Chapter 3

Extended Non-destructive Testing for Surface Quality Assessment

Mareike Schlag, Kai Brune, Hauke Brüning, Michael Noeske, Célian Cherrier, Tobias Hanning, Julius Drosten, Saverio De Vito, Maria Lucia Miglietta, Fabrizio Formisano, Maria Salvato, Ettore Massera, Girolamo Di Francia, Elena Esposito, Andreas Helwig, Rainer Stössel, Mirosław Sawczak, Paweł H. Malinowski, Wiesław M. Ostachowicz, and Maciej Radzieński

Abstract This chapter introduces various extended non-destructive testing (ENDT) techniques for surface quality assessment, which are first characterized, then enhanced, and finally applied to assess the level of pre-bond contaminations intentionally applied to carbon fiber reinforced plastic (CFRP) adherends following the procedures described in the previous chapter. Based on two user cases comprising different scenarios that are characteristic of either aeronautical production or repair, the detailed tests conducted on two types of sample geometry, namely flat coupons and scarfed pilot samples with a more complex shape, form the basis for applying the advanced ENDT procedures for the monitoring of realistic and real aircraft parts, as will be described in Chap. 5. Specifically, the reported investigations were performed to assess the surface quality of first ground and then intentionally contaminated CFRP surfaces using the following ENDT tools: the aerosol wetting test (AWT), optically stimulated electron emission (OSEE), two differently implemented approaches based on electronic noses, laser-induced breakdown spectroscopy (LIBS), Fourier-transform infrared (FTIR) spectroscopy, laser-induced fluorescence (LIF), and laser vibrometry.

M. Schlag (✉) · K. Brune · H. Brüning · M. Noeske
Fraunhofer Institute for Manufacturing Technology and Advanced Materials IFAM, Wiener Str.
12, 28359 Bremen, Germany
e-mail: mareike.schlag@ifam.fraunhofer.de

C. Cherrier · T. Hanning · J. Drosten
Automation W+R GmbH, Messerschmittstraße 7, 80922 Munich, Germany

S. De Vito · M. L. Miglietta · F. Formisano · M. Salvato · E. Massera · G. Di Francia · E. Esposito
ENEA – National Agency for New Technologies, Energy and Sustainable Economic
Development, TERIN-FSD, Portici Research Center, P.le E. Fermi 1, 80055 Portici, Italy

A. Helwig · R. Stössel
Airbus Defence and Space GMBH, Willy-Messerschmitt-Straße 1, 82024 Taufkirchen, Germany

M. Sawczak · P. H. Malinowski · W. M. Ostachowicz · M. Radzieński
Institute of Fluid–Flow Machinery, Polish Academy of Sciences, Fiszerza 14, 80-231 Gdańsk,
Poland

Keywords ENDT for surface quality assessment • Aerosol wetting test • Optically stimulated electron emission • Electronic noses • Laser-induced breakdown spectroscopy • Fourier-transform infrared • Laser-induced fluorescence • Laser vibrometry

3.1 Introduction

In the previous chapters, we detailed that one of the reasons inhibiting the certification of adhesive bonding for primary aircraft structures is the sensitivity of the bondline integrity to the presence of defects that can affect the strength of the joints. These defects are not accessible to visual monitoring during the bonding process. Furthermore, the most critical defects arising during the manufacture of adhesive joints are those that are not detectable by currently available NDT methods. This has led us to develop extended NDT (ENDT) methods capable of detecting such effects on CFRP adherends, whereby we evaluate their efficiency and assess their applicability benefits based on the analysis of specimens with increasingly complex sample geometries, starting from flat coupon samples that exhibit distinct levels of intentionally applied contaminations [1] and moving toward CFRP panels with more complex/curved geometries that might even exhibit multiple contaminations. The present chapter describes the respective contributions of the individual partners of the ComBoNDT consortium [2], thereby detailing the different specialist approaches within a jointly developed concept for quality assurance.

The subsequently detailed ENDT procedures for surface quality assessment constitute an essential input into the framework for the overall concept for the quality assessment of adhesively bonded joints described in this book. The results presented in this chapter were achieved in the research conducted into the applied ENDT methods. Looking ahead, we would like to highlight here that in certain contamination scenarios of the aircraft production and repair user cases, these pre-bond in-process methods were sensitive to impacts that were shown to affect a strength reduction of successively manufactured adhesive bonds and, therefore, could potentially be utilized to identify not-in-order (NIO) adherends during a surface quality assessment procedure.

3.2 Aerosol Wetting Test (AWT)

In this section, we introduce the aerosol wetting test (AWT) as a tool for surface quality assessment and detail how its performance was enhanced in the ComBoNDT project for the in-process monitoring of CFRP adherends.

3.2.1 Principle and Instrumentation

AWT allows the inline monitoring of the surface state, specifically through an inspection of its wettability.

Throughout the last decade, various aspects of this technology have been enhanced, whereby the most recent advances were achieved in the ComBoNDT project. Hereby, both the hardware and software were adapted in order to achieve more relevant and more reliable results in terms of measurement, data evaluation, and post-processing.

3.2.1.1 Measurement Principle

AWT allows the monitoring of a surface state by analyzing its wetting properties. In its most common implementation, an aerosol of ultra-clean water is sprayed onto the surface using an ultrasonic spray nozzle. Depending on the wetting behavior and wettability of the surface, the droplet pattern, diameter, and distribution vary, as exemplified in Fig. 3.1. The wetting behavior is then automatically analyzed based on the images recorded by a camera system and image processing algorithms.

This surface inspection method has various advantages, which are briefly:

Fig. 3.1 Aerosol wetting test (AWT) droplet pattern influenced by the local wettability of the substrate surface: a more wettable surface region (left) with less and larger droplets compared to a less wettable surface region (right) exposed to the same amount of droplets from a water aerosol generated by an ultrasonic nozzle

- The inspection speed and the size of the inspected surface.

AWT is particularly adapted to the measurement of the properties of the droplet pattern at the edge of a part. The inspection is conducted on a 30 mm wide area at a speed of 6 m per minute; therefore, it is especially suitable for inspecting specific, narrow bonding areas. In practice, each image is separated from the previous one and then the evaluation is performed. The values in this book are given based on calibrated image dimensions, such as the base area (30 × 30 mm).

- Its low impact on the surface.

This method is non-destructive and has a minimal influence on the investigated part. Approximately 0.2 μL of ultra-clean water is deposited by the spray per square centimeter. After drying (which takes less than a minute for most substrate materials), the surface typically does not show any residue since the water used is ultra-clean.

- Its simplicity of use and implementation.

The system enables the inspection of various parts with only a few limitations. The measurement can take place in various environments (for example, on a production line), on various materials, and it only needs a standard energy supply.

- The simplicity of achieving the results.

Once the images are captured, various image processing algorithms and decision-making processes run simultaneously. If the calibration of the system has been flawlessly achieved, the result can be integrated into a simple IO/NIO signal for the inspector, saving the more complex data for later analysis.

3.2.1.2 Software Enhancement

During the ComBoNDT project, various software modifications were made to the existing system, most significantly to the image processing algorithms. Once the images of the droplet patterns have been generated by the camera, the main task, which is also the hardest, is detecting the droplets (and their lateral boundaries) and separating them on the image from the background formed by the material texture.

At the beginning of the project, this was accomplished by a very straightforward image processing step (thresholding followed by morphological operations); however, it emerged that this approach is extremely unstable if there are variations of the surface properties (texture, structure...).

In a first step, this rather simple image processing method was replaced with a more complex one that can nevertheless be considered standard image processing. This enhancement primarily facilitates the detection of droplets on surfaces with slight variations in color or also light intensity. This first step was fully integrated into the research system and already is implemented on the system for inline detection.

However, for some complex surfaces or distinct contamination scenarios resulting in more varied and unpredictable droplet appearances and patterns, even this enhanced image processing was not sufficiently effective. Hence, further improvements were made, with the detection and evaluation of the droplet pattern being done by a convolutional neural network (CNN). We trained the network on various datasets generated by the AWT system (various materials, various contaminations, and/or activation of the surface). With a wide set of samples, the network was trained to separate the image pixels belonging to a droplet from the pixels belonging to the background.

We visualize the various stages of the up-to-date image processing in the table displayed in Fig. 3.2.

Following this use of a CNN to detect the droplets, further classical image processing approaches were integrated for an easier decision-making process. Consequently, a sequence of various filters was applied to the image, and local values for the standard parameters (e.g., wetted area percentage, deposited water droplet diameter, drop count to evaluate the droplet number density) were calculated and graphically displayed, as shown in Fig. 3.3.

Fig. 3.2 Various AWT image processing generations on various surfaces with distinct complexities. Droplet images with green frames highlight a successful droplet detection; some droplet detections (marked by a red frame) were not successful enough for a meaningful analysis

Fig. 3.3 Example output of the so-called heatmap after convolutional neural network (CNN) processing. The displayed example was obtained within a fingerprint contamination scenario

3.2.1.3 Hardware Enhancement

Some improvements were also made to the hardware, mainly concerning the AWT measurement head, which was fully redesigned. This was motivated by various considerations:

- Improving the optical system properties.
- Facilitating the use of a robot to perform the measurements on parts with complex geometries, which are presented in Chap. 5.

Specific hardware with high computing power was used in order to integrate the CNN image processing.

3.2.1.4 Up-to-Date Measurement Apparatus

By the end of the project, the updated AWT system consisted of three main components, namely the measurement head, the electrical cabinet, and the processing computer system, as presented in Fig. 3.4.

Fig. 3.4 Updated robot-aided bonNDTinspect AWT measurement head imaged during the full-scale demonstration (detailed in Chap. 5) conducted at Fraunhofer IFAM in Bremen

3.2.2 AWT Results

Here, we present our findings achieved by applying AWT to assess distinct contamination scenarios for CFRP adherends with different shapes.

3.2.2.1 AWT Results for the Coupon Level Samples

In the following investigations, the various test results for each of the distinct contamination scenarios and three different contamination levels are compared to the results for the clean ground reference samples, which differ depending on the respective production or repair user case.

The results shown here are always presented for those two droplet pattern features out of the four subsequently listed ones that showed the best differentiating correlation with the respectively applied contamination levels. The four evaluated features are as follows:

- Average droplet diameter.
- Wetted percentage, i.e., the percentage of the surface covered by water.
- Number of droplets per surface area, i.e., the droplet density.
- Average droplet compactness, whereby the compactness of each droplet is calculated by determining the area to perimeter ratio.

Fig. 3.5 Evaluation results for the AWT features of droplet diameter and number of droplets as obtained for the CFRP samples from the MO scenario

3.2.2.2 Detection of the Moisture of CFRP Substrates (P-MO)

The moisture contamination of CFRP parts from the production user case was successfully revealed and distinguished for the three different contamination levels achieved by material exposure to environments with distinct relative humidities, as shown in Fig. 3.5.

3.2.2.3 Detection of Release Agent (P-RA)

Release agent contamination was successfully revealed and distinguished for the three different contamination levels achieved by depositing distinct amounts of a silicon-containing release agent onto the surface, as shown in Fig. 3.6.

Fig. 3.6 Evaluation results for the AWT features of droplet diameter and wetted percentage as obtained for the CFRP samples from the scenario involving a silicon-containing release agent deposited at atomic concentrations, characterized by XPS investigations

Fig. 3.7 Evaluation results for the AWT features of wetted percentage and number of droplets as obtained for the CFRP samples from the de-icing fluid scenario involving a potassium-containing de-icing fluid deposited at atomic concentrations, characterized by XPS investigations

3.2.2.4 Detection of Fingerprints on Production Samples (P-FP)

The fingerprint contamination within the production user case was contrasted and detected using AWT, although discrimination between the different contamination levels could not be achieved. For locally deposited contaminations, such as the fingerprints used here, the detection was also successfully achieved with local image processing algorithms, which allowed the characterization of the size and position of the contamination.

3.2.2.5 Detection of De-icing Fluid (DI)

The de-icing fluid contaminations were clearly revealed by AWT when comparing the droplet patterns obtained on intentionally contaminated CFRP specimens with those of clean reference samples. However, the different contaminations levels could barely be differentiated from each other, see Fig. 3.7.

3.2.2.6 Detection of Fingerprints on Repair Samples (R-FP)

Contaminations applied to CFRP surfaces for the fingerprint scenario within the repair user case were barely detected with AWT, and the distinct contamination levels were not differentiated.

3.2.2.7 Detection of Thermal Degradation (R-FP)

The effects of the thermal impact on CFRP coupon specimens were clearly detected by AWT. However, the different contamination levels were only barely differentiated.

		No detection	Partial detection	Clear detection	Partial discrimination of contamination level	Discrimination of contamination level
Production	Moisture (MO)					X
	Release agents (RA)					X
	Fingerprint (FP)			X		
	RA + FP				X	
Repair	De-icer (DI)				X	
	Fingerprint (FP)		X			
	Thermal degradation (TD)				X	
	TD + DI				X	

Fig. 3.8 Summary of the detection capacity (marked X) observed for the flat CFRP coupon samples for the production or repair user cases (first column) within the respective contamination scenarios (second column)

3.2.2.8 Summary of the Performance of AWT for Contaminated CFRP Coupon Samples

The summary presented in Fig. 3.8 shows the detection capacity of AWT for various contamination scenarios. The samples considered here are the flat CFRP coupon samples, which may not be directly relevant for the evaluation of the performance of the AWT method in terms of real parts.

3.2.3 AWT Results for the Pilot Level Samples

The AWT results obtained for the scarfed CFRP pilot samples are presented in the following. They cannot be directly compared with the results for the coupon samples or those of the realistic parts. Indeed, the variations between part type, geometry, and surface have a significant influence on the AWT measurement and evaluation results.

Therefore, we perform comparisons only among similar parts of the same type. The analytical process was set up following the objective of detecting surface contamination on the respective part.

3.2.3.1 Pilot Samples for the Production User Case with Combined Release Agent and Fingerprint Contamination

Regarding the surface constitution/texture, the pilot samples of the production user case showed a strongly structured surface and were slightly curved. The AWT droplet detection was partially successful with the first image processing improvement, and it was successful in all cases using neural network processing, see Fig. 3.9.

In this case, the geometrically strongly structured background as well as the combination of two contamination processes involving two types of deposited contaminants led to a more difficult differentiation of the various contamination levels, see Fig. 3.10.

Fig. 3.9 Overview of the findings from different AWT droplet image evaluation and processing procedures for the production pilot samples, starting from an original image (left), after performing the droplet segmentation with standard image processing (labeled “old segmentation”), and after training a CNN

Fig. 3.10 AWT findings when evaluating the feature of wetted percentage for distinct levels of the intentionally deposited combined “release agent (RA)+fingerprint (FP)” contamination within the production user case with pilot CFRP samples

3.2.3.2 Repair Scenario Pilot Samples with Combined “Thermal Impact+De-icing Fluid” Contamination

We would like to reiterate here that in contrast to the smooth CFRP specimens of the respective production user case, the pilot samples within the repair user case were shafted CFRP samples. In the following, we focus on the contamination scenario that is based on distinct levels of combined thermal degradation and subsequent de-icing fluid contamination.

Similar to the production pilot samples, the detection of the applied water droplets following the AWT procedure was challenging, even though the surface did not show a very strong texture/structure. However, the deposited waterborne de-icing fluid contamination (as similarly observed on coupon samples) leads to a very good

spreading of the droplets. Therefore, identifying individual droplets during the detection step of the AWT data evaluation process was harder since the droplets appeared to be “open” on the captured images instead of being assigned a roundish and “closed” contour. This type of droplet is not detectable using standard image processing. Once again, for such a scenario, the processing of the images with the CNN proved to be quite efficient, see Fig. 3.11.

Both the detection of contamination and the differentiation from the reference CFRP surface state were easily achieved through the observation of the AWT “droplet diameter” feature. The differentiation of various contamination levels was also possible here, see Fig. 3.12.

Fig. 3.11 Starting from the captured original AWT image, this sequence was obtained from distinct droplet segmentation approaches using standard image processing (“old segmentation”, left) and convolutional neural network (“CNN segmentation”, right) when applying AWT to intentionally contaminated CFRP pilot samples within the repair user case

Fig. 3.12 AWT findings when evaluating the “droplet diameter” feature obtained for the CFRP pilot samples prepared within the combined “thermal impact+de-icer” contamination scenario

3.2.4 AWT Performance in Inline Surface Quality Assessment

In order to establish and enhance the performance of AWT when inspecting the surface states of CFRP parts relevant for specific aeronautical user cases, we iteratively determined and advanced the abilities of the system on flat coupon samples, pilot samples, and realistic parts and then conducted an assessment of the potential inline application of the technology. As explained, this technology relies on a comparative assessment of the surface state. Hereby, the very powerful systematic AWT inspection procedure, based on a convolutional neural network (CNN), must be taught to differentiate contaminations. Once the system had been trained to correctly detect the droplets and to differentiate the contaminations, its use in inline applications was straightforward.

The inline application allows fast and non-destructive monitoring and classification of the surface states and clearly exceeds the performance of the NDT approaches used so far (e.g., the water break test). Most contaminations investigated during the ComBoNDT research project in distinct scenarios with various degrees of contamination were successfully detected, and even the relevant contamination levels investigated here could be differentiated.

In conclusion, we developed sensitive and productive AWT procedures that not only facilitated the differentiation between the surface states of clean and intentionally contaminated parts but also permitted discrimination between distinct levels of contamination for several contamination scenarios. As the significance of AWT investigations and the thus obtained findings are based on contrasts in the wetting behavior of the inspected surfaces, our investigations plausibly indicate that AWT is a very surface-sensitive technique that enables a significant differentiation between clean surfaces and surfaces with sub-monolayer and monolayer contamination. However, AWT does not allow discrimination between surface states composed of a few or several molecular layers of contaminants. Finally, the integration of the technology in inline applications without major constraints was achieved.

3.3 Optically Stimulated Electron Emission (OSEE)

In this section, we introduce optically stimulated electron emission (OSEE) as a tool for surface quality assessment and detail how its performance was enhanced in the ComBoNDT research project for the in-process monitoring of CFRP adherends. Using OSEE for the surface inspection of carbon/epoxy composite and CFRP substrates has been described in several works over the last decades [3, 4], and the method is presently gaining visibility in surface quality assessment prior to bonding [1, 5, 6].

