

# Preliminary Tests for the Development of New NDT Techniques for the Quality of Adhesive Bond Assessment

Bastien EHRHART<sup>\*</sup>, Bernd VALESKE<sup>\*</sup>, Malaika SARAMBE<sup>\*\*</sup>, Nicolas CHOBAUT<sup>\*\*</sup>, Alexis GENDARD<sup>\*\*</sup>, Clemens BOCKENHEIMER<sup>\*\*</sup>

<sup>\*</sup> Fraunhofer Institute for Non-Destructive Test Methods (IZFP), (Campus E3.1, 66123 Saarbruecken, Germany)

<sup>\*\*</sup> Airbus Operations GmbH (Department Materials and Processes ESWNG, Airbus Allee 1, 28199 Bremen, Germany)

**Abstract.** Although the aerospace industry already has experience with adhesive bonding on carbon fibre reinforced polymers (CFRP) technology, a great potential for the manufacturing of high-loaded structures exists. A prerequisite for such an application is that the quality of the adhesive bond can be controlled. Several non-destructive testing (NDT) methods exist for the characterisation of defects like pores, delamination or debonding within adhesive bond. No existing NDT technique however allows a control of the optimal physical and chemical properties of the adherend surface yet, which is believed to be decisive in the mechanical performance of the adhesive bond. This lack is an obstacle to a wider application of adhesive bonding technology. Therefore, to ensure the optimal properties of the adhesive bond, that are depending on the adhesive and the adherend surface properties, “new” NDT methods for the characterisation of the adherend CFRP surface need to be developed.

This paper covers some recent research activities led in this field within Fraunhofer and Airbus Operations GmbH. Preliminary test programs were launched in accordance with Airbus standards in order to reveal the potential of a few pre-selected “new” NDT technologies. They involved also comparison between conventional laboratory measurements and mechanical destructive tests for the correlation of the contamination and damage effects on the CFRP. Tests have been performed on 3 different applications scenarios: moisture uptake in CFRP, thermal damage in CFRP, Skydrol/Water contamination in CFRP. First results demonstrated that portable X-Ray Fluorescence (XRF), Laser-induced Breakdown Spectroscopy (LIBS) were able to detect traces of Skydrol contamination while a portable Infrared Spectrometer was successfully implemented in all experimental cases, from the systematic detection of heat damaged composites to different moisture contents. Interesting results were also obtained from other technologies such as active thermography.

This approach relying on the characterisation of properties of the composite material has shown interesting possibilities so that further development of each technology is running and shall provide even better results in the future.

## 1. INTRODUCTION

Although the aerospace industry already has experience with adhesive bonding on carbon fibre reinforced polymers (CFRP) technology, a great potential for manufacturing of high-loaded structures exists. A prerequisite for such an application is that the quality of the adhesive bond can be controlled. Various non-destructive testing (NDT) techniques are

adequate for the characterisation of defects like pores, delamination or debonding within adhesive bond. No existing NDT technique however allows a control of the optimal physical and chemical properties of the adherend surface yet, which is believed to be decisive in the mechanical performance of the adhesive bond. This lack is an obstacle to a wider application of adhesive bonding technology. Therefore, to ensure the optimal properties of the adhesive bond, that are depending on the adhesive and the adherend surface properties, “new” or also called “Extended” NDT methods for the characterisation of the adherend CFRP surface need to be developed. For this purpose, several techniques have been selected over the last months for preliminary tests on precise application scenarios.

The objective of this paper is to illustrate the achievements realised by these methods for the characterisation of the adherend surface and so, demonstrate the validity of this approach.

## **2. POTENTIAL EXTENDED NDT TECHNIQUES**

The selected techniques and their parameters for the tests performed in the feasibility studies are introduced.

### *IR Spectroscopy - portable spectrometer FT-IR Exoscan®*

The spectrometer Exoscan® was alternatively equipped with the Attenuated Total reflectance (ATR), the diffuse reflectance, or the 45° external reflectance sampling probes. The scanned area is of around 4,7-7,9 mm<sup>2</sup>, and each sampling probe has its advantage for the characterisation of liquids, plastic films, smooth and rough surfaces and requires an intimate contact with the specimen. The Exoscan also involves a Michelson interferometer (8 cm<sup>-1</sup> resolution) and a TGS detector. Five measurements at different spots were done on each specimen. For each measurement, the device compiled 128 spectra.

