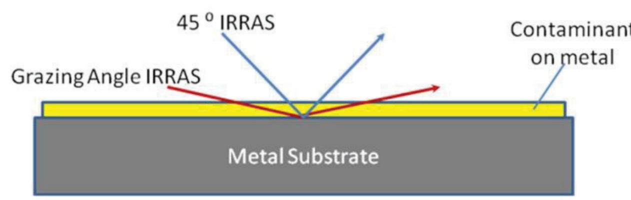


**Figure 1.** Diagram showing the sample interface of infrared reflection absorption spectroscopy (IRRAS) in both the grazing angle (red) and specular reflectance (blue) geometries. The grazing angle geometry has an increased pathlength through the contaminant

The intensity of an IR absorbance measurement is directly proportional to both the concentration of the sample and the pathlength of the light traveling through the sample according to Beer's Law (Absorbance = Concentration * Pathlength * Molar absorptivity). In an IRRAS experiment, the pathlength can be increased by using a very shallow angle with respect to the substrate surface. If the angle of incident light is greater than 75 degrees from normal, the experiment is typically referred to as a grazing angle measurement. Figure 1 also shows pictorially the difference in pathlength comparing reflection at 45 degrees (typical specular reflectance measurement) to a grazing angle reflectance at 80 degrees to normal. In addition to the increased pathlength, grazing angle reflectance shows additional sensitivity compared to a typical specular reflectance measurement. The increase in sensitivity is due to enhancement of the electric field of the p-polarized light at the surface. One can visualize the p-polarize light as creating a standing wave on the surface thus greatly increasing the effective path length. The greatest enhancement in the field strength for smooth metallic surfaces is near 88 degrees from normal; this is instrumentally unpractical, so grazing angle sample optics typically have a average angle near 80 degrees.

The 4100 ExoScan FTIR is a portable, handheld IR spectrometer for surface analysis. It has been designed specifically for reflection techniques; one if the three available sampling interfaces is a grazing angle geometry. The 4100 ExoScan grazing angle has a nominal angle of 82 degrees. The high throughput optic system yields over 80% throughput, producing excellent signal-to-noise even on short measurements. The 4100 ExoScan is also available with specular reflectance (45°) and attenuated total reflectance (ATR) sample interfaces making it a versatile instrument for many sample types. The 4100 ExoScan is fully portable, requiring no power or computer connections. The data is collected and results are displayed on a PDA computer; the results can also be transferred to a PC for further evaluation. Additionally, the 4100 ExoScan measures the full IR spectral range for identification and quantification of most contaminants, and it is impervious to atmospheric conditions.

## Contaminant measurement using the Agilent 4100 ExoScan FTIR

All IR spectrometers, including the 4100 ExoScan FTIR, are sensitive to many different organic and inorganic contaminants. Figure 2 shows spectra obtained with the 4100 ExoScan of a thin layer of hydrocarbon oil and a thin layer of silicone, each on an aluminum surface.

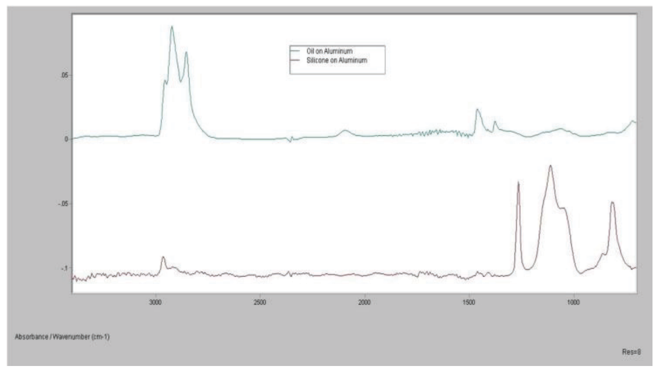


**Figure 2.** Hydrocarbon oil (blue) and silicone oil (red) on an aluminum substrate measured with the Agilent 4100 ExoScan FTIR.

As can be seen from the spectra, the 4100 ExoScan FTIR can easily distinguish different types of contaminants, enabling the user to select the proper cleaning procedure to remove the contaminant.

The 4100 ExoScan FTIR was designed to provide easy to understand answers for both skilled and unskilled users. The spectra shown above and below are informative for a skilled user to determine the amount and type of signal present, but the successful use of the 4100 ExoScan in field applications requires that the results be presented in a simplified form. Methods can be generated in the 4100 ExoScan to produce numeric results related to the amount of sample on the surface. Limits are provided, allowing the results to be displayed as red, yellow or green if the sample is in a critical, marginal or safe range respectively. Figure 3 shows the results screen for a measurement of oil contamination. In this case the amount of silicone was above the marginal but below the critical limit, so the result is display in yellow. This indicates to the user that the area should be cleaned and re-measured before proceeding.