3.3.1 Principle and Instrumentation

OSEE is a surface analytical technique that relies on recording the photocurrent emitted from a sample surface region illuminated with UV light, typically under environmental conditions that prevail in cleaning or adhesive bonding processes. There are two modes of operation. During “microscopic” OSEE mapping, the sample is scanned using an electron collector, typically by applying lateral movements with a speed ranging from 1 mm to 1 cm per second. Meanwhile, during “spectroscopic” local measurements, the photocurrent is measured at fixed positions upon varying and recording the hold-up time. We performed our OSEE experiments under ambient conditions using an SQM300 surface quality monitor (purchased from Photo Emission Tech., Inc. (PET), USA).

Regarding the principle of an OSEE measurement in more detail, during the local inspection, regions of the sample surface are exposed to UV light from a mercury vapor lamp with prominent emission maxima at 4.9 and 6.7 eV. As the work function of the respective substrate surface amounts to approximately 5 eV, the emission maximum at the higher energy of 6.7 eV essentially contributes to the photoelectrons emitted by the sample surface, and the emitted electrons exhibit kinetic energies of less than approximately 2 eV. A sub-micrometer information depth of this method is observed when investigating the surface of a solid sample covered with a film exhibiting a thickness of some nanometers. This allows for the sensitive detection of thin films on substrates that do not significantly trap electric charges upon photoelectron emission. The interaction of the emitted photoelectrons with the ambient atmosphere is dominated by an electric field effective at the collector of the sensor to an extent that permits sensor-surface distances in the millimeter range during OSEE measurements. Carefully controlling the distance between the sensor and the surface is a prerequisite for effectively applying the setup presented in Fig. 3.26, see Fig. 3.13.

To mount the substrates for analysis, we equipped a commercial OSEE device with an electrically conductive and earthed moving table upon which we positioned the analyte sample using movements in two perpendicular horizontal directions (x and y) under the sensor. The vertical distance between the sample surface and the sensor (z) was set using a micrometer screw attached to the holder of the sensor. The enhanced OSEE setup developed during the ComBoNDT research project permitted vertical sensor movements with the aid of an electric motor, and the most advanced OSEE procedure was achieved with robot-aided three-dimensional sensor positioning. In OSEE implementations depending on a moving table for positioning the CFRP specimens, a surface scan was performed, with the table programmed to move according to a certain step size and number of steps in both horizontal directions, defined by the user through the machine-associated software. As the scan advanced, a photocurrent was obtained for each part of the scanned surface, and an apparently dimensionless value (which actually indicates a current converted into a voltage [7], given in centivolts), henceforth denoted as the OSEE signal, was indicated on a display and digitally recorded. Finally, a digital worksheet with the emission values for the entire

Fig. 3.13 Diagram showing the components and the principle of optically stimulated electron emission (OSEE) for measuring a photocurrent to reveal the surface state of a substrate

analyzed sample, i.e., an OSEE map, was obtained as a result of the test. For further evaluation of these maps especially for non-localized contaminations, the mean value of all the data points in the map together with its standard deviation was calculated.

3.3.2 OSEE Results

In the following, we report the OSEE enhancements and findings obtained in the ComBoNDT research project, in which the consortium partners at Fraunhofer IFAM performed the in-process monitoring of CFRP adherends with different shapes that are relevant for distinct technologically relevant user cases and which had undergone an intentional application of various contamination scenarios.

3.3.2.1 OSEE Results Obtained on CFRP Coupon Level Samples

First, we detail the advancements of the OSEE technique. Then, we report the respective OSEE results for the production user cases, characterized by a grayish abrasive dust obtained during the grinding of the CFRP surface, and the repair user cases, characterized by black abrasive dust obtained during the grinding of the CFRP surface. When assessing the surface quality of the coupon level CFRP specimens, we used OSEE to investigate a set of three 10 cm wide square samples to examine the surface state. For each sample, a surface scan was performed using a 6 mm wide aperture

at a constant sensor-surface distance, with the table being programmed to move according to 15 steps with a width of 5 or 6 mm (in both horizontal directions), as defined by the user through the machine-associated software.

In going beyond the commercially available state of the art, and thereby increasing the technology readiness level of the OSEE technique, three principal advances were performed within the ComBoNDT project. First, we aimed at improving the reliability of the technique by considering the influence of topography, especially the sample-sensor distance, on the sensor signal and by controlling or also avoiding electrostatic charging effects. Second, we sought an adaption of the device setup and control systems to the automated scanning of CFRP surfaces used in real manufacturing processes within the production or repair user cases. Third, we manufactured the electronic parts for the OSEE adaptation (e.g., serial interface, power supply, and relay board) as defined by Fraunhofer IFAM within the project. The achieved advancements are presented in Fig. 3.14.

Fig. 3.14 Images showing the technological advancements achieved for optically stimulated electron emission (OSEE) in the ComBoNDT research project: The developed motor-driven shutter for the UV light source (left; below the electron collector) and the drive for the sensor holder, permitting a variation of the distance between the sensor and the substrate surface (right)

In terms of the abovementioned “microscopic” and “spectroscopic” operation modes of OSEE, a hybrid operation mode was developed and implemented. Based on rapidly opening a shutter in the light path of the UV source after having reached a measurement position (by laterally moving the newly developed x, y scanning table), an instant time-dependent (“in-time”) sample mapping was facilitated that allowed combining the x, y mapping option while recording the local charging behavior or also recording the local height (i.e., sensor-surface distance) dependence of the OSEE signal. Specifically, by introducing an automatized variation of the sample-sensor distance based on a third precision drive (for the vertical z-direction), the variation of the OSEE signal upon changing the sensor-surface distance became possible. This also enables an assessment of surface topographies that are more complex than flat surfaces.

Production user case based on CFRP coupons

For the production user case based on CFRP coupon specimens, we investigated three different contamination scenarios, and the respectively obtained OSEE results were compared to the reference surface state of the production samples (P-RE):

- First, different levels of surface contaminations with a silicone-based release agent (P-RA) were prepared, as described in Chap. 2, and the degree of contamination was quantified by XPS analysis.
- Second, for the production fingerprint scenario (P-FP), samples were contaminated by different amounts of a synthetic sweat formulation according to DIN ISO 9022-12, as also detailed by Moutsompegka et al. [8].
- Third, a moisture scenario during production (P-MO) was considered.

Figure 3.15 presents the respectively obtained OSEE maps for the three samples prepared following the clean reference (P-RE) scenario. With the instrumental settings applied, an average OSEE intensity of 754 ± 152 a.u. (arbitrary units) was obtained.

In the following, we present plots showing the average OSEE intensity for the three contamination scenarios P-RA, P-FP, and P-MO in comparison to that obtained for P-RE.

Fig. 3.15 Optically stimulated electron emission (OSEE) maps (15×15 pixels) for the three samples prepared following the clean reference scenario of the production user case (P-RE), based on CFRP coupon specimens resulting from a grinding process that was characterized by producing a grayish abrasive dust

Fig. 3.16 Average OSEE intensities for the three samples within each sample set, P-RA-1, P-RA-2, and P-RA-3, as part of the P-RA scenario, based on different contamination degrees achieved with an intentionally deposited silicone-based release agent, compared to the OSEE results for the P-RE scenario

As may be inferred from Fig. 3.16, all the surfaces corresponding to contamination levels P-RA-1, P-RA-2, and P-RA-3 within the P-RA scenario can be clearly detected and differentiated from the surface state corresponding to P-RE.

As may be perceived from Fig. 3.17, the average OSEE intensities obtained for surfaces corresponding to moisture levels P-MO-1, P-MO-2, and P-MO-3 within the P-MO scenario can be clearly detected and differentiated from the clean CFRP surface state corresponding to P-RE.

As may be seen in Fig. 3.18, all the surfaces corresponding to contamination levels P-FP-1, P-FP-2, and P-FP-3 within the P-FP scenario can be clearly detected and differentiated from the surface state corresponding to P-RE, even when evaluating $7.5 \text{ cm} \times 7.5 \text{ cm}$ wide areas, which exceeds the area covered by the respectively applied fingerprint (the size of a human thumbprint).

Repair user case based on CFRP coupons

For the repair user case based on the coupon level CFRP specimens, three different contamination scenarios were investigated, and the respectively obtained OSEE results were compared to the reference surface state of the repair samples (R-RE):

- For the first repair scenario (R-DI), the surfaces were intentionally contaminated with different amounts of de-icing fluid (also called de-icer, an aqueous potassium format solution).
- The second scenario (R-FP) involved contaminations with hydraulic Skydrol fluid [8], the main ingredients of which are phosphate esters.

Fig. 3.17 Average OSEE intensities for the three samples within each sample set, P-MO-1, P-MO-2, and P-MO-3, as part of the P-MO scenario, based on different moisture degrees achieved through intentional exposure to distinctly humid environments, compared to the OSEE results for the P-RE scenario

Fig. 3.18 Average OSEE intensities for the three samples within each sample set, P-FP-1, P-FP-2, and P-FP-3, as part of the P-FP scenario, based on locally applied contaminations of different degrees, achieved by intentionally depositing a sodium-containing synthetic sweat formulation, compared to the OSEE results of the P-RE scenario

- The third repair scenario considered a thermal impact affecting CFRP surface degradation during repair (R-TD).

We highlight here that the OSEE intensity values for the samples prepared according to the R-RE scenario showed significantly higher OSEE intensities than those prepared according to the P-RE scenario. We attribute this finding to a more profound grinding in the case of the R-RE samples, which led to a higher area ratio of the exposed carbon fibers; we expect carbon fibers to contribute a higher OSEE intensity than the polymer matrix of the composite material. The OSEE settings

Fig. 3.19 Optically stimulated electron emission (OSEE) maps (15×15 pixels) for the three samples prepared following the clean reference R-RE scenario of the repair user case, based on CFRP coupon specimens resulting from a grinding process that is characterized by producing black abrasive dust, measured with adjusted OSEE settings

adjusted for the CFRP specimens of the R-RE scenario were applied for all the samples investigated within the repair user case.

Figure 3.19 presents the OSEE maps obtained for the three samples prepared following the R-RE scenario. With the instrumental settings applied, an average OSEE intensity of 739 ± 106 a.u. was obtained. We highlight here that, based on our OSEE investigations, the I-R-OSEE-RE-1 sample had presumably been polished more strongly on the right side than on the left. We note that any OSEE map obtained on ground CFRP substrates reveals both the lateral homogeneity of the sample surface (based on the standard deviation of the OSEE signal) and the depth of polishing (based on the intensity of the OSEE signal).

In the following, plots showing the average OSEE intensity of the three scenarios R-DI, R-FP, and R-TD (provided that they were investigated) are presented in comparison to that obtained for R-RE.

As may be inferred from Fig. 3.20, the surface states corresponding to contamination levels R-DI-2 and R-DI-3 within the R-DI scenario can be clearly detected and differentiated from the surface state corresponding to R-RE. However, the surface state of the sample with level R-DI-1 cannot be differentiated from that of the R-RE sample with the OSEE settings applied.

As shown in Fig. 3.21, when applying the used OSEE settings, the average OSEE intensities obtained for surfaces corresponding to the thermal degradation level R-TD-1 within the R-TD scenario cannot be clearly differentiated from the surface state corresponding to R-RE. Moreover, the six samples corresponding to the surface states R-TD-2 and R-TD-3 were not investigated by OSEE due to their visually perceivable strong deformation.

Figure 3.22 presents the respectively obtained OSEE maps for the three samples prepared following the R-FP scenario. For all three samples investigated, the OSEE intensities measured around the centers of the samples were diminished compared to the R-RE state. The lateral inhomogeneity within the OSEE maps of samples I-R-OSEE-FP-1-3 and I-R-OSEE-FP-2-3 (corresponding to two different levels of exposure within the R-FP scenario) is interpreted to result from the different spreading of the fluid applied with the fingerprint since that application was performed centrally

Fig. 3.20 Average OSEE intensities for the three samples within each sample set, R-DI-1, R-DI-2, and R-DI-3, as part of the R-DI scenario, based on locally applied contaminations of different degrees, achieved with an intentionally deposited potassium-containing de-icing fluid, compared to the OSEE results of the R-RE scenario

Fig. 3.21 Average OSEE intensities for the three samples within the sample set R-TD-1 compared to the OSEE results for the clean and freshly ground CFRP reference R-RE scenario. The three samples within each of the sets R-TD-2 and R-TD-3, as part of the R-TD scenario, were not investigated due to their visually perceivable strong deformation

Fig. 3.22 Optically stimulated electron emission (OSEE) maps (15 × 15 pixels) for three samples prepared following three different levels of contamination within the R-FP scenario, based on locally applied contaminations of different degrees, achieved by intentionally depositing Skydrol hydraulic oil

within the OSEE mapping area using a fingerprint with the width of a human thumbprint.

As shown in Fig. 3.23, all the surfaces corresponding to contamination levels R-FP-1, R-FP-2, and R-FP-3 within the R-FP scenario can be clearly detected and differentiated from the surface state corresponding to R-RE, even when evaluating 7.5 cm × 7.5 cm wide areas, which exceed the area covered by the respective originally applied fingerprint, which was originally the size of a human thumbprint.

Combined contaminations

Combined contaminations include the RA+FP scenario within the production user case and the TD+DI scenario within the repair user case. In both cases, we investigated

Fig. 3.23 Average OSEE intensities for the three samples within each sample set, R-FP-1, R-FP-2, and R-FP-3, as part of the R-FP scenario based on locally applied different contamination degrees, achieved by intentionally depositing Skydrol hydraulic oil, compared to the OSEE results of the clean CFRP reference R-RE scenario

two levels of contamination in addition to the respective references. On the surfaces of the P-RA+FP samples, we applied two distinct levels of release agent contamination (RA) before the application of the salt-based fingerprint in the center of the sample area. For the R-TD+DI samples, there were two levels of de-icing fluid contamination (DI) applied after the thermal degradation treatment (2 h in an oven at 220 °C).

As was shown in Sect. 2.1.2.2, samples contaminated following the P-RA scenario showed much lower OSEE signals than the clean reference CFRP samples prepared according to the P-RE scenario. The sample surface states comprising combined contaminations show similar OSEE intensities to the sample prepared within the P-RA-2 scenario; thus, these combined contamination levels can be clearly differentiated from the surface state corresponding to P-RE.

Specifically, the OSEE maps obtained for the samples prepared following the P-RA-1+FP3 (cf. Fig. 3.24) and P-RA-2+FP3 scenarios (cf. Fig. 3.25) reveal the positions where the fingerprints were applied since the respective regions show higher OSEE intensities than the surrounding surface regions.

Finally, within the considered repair user case, the OSEE results for surface states corresponding to R-RE were compared with the OSEE results obtained for sample

Fig. 3.24 Optically stimulated electron emission (OSEE) maps (15×15 pixels) for the three samples prepared following the P-RA-1+FP3 contamination scenario, measured with adjusted OSEE settings. Presumably fingerprinted (FP) regions showing higher OSEE signals are marked with dashed ellipses

Fig. 3.25 Optically stimulated electron emission (OSEE) maps (15×15 pixels) for the three samples prepared following the P-RA-2+FP3 contamination scenario, measured with adjusted OSEE settings. Presumably fingerprinted regions showing higher OSEE signals are marked with dashed ellipses

Fig. 3.26 Average OSEE intensities for the three CFRP coupon samples within each sample set of the R-TD-1+DI-1 and R-TD-1+DI-2 combined contamination scenarios within the repair user case; here compared to the OSEE results of the R-RE scenario

surfaces exhibiting combined contaminations following the R-TD-1+D-1 and R-TD-1+DI-2 contamination scenarios. The respective average OSEE intensities are compared in Fig. 3.26. The sample surface states with the combined contaminations can be differentiated from the surface state corresponding to R-RE. Somewhat remarkably, the surface states of samples within the R-TD-1+DI-1 scenario can be differentiated from those of the R-RE samples, in contrast to samples prepared following the R-DI-1 and R-TD-1 scenarios.

3.3.2.2 OSEE Results on Pilot Level Specimens

In the following, we present selected findings obtained when applying the available OSEE technology for assessing the surface quality of CFRP pilot level specimens from the production user case.

One key feature of the investigated pilot level specimens from the production user case was the peel ply surface of a CFRP part. This peel ply surface resembles a closed epoxy film that forms the outermost layer of the sample. For the OSEE technique to work, it is necessary that the studied samples show at least some amount of electron emission. However, probably due to the closed and electrically insulating terminal epoxy film, we did not observe any significant electron emission. The closed polymer film on top of subjacent carbon fiber layers appears to prohibit a measurable OSEE signal. We tried several approaches with the aim of achieving measurable signals, e.g., using the highest possible detector sensitivity setting and decreasing the distance to the sample in order to increase the flow of the UV light and decrease the distance for the electrons to travel. These changes have proved to be useful on other kinds of material surfaces in the past; nevertheless, with the closed epoxy film on this type

of CFRP part, no signal was observed. The samples from the production scenario were therefore categorized as not measurable with the OSEE technique as long as charging compensation was not facilitated.

3.3.2.3 Technological Advancements of the OSEE Method Toward Industrial Automation

During the ComBoNDT research project, several enhancements were made to the setup to implement the existing OSEE sensor in an industrial environment. A key requirement for applying the OSEE technique when investigating specimens with curved surfaces is maintaining a constant height of the sensor (especially the essential component, i.e., the electron collector in the sensor head) above the CFRP surface. To achieve this, the OSEE sensor was adapted to be mounted on and used with an industrial robot.

Specifically, the main work here was the construction of an adapter plate for the mechanical connection of the OSEE sensor itself to the flange of a suitable industrial robot. At the Fraunhofer IFAM site in Bremen, a KUKA KR 20 device with a KUKA KR C4 control system was used. The flange with which such a robot is equipped follows an international norm, which was taken into account when making the layout for the holes on the robot side of the adapter plate. On the OSEE side of the adapter plate, a simple clamping mechanism was chosen to hold the OSEE sensor head in place. This clamping mechanism allowed easy access to the sensor head for the maintenance or direct manipulation of the sensor head itself. It also facilitated adjusting the height of the sensor compared to the sample surface in case that this crucial parameter needed to be changed without making adjustments to the programming and motor-driven positioning system running the robot itself.

The plate was made from aluminum, and all the necessary holes and cut-outs were manufactured using a CNC-controlled milling machine. The clamping mechanism was constructed in the same way as it was provided with the commercially available OSEE sample positioning system in the lab to enable an easy exchangeability of the used components. The resulting design of the OSEE sensor head connected to the industrial robot is shown in Fig. 3.27.

To ensure that the adapter plate worked correctly in terms of mechanical stability, several tests were performed. These examinations included test runs with different speed settings for the robot motion as well as different acceleration and brake settings. Not only was the mechanical stability of the mounted head itself checked every time, but also the repeatability of the motion performed by the robot was assessed. For these tests, extensive adjustments were made to the used programming within the KUKA KR C4 control system. These tests also ensured that the solutions established for the cable connections to the sensor head in terms of electrical power and sensor data worked as expected.