### *X-Ray Fluorescence*

A X-Ray wavelength is used to dislodge a tightly-held inner electron of an atom. The atom becomes thus unstable and an outer electron replaces the missing inner electron while emitting itself an X-ray, the so-called fluorescence. Each element has a precise electronic arrangement so that this mechanism can be used to identify the elemental composition of a specimen. The device used is a NITON XL3t GOLD from the company Analyticon Instruments. It has 30 seconds integration time and is calibrated to focus only on relevant light chemical elements (P, Si, S...).

### *Laser-Induced Breakdown Spectroscopy*

Laser-Induced Breakdown Spectroscopy (LIBS) involves a high-powered laser pulse focused on the specimen. The interaction between matter and high-density photons generates a plasma which is analyzed by a spectrograph to establish a ratio between a reference element and the targeted element.

### *Active Pulse Thermography*

The Active Pulse Thermography set up involved the use of two flash lamps of 3200 J as excitation sources. The light pulse duration was set at 20 ms. Some part of the IR radiation incident on the object surface is absorbed and transformed into a thermal energy, which propagates by thermal diffusion from surface inside the object. An infrared Silver 480 M

camera from Cedic Infrared System, operating in the 3-5  $\mu\text{m}$  spectral range was used. A sequence of 150 images was recorded over a period of three seconds after the flash impulse.

### 3. RESULTS ON PRELIMINARY TESTS

#### 2.1 Skydrol & water contamination in CFRP

##### *Presentation*

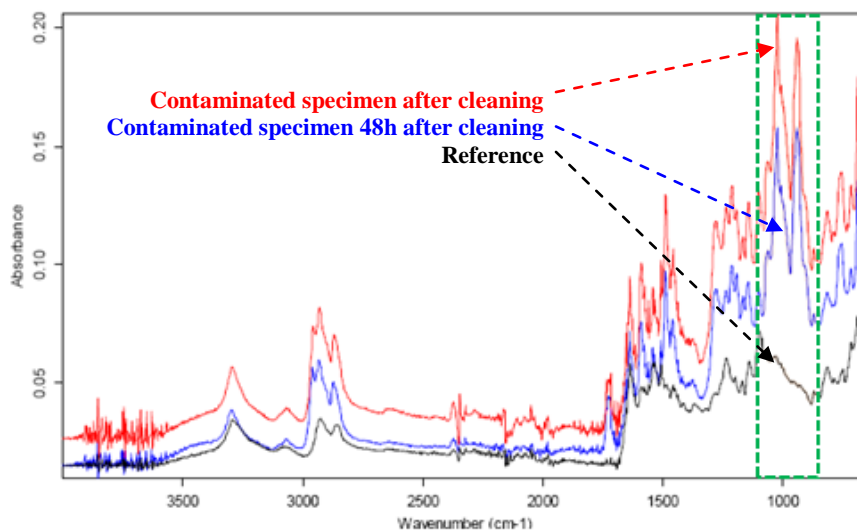
Skydrol is a fire-resistant hydraulic fluid based on phosphate ester which is used to convey power via pressure in order to command flaps, slats, rudder, etc. In each part of the aircraft made of CFRP and in the presence of Skydrol, a contamination due to a leakage of the hydraulic system can occur. Skydrol and water react to form a phosphoric acid that can etch the CFRP. Other alkaline solutions may form and cause a similar effect. After the standard cleaning and drying processes, Skydrol traces may remain on the surface and diffuse into the interface of the adhesive bond and weaken any bonded repair or even prevent its adhesion completely.

For the purpose of the skydrol contamination, a mix of skydrol 500-B4 and de-ionised water (50/50) was prepared according to Airbus specifications. CFRP specimens with unidirectional fibres were available at the clean reference state and at 850 h contaminated state. Both sets of specimens underwent the mandatory cleaning process defined by Airbus, including solvent wipe, sandpapering, water break test and its compulsory dry-out.