**Figure 3.** 4100 ExoScan FTIR Results screen showing a marginal oil contamination on a metal surface

## Limit of detection of surface contamination

To determine the limit of detection for contaminants on smooth metal, a series of test samples were made by spray coating a silicone mold release (Frekote) on sheet metal aluminum plates. The silicone was applied by spraying a precise amount of material on the surface in two sweeps. The concentrations were verified by measurement on a laboratory IR spectrometer with an established method. The average concentration of six measurements for each panel was calculated; the concentrations ranged from 1.6 to 8.8 µg/cm$^2$. Table 1 shows the average concentrations of each sample in this test set.

**Table 1.** Surface concentrations of silicone mold release agent on aluminum

| Sample | Concentration (µg/cm$^2$) |
|---|---|
| 1 | 1.6 |
| 4 | 3.2 |
| 6 | 6.1 |
| 10 | 8.8 |

Several spectra of each panel were measured using the 4100 ExoScan FTIR. Spectra were measured using 8 cm$^{-1}$ spectral resolution; 32 scans were co-added yielding a 10 second data collection time. Representative spectra from this sample set are shown in Figure 4. The three prominent bands of silicone at 1265, 1112 and 820 cm$^{-1}$ are easily distinguished, even at the lowest concentration measured.

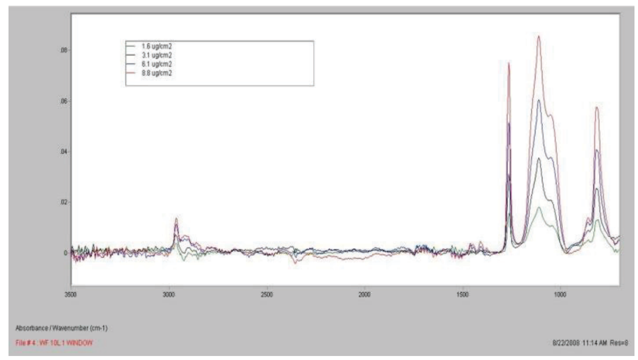

**Figure 4.** Spectra of silicone mold release agent on aluminum measured with the Agilent 4100 ExoScan FTIR using the grazing angle sample interface. Spectra were collected at 8 cm$^{-1}$ resolution with a 10 second collection time.

A calibration curve was plotted using the area of the silicone band at 1265 cm$^{-1}$. The calibration is shown in Figure 5. The calibration is linear with an excellent correlation of 0.997. The limit of detection was calculated by measuring baseline area from 2210 to 2120 cm$^{-1}$. This area was multiplied by 3 (3x the baseline noise) to give the limit of detection of 0.17 µg/cm$^2$. It should be noted this LOD is a worst case prediction; the measurement of entire silicone band area or measurement over a longer period of time would produce a lower LOD.

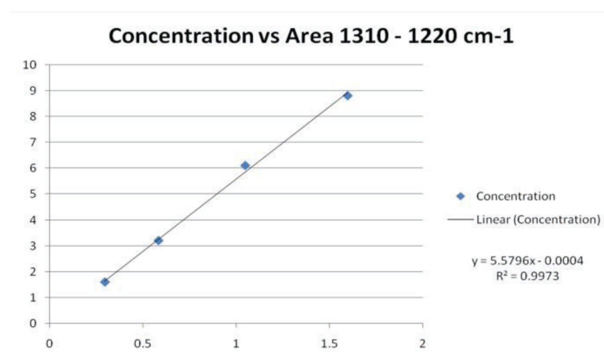


**Figure 5.** Calibration curve for silicone mold release agent on aluminum from 1.6 to 8.8 µg/cm$^2$

## Conclusion

The quality and strength of an adhesive bond is directly proportional to the cleanliness of the surface being bonded. In addition to stringent cleaning procedures, measurement of bonding surfaces post-cleaning can provide a needed quality control step. The 4100 ExoScan FTIR system, equipped with grazing angle sample optics, can provide the level of sensitivity required for the detection and identification of a large number of organic and inorganic contaminants on metal surfaces. Even with a quick 10 second measurement, a limit of detection of 0.17 μg/cm$^2$ was obtained for a silicone mold release agent on aluminum surfaces. Methods can be created to present the measurement results in easy to understand categories for use by field personnel. The 4100 ExoScan FTIR enables field measurement of surface cleanliness at detection levels required for efficient bonding.

*In addition to the 4100 ExoScan FTIR, Agilent offers the 4200 FlexScan FTIR. The 4100 ExoScan and 4200 FlexScan both provide easy, handheld FTIR analysis, but with slightly different form factors. The 4200 FlexScan has the same optical components as the 4100 ExoScan, but the optics and electronics are separated by a cable. This makes the handheld component smaller, while still providing the spectroscopic performance needed for a variety of applications.*

*The 4200 FlexScan has a 3 pound optical head attached to a 4 pound battery and electronics pack. Although the form factor is different, use of the two systems, including the software, is identical. While the 4100 ExoScan provides an integrated, compact package, the 4200 FlexScan has a smaller size to fit into spaces with tight clearances.*

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