As described above, one key element of the OSEE technique is the need to ensure a constant distance between the measuring head and the sample. To achieve this goal, it was considered important to have a verification mechanism to constantly

Fig. 3.27 OSEE sensor head mounted to a KUKA KR 20 standard industrial robot for test measurements on the CFRP pilot samples to be investigated in the ComBoNDT research project at the technical center at Fraunhofer IFAM in Bremen; bottom: A more detailed image of the clamping mechanism holding the sensor head in place

check this parameter and provide feedback to a control unit. Therefore, some further enhancements in terms of manipulating the OSEE head were made by incorporating a distance sensor into the measuring setup. For this purpose, a laser line scanner was used. This sensor device was mounted close to the OSEE measuring head with the laser line being projected directly onto the spot that was illuminated by the UV light of the OSEE sensor and from which the OSEE captured the emitted electrons for the photocurrent measurements. This enabled safeguarding of the constant evaluation of the distance between the OSEE sensor and the sample. The laser line scanner can

Fig. 3.28 Setup comprising a laser-based distance sensor for use in conjunction with the OSEE sensor head and an industrial robot; a laser line scanner (on the left) is attached to the manipulator that holds the OSEE measuring head in such a way that the setup enables constant checking of the distance between the sensor and the sample and the measuring of the optically stimulated electron emission at a constant distance between the sensor and the CFRP surface

also be connected to the programmable logic controller (PLC, henceforth referred to as SPS), which pilots the whole measuring process, as displayed in Fig. 3.28.

With these modifications, the precision of the robot motion was all that limited the areas accessible for the scheduled use of the OSEE device as an ENDT technique. As long as it is possible to follow the surface geometry of a part with a constant distance, the OSEE facilitates the inspection of large surfaces at a high speed.

3.3.3 *Performance in Inline Surface Quality Assurance*

In this section, we summarize the findings highlighting the performance of the OSEE-based ENDT technique for the surface quality assessment of CFRP specimens in distinct user cases.

In a first and trendsetting approach within the ComBoNDT research project, we technologically advanced OSEE and successfully applied this ENDT technique to map CFRP test coupons prepared by intentionally depositing distinct contaminants within several contamination scenarios, among them scenarios comprising combinations of contaminations that might have adverse (and, thus, possibly compensatory) effects on the OSEE signal. Specifically, the reference (RE) states of the production (P-RE) and repair (R-RE) user cases were clearly differentiated from each other, and the suitability of using OSEE to assess the results and reproducibility of a CFRP

surface grinding process was indicated. When investigating samples from production scenarios, we applied adjusted OSEE settings that differed from the ones applied for samples from the contamination scenarios of the considered repair use case. In a nutshell, when comparing the sample surface states obtained within different contamination scenarios of the production user case with the ones prepared following the P-RE scenario, OSEE enabled all sample sets from the P-RA, P-MO, and P-FP scenarios as well as the sets with combined contaminations (P-RA-1+FP3 and P-RA-2+FP3) to be differentiated from P-RE. Moreover, within the contamination scenarios of the repair user case, OSEE enabled all sample sets from the R-FP scenarios, most of the samples from the R-DI scenarios (namely those with higher levels of contamination than R-DI-1) as well as sets with combined contaminations (R-TD-1+DI-1 and the scenario R-TD-1+DI-2) to be differentiated from R-RE. However, the surface states of the samples from the R-TD scenarios and samples of the R-DI-1 scenario were not differentiated from those of the R-RE samples. Clearly, if the adhesive joints manufactured based on these adherend surfaces showed inferior mechanical properties compared to joints prepared following the R-RE scenario, then these findings would stand in opposition to recommending OSEE as the ENDT method of choice in this user case. Finally, when referring to the lateral homogeneity of the CFRP test coupons, OSEE indicated several peculiarities: The inhomogeneous grinding of one coupon sample from the repair scenario, the spreading of fingerprinted fluid within the R-FP scenarios, and the position of fingerprints within samples exposed to combined contaminations in the P-RA-1+FP3 and P-RA-2+FP3 scenarios.

Aiming at assessing the surface quality of the pilot level CFRP specimens, we further improved the OSEE technique to permit its use in an industrial environment by incorporating a laser line scanner in the measuring setup to precisely control the distance between the sensor and the studied sample, which might have a more complex shape than a flat sheet. Concerning the investigations conducted on the pilot samples from the production user cases, the OSEE method encountered some severe limiting challenges concerning its use as a measuring system for these kinds of samples. In the case of the pilot samples of the production user case, the closed epoxy film of the peel ply surface prevented a measurable OSEE signal from being obtained. ENDT procedures using OSEE as a measurement technique evaluate relative changes to a given reference signal, e.g., the one characteristic of a clean CFRP surface. Therefore, the procedure was not suitable for assessing the surface quality of the pilot samples of the production user case as the surfaces of the reference substrate did not provide a sufficient signal strength. In our opinion, the encountered challenges, in the form they are presented here, do not appear to be unsolvable if further development is invested in a more customized embedding of the powerful OSEE technique in a setup that enables the elevated positive charging of electrically non-conductive analyte surfaces to be counteracted.

Moreover, we achieved an integration of the OSEE technology in inline applications, e.g., a robot-aided approach, without fundamental constraints. We present an approach to assembling the OSEE sensing technique in a setup that provides further information on the geometrical constellation of the measurement situation. We suggest that a real-time height adjustment and an improved method of signal

detection facilitating an automated adjustment of the signal range could provide new ways to use this technique, even on materials that present the challenges observed during the ComBoNDT project. Within the project, it was not possible to implement these improvements. However, as techniques to change the sensitivity of analog–digital converters become more and more available, these challenges could be tackled in a future project.

We would like to underline that OSEE is a highly sensitive inspection method that allows the detection of even very low levels of contamination [1]. Often, a monolayer of a contaminant on an otherwise well-emitting material can be safely detected, as was demonstrated here, e.g., in the case of release agent deposits that we diagnosed using x-ray photoelectron spectroscopy. Nevertheless, establishing OSEE-based ENDT procedures may encounter difficulties with some of the technical surfaces found in industrial applications that, for example, rely on manually performed abrasive surface pretreatment. Such technical surfaces, which are often laterally inhomogeneous in their surface composition or surface conditions, show a considerable variance in their OSEE signal. This may make it difficult to locally differentiate between contaminations and substrate effects. In other words, assessing merely the feature of optically stimulated electron emissivity does not enable the identification of the substantial source of signal variations and provides a signal contrast that is not sufficiently specific to assess analytical challenges, such as the material-related identification of (mixed) contaminants or the essential elements thereof. We estimate that these challenges can be compensated for to a certain level using modern data analysis methods for such applications that benefit from the high sensitivity of the OSEE technique.

3.4 Electronic Nose

In this section, we introduce the electronic nose technique, highlighting two distinct instruments serving as ENDT tools for surface quality assessment and detailing how their performance was enhanced in the ComBoNDT research project for the in-process monitoring of CFRP adherends representative of close to potential aeronautical user cases.

3.4.1 *Principle and Instrumentation*

Electronic noses (e-noses) are chemical multi-sensor devices, based primarily on microsensors, which are capable of conducting low-cost analyses of complex gas mixtures through chemical fingerprinting. Coupling an array of chemical sensors to pattern recognition algorithms is an idea dating back to the 1980s and began significant development during the 1990s. Due to low overall costs in terms of purchase, operation, and maintenance as well as interesting research results, they looked—and

still look—very promising and appealing for the development of industrial-grade ENDTs [9]. A significant number of commercial platforms have been available since 2000 for the comprehensive detection of components in mixtures as well as identification and/or quantification in medical diagnostics, environmental monitoring, and the food industry [10]. Despite some success stories, increasing the application of this technology to a wider range of industrial scenarios and user cases is currently obstructed by technological limitations [11]. Apart from the well-known specificity and sensibility issues that affect single sensors, the variability of fabrication outcomes severely hampers the use of a shared calibration function for e-noses. Thus, ad hoc calibration procedures need to be implemented for each individual e-nose device. The development of calibration transfer strategies could help overcome these limitations but, currently, there are no definitive results [12, 13]. Drift effects (mostly due to aging and poisoning) in sensor devices as well as environmental parameters have affected the mass adoption of e-noses in the high-value production industry because they jeopardize operative requirements. Presently, most research contributions in advancing e-noses still target the headspace analysis of liquid/solid samples in controlled environments, which may amount to underestimating the challenges of on-field applicative scenarios. From the point of view of today's user, we would like to highlight that on the one hand, specific requirements such as high reliability, fast response, and the possibility to be operated by a chemically non-expert workforce can be, in principle, met by up-to-date e-nose platforms. On the other hand, some instrumental operative requirements, including the need for operation in uncontrolled or even harsh environments [14], may still prove very challenging due to the abovementioned lags and issues.

Conversely, and from a prospective point of view, we observe that along with the requests for novel integrated health monitoring systems, the need for new NDT technologies that should be capable of coping with the new challenges brought by the lightweight aircraft industry is steadily growing [15, 16]. The adoption of lightweight composite materials like CFRP for primary structural components is a major trend-setting milestone and may contribute to a significant reduction of per-mile-passenger transportation costs. It is estimated that this could allow for a dramatic increase in cost efficiency for ground operations (up to 50%), a reduction in fuel usage (up to 20%), and consequently, a CO₂ emission rate reduction at the fleet level of up to 15% [2]. CFRP parts are assembled and joined by adhesive bonding, a critical and special process that requires the adherend panel surfaces to have a high grade of cleanliness. If not, the mechanical properties of the assembly itself could be severely compromised, leading to a high risk of potential structural failure [17]. Surface contamination can be caused by various processes that occur during the assembly or operative life of CFRP panels. Adherends with improperly removed deposits of contaminants, such as hydraulic oil or de-icing fluid, may come in contact with a CFRP surface during aircraft operation, while the release agents used in CFRP molding processes during composite production can severely affect the mechanical properties of a resulting adhesively bonded joint. Such deposits may produce chemical damage to the surface or create a physical screen to the adhesion, while the thermal degradation of the CFRP adherend surface can affect the adhesion properties of the panel, thus compromising

the mechanical strength of the bond. Several authors have measured the mechanical parameters of adhesive bonds based on contaminated CFRP panels (e.g., [18]). In particular, Tserpes et al. showed a reduction in the fracture toughness (G_{IC}) in excess of 25% for Skydrol®500-B contamination and of more than 60% for significant release agent contamination [19]. Specifically, a 7% silicon-containing substance (calculated as at.% based on XPS investigations) remaining on the surface after demolding can lead to a total lack of adhesion [20].

Bearing in mind these production–technological challenges and the instrumental current state of the art, we anticipate that customized e-noses may represent a suitable technology that can contribute to addressing the lack of a verified procedure for assessing bond quality, which has ultimately been slowing down the adoption of CFRP for primary structures. ENEA and Airbus, both partners in the H2020 ComBoNDT research project [2], have been and continue to be focused on developing e-nose ENDT solutions for surface cleanliness checks to be applied in composite pre-bond quality assurance. In the ComBoNDT project, this endeavor required the design of ad hoc sampling and measurement subsystems, the careful selection of an ad hoc sensor array as well as the design of proper machine learning algorithms to cope with the requirements of this safety-critical application field. The subsequently reported work accounts for the in-project development process, which aimed to reach and demonstrate a high TRL for the use of the e-nose as a detector of surface contaminations before bonding.

3.4.1.1 Generic E-nose Architecture Considering CFRP Contamination Scenarios

The basic idea underlying any e-nose design is a close coupling between an array of chemical sensors and a pattern recognition system. The latter can be focused on detection, classification, or quantification [21, 22]. The sensor array is usually designed to focus on broad sensitivity and diversity in order to augment the chemical fingerprinting capabilities. Metal oxide (MOX) sensors, polymeric sensors, and electrochemical sensors, often combined with photoionization detectors (PID) and/or ion mobility spectrometers (IMS), have been widely employed in e-nose devices. Hybrid arrays are also found in the literature, always with the aim of enhancing the diversity of potential applications and user cases.

In more detail, MOX sensors are chemiresistors, i.e., their electric resistance changes as a consequence of their interacting with the environment in which they are deployed. These sensors and their signals are non-specific since they are responsive to a wide variety of volatile organic compounds (VOCs) and environmental conditions (e.g., humidity). Their signal dynamics and sensing window are perhaps the largest in the gas sensor realm, and they are cheap and easy to integrate on electronic boards. On the other hand, the signal stability and response repeatability are the principal drawbacks for this family of gas sensors. An array of MOX sensors can be successfully implemented in a closed chamber of an e-nose, working in a “differential mode” to overcome the limited repeatability and poor signal stability. In this

so-called differential mode, sensors are exposed to filtered air before and after being exposed to the air analyte sampling. Features linked to the signal variation, which occurs when the sensor resistance is disturbed by an odor sample, can represent a repeatable odor pattern. A sensor equipped with PID can be considered as a VOC exposure meter. This detector is based on the photoionization of a gas by means of an UV lamp, and it can detect VOC particles ranging from sub-ppm to thousands of ppm. PID-based sensors cannot discriminate VOC species; they only account instantaneously for the species photo-ionized in the excitation process overall. In this way, they can be useful in understanding the integral level of the odor exposure on the e-nose sensor array.

Similar to a nose in the biological sense, the structure and flow conditions in the pneumatic section of an e-nose are of paramount importance in co-determining its final performance. Forced flow is usually adopted in benchtop scale solutions, while open sensing is generally adopted in battery-operated, long-term deployments of smart multi-sensor systems. In the first case, especially in benchtop devices, the sensor array is first exposed to pure synthetic or filtered air in order to assess the baseline results. Sensor baseline generation under clean air conditions is a vital aspect of e-nose performance, and a new technique of sensor baseline estimation without the need for an external gas supply is also available [23].

Following e-nose data acquisition, pattern recognition subsystems are employed, which are primarily designed to provide classification capabilities. Both supervised and unsupervised pattern recognition designs have been widely explored. Among the plethora of different supervised designs, k-nearest neighbors algorithms (k-NN), support vector machine (SVM), neural networks, and partial least squares discriminant analysis (PLS-DA) systems are the most commonly adopted. While most of these approaches are strongly non-linear and aim at modeling significant non-linearities found in the multivariate sensor models, PLS-DA combines a linear transformation to reduce the number of evaluated dimensions with the discrimination capabilities of Fisher discriminant analysis. Dimensionality reduction is also usually tackled by principal component analysis (PCA), resorting to the first principal components. Recently, this approach has been reported less often, essentially because discriminant characteristics may be embedded in relatively low variance components.

Indeed, for the design of the e-nose pattern recognition subsystem, feature extraction and selection comprise one of the most important steps. Designing appropriate features and selecting the most informative combination is in fact one of the main performance drivers. Steady-state responses, when appropriately normalized for the reduction of baseline drift issues, can be sufficient for obtaining a discriminant fingerprint for several analytes and mixtures. However, most of the time-dynamic features based on the sensor response during exposure, presentation, and flushing transients are essential for obtaining an adequate classification performance [24, 25]. With respect to ongoing developments, we may state that quantification issues and problems are primarily tackled using non-linear approaches exploiting the regression capabilities of neural networks, support vector machines, and Gaussian processes as well as other data-driven approaches. Recently, the analysis of dynamic behavior has attracted interest also for quantification problems, exploiting a model that can

Table 3.1 Graded concentration ranges of contaminants intentionally applied to CFRP reference (RE, for production or repair) substrates as identified and defined by partners of the ComBoNDT research project for aeronautical user cases in a way that yielded a loss of bond strength of up to 30% of the initial strength

Contamination scenario	Contaminant	Concentration ranges
Production	Release agent (RA)	3–8% (Si at.%) ^a
	Moisture (MO)	0.4–1.4% (mass uptake)
	Fingerprint (FP)	0.2–0.7% (Na at.%) ^a
Repair	De-icer (DI)	6–12% (K at.%) ^a
	Hydraulic fluid (FP)	<0.5 g/m ²

^a Atomic surface concentrations (in at.%) for the listed species were measured by XPS analysis

take into account the intrinsic dynamic behavior of the sensor response toward target gases and non-target interfering substances.

In the specific framework of the quality assessment of CFRP structures through ENDT methods focusing on surface cleanliness, the essential steps were determining and listing the chemical targets to be considered. Within the contemplated aeronautical user cases, this basic requirement was identified and defined by partners of the European Union (EU) ComBoNDT research project, a consortium that includes Airbus, the main EU aerospace industry stakeholder. This list is based on production or repair user cases and comprises hydraulic fluid, water (humidity), fingerprints applied unconsciously and locally by workers, release agents, and de-icing fluid, and is further complemented by thermal impacts and even damages. More details about this topic can be found in Chap. 2. The contamination scenarios are then divided according to the specific workplace at which the contamination can occur, namely within production or repair areas.

The interaction of these chemically nameable substances with CFRP structures can undermine the composite adherends at different levels, eventually affecting the mechanical strength of the adhesive bond between CFRP panels. Specifically, release agents are silicon(and siloxane)-based formulations used during the molding and demolding process of composite panels, and they can penetrate up to hundreds of nm into the CFRP panel matrix. Another source of the potential weakening of adhesive bonds stems from the presence of sodium chloride residue left by occasional fingerprints. Therefore, a fingerprint simulant prepared according to DIN ISO 9022-12, containing sodium chloride, urea, ammonium chloride, lactic acid, acetic acid, pyruvic acid, and butyric acid in demineralized water was added to the contaminant list. Additionally, the hydraulic fluid considered in this study was a fire-resistant phosphate ester-based liquid that, under certain conditions, can release phosphoric acid and alcohols. Finally, the considered de-icing fluid was a potassium formate-based formulation involved in runway or aircraft de-icing. Moisture exposure of CFRP parts as well as thermal impact and damages (TD) were also investigated.

Different contamination levels (as detailed in Table 3.1) were determined in a way that yielded a loss of bond strength of up to 30% of the initial strength (with respect to using two reference specimens, called RE, as adherends).

In addition to the flat coupon level samples (see Chap. 2) that had undergone these intentional contamination procedures comprising individual contaminants, according to the high TRL required for the measurement techniques, we also tested two e-nose setups against CFRP samples that had mixtures of two different contaminants applied to them. In particular, we investigated CFRP panels contaminated with a combination of release agent and (artificial sweat) fingerprints for the production user case (P-RA-FP) and thermally impacted panels that had additionally been contaminated by an application of de-icing fluid within the repair user case (R-TD-DI).