All characterisation methods were tested once directly after the cleaning procedures and also once again 48 hours after in order to evaluate any possible retro-diffusion of the contaminant from the inner core to the near surface.

##### *Skydrol traces detection with IR Spectroscopy*

A significant difference in the absorbance appears between the reference (black spectrum) and contaminated (red and blue spectra) specimens, despite the cleaning process (Figure 1). Two important peaks corresponding to the bands of phosphoric ester C-O around 1000 and 1100  $\text{cm}^{-1}$  can be detected. The presence of contaminant traces is thus qualitatively assessed.

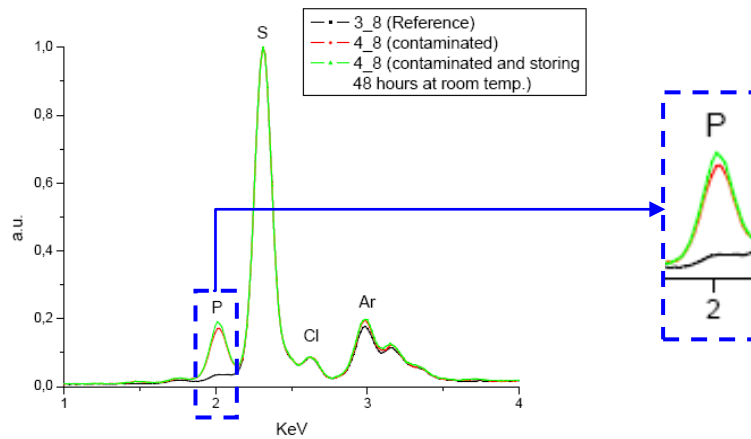


**Figure 1:** IR spectra from the measurement on a reference (black) and a 850 hours contaminated specimen at 0 (red) and 48 hours (blue) after cleaning process (source: Fraunhofer IFAM)

No significant changes are however visible between the IR-spectra at 0 hour and 48 hours after the cleaning process, what suggest that no retro-diffusion takes place.

*Skydrol traces detection with X-Ray Fluorescence*

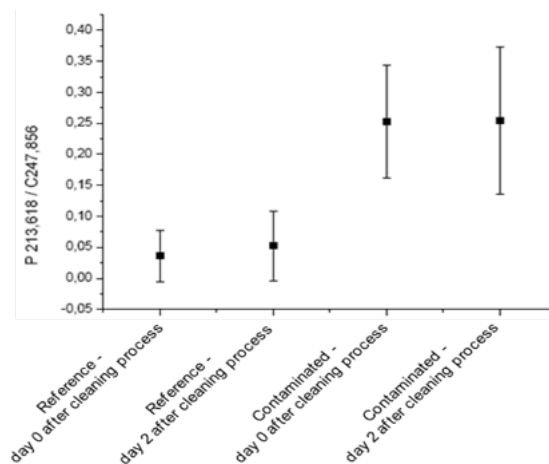
**Figure 2** displays the spectra from the XRF measurements. A difference in intensity at 2 keV corresponding to phosphorus is observed, illustrating the presence of phosphorus either from the phosphoric ester or phosphoric acid. The difference is however only to be seen between the reference clean specimen and the contaminated one. No significant difference in the spectra 0 hours and 48 hours after cleaning is observed. Again, this Extended NDT method suggests that over 48 hours at room temperature, no retro-diffusion takes place.



**Figure 2:** X-Ray Fluorescence spectra from reference (black) and a 850 hours contaminated specimen at 0 (red) and 48 hours (green) after cleaning process (source: Fraunhofer IFAM)

*Skydrol traces detection with Laser-Induced Breakdown Spectroscopy*

The result from LIBS is given in **Figure 3**. The Y-axis shows the ratio phosphorus/carbon detected for each specimen (reference or contaminated) corresponding to an average of 25 tests done on each specimen. The scattering of the results is also displayed.