Additionally, user cases based on curved pilot level CFRP samples in which contamination was applied on both convex and concave surfaces were assessed by e-nose inspection. Finally, the e-nose systems were tested for the monitoring of realistic parts as part of joint tests oriented toward TRL assessment (defined within ComBoNDT).

3.4.1.2 Details of the ENEA E-nose

During the ComBoNDT project, the consortium partner ENEA continuously developed its e-nose approach featuring two main successive versions aimed at handling the increasingly high demands of the project's contamination scenarios, starting from planar coupons and reaching the realistic parts level. A description of these two main versions is given here.

The first version, the ENEA e-nose ver.1 (SNIFFI, [26]), is a closed-chamber gas sensing system. It is equipped with a chamber containing the sensor array, into which the air analyte sample enters by means of an air pump. Figure 3.29 shows the main components and functional connections of the ENEA e-nose ver.1.

The embedded architecture is organized in different layers, each one requiring different expertise, as shown in Fig. 3.30.

The sensor array is based on six four-pin slots that can host up to six heated chemo-resistive commercial sensors. During the ComBoNDT project, three couples of MOX Figaro Sensor family (Tgs2600, Tgs2602, and Tgs2620) were used. This commercial sensor array can be completed with up to six prototype sensing films using plug-and-play USB-like transducers that have been specifically designed to be mounted on a custom sensor board, as shown in Fig. 3.31. In particular, ENEA developed the graphene chemo-resistive devices chosen to complete the array. The features characterizing the environmental status and total VOC contamination of the chamber volume are measured by means of temperature and humidity sensors (Sensirion SHT75) and a PID, i.e., a photoionization detector (PID-AH, AlphaSense Inc.). The sensor chamber is built using a Teflon polymer to ensure a base sensor board with good electrical insulation as well as an aluminum cover to ensure good heat dissipation, see Fig. 3.31.

Fig. 3.29 Functional block diagram of the system representing the ENEA e-nose version ver.1 developed in the ComBoNDT research project for CFRP surface quality assessment

Fig. 3.30 Embedded layer-wise architecture of the ENEA e-nose ver.1 system

The ENEA e-nose ver.1 has two operating modes, allowing for switching between two different inlets to perform different application-oriented sampling tasks (as detailed in the block diagrams in Figs. 3.29 and 3.32):

- A front inlet for the air sampling of odors coming from a headspace (e.g., a bottle, an air sampler bag) (see the photograph in Fig. 3.33).

Fig. 3.31 Sensor chamber on the sensor board of the ENEA e-nose ver.1 system; left image: open state with the 12 chemiresistors, photoionization detector (PID) and temperature (T) and humidity (RH) sensors; right image: closed state

Fig. 3.32 Block design of the ENEA e-nose ver.1 system

- A bottom inlet, heated by a 20 W halogen lamp, to perform analysis focusing on surface contamination (see the image in Fig. 3.33).

Finally, this e-nose has a line of purified air that is used to conduct cleaning phases, maintain the gas sensors in a stable steady state, and properly dilute sampled air.

A high-level logic control layer based on low-cost open-source hardware drives the actuators and the sensor conditioning board. The graphic user interface (GUI) (based on a web server) allows the following operations to be performed: creation, saving, and recalling of measurement recipes; monitoring of sensors' real-time status' wireless Wi-Fi access; and transmission of the sensor log. The repeatability of the

Fig. 3.33 Air inlets of the ENEA e-nose ver.1; on the left: a front inlet for headspace analysis (bottle or sampler bag); on the right: a bottom inlet and a spotlight halogen lamp to analyze surface contamination

sampling analysis is guaranteed by automated measurement cycles. A standard cycle can be repeated many times and is divided into four phases, the duration of which can be set by the user, as presented in Fig. 3.34.

We further developed the e-nose prototype (ver.1) described thus far to match the higher TRL targets foreseen by the ComBoNDT project objectives. Based on the analysis of the preliminary results for the CFRP coupon samples, we deemed it necessary to improve several aspects, in particular the sampling operating mode.

Fig. 3.34 Outline of a single generalized measurement cycle of the ENEA e-nose ver.1

Fig. 3.35 Block design of the advanced e-nose prototype, ENEA e-nose ver.2 [27]

Fig. 3.36 Functional block diagram of the advanced e-nose prototype, ENEA e-nose ver.2

Figures 3.35 [27] and 3.36 present the design of the resulting second version, the e-nose prototype ver.2.

Aiming to analyze CFRP surface contamination without external interference, we first designed a new sampling head that allows the sampling area to be isolated from the outside, as detailed in Fig. 3.37. In this “sealed” sampling area, a flow of clean reference air is directed toward the sample surface while irradiation from an infrared emitter stimulates the desorption of the analytes from the investigated surface. The air sample is then pumped toward the sensor chamber. We paid special attention to the cleaning phase of the sampling chain. To improve the desorption capabilities, a 50 W halogen lamp was used in this new device. In addition, a sampling head suitable for curved samples was designed and realized. The sensor chamber and sensor array design were essentially unchanged, whereas the control actuator drive and sensor conditioning board were modified according to the new setup of the sampling head. The control actuators also offer the possibility of driving a remote sampling head.

Fig. 3.37 Details of the advanced ENEA e-nose ver.2 prototype showing an open view of the sensor chamber, the GUI of the control system, details of the sampling head and the probe head, and a plot with an exemplary sensor signal outputs

3.4.1.3 Details of the Airbus E-nose and Desorber Device

Unlike the ENEA e-nose system, the Airbus approach relies on a custom-made e-nose in combination with an optimized sample-taking apparatus. The core part of this system is shown in Fig. 3.38 and consists of a ruggedized version of a multi-purpose e-nose marketed by the AIRSENSE Analytics company under the name

Fig. 3.38 Portable e-nose from AIRSENSE Analytics

Fig. 3.39 E-nose system and desorber device—image of the assembly (20" rack) in the laboratory

PEN (Portable Electronic Nose) [28]. This system contains an array of ten different MOX gas sensors. All sensors are operated according to their specific supplier recommendations.

The system was retrofitted with temperature sensors and a humidity sensor and was integrated into a mobile rack. Some further ruggedization was necessary to enable shop floor compatibility. To equip this multi-purpose core system for its intended use of contamination detection, it was fitted with an external sampling head called a “desorber device” (see Fig. 3.39) invented by Airbus and advanced to TRL six during the ComBoNDT project.

The integrated desorber system features a fully automated measurement process. In principle, the same procedure as that used for the ENEA system and depicted in Fig. 3.34 may be used. The system controls all relevant measurement parameters automatically, and the status of the system is displayed on a liquid-crystal display (LCD). The desorber system controls the sample heating and operates the humidity sensors and the pyrometer, which were integrated into the desorber device sampling head presented in Fig. 3.39.

To take the step from the laboratory to shop floor conditions, we conducted investigations to replace the synthetic air cylinders as a zero-gas supply. The system had to be adapted to work with oil-free compressed air, which is easily available on the production floor. Hereby, a particle filter, charcoal filter, and hydrocarbon oxidizer were deemed necessary to ensure sufficient clean air quality.

3.4.2 *E-nose Methodology*

In this section, we first detail the experimental methodology for assessing e-nose data as well as the pattern recognition technique. Finally, we present the obtained results for the CFRP specimens from the distinct user cases, according to their shape and the respectively considered contamination scenarios.

3.4.2.1 *Experimental Methodology*

The ENEA e-nose ver.1 was used to conduct measurements on CFRP surfaces by means of two different methods. The first was the standard measurement method, named the “0 method”, which makes use of only the IR irradiation of the sample. The second one, named the “PC method”, enhances the extraction of volatiles by treating the surface with a suitable low-boiling solvent. The process involves first spraying a few milliliters of ethanol over the surface of the sample with an airbrush and soon thereafter performing the e-nose measurement. The adoption of the PC method was motivated by the need to improve the desorption of the volatiles. In principle, this treatment also enables differentiation between different surfaces and surface states, also on the basis of their capability to retain and desorb the solvent (e.g., ethanol) as a function of the surface contamination. The measurements carried out with the advanced ENEA e-nose ver.2 were accomplished using only the standard method described above. For all measurements, the time exposure to the IR emitter was tuned to heat the CFRP to a temperature above 120 °C (but below 150 °C to avoid permanent CFRP damage). To ensure the repeatability of the results, a measurement strategy was adopted, which was mainly intended to avoid the presence of residual contamination inside the sample line after the sensing phase. To this end, a blank sample was analyzed periodically (at least once per hour), which also allowed the repeatability of the sensing responses to be verified. A cleaning procedure was implemented to prevent residual contamination in the sampling line.

To control and perform the right measurements, an assessment of the data is necessary to visualize the output sensors' features describing the odor pattern of the sample immediately after a measurement cycle. This offers the possibility to rapidly compare measurements and thus to understand if the results are reliable or if a cleaning phase of the system or a change in the measurement cycle parameters is necessary. Solid-state sensors can show a certain tendency to signal drift, and this could jeopardize the comparison among different samples. To overcome this issue, we processed the raw sensing responses to extract parameters that could be used to compare different samples. Essentially, each sensing response R was normalized to its own baseline R_0 , and the percentage of the relative response R_{sp} was calculated as follows:

$$R_{sp} = \frac{\max|R - R_0|}{R_0}$$

Subsequently, a signal differential was performed (always relative to the baseline value) and the maximum was calculated. This is the same as having calculated the rate of the sensing responses and the maximum rate of the response itself. In our experience, these parameters are less affected by sensor drift and saturation, although they contain the same discrimination features of the sensor response [29]. Finally, a simple comparison was performed by calculating the ratios of the maximum response rate of each sensor with respect to that of the fastest sensor.

As a result of this signal elaboration, after the measurement cycle, the operator can see the entire sensor performance, as shown in Fig. 3.40, see Fig. 3.41.

The presented histogram gives an overview of how the individual sensors react to the analyzed odor. The red bars represent the adsorbing phase, while the blue ones

Fig. 3.40 Underside view of the desorber device sampling head. Excitation and heating are possible via infrared (IR) irradiation or ultraviolet light-emitting diodes (UV LEDs)

Fig. 3.41 The e-nose sensor response rate and an odor map obtained during a measurement cycle; on the left: a histogram of the sensor reaction to the odor during the adsorbing phase (red) and desorbing phase (blue); on the right: a contour map of the sensor signal distortion during a measurement cycle

refer to the desorbing phase. Moreover, a contour map is shown, which is useful for the e-nose technical specialist to understand if there are anomalies in the measurement cycle and if the recorded sensor signal distortion is well suited to the odor pattern. Signal distortions can be related to changes in odor intensity or abnormalities due to imperfect air filtering, or they can be ascribed to an odor fingerprint. The map then represents the differences between the signal shape of each individual sensor and that of the others. The map is divided into areas. The C (labeled C1 and C2) areas depict the sensor behavior earlier on, during the baseline phase in filtered air; an optimal behavior is the lowest distortion (light blue color). Areas labeled with A (or Ar) and D (or Dr) display the signal distortion intensity in the adsorbing and desorbing phase, respectively. Performing such feature visualization allows an experienced specialist to validate measurements and helps to prevent an applied pattern recognition technique from being confused by bad measurements. We would like to stress that this approach is completely modular and can be easily adapted to any sensor array.

Pattern Recognition Technique

Before actually tackling the pattern recognition task, the feature extraction process took place based on the measured e-nose data. From each sensor signal, five features were computed. The first three are specifically computed by averaging sensor response value through a specified time range. The obtained value then underwent a baseline normalization procedure being divided by the average sensor response recorded during the baseline acquisition time.

In Table 3.2, we present the computed feature array, including the steady-state and dynamic features. After the feature extraction, the data were normalized on a per column (sensor) basis to zero mean and unitary variance. We would like to highlight that several algorithms were implemented in order to select relevant features, including linear discriminant analysis, an entropy-based procedure (tree classifier), and a feature ranking algorithm based on K-nearest neighbors (*relief-f*).

Table 3.2 Description of the extracted features; the first five are computed for each of the seven e-nose sensors and the last two are from included temperature and humidity sensors

# Feature	Description	Computation time range (s)
Feature 1	Steady-state response (wrt averaged baseline)	[150, 180]
Feature 2	Steady-state response—IR Off (wrt averaged baseline)	[181, 200]
Feature 3	Desorption status (wrt averaged baseline)	[250, 300]
Feature 4	Uptake derivative	[60, 120]
Feature 5	Desorption derivative	[210, 250]
Feature 6	Temperature	[0, 330]
Feature 7	Relative humidity (RH)	[0, 330]

With the subsequently detailed e-nose data obtained for CFRP specimens, preliminary data analysis was performed using principal component analysis (PCA) to further reduce dimensionality and extract most of the signal's variance. The centers of the clusters, computed as the mean of the scores related to each class, were highlighted as well as their standard deviation (1-sigma) ellipses. This representation aimed to show a preliminary qualitative evaluation of the (inner and outer) variance distribution for contamination classes through cluster localization and spatialization. Furthermore, PCA was used as an anomaly detection method by relying on the first PC projections extracted from a distribution obtained for reference samples. In this way, a threshold level was set, delimiting a 2-sigma coverage on the supposed multivariate Gaussian distribution of the reference samples. Each sample whose representation fell outside this limiting border was detected as a contaminated sample. In some cases, more powerful pattern recognition schemes were implemented to cope with the subtleties of the different tasks. Details are given in the following sections. Finally, shallow neural networks were used, instead, for regression tasks aimed at estimating the level of contamination.

3.4.2.2 E-nose Results on Coupon Level Samples

In the following, we detail the findings achieved using the Airbus and ENEA e-nose setups and related procedures for flat CFRP coupon level samples in the ComBoNDT research project.

Airbus E-nose Setup

The received CFRP samples were measured in a random order using the device setup described above. Before starting a detailed multivariate data evaluation, the gathered raw data were normalized using a mean center function around zero followed by a scaling of the variables to their unit standard deviations. With this normalized data matrix, a PCA was done, and a PLS-DA was performed for classification purposes.

Figure 3.42 provides an insight into the PLS-DA results obtained when investigating intentionally contaminated CFRP coupons using the Airbus e-nose setup. On the 2D score plot of the latent variables (LV) LV1 and LV2, three different clusters of findings can be identified from the e-nose measurements. Dark blue rectangles form the cluster of the reference sample measurements (RE). In the second cluster, pink stars belong to samples that have been contaminated with de-icing fluid and the light blue triangles represent the combined repair samples (R-Combi). All other performed measurements form a third cluster on the 2D view. The respective abbreviations for the contamination scenarios were already introduced in Table 3.1.

By turning to a 3D analysis by adding the third latent variable (LV3), discrimination concerning the third cluster of measurements becomes feasible. When we investigated for even higher numbers of latent variables (LV4 and LV5), improved separation of the production scenario samples occurred (results not shown here).

Fig. 3.42 LV1/2 score plot of the e-nose measurements for flat CFRP coupon level samples. Scores based on features from distinct contamination scenarios are color-coded; details are given in the text

After the multivariate data analysis of the obtained measurement data, we offer the following summing up statements for the ENDT investigations of CFRP coupons using the Airbus e-nose setup:

- Clean reference samples (RE) and samples contaminated with de-icing fluid (DI) cluster in their own quadrant in the LV1 versus LV2 score plot and can be easily and clearly identified.
- By evaluating LV3, thermally damaged samples (TD) and repair scenario fingerprint samples (R-FP) can be separated and identified.
- Spatial separation of release agent (RA) samples and production fingerprint (P-FP) samples is possible, but the degree of separation is rather low (LV4, LV5).
- The “clean sample or dirty sample” decision (that is, related to the “sample ready to bond or not ready bond” decision) can be made for all the investigated contaminations.

3.4.2.3 ENEA E-nose Setup

Before detailing the findings obtained with the ENEA e-nose for the ENDT inspection of CFRP coupon level samples, we report in Table 3.3 the number of panels and corresponding features (37) sampled in the frame of the production user case by means of two different sampling methods.

Concerning the fingerprint (FP), moisture (MO), and release agent (RA) contamination scenarios within the production use case, the results presented in Fig. 3.43 which were obtained with the 0 method for the sampling of analytes did not reveal the capability to distinguish between reference and contaminated samples, at least in the considered PCA subspace.

Based on these preliminary results, we decided not to go further in the investigations of CFRP specimens from the production use case but instead focused on coupon panels from the defined repair user case to test the performance of e-nose ver.1. In

Table 3.3 Number of sample measurements with the CFRP coupon sample-based production use case for both the applied e-nose sampling methods; more details are given in the text

	Production use case
0 method	25
PC method	44

Fig. 3.43 E-nose findings when performing PCA on the 0 method sampled coupon level CFRP panels

Table 3.4 Number of sample measurements with the CFRP coupon sample based on the repair use case; more details are given in the text

	Repair use case
0 method	25
PC method	41

Table 3.4, we present the number of samples taken for the analysis of specimens from the repair user case.

Assuming a two-class classification problem (FP/Skydrol versus ALL), we performed a preliminary data analysis using PCA so as to highlight the capabilities of the e-nose ver.1 to discriminate fingerprint/Skydrol hydraulic oil contamination at each contamination level from any other contaminated and reference CFRP samples. In this way, both sampling methods showed a limited capability to discriminate FP/Skydrol contaminated samples from the others in the PCA subspace. Meanwhile, the PC sampling method enhanced the separation capabilities, obtaining a clear separation for FP level 3 contaminated samples, as shown in Fig. 3.44.

Encouraged by these results, we performed a feature selection step for the samples investigated and recorded with both methods. Based on the ranking feature algorithm *relief-f*, ten relevant features were extracted for the PC method. Specifically, a subset

Fig. 3.44 E-nose findings when performing PCA on the PC method sampled flat CFRP panels

of steady-state and desorption rate features for MOX sensors was selected by the algorithm. By using the selected feature vector along with a logistic regression classifier, the *receiver operator characteristic* (ROC) curve was drawn (see Fig. 3.45). Its area under the curve (AUC) performance indicator was then computed, obtaining a value of 0.84. In this way, we have shown that a total correct classification (CC) rate of 78% can be achieved, at a false negative rate of 31% (Table 3.5).

Fig. 3.45 AUC of the logistic regression classifier when evaluating the e-nose findings for the CFRP coupons

Table 3.5 Parameters of the classifier performance assessment for evaluating e-nose data obtained for CFRP coupons. One class representing FP-contaminated samples (at all contaminated levels)

Classification Parameter Rate	
Correct Classification	78%
False Negative	31%
False Positive	35%
AUC	0.84

Confusion Matrix			
True class	0	23	5
	1	4	9
		0	1
	Predicted class

Fig. 3.46 Neural network regression results obtained with e-nose ver.1 data, considering all samples (note 0 level contamination). The results have been obtained using a leave-1-out cross-validation procedure. Note that the contamination level is underestimated and that the regressor is basically capable to discriminate the highest level of contamination samples from uncontaminated samples

Further analyses were conducted to compute the contamination quantification capabilities of the e-nose ver.1. In particular, a simple multivariate regression algorithm (FFNN) was used to estimate the level of contamination by a linear continuous encoding of the level score ranging from 0 to 3. Results shown in Fig. 3.46 show that the selected regression algorithm when applied to all e-nose ver.1 captured data is not capable to directly estimate the contamination level of a sample. Actually, it is only capable to discriminate the third (highest) FP contaminant level, and its mean absolute error (MAE) evaluation resulted in a 0.69 value.

In Fig. 3.47, we show the results obtained for the correctly identified contaminated samples. In this case, the regression method offers much better performance, highlighting a progressive behavior when evaluating contamination levels of increasingly contaminated samples. The MAE score, in this case, reaches a 0.5 value. This suggests that experimental conditions variability severely hampers the inherent discrimination and quantification capability for some of the samples. However if the conditions favor the correct measuring of the samples, then its identification as contaminated and the consequential contamination level quantification may be successful.

Samples recorded with the 0 method were screened with a discriminant analysis (DA) approach in order to select the most discriminative features. In particular, we restricted our analysis to the three features obtaining the best DA scores. Specifically, all the selected features were uptake derivatives of MOX sensor responses. Two of these were selected for the final classification task, namely the uptake derivatives

Fig. 3.47 Regression results obtained with the ENEA e-nose ver.1 when considering correctly identified contaminated samples

with respect to MOX1 and MOX5, which were used in the classification task to differentiate the FP/Skydrol contaminated coupons from the CFRP reference (RE) samples. This selection allowed a simple tree classifier to achieve a correct classification rate of 86.44% (false negatives FN = 0%, false positives FP = 27%, as listed in Table 3.6).

Table 3.6 Confusion matrix as obtained by a classification tree (CT) when discriminating uncontaminated reference samples from FP/Skydrol contaminated samples

Confusion Matrix			
True class	0	8	3
	1	0	11
		0	1
Predicted class

Fig. 3.48 E-nose with the desorber device imaged with the sampling head approaching CFRP parts with different sample geometries

3.4.2.4 E-nose Results for the Pilot Level Samples

Subsequently, we detail the findings achieved, respectively, with the Airbus and ENEA e-nose setups and related procedures for curved CFRP pilot level samples in the ComBoNDT research project.

Airbus E-nose Setup

The received CFRP samples were measured in a random order with the above-described device setup. The images in Fig. 3.48 show the desorber device sampling head taking analyte samples from CFRP parts with different sample geometries.

CFRP Pilot Level Samples from the Production User Case

The considered CFRP pilot level samples of the related production user case were curved specimens with convex and concave surfaces. All surfaces could be measured successfully with the e-nose desorber device. The contemplated contamination scenario was implemented by depositing on the surface a combination of release agent (RA), at two different concentration levels (RA1 and RA2), and fingerprints (FP) containing artificial sweat, whereby the contaminants were applied to both sides of the sample. We measured all the samples only once to avoid errors due to differential outgassing of contamination volatiles. With the normalized data matrix, a PLS-DA was performed for classification purposes.

In Fig. 3.49, we present the results of the respective PLS-DA analyses. The graph on the left side of this figure shows that the applied algorithm enables the contaminated samples to be distinguished from the reference samples with a clean surface. The right-hand graph shows the results, highlighting the additional distinguishing

Fig. 3.49 Results of the class prediction of the PLS-DA of data obtained by e-nose measurements on the CFRP pilot samples from the production user case; left: prediction of two classes (clean reference class 2; contaminated class 1); right: prediction of three classes, including a discrimination between the two different contaminant concentrations

among the contaminated sample sets into two classes, providing the information on different concentrations of contaminants and thus facilitating a quantification.

CFRP Pilot Level Samples from the Repair User Case

The pilot level CFRP samples of the repair user case were prepared by introducing a scarfed surface. We successfully measured all surfaces with the desorber device. The applied scenario affecting the sample surfaces was a combination of a thermal impact (TD) and the deposition of contaminants based on de-icing fluid (DI).

We observed that all measured samples showed a very high sensor response when compared to the CFRP coupons. Specifically, even the scarfed reference samples reacted as if they were coupon samples with certain contaminations. This behavior could originate, on the one hand, from the thermal damage of the sample caused by the scarfing process or, on the other hand, from a solvent or chemical substance being used during or after the scarfing process, e.g., to clean the sample. Based on these observations, to experimentally verify these presumptions, some samples (reference, thermal impact (TD), and the “TD-DI” combination) were placed in a vacuum oven at 120 °C for one day. After this desorption process, the samples were measured again.

Figure 3.50 displays the results of the PLS-DA analysis. We infer that after applying the PLS-DA algorithm, we are able to distinguish among thermally damaged samples, samples with additional de-icing fluid contamination, and samples with a clean surface.

Performing a cross-validation step with the obtained data, the confusion table of cross-validation presented in Table 8 is returned.

Table 3.7 shows that the CFRP surface obtained after applying DI contamination can be clearly distinguished from the surfaces of the other samples and that thermally

impacted samples are identified correctly in eight out of eleven cases. A small amount of incorrect classification exists between reference samples and thermally damaged samples. Considering this error, it should be noted that the reference samples are also scarfed samples and might bear an odor characteristic of thermal damage due to the mechanical scarfing treatment.

ENEA E-nose Setup

The pilot sample set was characterized by the advanced ENEA e-nose ver.2.0. The measurements were performed according to the standard method, i.e., the 0 method sampling procedure. Our classification task within the production user case aimed to differentiate the contaminated CFRP panels from the reference ones to achieve a GO/NOGO classification. Reference samples were labeled as belonging to the RE class, while the contaminated class, including all panels (RA1FP3 and RA2FP3) having undergone combined contamination, was tagged as the RAFP3 class. For this task, a PLS-DA approach was selected. Training was performed on a normalized

Fig. 3.50 Results of the class prediction of the PLS-DA of data obtained by e-nose measurements on the repair user case pilot level CFRP samples

Table 3.7 Confusion matrix obtained when cross-validating data from the e-nose measurements on CFRP pilot level specimens from the repair user case comprising specimens prepared following three different contamination scenarios (RE, TD, and TD-DI); more details are given in the text

Actual class	RE	TD	TD-DI
Predicted as RE	22	3	0
Predicted as TD	3	8	0
Predicted as TD-DI	0	0	23

Fig. 3.51 Computed cross-validated response for the class comprising contaminated (RAFP3) CFRP pilot level specimens versus the reference samples (REF). The red dotted line indicates the contaminated class threshold crossing which will determine a sample classification as a contaminated one

data matrix of 37 features and 69 total panels. An internal leave-one-out cross-validation procedure¹ was used to select the optimal number of components, while external cross-validation with 20% of samples used as a test set at each validation run was used for the performance estimation. The results demonstrated a 0.83 correct classification rate level.

Table 3.7 shows the results of the classification of the 69 samples. The classification threshold was set by the PLS-DA method, see Fig. 3.51.

The trained classifier provides the wrong estimations for just 12 out of the 69 samples, as confirmed by the confusion matrix shown in Table 3.8.

Furthermore, the value of the area under the ROC curve (AUC) (presented in Fig. 3.52) approaches unity, confirming the classifier performance.

These results show how the advanced second version of the e-nose was finally implemented to achieve a good performance; also in the production user case, it was capable to identify the contaminated samples among the pilot samples.

¹This procedure selects all samples for training purposes except one, set apart for evaluating the performance of the trained algorithm. The process is repeated for a number of times equal to the dimension of the originating sample set. In this case, the classification rate obtained by the test samples is used to forecast the performances of several models, each one using a different set of principal components.

Table 3.8 Confusion matrix obtained for the e-nose measurements on CFRP pilot level specimens of the production user case comprising specimens from two different contamination scenarios (RE and RAFP3); more details are given in the text

Actual class	RE	RAFP3
Predicted as reference	36	6
Predicted as contaminated	6	21

Fig. 3.52 ROC curves (left) and plots of sensitivity (blue) and specificity (red) values for the e-nose data as the class threshold is changed (right) for the classes comprising non-contaminated (upper) and contaminated (lower) CFRP pilot level specimens of the repair user case

3.4.3 Final Remarks

Regarding the Airbus e-nose setup, during the different test campaigns, the device proved its capability in terms of contamination detection on the provided samples and chosen application cases. During the coupon sample investigations, the system showed its ability to distinguish the different contaminations in both the production and repair user cases. At the pilot sample level, the desorber measuring head managed to take air-tight odor samples from concave and convex real-world geometries while dealing with new and previously unknown scarfed surfaces. During the three-day test event on technologically realistic parts at IFAM, the detection system substantiated its ability to also function in surroundings other than a gas testing facility and once again showed great sensitivity in detecting volatile chemical compounds.

Quantitative determination of moisture content using the e-nose system in combination with the desorber device is feasible for the desired material. The achieved error of prediction of less than 0.0763 wt% is very encouraging. Enlarging the dataset with additional measurements will further reduce the error of prediction to values of RMSECV (about 0.035 wt%). One big advantage of the e-nose in the combined method of operation is that information on the chemical surface condition (clean or contaminated) can be obtained at the same time with a very good value in terms of the moisture content.

If more precise measurements of the moisture content are required, the measuring setup of the e-nose system can be changed to a pure moisture measurement setup. Under this setup, the resolution of moisture detection will be increased, and the error of prediction can further be reduced.

At the coupon level, the first e-nose version by ENEA was not capable of dealing with the challenges of the production user case, although it was able to reach a 78% correct classification rate for FP detection in the repair user case. After the coupon level tests campaign, the ENEA e-nose was significantly improved by developing a new sampling head and filtering subsystems. The second version proved its capability to detect contaminated samples in both the production and repair user cases at the pilot and realistic parts challenge levels. In particular, the second version was able to achieve more than 80% accuracy in detecting RA-FP mixed contamination samples at the pilot level and obtained a perfect score during the realistic parts testing event in Bremen.

Based on the analysis of these results, e-nose technology appears very close to the maturity stage for the detection of surface contamination prior to the bonding phase. Of course, the e-nose methodology can only be effective whenever residual volatile compounds are present on the surface under analysis. The results of the ComBoNDT campaign are significant for the detection task and are encouraging with respect to the possibility to distinguish different contaminants, even when the concentration level was close to what we would expect to find in real-world scenarios. Quantification capabilities at this level, however, still appear to be difficult to achieve. Currently, the primary limitations of the techniques are due to measurement times, which can slow down the screening of large surfaces.

In summary, during the ComBoNDT project, two different approaches to contamination detection using e-nose were followed. On the one hand, a custom-made-of-the-shelf system (Airsense, Airbus E-Nose) was employed to reach a high TRL in a very short time. The system had to be retrofitted with additional sensors, and in order to achieve stable results on a shop floor environment without the influence of interfering odors from solvents and volatile compounds, a desorber device also had to be developed. On the other hand, the e-nose system from ENEA was developed almost from scratch and went through several optimization steps. Both approaches proved their eligibility and showed outstanding detection capabilities, as described above.

Both approaches offer advantages. The ENEA approach can be considered as an open-source system. The measurement setups (e.g., duration, flow, temperature) as well as sensor signal feature extraction and all other parameters are easy to set and

change, whereas the custom-made device can only be controlled or influenced in a way that the manufacturer allows by providing an insight into the device's firmware. The Airbus approach, employing a working gas sensor system, saved a lot of time, which was used to work on a smart sample-taking device. With the integration of the e-nose and desorber device in one system, interfering influences from a shop floor environment can be ignored. The implementation of signal processing and multivariate data analysis could easily be achieved, tested, and adapted using the "open-source" ENEA system. Measurement control, data recording, feature extraction, and multivariate data analysis were successfully performed, displaying the results on a GUI designed and programmed by ENEA at the end of the project.

As already mentioned above, both approaches have their advantages, and the greatest advancements in the technology were achieved in the areas where research and experience could improve the system via further hardware and software developments. The only conclusion must be to combine these enhancements—smart sample taking and total system control—in an integrated common device to further advance sensor system performance.

3.5 Laser-Induced Breakdown Spectroscopy (LIBS)

In this section, we introduce laser-induced breakdown spectroscopy (LIBS) as a tool for surface quality assessment and detail how its performance was enhanced in the ComBoNDT project for the in-process monitoring of CFRP adherends.

3.5.1 *Principle and Instrumentation*

LIBS is a spectroscopic method for elemental analysis that is routinely used to determine the elemental compositions of solids, liquids, and gases. For surface technology applications, a high-power laser pulse is focused onto the sample, whereby a small amount of material (typically hundreds of ng to a few μg) evaporates and forms a micro-plasma above the surface [30]. In this way, surface species are excited, and due to the following relaxation process, element-specific radiation is emitted. The emitted light is subsequently separated by its wavelength and is detected using a (often high-resolution) spectrometer; then, the measured intensities of the optical emission are evaluated using dedicated software for qualitative and quantitative analysis. Quantification to assess the surface composition is possible through, e.g., peak ratios in combination with a suitable calibration of the method [6]. For the detection of surface contaminants with LIBS, the contaminant needs to contain (atoms of) the elements that are detectable by means of LIBS and that are not (or only in a very defined amount) part of the clean surface. Detection limits can be in the range of ppm but depend on the material, contaminant, and experimental setup, and they need to be

Fig. 3.53 Diagram showing the measurement principle in LIBS

determined separately for each combination of materials and species to be detected [1].

In comparison to conventional surface analysis methods, LIBS requires relatively short measurement times in the order of a few seconds. Measurements can be performed under atmospheric conditions without the need for sample preparation. In addition, LIBS can be adapted to inline applications [31].

Regarding the findings reported here, the LIBS measurements were performed with the LIPAN 4000 system from LLA Instruments GmbH, Berlin, Germany. Laser pulses from a Q-switched Nd:YAG laser with a 1064 nm laser wavelength, a pulse width of 6 ns, and a repetition rate of 20 Hz were used for excitation. In addition, tests were also performed with another Nd:YAG laser system that emits laser light with a wavelength of 266 nm at a rate of 10 Hz with a 7 ns pulse width. Figure 3.53 gives an overview of the LIBS setup.

Spectra were obtained and analyzed using an Echelle spectrometer (LLA Instruments GmbH, Berlin, Germany), which allows simultaneous detection of wavelengths from 200 to 780 nm with a spectral resolution of a few pm. The spectrometer was combined with an ICCD camera (1024 * 1024 pixels). Measurements were typically done at laser energies ranging from 95 to 180 mJ, depending on the laser light wavelength. The control of the spectrum recording and the evaluation of the spectra were performed using the ESAWIN software developed by LLA Instruments GmbH. The software has a large database that allows the automated identification of many relevant atomic emission lines in the optical spectral region.

3.5.2 LIBS Results

In the following, we report the LIBS advancements and findings obtained in the ComBoNDT research project, in which the consortium partners at Fraunhofer IFAM performed the in-process monitoring of CFRP adherends of different shapes that are relevant for distinct technologically relevant user cases and had undergone the intentional application of various contamination scenarios.

3.5.2.1 LIBS Results on Coupon Level Samples

We investigated three different contaminants and clean reference samples on flat 10 cm × 10 cm coupon level samples for a production user case comprising distinct contamination scenarios. In the following, the results for CFRP surface states obtained by applying the different contaminants are presented in comparison with the clean reference samples. Coupon samples with different amounts of moisture are not discussed due to the inability of LIBS to detect this contaminant (i.e., water in CFRP).

Release agent (RA) contamination scenario:

The silicon-containing release agent Frekote® 700NC was used in the RA scenario. For the contaminated samples, silicon emission lines were detected with LIBS. In Fig. 3.54, the LIBS spectra of a clean CFRP sample and an RA-contaminated sample are shown together. The relevant atomic emission lines (carbon and silicon) used for sample evaluation are marked.

Three correspondingly prepared RA-contaminated CFRP coupon samples for each degree of contamination (named 1, 2, or 3) and three clean reference samples were investigated with a 1064 nm single laser pulse energy of 180 (±10) mJ and 60 LIBS measurements on each sample specimen. The mean values and 95% confidence intervals were calculated from the three samples, respectively, and the resulting relative LIBS intensities (given as Si/C intensity ratios) are correlated to the respective XPS results in Fig. 3.55. The lowest level of contamination, namely I-P-RA-1, is

Fig. 3.54 LIBS spectrum obtained from a clean (black line) and an RA-contaminated CFRP coupon sample (red line) with the indication of relevant emission lines for carbon and silicon species

Fig. 3.55 Correlation between the 1064 nm LIBS relative intensities (Si/C) and silicon surface concentrations (in at.%) measured with XPS

clearly detectable compared to the clean reference sample and can additionally be differentiated from the two subsequent contamination levels (I-P-RA-2 and I-P-RA-3).

The same set of CFRP samples was investigated using the same LIBS setup coupled with a different laser using an excitation wavelength of 266 nm. The single laser pulse energy was reduced to 95 (± 10) mJ. The results are shown in Fig. 3.56. An increased Si/C ratio for the contaminated samples is observed and both the reference sample and the three contamination levels can be clearly detected and differentiated.

The detection limit using the 266 nm laser for excitation is expected to be even lower than the contaminant surface concentration on the tested composite sample, with approximately 3 at.%(XPS). To increase the silicon concentrations on the CFRP surface, a differentiation of the level of contamination is better using 1064 nm for the plasma excitation. We explain this phenomenon by achieving different information depths depending on the laser excitation: Using the 1064 nm light, the information depth is comparably high. The CFRP adherend surface contributes to a great extent to the plasma emissions (we observe a large carbon signal and a comparably low silicon signal intensity). When using the 266 nm laser for plasma generation, the information depth is lower and the surface-near regions (e.g., deposited contaminants) contribute significantly more strongly to the measured signal. This results in an increased Si/C ratio and enables very surface-sensitive measurements.

Fingerprint (P-FP) contamination scenario:

LIBS investigations were performed on the CFRP adherends with an analogous procedure, as applied in the case of the samples from the RA scenario that had been locally contaminated with an artificial fingerprint (FP) solution (see Chap. 2).