**Figure 3:** Results for LIBS method comparing reference and 850 hours contaminated specimens at 0 and 48 hours after cleaning process (source: Fraunhofer IFAM)

With a ratio P/C around 0.25, the LIBS provide also a clear conclusion regarding an uptake of phosphorus in the case the contaminated specimen, whereas the ratio for the

reference specimen is close to 0. The important scattering in the case of the contaminated specimen still allow a qualitative detection of the phosphorus. However, no retro-diffusion of contaminant was observed 48 hours after the cleaning process.

## 2.2 Moisture contamination in CFRP

### *Presentation*

During the manufacturing process, CFRP panels undergo several pre-treatment such as wet abrasion and water break test to make sure the surface is clean and ready for further use.

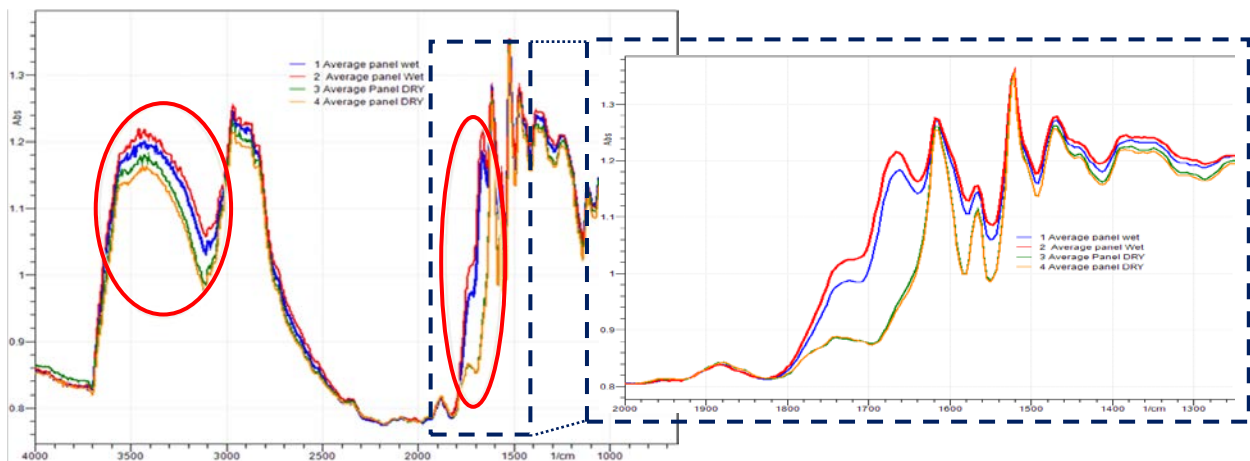
In some cases, due to water remaining on panels or storage in a humid atmosphere for example, the surface is contaminated by moisture with a concentration up to a few wt%. Moisture is however to avoid because it lowers the quality of the adhesion and leads to a loss of performance in the CFRP. Large CFRP parts whose exposure is not sure are by default dried-out. This step is yet mandatory and costly in time and money.

Typically, moisture concentrates in the resin and its amount does not exceed about 2 wt.%. Extended-NDT methods shall be able to detect quantitatively the moisture rate in the CFRP panels which can reach up to several m<sup>2</sup> over different geometries.

The specimens were stored over more than 3 months in a climatic chamber (80 °C / 85 % r.H.) to simulate the moisture contamination and obtain a complete saturation. To design specimens with a reference dry state, specimens were also stored over days in an oven with air circulation at 60 °C.

### *Moisture detection with IR Spectroscopy*

After a demonstration of the repeatability of the measurements on the faces of the CFRP, tests were done on 4 coupons. Two were moisture saturated and two dry. **Figure 4** shows all 4 averaged spectra.



**Figure 4:** Comparison of IR Spectra averaged from 2 wet + 2 dry specimens showing differences in intensity around 3100-3600 cm<sup>-1</sup> and 1600-1800cm<sup>-1</sup> (source: A2 Technologies)

The wave number regions of 3100-3600 cm<sup>-1</sup> and 1600-1800 cm<sup>-1</sup> show the greatest differences between dry and wet conditions:

3100-3600 cm<sup>-1</sup> is the OH Stretching vibration region, influenced by the presence of water. The peak height (absorbance) increases with the moisture content while the peak width remains unaffected;