Fig. 3.56 Correlation between the 266 nm LIBS relative intensities (Si/C) and silicon surface concentrations measured with XPS

Using mean values from an area of $3.6 \text{ cm} \times 2 \text{ cm}$ (1600 LIBS shots), the lowest level of contamination (named I-P-FP-1) is clearly detectable compared to the clean reference sample with both laser excitation wavelengths (1064 nm and 266 nm), see Fig. 3.57 for 1064 nm and Fig. 3.58 for 266 nm. Differentiation of the different contamination levels is, to some extent, possible with a laser wavelength of 1064 nm.

Fig. 3.57 Correlation of the 1064 nm LIBS relative intensities (Na/C) with sodium surface concentrations measured with XPS

Fig. 3.58 Correlation of the 266 nm LIBS relative intensities (Na/C) with sodium surface concentrations measured with XPS

Just as for the RA scenario, for measurements using a 266 nm laser for plasma excitation, the information depth is comparably lower and the surface-near regions (e.g., contaminants) contribute significantly more strongly to the measured signal. This results in a clearer detection of contaminants on the I-P-FP-1 samples and a more significant discrimination from the reference CFRP surface state, but it does not allow for a differentiation of the three contamination levels (FP-1 to FP-3). The chosen evaluation method calculates the mean values from the areas with (fingerprinted region) and without (surrounding areas) contamination.

In this case, as in any case of punctual contamination, we suggest improving the detection result for contaminated regions by evaluating every single LIBS measuring spot and plotting the result in a space-resolved 2D diagram (hereafter named a map). Clean and contaminated areas on the sample can, thus, be identified, and the risk of missing small spots of contaminants (due to averaging comprising spots from surrounding and not contaminated regions) is reduced. Half of an artificial fingerprint and part of the clean surrounding areas were measured and evaluated, and the results are shown in Fig. 3.59 (for an excitation wavelength of 1064 nm) and Fig. 3.60 (266 nm), respectively. Green areas indicate regions with Na/C signal intensity ratios as found on a clean surface, while orange and red color-coded (with darker colors referring to a higher Na/C ratio) areas indicate an increased Na/C ratio and, thus, FP-contaminated areas.

Regarding the production user case, similar to the contamination scenarios within the repair user case, we investigated three different contaminants and clean reference samples on flat 10 cm × 10 cm CFRP coupon level samples. In the following, the results for the surface states based on the different contaminants are presented in a comparison with the findings for the clean reference samples. Coupon samples with

Fig. 3.59 LIBS map showing a space-resolved 2D diagram of the 1064 nm relative signal intensities (Na/C)

Fig. 3.60 LIBS map showing a space-resolved 2D diagram of the 266 nm relative signal intensities (Na/C)

different degrees of thermal impact and resulting degradation are not discussed due to the lack of a contamination-specific tracer element, which is essential for LIBS to detect different surface states.

De-icing fluid (DI) contamination scenario:

The de-icing fluid (DI) applied in this contamination scenario contained potassium as a tracer element, which enabled the contaminant detection and quantification with LIBS. Measurements with a 1064 nm laser wavelength were performed with an approximately 180 mJ single pulse energy and 60 measurements in an area of 4.5×9 cm. The LIBS intensities (K/C) correlate well with potassium concentrations

measured with XPS, as shown in Fig. 3.61. We achieved a detection and differentiation of different levels of contamination with this set of settings. Using 266 nm as the excitation wavelength (approximately 95 mJ single pulse energy and 64 LIBS measurements in an area of $4\text{ cm} \times 4\text{ cm}$), DI contamination was also successfully detected; see Fig. 3.62. Differentiation of the higher contamination levels DI-2 and

Fig. 3.61 Correlation between the 1064 nm LIBS relative intensities (K/C) and potassium surface concentrations measured with XPS

Fig. 3.62 Correlation between the 266 nm LIBS relative intensities (K/C) and potassium surface concentrations measured with XPS

Fig. 3.63 1064 nm LIBS relative intensities (P/C) for distinct degrees of CFRP surface contamination with a phosphorous-containing hydraulic oil

DI-3 was not achieved. The comparatively large standard deviations of the XPS results for the surface concentrations (potassium) on DI contaminated samples indicate that the DI is non-uniformly distributed on the CFRP surfaces. Hence, depending on the area investigated with LIBS, different intensity ratios might be the result.

Fingerprint (P-FP) contamination scenario:

For this scenario, the same LIBS settings as elaborated for the DI detection were used. In this case, the fingerprints comprised a phosphorous-containing hydraulic oil. FP detection was successfully performed with both the 1064 and 266 nm plasma excitation wavelengths; see Fig. 3.63 (1064 nm) and Fig. 3.64 (266 nm). The three different contamination levels could be distinguished. However, the confidence interval for sample FP-2 was quite large when measured with the 1064 nm laser. A correlation with the XPS results was not achieved in this case. Comparing both measurements, we infer that the 266 nm laser excitation wavelength is again more surface sensitive, and thus gives larger P/C ratios (compared to the release agent (RA) scenario in the production user case).

Thermal degradation (TD) scenario:

Since thermally degraded surfaces do not contain a chemical element that exclusively and specifically marks the treated samples, a clear detection of CFRP samples that had undergone a TD impact was not achieved with LIBS in the current setup. Using a multivariate approach, there was no clear differentiation between the sample sets, and the prediction of unknown sample states failed. Improvements may be reached

Fig. 3.64 266 nm LIBS relative intensities (P/C) for distinct degrees of CFRP surface contamination with a phosphorous-containing hydraulic oil

by using a setup dedicated to oxygen detection, which was not the focus of our current LIBS setup.

Summary of the LIBS results for coupon level samples:

Table 3.9 summarizes the LIBS results for the coupon level samples. For the production user case, the detection of the contaminant was possible for the RA and FP scenarios. A clear differentiation of the three contamination levels was possible for

Table 3.9 Categorizing summary of the LIBS results for the coupon level CFRP samples of distinct contamination scenarios in the production and repair user cases

		Detection of contaminants	Differentiation of cont. levels
production	MO	✖	✖
	RA	+	+
	FP	+	▬
repair	DI	+	+
	FP	+	+
	TD	✖	✖

+

 Clear

▬

 Partially/Improvement necessary

✖

 No

the RA scenario. Concerning the repair scenarios, the detection as well as the differentiation of the levels of contamination were successfully demonstrated for the FP and DI scenarios.

3.5.2.2 LIBS Results on Pilot Level Samples

The LIBS measurements on pilot level CFRP specimens from the production user case were performed on curved CFRP surfaces after peel ply removal. The laser wavelength of 1064 nm was used with a 180 mJ laser pulse energy. The inspected area was 4 mm × 4 mm with 1600 LIBS single shots within this area.

Combined contamination of RA and FP:

Two contaminants were applied to the samples: a release agent (RA) and a fingerprint with artificial sweat (FP). On the coupon level samples, these two contaminations could be detected individually using LIBS. For the combined FP and RA contamination, Fig. 3.65 shows the evaluation of the silicon emission line that is specific for the silicon-containing RA. The Si/C ratio increases with increasing RA concentration on the CFRP surface. We clearly detected the low RA concentration (compared to a clean reference sample) and also distinguished it from the higher RA concentration. Figure 3.66 shows the good correlation of the LIBS results (giving the Si/C signal intensity ratio) with the XPS results (giving the silicon surface concentration).

Fig. 3.65 Evaluation of the Si/C LIBS signal for the pilot level CFRP samples with combined release agent (RA) and fingerprint (FP) contaminations

Fig. 3.66 Evaluation of the Si/C LIBS signal for the pilot level CFRP samples correlated to the XPS results

Based on the visual inspection, we inferred that the FP contamination did not spread over the entire sample surface (as it is the case for the release agent) but is located somewhere in the middle of the samples. In order to detect this contamination, an area of $4\text{ cm} \times 2.4\text{ cm}$ containing 240 LIBS measurement spots was inspected for each sample. We did not obtain a clear FP detection (as for the coupon level samples). In Fig. 3.67, the Na/C LIBS mapping result for the reference sample is shown, and in Fig. 3.68, we present the corresponding mapping for the contaminated sample II-P-RA1-FP3. There is an overall increased sodium concentration (characteristic of the artificial sweat in the fingerprinted surface regions) for the contaminated sample (in the more orange and red areas), but the detection of a clear fingerprint shape was not possible.

Within the repair user case based on pilot level samples, the LIBS measurements were performed on the CFRP surfaces after scarfing. The laser wavelength of 1064 nm was used with a 180 mJ laser pulse energy. The inspected area was $0.4\text{ cm} \times 0.4\text{ cm}$, with 1600 LIBS single shots within this area.

Combined DI and TD contamination scenario:

The scarfed CFRP specimens underwent two contaminations and showed the surface modifications resulting from contact with de-icing (DI) fluid and exposure to thermal impact (TD). On coupon level samples, LIBS was a suitable method for the detection of DI, but not for TD. For the pilot samples, we, therefore, focused our measurements on the detection of potassium-containing DI.

The LIBS results for K/C are shown for all measured samples in Fig. 3.69. We obtained a clear detection of DI in comparison to the reference CFRP sample. Also,

Fig. 3.67 LIBS map for the Na/C signal intensity ratio on a pilot level CFRP reference sample

the two levels of combined contamination were differentiated. The LIBS results correlated well with the XPS results for potassium concentration on the surface, as shown in Fig. 3.70.

Summary of results for the pilot level CFRP specimens:

Concerning the measurement of the pilot samples for the respective production user case, LIBS enabled detection and even a differentiation of the different levels of release agent. The fingerprint composed of artificial sweat was detected, but the

Fig. 3.68 LIBS map for the Na/C signal on a pilot level CFRP sample II-P-RA1-FP3

respective ENDT procedure might even be improved. The detection was not as clear as for the coupon level samples. We suggest that one reason for this outcome might be the rough surface structure (the peel ply was removed without subsequent abrasion treatment) of the examined samples.

Within the repair user case comprising pilot level CFRP specimens, LIB investigations were performed on scarfed samples. The geometry was easily accessed and handled by the LIBS system. The deposited de-icing fluid was neither detected nor

Fig. 3.69 Evaluation of the K/C LIBS signal for the pilot level CFRP samples in the repair user case

Fig. 3.70 Correlation of the K/C LIBS signal for the pilot samples in the repair user case with the XPS results for the potassium surface concentration

quantified. Thermal degradation was not detected (as when inspecting coupon level samples) because no element contrast was present in this scenario.

3.5.3 Performance in Inline Surface Quality Assurance

In the following, we summarize the findings revealing the performance of laser-induced breakdown spectroscopy (LIBS) as an ENDT technique for the surface quality assessment of CFRP composite specimens in distinct user cases. These comprised first a production and a repair user case, both based on coupon level samples, then pilot level CFRP samples with a more complex shape applied in a production and a repair user case, and finally user cases relying on technologically realistic CFRP parts.

In a first and trendsetting approach within the ComBoNDT research project, we applied LIBS to map CFRP test coupons prepared by intentionally depositing distinct contaminants within several contamination scenarios. Some of these scenarios comprised contaminants containing chemical components that feature elements that are not found on clean CFRP substrates and thus, may be used as tracer species for LIBS-based surface assessment procedures. We advanced these spectroscopic procedures to achieve technologically relevant detection limits and to accomplish fast data acquisition and evaluation that permit surface investigations by applying a high area density of LIBS spots. In this way, even locally applied contaminants relevant for aeronautical environments were detected.

3.6 Fourier-Transform Infrared Spectroscopy (FTIR)

In this section, we introduce Fourier-transform infrared spectroscopy (FTIR) as a tool for surface quality assessment and detail how its performance was enhanced in the ComBoNDT project for the in-process monitoring of CFRP adherends.

3.6.1 Principle and Instrumentation

In FTIR spectroscopy, molecules close to the surface are excited by infrared light. This excitement results in a partial absorption of the infrared radiation by the molecules, as depicted in Fig. 3.71. The absorbed infrared radiation is missing in the received infrared spectra, providing information about the chemical composition of the surface. The measured FTIR spectra have complex structures that can be interpreted by a partial least squares (PLS) algorithm that correlates the material properties given in the calibration with significant features in the FTIR spectrum recorded on a substrate. In the second step, the calibration can be used to predict

Fig. 3.71 Working principle of diffuse reflection FTIR spectroscopy

the material properties from an FTIR spectrum made on a substrate with unknown properties. The advantage of this evaluation algorithm is that the FTIR spectra can be interpreted quantitatively.

The measurements were conducted with an Exoscan 4100 portable handheld FTIR spectroscope. The test parameter was set to 64 scans at a resolution of 8 cm^{-1} . All measurements were performed in diffuse reflection.

3.6.2 FTIR Results

The following subchapter summarizes the results obtained for the three sample levels. Since no sensitivity toward release agent or fingerprint contamination was found during this experiment, a successful evaluation of these samples was not possible; therefore, the results are not described in this chapter.

3.6.2.1 FTIR Results on Coupon Level Samples

The coupon level samples were used to create a PLS algorithm model. For this purpose, FTIR spectra recorded on surfaces with different contaminations were used to build a calibration model. The presented results show the validations of these models with additionally recorded FTIR spectra. Figure 3.72a depicts the validation of a thermally degraded CFRP surface. The results show a satisfactory prediction

Fig. 3.72 **a** Prediction of the temperature during thermal degradation based on the PLS algorithm from the FTIR spectra recorded on a CFRP surface; **b** prediction of the amount of potassium on the surface based on the PLS algorithm from the FTIR spectra recorded on a CFRP surface contaminated with de-icing fluid; **c** prediction of the moisture uptake on the surface based on the PLS algorithm from the FTIR spectra recorded on a CFRP surface after moisture conditioning

accuracy with a root mean square error of prediction (RMSEP) of about 8 °K and a coefficient of determination (R^2) of about 0.94.

For the prediction of the amount of residual de-icing fluid, the amount of potassium (K) from XPS measurements was used as a calibration reference. The prediction quality is quite satisfactory, with a root mean square error of prediction (RMSEP) of 1.4 at. % K. The uptake of moisture is a well-known property of CFRP material. In Fig. 3.72c, the prediction of moisture uptake correlates with an accuracy of 0.086 wt% (RMSEP) and an R^2 of 0.938. This prediction accuracy is in good accordance with similar investigations. In [32], a method was described that uses additional conditioning of the surface with an intermediate heating step. This investigation shows at an early stage that it is possible in principle to also measure non-homogenously saturated samples.

3.6.2.2 FTIR Results on Pilot Level Samples

The measurements for a thermally degraded scarfed surface are depicted in Fig. 3.73a. Both the reference and the thermally damaged sample showed a high scattering of the predicted temperature. It is assumed that this phenomenon was caused by the sample preparation. The samples on the coupon level were scarfed in a gentle manner to remove only the resin above the top fiber layer. In contrast, the pilot level samples were scarfed with an elevated pressure to reach an appropriate scarfing depth for the repair patches. Such friction leads to high temperatures on the surface. The fact that the information depth of FTIR spectroscopy is limited to near-surface areas can explain the predicted temperatures and their scattering. Further development of the method could include a defined surface preparation after scarfing in order to prevent a high-temperature impact.

Fig. 3.73 **a** Prediction of the temperature during thermal degradation based on the PLS algorithm from the FTIR spectra recorded on thermally degraded and de-icing fluid contaminated scarfed CFRP surfaces; **b** prediction of the temperature during thermal degradation based on the PLS algorithm for thermal-oxidative degradation; **c** prediction of the amount of potassium on the surface based on the PLS algorithm from the FTIR spectra recorded on scarfed CFRP surfaces with thermal degradation and additional de-icing fluid contamination

In order to check the repeatability of the FTIR method, un-scarfed areas of the sample were also investigated. For this evaluation, an in-house PLS model was used that was available from previous investigations on thermal-oxidatively degraded surfaces. In Fig. 3.73b, the evaluation shows a quite significant differentiation between the reference and thermally degraded surfaces. The evaluation of the measured amount of de-icing fluid is displayed in Fig. 3.73c. It was observed that contamination from de-icing fluid was detected on all samples. Furthermore, a clear increase in the amount of predicted potassium could be detected between the reference sample and the contamination levels I and II. For the reference sample, a high scattering was obtained.

3.6.3 Performance in Inline Surface Quality Assurance

During the different measurement series, FTIR spectroscopy demonstrated high sensitivity in detecting and quantifying thermally damaged parts, the amount of moisture uptake inside an assembly, and de-icing fluid contaminations on CFRP surfaces.

Moisture uptake could be correlated successfully with an error of 0.09 wt%. This sensitivity is sufficient to set a reliable process window to prevent bondline failure due to unknown moisture uptake.

Coupon level investigations proved the capability of determining thermally damaged samples with an error of 8 °K. This is a very good result for sanded CFRP surfaces. However, this accuracy was not achieved for the pilot samples. At present, it is assumed that the heat friction during the scarfing process leads to high temperatures and causes thermal damage on the sample surface with higher local variations.

On the coupon sample level, the surface contamination with de-icing fluid was well predicted with an error of only 1.4 at.% K. These results were subsequently validated with the contaminated pilot samples, with appropriate separation of lower (DI-I) and higher (DI-II) levels of de-icing concentration. For measurements on the demonstrator part, the de-icing fluid was found on the contaminated area as well as on the reference side (in smaller concentrations). It is assumed that during the drying step in the oven, the de-icing fluid was spread across the whole surface of the sample.

With this newly gained knowledge and the identified tasks, the process of FTIR sampling can be significantly improved. Hence, FTIR spectroscopy has made another step toward finally being employed on the shop floor.

3.7 Vibrometry Inspection

In this section, we introduce scanning laser Doppler vibrometry (SLDV) as a tool for surface quality assessment and detail how its performance was enhanced in the ComBoNDT project for the in-process monitoring of CFRP adherends.

3.7.1 *Principle and Instrumentation*

A scanning laser Doppler vibrometer is a non-contact measuring device that makes use of the Doppler effect to register the vibration velocity. A beam of laser light is focused on a point on the measured surface, see Fig. 3.74. The light is reflected and due to the Doppler effect, its frequency is shifted proportionally to the velocity of the measured point. A built-in SLDV interferometer is used to estimate this shift, thus measuring the point velocity. A set of motors and mirrors in the scanning head enables laser beam steering and, together with developed software, scanning along a defined grid of points. Possibilities for SLDV application in research related to guided wave measurements have been extensively studied over recent years. In [33], a combination of experimental analysis using laser vibrometry and numerical analysis for the thin aluminum plate is presented. Ruzzene [34] proposed a technique for full wavefield analysis in the wavenumber/frequency domain for damage detection. This is a filtering technique that improves damage localization results. The author performed numerical and experimental analyses of simple aluminum plates with crack and disbanded tongue and groove joints. In [35], scanning laser vibrometry and imaging techniques were utilized for the detection of hidden delaminations located in a multi-layer composite. The authors analyzed the wave interactions with delamination and utilized several image processing techniques, such as Laplacian filtering. It should be noted that the mentioned work presented a completely non-contact system for elastic wave generation and sensing. Elastic wave generation was performed using a continuous wave (CW) laser source in connection with a photodiode that excited a piezoelectric transducer. Elastic wave sensing was performed

Fig. 3.74 The experimental setup

using a conventional scanning laser vibrometer. Non-contact elastic wave generation based on a thermoelastic effect was utilized in [36]. The authors utilized broadband excitation based on a low-power Q-switched laser. The research presented here used a piezoelectric transducer (Sonox P502) with a diameter of 10 mm, which was attached to the surface to excite guided waves in the samples. An excitation signal in the form of a $5 \mu\text{s}$ Hanning was generated by an arbitrary waveform generator and amplified to $\pm 180 \text{ V}$ by a signal amplifier. The excitation was synchronized with the SLDV system.

3.7.2 Vibrometry Inspection Results

3.7.2.1 Vibrometry Inspection Results on Coupon Level Samples

To excite guided waves in the coupon samples, the piezoelectric transducer was attached to the back surface of the specimen in the top-right corner, as depicted in Fig. 3.75. Measurements were made along a diagonal line of 592 equally spaced points. At each point, 100 time samples were registered with a 512 kHz sampling frequency (192 ms total registered time). Each measurement was repeated 10 times and used for averaging to improve the signal-to-noise ratio. The specimen was laid flat on foam to minimize any propagating wave distortion.

Fig. 3.75 The specimen

An example of a registered signal, presented in Fig. 3.76, is in the form of a time response at one point situated on a diagonal line, 50 mm from the top-right corner of the specimen.

The complete registered data are presented in the form of a waterfall plot in Fig. 3.77.

Due to the high wave amplitude diversification, the same results are presented in the logarithmic amplitude scale in Fig. 3.78. Three wave modes are visible, one dispersive and two nondispersive (parallel lines).

Fig. 3.76 Time response at one point at $d = 50$ mm

Fig. 3.77 Waterfall plot

Fig. 3.78 Waterfall plot in the logarithmic scale

Fig. 3.79 Waterfall plot with space-amplitude compensation

Guided Wave Amplitude Compensation in Space

As the waves propagate along the specimen due to the damping phenomenon and the geometrical wave spread, the amplitude decreases dramatically with distance traveled. To compensate for this effect, an amplitude compensation procedure was proposed.

The average energy of the propagating waves at every measured point was determined as follows:

$$E(d) = \frac{1}{T} \sum_{t=0}^{T-1} \sqrt{w[d, t]^2}, \quad (3.1)$$

where T is the total number of measured time samples. Subsequently, the registered signal at each point was divided by its average energy:

$$\tilde{w}(d, t) = \frac{w(d, t)}{E(d)}. \quad (3.2)$$

The results, taking into account the amplitude compensation in space, are presented in the form of a waterfall plot in Fig. 3.79.

Fig. 3.80 Wavenumber–frequency relationship

Two-Dimensional Fourier Transform

To transform the registered data from the space–time domain into the wavenumber–frequency domain, the two-dimensional Fourier transform (2D FT) was used:

$$W(k, f) = \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} w(d, t) e^{-j2\pi(kd + ft)} dd dt. \quad (3.3)$$

The discrete form of the two-dimensional Fourier transform may be noted as follows:

$$W[k, f] = \frac{1}{\sqrt{DT}} \sum_{d=0}^{D-1} \sum_{t=0}^{T-1} w[d, t] e^{-j2\pi\left(\frac{kd}{D} + \frac{ft}{T}\right)}, \quad (3.4)$$

where D and T are the total numbers of space and time samples, respectively.

Examples of the results in the wavenumber–frequency domain are presented in Fig. 3.80.

The same operation was repeated for the signal with the compensated amplitudes in space, leading to improved results, which are presented in Fig. 3.81. Such a curve is typical for a sample made of the given material with the given thickness. Next, a thresholding procedure was applied in order to create a binary curve. For the binary data, linear fitting was conducted. The reciprocity of the value of the slope obtained

Fig. 3.81 Wavenumber–frequency relationship with space–amplitude compensation

from the fitting gives a linear approximation of the elastic wave group velocity c . This velocity was taken for the comparison of the coupon samples.

Two groups of samples were investigated in the coupon level samples; the sample set investigated for the production user case comprised three reference samples (RE), nine samples contaminated with release agent (RA), nine samples contaminated with fingerprints containing artificial sweat (FP), nine samples containing moisture (MO), and six samples with a mixed contamination of release agent and fingerprints. Because moisture samples were investigated in this set, it was important to compare them with very dry samples. The reference samples were measured for the first time after arrival from Fraunhofer IFAM (Bremen, Germany) and the wave velocity was estimated. Next, the samples were dried in an oven with air circulation. It was observed that the mass drop for the I-P-RE-1, I-P-RE-2, and I-P-RE-3 samples was 0.19%, 0.63%, and 0.18%, respectively. The second measurement was made after drying. The estimated wave velocity values for the three samples before and after drying are plotted in Fig. 3.82. A significant drop in velocity was observed for the second sample (I-P-RE-2). The observed relative change in velocities due to drying was 1.80%, -15.63% , and 0.73% for the I-P-RE-1, I-P-RE-2, and I-P-RE-3 samples, respectively. For the next analyses, the dried reference samples were taken.

Figure 3.83 depicts the results obtained for the feature velocity when investigating samples with single contaminations in the production user case based on CFRP coupons. No correlation between the contamination level and wave velocity is observed for the release agent contamination (RA). An exceptionally high value of velocity is observed for the I-P-RA-2-2 sample, while the I-P-RA-2-1 sample has the

Fig. 3.82 Vibrometry results; comparison of the reference (RE) CFRP coupon samples of the production user case

Fig. 3.83 Vibrometry results for the feature c (velocity of wave propagation) obtained during the surface quality assessment of CFRP coupons within the production user case; each sample had undergone one single modification. More details are given in the text

Fig. 3.84 Vibrometry results obtained with CFRP coupons in the production user case; the findings for samples prepared by applying combined contaminations are compared to the ones for the reference (RE) samples and the samples with the respective single contaminations

lowest value among all the RA samples, even though it has the same contamination level. In the case of the fingerprint contamination (FP), there is a slight increase in the wave velocity going from the lowest level (I-P-FP-1-x) to the highest level (I-P-FP-3-x). The numbering of the moisture samples cannot be treated as being representative of contamination content because each of the samples absorbed different amounts of moisture during conditioning. The sample with the highest velocity (I-P-MO-1-1) gained 0.59% of mass, the same amount as the I-P-MO-3-1 sample, which has the lowest velocity. The highest mass increase (0.71%) is observed for the I-P-MO-2-2 sample, but this is not distinguished by an extreme value of the velocity. The moisture case is further studied in a separate subsection.

In the next step, the samples with combined contaminations were studied. The combined case comprised both fingerprint and release agent contaminations, so the comparison was made not only with the reference samples but also with the RA and FP samples with single contaminants at the respective levels. The results are depicted in Fig. 3.84. It should be noted that the wave velocity values for the samples with combined contaminations are on the level of the dry reference samples. The velocity for single contamination samples was higher in most of the cases.

The CFRP coupon sample set investigated for the repair user case comprised three reference (RE) samples, nine thermally treated (TD) samples, nine samples contaminated with de-icing fluid (DI), nine samples contaminated with oily fingerprints (FP), and six samples with mixed modification obtained by a combination of thermal impact and subsequent contamination with de-icing fluid. In comparison to

Fig. 3.85 Vibrometry results for the CFRP coupons from the repair user case; findings related to the feature c (velocity) are presented for all the investigated samples with a single modification

the findings within the production user case, the reference samples differ more from each other, see Fig. 3.85. Especially for the first sample (I-R-RE-1), the value of velocity is significantly low. The non-uniformity of the estimated velocities could be related to the surface preparation of the samples. The samples for the repair user case were ground down to the fibers. For the velocity values for the samples with modifications, there is no correlation with the de-icing fluid contamination level. Relatively good repeatability is observed for the fingerprint contamination. The samples with the same level of contamination are characterized by similar values of velocity; however, they cannot be distinguished from the reference samples. In the case of the thermal treatment, the highest value of velocity was observed for the lowest temperature of treatment, namely 220 °C (I-R-TD-1-x).

In the next step, the samples with combined modifications were studied. The combined case comprised thermal degradation and de-icing fluid contamination, so the comparison was made not only with the reference samples but also with the respective TD and DI samples. Generally, a higher level of combined modification results in an increase in the velocity value, see Fig. 3.86. However, only two samples (I-R-TD1+DI-2-2 and 2-3) are characterized by a higher velocity than the reference samples. Moreover, the combined modifications cannot be distinguished from the respective single modifications (DI and TD).

Fig. 3.86 Vibrometry results for the CFRP coupons from the repair user case; findings for the combined modifications are compared against those obtained for the reference (RE) samples and for coupons with the respective single modifications that contribute to the combined modification

Focus on the Moisture Uptake

After inspecting all coupon samples, it was decided to further investigate the samples with moisture contamination. This was because a significant influence of the drying of the I-PRE-x samples was observed. Additional analysis was conducted, and the undried reference samples were also treated as being contaminated with moisture. Because the moisture absorption of each sample was different, it was decided not to use the sample symbols but rather to represent moisture intake as the percentage of mass increase. The new results are plotted in Fig. 3.87. This time, there were 12 cases with moisture because the undried reference samples were included in the set. The wave velocity value is on the same level for a considerable number of samples, starting at 0% moisture content and ending at about 0.7%.

A correlation of the velocity with moisture content was not observed. This scattering of the results could be related to the fact that the considered samples were not saturated with moisture. This could explain the fact that we observed distinct results for samples with similar mass increases. The moisture content on the wave path may vary between samples with the same mass increase. Moreover, the moisture content on the wave path may also vary from point to point for a single sample. Also, according to the numerical investigation, the moisture increase influences the wave amplitude far more than it does the wave velocity value. Therefore, it was decided to analyze the vibration energy from point to point. At each measurement point i , the RMS value was calculated:

Fig. 3.87 Estimated wave velocity plotted against mass increase due to moisture

$$RMS_i = \sqrt{\frac{1}{N} \sum_{n=1}^N X_{i,n}^2}, \quad (3.5)$$

where $X_{i,n}$ is the n -th time sample of a signal X measured at point i . The indices that are assumed to give the average state of the surface are the mean value of RMS_i , defined as

$$E = \frac{1}{M} \sum_{i=1}^M RMS_i, \quad (3.6)$$

where M is the number of measurement points, and the three-sigma is defined as three times the standard deviation:

$$3\sigma = 3 \times \sqrt{\frac{1}{M-1} \sum_{i=1}^M (RMS_i - E)^2}. \quad (3.7)$$

The three-sigma value consists of 99.7% of all data, meaning this encompasses almost all the calculated RMS values. The results are depicted in Fig. 3.88. Again, the samples with moisture contamination cannot be distinguished from the dry samples.

The problem in identifying the samples with moisture contamination could lie in the fact that only a linear measurement is done along the diagonal of the samples. If the samples are not saturated, one cannot be certain where the moisture is located in the sample because only the mass of the sample is taken as the indicator of the

Fig. 3.88 Results of the RMS analysis for the moisture contaminated samples; **a** E index, **b** three-sigma index

Fig. 3.89 Result of the whole area analysis for moisture contaminated samples; **a** E index, **b** three-sigma index

moisture content. For this reason, a new set of measurements was conducted. The time signals were registered in a dense grid of measurement points defined at the whole sample surface. Again, the E and three-sigma indexes were calculated. It should be noted that these measurements were taken after some time, so the moisture content was slightly different than the results depicted in Fig. 3.88. The new results for the whole area scan are presented in Fig. 3.89. It can be observed that the dry reference samples (zero moisture content) differ slightly from each other. This could be caused by slight differences in surface quality that influence the reflection of the vibrometer laser beam. However, the more important observation is that the reference sample results clearly differ from those of the samples with moisture.

3.7.2.2 Vibrometry Inspection Results for Pilot Level Samples

In the next step, pilot samples were investigated using whole area analysis. The production samples contaminated with both release agent (RA) and fingerprints (FP) had a curved shape, so they were measured from both sides. The results for the convex side are presented in Fig. 3.90. The values for the reference samples do not differ significantly. The E and three-sigma values for contaminated samples are dispersed. The II-P-RA1+FP3-2 and II-P-RA2+FP3-2 samples have similar values as the reference samples. Looking at the results for the concave side, see Fig. 3.91, it can be noted that the scale is 10 times larger. This could be related to the different

Fig. 3.90 Results of the full-field analysis for the production pilot samples with combined RA+FP contamination; convex side; **a** E index, **b** three-sigma index

Fig. 3.91 Results of the full-field analysis for the production pilot samples with combined RA+FP contamination; concave side; **a** E index, **b** three-sigma index

Fig. 3.92 Results of the full-field analysis for the repair pilot samples with combined TD+DI modification; **a** E index, **b** three-sigma index

surface quality and shape of this side. The behavior of the reference samples is no longer uniform. The difference between the reference and contaminated samples is also not evident.

The pilot samples for the repair user case comprised a mixed modification by thermal degradation (TD) and de-icing fluid contamination (DI). These samples were scarfed samples with a smoothly decreasing thickness. They were measured only from the side with decreasing thickness. The results are depicted in Fig. 3.92. Apart from the three reference samples, one sample that was only treated thermally was measured (TD1) for comparison with samples with mixed modification. The reference samples differ from each other. The TD1 sample result is within the interval given by the reference sample measurements. There is no clear separation between the TD1+DIx results and the values for the reference samples.

3.7.3 Final Remarks

In the research reported in this subchapter, the laser vibrometry measurements were first conducted at points defined along the samples' diagonal. A signal processing method was applied that allowed the wavenumber to be extracted as a function of frequency. Based on this relationship, the wave group velocity was estimated. The most promising results were observed for the moisture contamination, although the samples were not fully saturated with moisture. The used approach was local, so only a limited part of the sample was measured (diagonal measurement). However, as the waves propagated in the whole sample, the change in the wave field caused by the surface modification may have been too weak to be noticed after the wave had traveled a considerable distance (from the transducer to the edges and then to the

measurement point). Considering that the presence of degradation or contamination can have a very slight influence on the wave, a new approach was proposed based on full-field measurements. The time signals were registered in a dense grid of measurement points defined at the sample surface. It was decided to choose an index that could give information about the average state of the surface because it was assumed that the real distribution of the contaminant/degradation is unknown. It was observed that the samples contaminated with moisture clearly differed from the reference samples. However, a sensitivity to the moisture level was not observed in the results. The pilot samples for the production user case were measured from both sides due to their curvature, and the results obtained for the reference samples on the convex side were comparable; however, this was not observed for the concave side. Regarding the contaminated samples, it cannot be clearly stated that they differ from the referential samples. In the case of the pilot samples from the repair user case, the reference samples differ from each other. There is no clear separation between the results for the modified samples and the values for the reference samples. The same approach applied to the realistic part also showed no sensitivity to the contamination of the surface. This could be associated with the type of contamination used.

3.8 Laser-Induced Fluorescence (LIF)

In this section, we introduce laser-induced fluorescence (LIF) as a tool for surface quality assessment and detail how its performance was enhanced in the ComBoNDT project for the in-process monitoring of CFRP adherends.

3.8.1 Principle and Instrumentation

LIF is a technique based on the analysis of the spontaneous emission of atoms or molecules excited with a laser, whereby the analyzed material can be in the gas, liquid, or solid-state phase. Typical instrumentation for LIF analysis consists of a laser to illuminate the investigated material and a detection system to record the fluorescence. Depending on the chemical composition of the analyzed material, the laser can be tuned to match the wavelength to the absorption lines or bands of specified atoms or molecules, producing an electronically excited state that can radiate. The fluorescence emission can be detected using bandpass filters and sensitive detectors, i.e., photomultipliers in the case of specified spectral band analysis or monochromators equipped with sensitive CCD detectors for full spectra recording. Since the fluorescence signal is much weaker than the excitation laser radiation, a laser cutoff filter is recommended in the detection system. The LIF analysis can be provided in two regimes: (i) the time-integrated mode, in which the spectra are integrated over a long time—in this mode both CW and pulsed lasers can be used for sample excitation;

(ii) the time-resolved mode, in which the fluorescence decay is taken into account—this mode requires a short pulse duration of the excitation laser. The fluorescence spectrum is usually represented as a combination of vibrational, rotational, and fine structures, depending on the chemical composition and spectral range. In the case of composite materials characterized by complex chemical composition, the fluorescence bands usually overlap, but subtle changes in the structure of the material can still be seen as changes in the intensity or profile of the fluorescence spectrum.

The main advantages of the LIF technique are its sensitivity, spatial and temporal resolution as well as the non-invasive nature of the analysis. Measurements can be provided for the individual points on the material, or large areas of the surface can be scanned with a laser to visualize the local structure or composition changes [37]. The analysis does not require sampling, and the measurement can be performed on the tested object. The detection of kerosene and hydraulic fluid on CFRP surfaces has been previously reported [38]. Good results were obtained for 266 nm excitation. In another work [39], three wavelengths were studied (266, 355, and 532 nm). The detection of hydraulic fluid, release agent, and moisture contaminations as well as thermal treatment has also been presented. It was shown that at 532 nm, the thermal treatment can be easily distinguished from the remaining cases. Moreover, it was shown that samples treated at 190, 200, and 210 °C are characterized by increasing LIF intensity and can be distinguished from each other and from reference samples.

For the results presented in the next sections of this chapter, the sample excitation was provided by a CW DPSS Nd:YAG laser operating at 532 nm (Spectra Physics). The laser power was set to 0.2 W and the laser intensity was 1 W/cm² (5 mm laser spot diameter). The spectra of the laser-induced fluorescence (LIF) were recorded in the time-integration mode. The emission spectra were dispersed by a SR-303i 0.3 m spectrograph equipped with gratings of 600 and 150 grooves/mm and coupled to a time-gated ICCD camera DH 740 (Andor Tech). Spectra were acquired in the range of 300–800 nm with resolutions of 0.3 nm or 1.2 nm. An illustration of the setup is presented in Fig. 3.93.