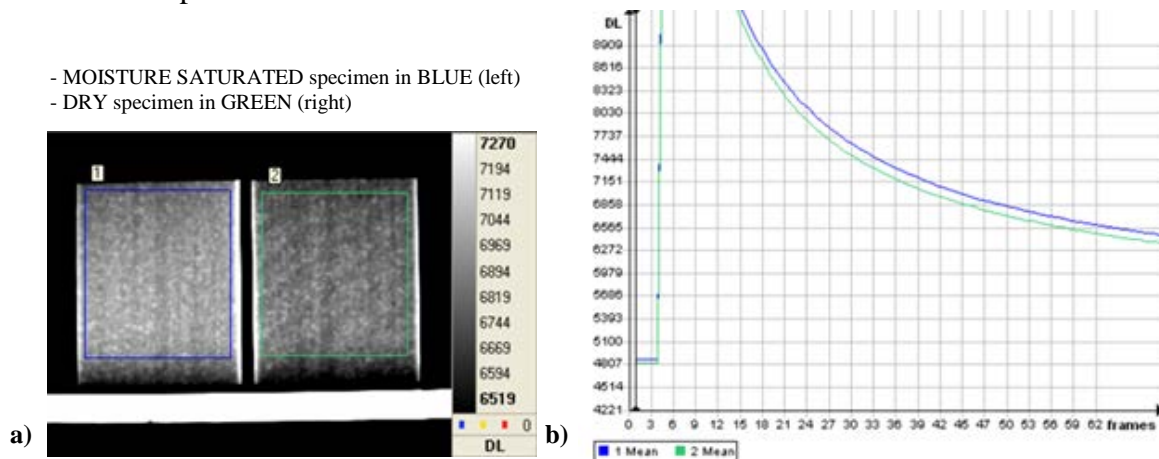
1600-1800cm<sup>-1</sup> is the OH bending mode vibration of the hydroxyl of the water and shows highly different intensities in the spectra whether the specimen is dry or wet: as visible in the enlargement (**Figure 4** right) a new peak appears at ~1666 cm<sup>-1</sup> while a strong

attenuation of the peak at  $\sim 1566\text{ cm}^{-1}$  is visible for wet specimens. A small shoulder between  $\sim 1744\text{ cm}^{-1}$  and  $\sim 1729\text{ cm}^{-1}$  can also be attributed to changes in the chemical environment of carbonyl groups. A correlation between the moisture content and the IR absorption could successfully be shown thanks to the Exoscan.

### *Moisture detection with Active Pulse Thermography*

The thermographic image (Figure 5a) shows on the left the “wet” specimen and on the right the “dry” specimen. Figure 5b gives the time-temperature curve, which displays the averaged value of level of grey over the selected area bordered in Figure 5a.

In the time-temperature graph, it can be observed that the green curve (dry specimen) decreases faster than the blue one (wet specimen). This characterizes a higher effusivity (capacity of an object to exchange thermal energy with its environment) meaning also a faster outcome of the thermal energy absorbed, possibly because of the moisture absorbed. The difference is however still too sensitive and thermography requires a higher resolution for further experiments on this field.



**Figure 5:** Time-temperature curve (a) and Thermographic image (b) of saturated and dry CFRP specimens (Source: Fraunhofer IZFP)

## 2.3 Heat Damage in CFRP

### *Presentation*

Thermal degradation can occur in several parts of the aircraft (e.g. Rudder), due to local overheating/lightning strike and many more other accidental damage. High temperature ranges on short periods or lower temperature ranges on longer periods can cause damages in the (resin) matrix of the CFRP and thus, lead to a loss of its mechanical properties through a loss of its own integrity.

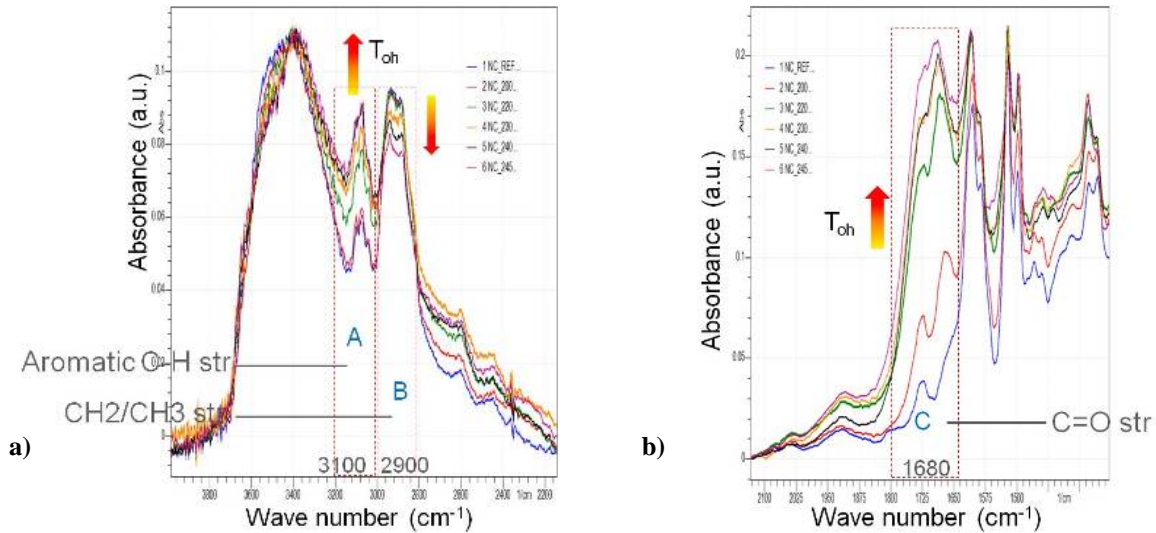
The focus is made on the detection of heat damage in composite matrix. As heat alters the chemical composition of the degraded element, characteristic molecular groups are expected to form in the material and shall be detected by the Extended NDT technologies.

For the needs of this test, CFRP specimens were exposed to heat in an oven with air circulation at a range of temperatures between the curing temperature of the composite ( $180\text{ }^{\circ}\text{C}$ ) and the limit temperature at which the delaminations appeared ( $250\text{ }^{\circ}\text{C}$ ).



### Detection of heat damage with IR Spectroscopy

Six specimens were scanned and their absorption spectrum was plotted on the same graph for comparison purpose (Figure 6). Qualitatively, some differences in shape and intensity are observable between the individual spectra.



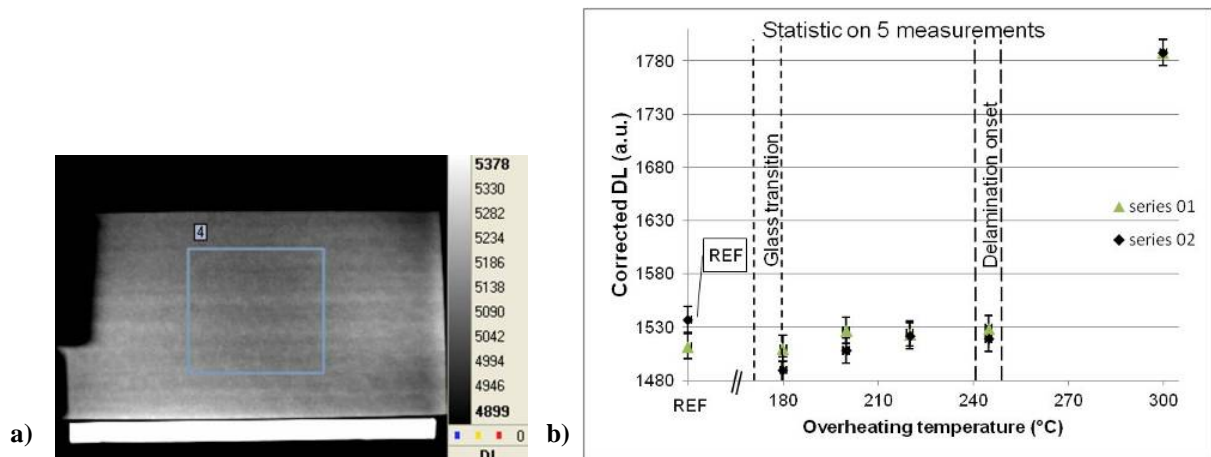
**Figure 6:** Magnification of IR absorbance spectra on regions featuring characteristic bands (45° ERAS)

Two bands around  $3000\text{ cm}^{-1}$  (see **Figure 6a**) change in intensity depending on the overheating temperature: the band labelled A around  $3100\text{ cm}^{-1}$  accounts for a stretch vibration of C-H bond in aromatics functional groups. The higher the overheating temperature is, the higher the absorbance is and hence the more C-H bonds are excited in stretching mode. The band labelled B around  $2900\text{ cm}^{-1}$  accounts for a stretch vibration of C-H bond in alkanes. One large band labelled C around  $1680\text{ cm}^{-1}$  (see **Figure 6b**) changes in shape and intensity with thermal degradation. It accounts for a stretch vibration of C=O bonds. The higher the overheating temperature, the higher the infrared absorbance.

### Detection of heat damage with Active Pulse Thermography

Measurements were performed on specimens within the blue square bordered region sketched in Figure 7a in order to generate an average value on a representative area. **Figure 7a** is a top view of a specimen excited by a flash and observed at a fixed time during cooling. The grey scale is a measure of the digital limit. The procedure (flash, recording and analysis) was repeated five times on each specimen for statistical reasons. The obtained value called “corrected DL” for the circumstance (mean value of five values) is plotted as a function of the overheating temperature in **Figure 7b**.

The reference specimens on the left side of the graph (**Figure 7b**) stand for specimens that have not undergone overheating. The corrected DL slightly decreases for a specimen overheated at  $180\text{ °C}$ . This could be explained by post-curing taking place during the overheating at  $180\text{ °C}$  and increasing the density of the specimen. A slight but insignificant increase of the measured value is noticeable for specimens overheated from  $180$  to  $245\text{ °C}$ . The specimen overheated at  $300\text{ °C}$  features a high corrected DL accounting for delaminations and proving the capability of pulse thermography as a conventional NDT technique.



**Figure 7:** a) Thermographic image of a reference specimen - The blue square delineates the area chosen for a statistical analysis and b) Influence of overheating temperature on corrected digital limit with mean values on a square area

#### 4. CONCLUSION

This paper introduces the results of the first test campaign performed with identified Extended NDT technologies on 3 top priority application scenarios: Skydrol&Water contamination in CFRP, Moisture contamination in CFRP and Heat Damage in CFRP. The four implemented Extended NDT technologies in those test campaigns were: the FT-IR Exoscan; the Active Pulse Thermography; the X-Ray Fluorescence and the Laser-Induced Breakdown Spectroscopy.

The FT-IR Exoscan is the only technology used in all cases: it demonstrated good capabilities with the substrate CFRP and managed to detect characteristic chemical bonds from all possible contaminants or generated degradation in the material.

The X-Ray Fluorescence was applied in test 1 for the detection of phosphorus. This technique was successful in its task by displaying a clear difference in the intensity corresponding to this element. This technology shall be considered for other applications where such a precise measuring task is required. This technique also has the same maturity and handling as the FT-IR Exoscan.

The Active Pulse Thermography has shown a good potential in both the detection of either moisture or heat damage in CFRP. The sensitivity is however yet too low to allow a precise characterisation of the material.

Finally, the Laser Induced Breakdown Spectroscopy was applied only in test 1 and clearly managed to detect phosphorus in contaminated specimen. Only few characteristics are however known, so that the gaps of this technology cannot be identified at this point.

The feasibility of Extended NDT is demonstrated through all tests run in the previously mentioned test campaigns. The FT-IR Exoscan and the X-Ray Fluorescence techniques are so far the only portable and commercialised technologies that could be used for in-service inspections. All other methods are still under development and are not yet portable. Their implementation, with also the Exoscan and the XRF devices should be possible in manufacturing environment.

Further development will involve more detailed application scenarios (e.g. measuring task, limit values, substrate type, surface treatments, environment requirements, etc.) and a larger range of specimens to characterise. The specimens shall also cover the complete issue addressed in the application scenario in order for the technology to show its complete potential and be optimised for the required measuring tasks.