3.8.2 LIF Results

3.8.2.1 LIF Results on Coupon Level Samples

In the set of coupon level samples, two groups of samples were investigated. The first examined production-related contaminations of the samples, and the second focused on repair-related modifications/contaminations of the samples. The sample set investigated for the production user case comprised three reference samples, nine samples contaminated with a release agent, nine samples contaminated with fingerprints (artificial sweat), and nine samples contaminated with moisture. The sample set investigated for the repair user case comprised three reference samples, nine thermally degraded samples, nine samples contaminated with de-icing fluid, nine samples contaminated with oily fingerprints (containing Skydrol hydraulic oil), and

Fig. 3.93 LIF equipment used for the investigations

six samples with mixed modifications obtained by combining thermal degradation and contamination with de-icing fluid.

Firstly, the reference samples from both user cases were compared. The fluorescence spectra were measured and then the area under the curve (LIF intensity) was taken for comparison, see Fig. 3.94. The production and repair user case samples differed significantly. The fluorescence intensity from the surface of the production samples was four times stronger than for the repair user case, see Fig. 3.95. The reason for this could stem from the surface preparation. The repair user case samples were ground down to the fibers in order to simulate the preparation for bonding repair, while the production user case samples were only slightly ground. Due to this difference, the modified samples from the repair user case should be compared with the respective reference samples. An analogous approach should be used for the production samples.

The results for the release agent contamination are depicted in Fig. 3.95. All the contaminated samples have a similar intensity to the reference samples. In the case of fingerprint contamination, the behavior is similar. The results for the contaminated samples are similar to the reference cases within the boundaries defined by the standard deviation, see Fig. 3.96. There is no correlation between the LIF intensity and the release agent or fingerprint contamination level.

Fig. 3.94 An example of registered LIF spectra

Fig. 3.95 LIF technique: Results for the three reference (RE) samples from each of the two user cases, namely a production (P) and a repair (R) aeronautical user case, involving flat CFRP coupons

Fig. 3.96 LIF results for the production (P) user case as obtained for each of the three CFRP coupons (1, 2, and 3) that had been intentionally treated following a release agent contamination (RA) scenario at three distinct contamination levels (1, 2, and 3)

The first results for the repair user case are presented in Fig. 3.97 for the de-icing fluid contamination. These results are characterized by high dispersion (wide standard deviation bars). Some samples (I-R-DI-1-1, 1-3, 2-1, 3-3) are characterized by significantly low-intensity values, but these do not correspond to the same contamination levels. The LIF intensity for oily fingerprint contamination, see Fig. 3.98 increases with increasing contamination. However, considering the intensity values for the reference samples, it becomes clear that these are located between the results for the two highest contaminations levels I-R-FP2-x and I-R-FP3-x. Considering the results for thermal degradation, a high response is observed at the first level (I-R-TD-1-x), see Fig. 3.99. This case was achieved by keeping the samples in an oven at 220 °C. The samples I-R-TD-2-x and I-R-TD-3-x were treated at higher temperatures, and there is no correlation between the intensity and the used temperature. Moreover, the response is very uniform. All six samples have a comparable level of mean intensity, and the standard deviation is low.

In a previously published work [39], there was a good detection of the thermal damage scenario with the LIF intensity measurement with 532 nm excitation. Different levels of thermal treatment correlated with the intensity level. The intensity value increased with the increasing temperature of the treatment. However, here we see different behavior. The first important difference is that the new samples (I-R-TD) were ground down to the fibers, whereby the previously investigated samples were measured just after the thermal treatment without any surface modification

Fig. 3.97 LIF results for the production (P) user case as obtained for each of the three CFRP coupons (1, 2, and 3) that had been intentionally treated following a fingerprint contamination (FP) scenario at three distinct contamination levels (1, 2, and 3)

[39]. It is possible that the thermal treatment only influenced the surface layer, which was removed by the grinding, and thus the intensity increase could no longer be observed. The second important difference is that the I-R-TD-2-x and 3-x samples were treated at higher temperatures than before. Crucially, the other side of the sample was not prepared/modified in any way. It was decided to measure this second side and compare the results with those previously obtained, see Fig. 3.99. The new result is presented in Fig. 3.100. Again, the highest intensity is observed for the I-R-TD-1-x samples and, as before, the I-R-TD-2-x and I-R-TD-3-x samples have intensity values on the level of the reference samples. There is also a clear difference in the vertical scale between Figs. 3.99 and 3.100. This could be related to the considerable time interval between these two measurements. Thus, the obtained results suggest that treatments at 260 and 280 °C have different influences on the sample and that the LIF intensity is not influenced.

With the knowledge that the 220 °C (I-R-TD-1-x) scenario can be detected and distinguished, the combined modification scenario for the remaining cases was investigated. This set was treated at the same temperature and subsequently contaminated with de-icing fluid. Figure 3.101 presents the results for this new set of samples with mixed modification (I-R-TD1+DI) in comparison with the clear reference samples (I-R-RE) and samples that had only undergone thermal treatment at 220 °C (I-R-TD1-x). The first observation is that the combined modification was detected. It clearly differs from the reference. The higher level of de-icing fluid (DI-2) contamination

Fig. 3.98 LIF results for the repair (R) user case as obtained for each of the three CFRP coupons (1, 2, and 3) that had been intentionally treated following a de-icing fluid contamination (DI) scenario at three distinct contamination levels (1, 2, and 3)

is not related to any increase or decrease in relation to the lower level (DI-1). What we can observe is that the intensities for the samples with mixed modification have higher values than for the pure thermal treatment (I-R-TD-1-x). However, taking into consideration the standard deviations, all the results after modifications (I-R-TD-1-x and I-R-TD1+DI) lie within the boundaries of standard deviation for the I-R-TD-1-1 sample, see Fig. 3.102.

3.8.2.2 Conclusions

The conducted research showed that the thermal treatment at 220 °C could be clearly distinguished from the samples based on the intensity measurement conducted on both sides of the sample. Above 220 °C, the LIF intensity gives results comparable to the reference samples. No sensitivity to any of the higher thermal treatment levels was observed. The thermal treatment level could not be determined for 532 nm excitation. Taking into account the results presented in this paper as well as previously published results [39], it can be concluded that thermal degradation up to 220 °C can be distinguished. Moreover, it was shown that the detection of thermal degradation at 220 °C was possible even if the surface was subsequently contaminated with de-icing fluid. The other contaminations investigated in the production and repair user

Fig. 3.99 LIF results for the repair (R) user case as obtained for each of the three CFRP coupons (1, 2, and 3) that had been intentionally treated following a fingerprint (with hydraulic oil) contamination (FP) scenario at three distinct contamination levels (1, 2, and 3)

cases of the ComBoNDT research project did not influence the LIF intensity in a way that the level of contamination could be distinguished. The results obtained for the Skydrol (FP) and release agent (RA) contaminations confirm previously published observations, namely that the LIF intensity observed for 532 nm excitation is not correlated to the amount of surface contamination. This was also observed for the realistic aircraft part, see Fig. 3.103.

3.9 Conclusion

We identified, defined, and intentionally implemented pre-bond contamination on CFRP surfaces in gradational levels. The respective CFRP parts were introduced as adherends in a qualified bonding process within two user cases involving different part geometries, namely flat coupons, curved pilot level specimens, and realistic or real CFRP parts, thereby contributing to the findings reported in Chap. 5. In this chapter, we described the findings obtained during the surface quality assessment with the ENDT methods that were advanced in the ComBoNDT research project for production and repair user cases relevant in aeronautical applications.

Fig. 3.100 LIF results for the repair (R) user case as obtained for each of the three CFRP coupons (1, 2, and 3) that had been intentionally treated following a thermal impact (TD) scenario at three distinct temperature levels (1, 2, and 3)

The in-process monitoring of CFRP composite surfaces was facilitated through the use of advanced setups and approaches based on the aerosol wetting test (AWT) performed with an enhanced bonNDTinspect[®] device by the consortium partner Automation W+R, optically stimulated electron emission (OSEE) performed by Fraunhofer IFAM, electronic nose (e-nose) testing performed by ENEA and Airbus, laser-induced breakdown spectroscopy (LIBS) performed by Fraunhofer IFAM, Fourier-transform infrared spectroscopy (FTIR) performed by Airbus, laser-induced fluorescence (LIF) performed by IMPPAN, and vibrometry inspection performed by IMPPAN.

Advanced ENDT procedures comprising in-process surface inspection with:

- an enhanced setup relying on AWT allowed for a differentiation between the surface states of clean and intentionally contaminated parts with the potential to discriminate between distinct levels of contamination for several contamination scenarios. This technology can be integrated into inline applications without major constraints.
- an enhanced setup relying on OSEE enabled detection of even small amounts of filmy contaminations. Therefore, this technique is most suited for specialized applications that require very clean and homogeneous surfaces.
- two enhanced setups relying on e-nose provided insight in the approach to combine custom-made-of-the-shelf (Airsense, Airbus E-Nose) with “open source” from

Fig. 3.101 The result for the repair user case for the thermal degradation of CFRP coupons; fluorescence intensity measured on the back face of the samples

scratch developed systems (ENEA). Considering smart sample taking and total system control seems to be the best path to further advance the sensor system performance of the e-nose method, which provides possibilities like a combined mode of operation to detect the chemical surface condition (clean or contaminated) at the same time as the moisture content.

- an enhanced setup relying on LIBS was used to map out contamination from coupon level sample to complex-shaped, technologically realistic CFRP parts. Using this approach, even locally applied contaminants can be detected on large areas in a realistic production environment.
- an enhanced setup relying on FTIR permitted detection and quantification of thermal degradation, the amount of moisture uptake inside an assembly, and de-icing fluid contaminations.
- an enhanced setup relying on LIF allowed for detection of thermal degradation at 220 °C.
- an enhanced setup relying on Vibrometry inspection facilitated moisture detection.

In summary, our investigations revealed that in certain scenarios within user cases relevant for aeronautical applications, the ENDT methods of AWT, OSEE, e-nose, LIBS, FTIR, LIF, and vibrometry inspection are sensitive to impacts on CFRP specimen surfaces that would induce a bond strength reduction if these CFRP parts were to be used as adherends in a bonding process. The advanced ENDT methods can, therefore, be utilized to identify not-in-order (n.i.o.) adherend surfaces and—based

Fig. 3.102 LIF results for the combined modifications of the surface compared with the thermal treatment at the first level and referential results

on the findings for design-relevant mechanical adhesive joint properties reported in Chap. 2—also not-ready-to-bond adherend surface states. In the final research chapter of this book (Chap. 5), we underline this perception and prognosis with findings highlighting the performance of ENDT for the monitoring of quality-relevant operand features in adhesive bonding processes involving parts of real aerospace structures with stringers.

Fig. 3.103 LIF results of the realistic aircraft part inspection; blue bars correspond to clean areas; red bars correspond to contaminated areas; the numbers denote the inspected areas

References

1. Tornow C, Schlag M, Lima LCM et al (2015) Quality assurance concepts for adhesive bonding of composite aircraft structures—characterisation of adherent surfaces by extended NDT. *J Adhes Sci Technol* 29:2281–2294. <https://doi.org/10.1080/01694243.2015.1055062>
2. ComBoNDT “Quality assurance concepts for adhesive bonding of aircraft composite structures by advanced NDT” (2015–2018) Project funded from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 636494
3. Smith T (1983) Surface quality unit for inspection by nondestructive testing (SQUINT). In: 15th national SAMPE technical conference
4. Parker BM, Waghorne RM (1991) Testing epoxy composite surfaces for bondability. *Surf Interface Anal* 17:471–476
5. Tornow C, Schlag M, Cavalcanti W et al (2018) In-process quality assurance procedures for surface preparation in adhesive bonding of lightweight composite structures. In: 6th world congress on adhesion and related phenomena
6. Ledesma RI, Yost WT, Palmieri FL et al (2019) Optically stimulated electron emission analysis of surface contamination levels on epoxy composites and effect on failure mode of adhesively bonded specimens, p 70005
7. Mahmud KT, Chawla MK (1989) OSEE determination of fluorocarbon lubricant film thickness on magnetic disk media. *Solid State Technol* 32:135–136

8. Moutsompegka E, Tserpes K, Noeske M et al (2019) Experimental investigation of the effect of pre-bond contamination with fingerprints and ageing on the fracture toughness of composite bonded joints. *Appl Compos Mater* 26:1001–1019. <https://doi.org/10.1007/s10443-019-09763-9>
9. de Vito S, Massera E, Miglietta M et al (2016) Detection and quantification of composite surface contaminants with an e-nose for fast and reliable pre-bond quality assessment of aircraft components. *Sens Actuators B Chem* 222:1264–1273
10. Nakamoto T (ed) (2016) *Essentials of machine olfaction and taste*. Wiley, Singapore
11. Röck F, Barsan N, Weimar U (2008) Electronic nose: current status and future trends. *Chem Rev* 108:705–725
12. Fonollosa J, Fernández L, Gutiérrez-Gálvez A et al (2016) Calibration transfer and drift counteraction in chemical sensor arrays using direct standardization. *Sens Actuators B Chem* 236:1044–1053
13. Fernandez L, Guney S, Gutierrez-Galvez A et al (2016) Calibration transfer in temperature modulated gas sensor arrays. *Sens Actuators B Chem* 231:276–284
14. Reidt U, Helwig A, Plobner L et al (2017) Detection of microorganisms onboard the international space station using an electronic nose. *Gravit Space Res* 5:89–111
15. Katnam KB, Da Silva LFM, Young TM (2013) Bonded repair of composite aircraft structures: a review of scientific challenges and opportunities. *Prog Aerosp Sci* 61:26–42
16. Petrone G, Bruno M, Bocchetto F et al (2016) An innovative health monitoring system for aircraft landing gears. In: *Proceedings of the European workshop on structural health monitoring (EWSHM 2016)*, pp 235–244
17. Markatos DN, Tserpes KI, Rau E et al (2013) The effects of manufacturing-induced and in-service related bonding quality reduction on the mode-I fracture toughness of composite bonded joints for aeronautical use. *Compos B Eng* 45:556–564
18. Moutsompegka E, Tserpes KI, Polydoropoulou P et al (2017) Experimental study of the effect of pre-bond contamination with de-icing fluid and ageing on the fracture toughness of composite bonded joints. *Fatigue Fract Eng Mater Struct* 40:1581–1591
19. Tserpes KI, Markatos DN, Brune K et al (2014) A detailed experimental study of the effects of pre-bond contamination with a hydraulic fluid, thermal degradation, and poor curing on fracture toughness of composite-bonded joints. *J Adhes Sci Technol* 28:1865–1880. <https://doi.org/10.1080/01694243.2014.925387>
20. Markatos DN, Tserpes KI, Rau E et al (2014) Degradation of mode-I fracture toughness of CFRP bonded joints due to release agent and moisture pre-bond contamination. *J Adhes* 90:156–173
21. Marco S, Gutierrez-Galvez A (2012) Signal and data processing for machine olfaction and chemical sensing: a review. *IEEE Sens J* 12:3189–3214
22. de Vito S, Esposito E, Salvato M et al (2018) Calibrating chemical multisensory devices for real world applications: an in-depth comparison of quantitative machine learning approaches. *Sens Actuators B: Chem* 255:1191–1210
23. Helwig A, Hackner A, Müller G et al (2018) Self-test procedures for gas sensors embedded in microreactor systems. *Sensors* 18. <https://doi.org/10.3390/s18020453>
24. Salvato M, de Vito S, Esposito E et al (2016) An holistic approach to e-nose response patterns analysis—an application to nondestructive tests. *IEEE Sens J* 16:2617–2626
25. Maier K, Helwig A, Müller G (2017) Room-temperature dosimeter-type gas sensors with periodic reset. *Sens Actuators B: Chem* 244:701–708. <https://doi.org/10.1016/j.snb.2016.12.119>
26. de Vito S, Miglietta ML, Massera E et al (2017) Electronic noses for composites surface contamination detection in aerospace industry. *Sensors (Basel)* 17. <https://doi.org/10.3390/s17040754>
27. Salvato M, de Vito S, Miglietta M et al (2017) Hydraulic oil fingerprint contamination detection for aircraft CFRP maintenance by electronic nose. In: *2017 ISOCs/IEEE international symposium on olfaction and electronic nose (ISOEN)*. IEEE, pp 1–3

28. AIRSENSE analytics GmbH portable electronic nose. <https://airsense.com/en/products/portable-electronic-nose>
29. Ricciardella F, Massera E, Polichetti T et al (2014) A calibrated graphene-based chemi-sensor for sub parts-per-million NO₂ detection operating at room temperature. *Appl Phys Lett* 104:183502
30. Pasquini C, Cortez J, Silva LMC et al (2007) Laser induced breakdown spectroscopy. *J Braz Chem Soc* 18:463–512
31. Ledesma R, Palmieri F, Connell J (2020) Laser induced breakdown spectroscopy of polymer matrix composites for real-time analysis of trace surface contaminants: a review. *Int J Adhes Adhes* 98:102528. <https://doi.org/10.1016/j.ijadhadh.2019.102528>
32. Heckner S (2017) Zerstörungsfreie Prüfmethode zur Oberflächencharakterisierung von kohlenstofffaserverstärkten Kunststoffen. Dissertation, Technische Universität München
33. Ruzzene M (2004) Simulation and measurement of ultrasonic waves in elastic plates using laser vibrometry. In: AIP conference proceedings. AIP, pp 172–179
34. Ruzzene M (2007) Frequency–wavenumber domain filtering for improved damage visualization. *Smart Mater Struct* 16:2116–2129. <https://doi.org/10.1088/0964-1726/16/6/014>
35. Sohn H, Dutta D, Yang JY et al (2011) Delamination detection in composites through guided wave field image processing. *Compos Sci Technol* 71:1250–1256. <https://doi.org/10.1016/j.compscitech.2011.04.011>
36. Flynn EB, Lee, JR, Jarmer GJ et al (2012) Frequency-wavenumber processing of laser excited guided waves for imaging structural features and defects. In: Proceedings of the 6th European workshop on structural health monitoring, Dresden, Germany
37. Ludeker W, Gunther KP, Dahn HG (1995) Comparison of different detection set-ups for laser induced fluorescence monitoring of vegetation. *EARSel Adv Remote Sens* 3
38. Wachinger G, Meer T, Sea B (2012) Detection of contaminants—a key aspect for composite adhesive repair bonding. In: ECCM15—15th European conference on composite materials
39. Malinowski PH, Sawczak M, Wandowski T et al (2014) Characterisation of CFRP surface contamination by laser induced fluorescence. In: Kundu T (ed) Health monitoring of structural and biological systems 2014. SPIE, 90640E

Open Access This chapter is licensed under the terms of the Creative Commons Attribution 4.0 International License (<http://creativecommons.org/licenses/by/4.0/>), which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license and indicate if changes were made.

The images or other third party material in this chapter are included in the chapter's Creative Commons license, unless indicated otherwise in a credit line to the material. If material is not included in the chapter's Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder.