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Abstract. Nowadays Toxic Industrial Components (TICs) and Toxic Industrial Materials (TIMs) are one of the most dangerous and diffuse vehicle of contamination in urban and industrial areas. The academic world together with the industrial and military one are working on innovative solutions to monitor the diffusion in atmosphere of such pollutants. In this phase the most common commercial sensors are based on "point detection" technology but it is clear that such instruments cannot satisfy the needs of the smart cities. The new challenge is developing stand-off systems to continuously monitor the atmosphere. Quantum Electronics and Plasma Physics (QEP) research group has a long experience in laser system development and has built two demonstrators based on DIAL (Differential Absorption of Light) technology could be able to identify chemical agents in atmosphere. In this work the authors will present one of those DIAL system, the miniaturized one, together with the preliminary results of an experimental campaign conducted on TICs and TIMs simulants in cell with aim of use the absorption database for the further atmospheric an analysis using the same DIAL system. The experimental results are analysed with standard multivariate data analysis technique as Principal Component Analysis (PCA) to develop a classification model aimed at identifying organic chemical compound in atmosphere. The preliminary results of absorption coefficients of some chemical compound are shown together pre PCA analysis.

Keywords - Dial; TIC, TIM,

1. Introduction

Nowadays the risk of a release of a chemical release is higher than in the past [1]. The real challenge is getting not only a better knowledge on risks, agents, protection-decontamination [2], detection and identification and investigation techniques, but also the establishment of a doctrine on prevention capabilities (referred to new non-proliferation methodologies), and learning to face non-conventional events and to manage their very consequences. The development of new technologies to

detect and identify chemical agents (CA) will be the focus of the paper, the author will approach new methodologies to face this problem [3].

The CAs release may be divided into two main categories: natural events (that provokes accidents having as consequences the CAs dispersion), man-made accidents that are respectively divided unintentional or intentional. [4]

One the most well-known unintentional events was the one occurred in 1976 in Seveso, Italy, where a dense vapor cloud was released from a chemical plant manufacturing pesticides and herbicides. In Europe, the Seveso accident prompted the adoption of legislation aimed at the prevention and control of such accidents. The toxic cloud contained tetrachlorodibenzoparadioxin (TCDD), a by-product of the trichlorophenol synthesis, also known as Seveso dioxin. TCDD has poisonous and carcinogenic properties with an LD_{50} of 0.02 mg/kg. Although no fatalities were reported, soon after its release a large amount of different toxic chemicals were dispersed in the environment and spread on a large area. This resulted in the immediate contamination of some ten square miles of land and vegetation. More than 600 people had to be evacuated from their housings and as many as 2000 were treated for dioxin poisoning [5] Moving to recent years, another chemical, accident related event is the one occurred in Viareggio, Italy, in 2009. The Viareggio derailment of a freight train and subsequent fire occurred on June 29, 2009, in a railway station in Viareggio, (province of Lucca), a city in Central Italy's Tuscany region. Some of the wagons were reported to have been carrying Liquefied Petroleum Gas (LPG). Two of these exploded and caught fire. Seven people were reported to have died in a building collapse.

In order to face the problem of a CA contamination there are several actions that have to be taken, the capability to rapidly detect and identify the contamination is an imperative. This knowledge allows the severity and extent of a hazard to be assessed so that areas that are clean or contaminated can be identified. Furthermore, the information acquired by these systems provides advice to military commanders and first responders, regarding the donning of individual protective equipment (IPE), sampling, handling and analysis procedures as well as medical countermeasures, should the need arise. An ideal detector can be described as one that can detect both CWAs and toxic industrial chemicals (TICs)/toxic industrial materials (TIMs) selectively within an acceptable time; sensitive enough to detect agent concentrations at or below levels which pose a health risk, and not be affected by other factors in the environment. The detector should have a rapid reaction and recovery time whilst being portable, easy to operate and produce data that is easily interpreted. As yet, the 'ideal' detector is not a commercial reality.

The Quantum Electronics and Plasma Physics Research Group[1] (QEP) of Department of Industrial Engineering has a long experience in stand off detection and identification development of apparatus based on laser systems [6-16] and in this paper a new demonstrator developed based on differential light absorption principle will be presented together with a PCA technique for data analysis applied by the our Department of Electronic Engineering. Preliminary result of absorption coefficient database joint with discrimination analysis will be reported and discussed.

2. Material and methods

Optical remote sensing, remote analysis by means of light, consist in a two-steps analysis: the first step consists in a proper excitation of the medium under study by sending into it radiation at optical frequencies, the second step consists in collecting from it a suitable light signal which has the property of being a direct or indirect carrier of the information needed about the interaction. Therefore, we need a suitable light source as a light transmitter. The receiving antenna usually could be a lens/objective or a telescope. It has the task to collect the light on a detector for the conversion of the optical signal in an electrical one in which is much easier to handle [17-29].

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[1] www.qepresearch.it

2.1 Experimental demonstrator and its principle of work

The literature present [17-29] affirms that the LIDAR (Light Detection And Ranging) techniques can be used only to provide an alarm in case of chemical release. In case of chemical events, it is essential to deploy also systems able to identify the chemical substances released. For this reason, the QEP research group are developing a mini-Dial system multi-wavelengths based named TELEMACO. The Dial technology usually employs two different wavelengths in order to measure the concentration profiles of an investigated molecule. In the case of organic substance unfortunately the absorption spectra show different overlaps causing interference phenomena that do not allow the recognition using the classical dial methodologies based only couples of laser lines [30]. The Dial multi-wavelengths methodologies, instead could be applied in order to identify the organic compounds using backscattering signals from different wavelengths Consequently, a fingerprint database is required, composed by a collection of absorption coefficients to identify molecules and to minimize the risk of wrong detections or false alarms. Actually data mining techniques have been developed to analyse the database of fingerprints in order to selected, for every organic compound, the minimum number of laser lines essential to identify the gas minimizing false alarm conditions.

Nowadays there is not such a collection of data in the scientific and technical literature. Furthermore the exactly value of absorption coefficients is influenced by the type of light source adopted. The mini TEA CO_2 laser (characteristics reported in table 1) is adopted for mini DIAL system TELEMACO. Preliminarily the mini TEA CO_2 laser is been used for absorption coefficient measurements made with cells filled with the investigated molecules. In this way we have obtained a preliminary results of proper fingerprint database, necessary for future application in atmosphere in order to identify dangerous molecules.

Table 1. TEA CO_2 Laser characteristics.

Transmitter TEA CO_2 laser	
Output power	10^9 W
Beam divergence	0.77 mrad
Spectral range	9:11 µm
Receiver	
Primary ROC	1300 mm
Primary diameter	250 mm
ZnSe focal length	10 mm
Detector type	HgCdTe
Detector Sensitivity D*	$3.38 \cdot 10^{10}$ cmHZ$^{1/2}$/W
Detector size	1 mm^2

There are two principal reason because the CO_2 laser has been chosen: first it is eye safe and, second because it covers a spectral band where there is good absorption for this kind of molecules. The preliminary measurements are carried out in laboratory in order to evaluate the different spectrum of several aggressive chemical compounds. A picture of absorption layout assembled in laboratory for in cell measurements using the same laser of TELEMACO is shown in Figure 1:

Figure 1. Laboratory absorption cell apparatus.

The absorption setup is based on a TEA CO_2 laser tuneable over 60 wavelengths, from 9 to 11 μm, and it has been fully equipped with an electronic micrometer to automatically rotate the diffraction grating and then is able to change the wavelengths.

The absorption coefficient $\alpha(\lambda_i)$ for the i-esima λ_i is calculated by the ratio between the transmitted I_T beam energy and the measured one by the sensor number 2 (Transmitted intensity - I_T) and by the sensor number 1 (Incident intensity - I_0). Indicating with β the reflectance of the beam splitter, the equations 1, 2 and 3 relate the three intensities:

$$I_1 = \beta \cdot I \quad (1)$$

$$I_0 = (1 - \beta) \cdot I \quad (2)$$

$$I_T = I_0 A_f A_g = (1 - \beta) \cdot I \cdot A_f A_g \quad (3)$$

where I is the intensity of the laser pulse Incident (I_1) reflected Intensity and (I_0) transmitted separated by beam splitter. The transmitted pulse is sent on absorption cell given a transmitted intensity (I_T) by cell and A_f and A_g represents respectively the attenuation of the laser beam due to the windows of the cell and the gas inside the cell (that is the CAs). In order to evaluate the gas attenuation it is need evaluate before the absorption due to at layout adopted as attenuation of the bean splitter and wavelength dependences or conversion coefficients of energy monitor. The dependency of

the values β and A_f and this can be achieved studying the response of an empty cell (CV) and calculating for this particulate case the ratio I_T/I_1. The solution at this problem in the follow equation is given:

At the first the transmitted intensity of at empty cell is measured:

$$I_T^{CV} = I_0 A_f = (1 - \beta) \cdot I \cdot A_f \quad (4)$$

So the ratio measured with the empty cell will be (5):

$$\left(\frac{I_T}{I_1}\right)_{CV} = \frac{(1 - \beta) \cdot I \cdot A_f}{\beta \cdot I} = \frac{A_f}{\beta} \quad (5)$$

Then the value is computed for the CAs inside the cell (6):

$$\left(\frac{I_T}{I_1}\right)_{CP} = \frac{(1 - \beta) \cdot I \cdot A_f \cdot A_g}{\beta \cdot I} = \frac{A_f}{\beta} \cdot A_g \quad (6)$$

So it is possible evaluate the attenuation A_g (7):

$$\frac{\left(\frac{I_T}{I_1}\right)_{CP}}{\left(\frac{I_T}{I_1}\right)_{CV}} = A_g \quad (7)$$

The absorption value, $\alpha(i)$, is related to the attenuation value by eq. (8):

$$A_g(i) = exp(-\alpha(i) \cdot p \cdot l) \quad (8)$$

Where p is the partial pressure of the gas, in [atm], and l is the length path of the laser beam into the cell, in [cm]. So it is possible to obtain the absorption value, $\alpha(i)$ (9):

$$\alpha(i) = \frac{1}{p \cdot l} \ln \frac{1}{A_g} \quad (9)$$

and the relative error (10):

$$\frac{\Delta\alpha(v)}{\alpha(v)} = \frac{\Delta P}{P} + \frac{\Delta l}{l} + \frac{I_1}{I_T} * \frac{1}{\ln\left(\frac{I_T}{I_1}\right)} * \Delta\left(\frac{I_T}{I_1}\right) \quad (10)$$

2.2 Multivariate data analysis method

Exploiting the information content of the multi-wavelength approach of the LIDAR, each single measurement is characterized by a pattern of absorption coefficients that represent a sort of fingerprint of the volatile compounds composing the air. To analyze this multidimensional data we need to process the experimental measurements by means of multivariate data analysis techniques.

Multivariate analysis consists of a collection of algorithms that can be used when measurements are characterized by a collection of descriptors. Historically, the great part of applications of multivariate techniques have regarded biological and behavioral sciences. Nevertheless, interest in multivariate methods has now spread to different fields of investigation. In this work we have analyzed the experimental results with two different data analysis techniques. The first one is an explorative and unsupervised technique called Principal Component Analysis (PCA).

PCA is a decomposition technique unsupervised used in multivariate data to obtain uncorrelated components. With PCA is maximized the variance of a linear combination of different features and allows to reduce the number of variables and to detect the presence of structure in the relationships between them.

Using PCA is possible to represent a dataset in a graphical representation carrying most of the data variance [32]. In the new representation space, the axes are obtained from a linear combination of the original axes and they are requested to be uncorrelated and orthogonal. In the direction of the largest variance of data is chosen the firs axis, called first "Principal Component". The second Principal Component orthogonal direction to the first PC with largest variance, and so on [32]. The second techniques is k-NN k- Nearest Neighbors one the golden standard classifiers [33]. k-NN is a simple algorithm that classifies new cases based on a similarity measure of k nearest neighbours selected among a pool of training examples.

3. Results

3.1 Experimental results and discussion

The absorption laboratory layout based on the same CO_2 laser source that will be used in TELEMACO DIAL systems is used to get the absorption spectra (see some of them in Figure 2, 3 and 4) that are principal characteristic of each CA.

The following figures 2,3,4 are three examples of the absorption spectra for toluene, trimethylbenzene and n-heptane taken placing few ppm of substance in the cell in two different conditions:

- Pure substances: condition obtained adding the substance in a cell after that a high vacuum has been reached (in the order of 0,1 bar)
- Substance in the air: air is added in the cell starting from the above mentioned set-up till the pressure of 1 atm is reached inside the cell.

These examples shows how clear are the absorption spectra for each substance both in "pure condition" and in "real scenario conditions". The differences between the absorption value of pure gas and an experimental condition closer to reality (air + substances) can be explained with the increase of internal pressure in this second condition,

The small discrepancy between the absorption values measured in two different conditions justifies the use of CAs + air to determinate the absorption value in order to realise a database of fingerprints. It is the starting point to get a fully database of absorptions spectra of the chemical aggressive agents indispensable for applied the dial techniques in order to identify chemical gas in atmosphere.
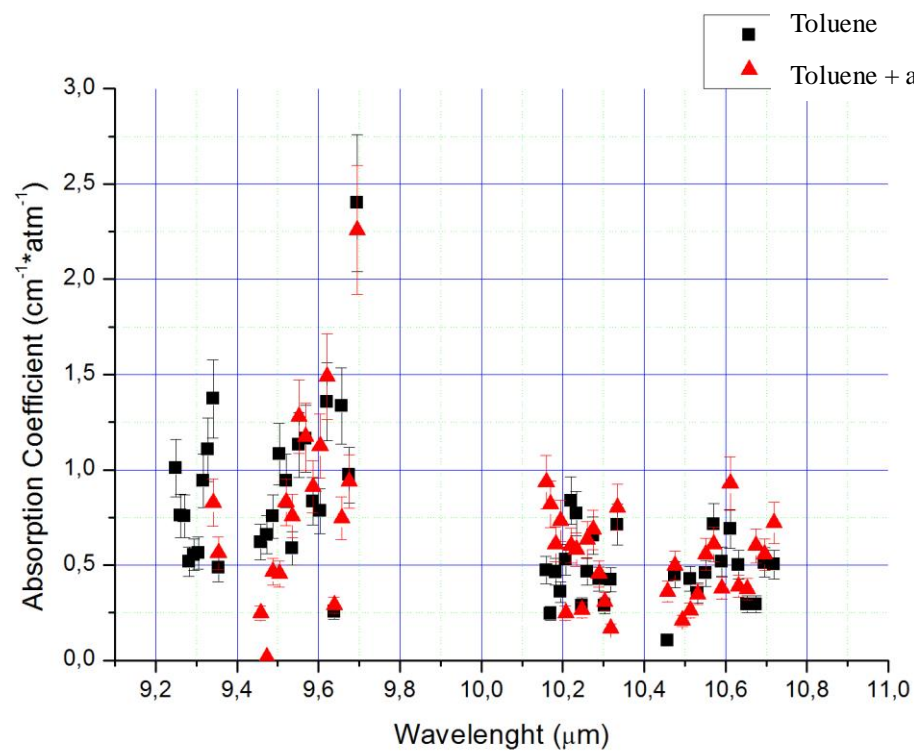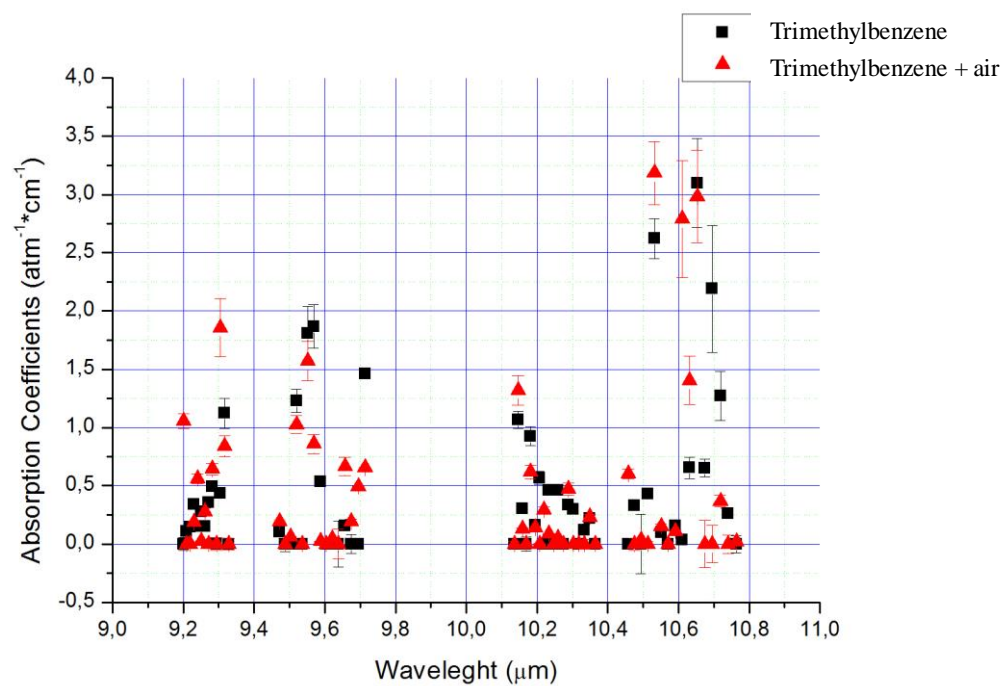
Figure 2. Absorption coefficients of toluene

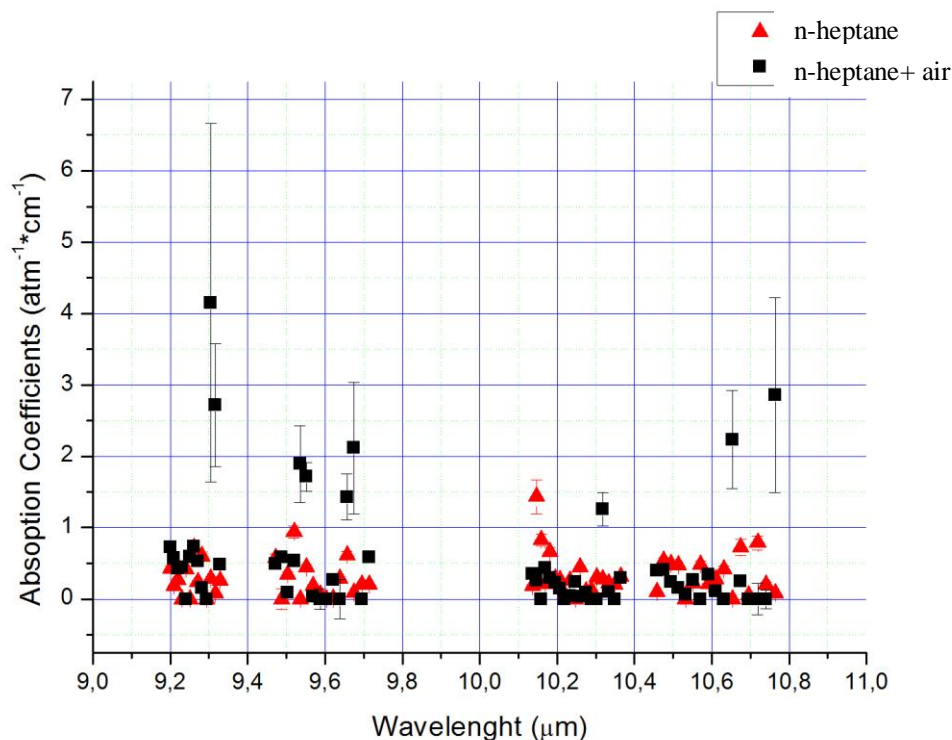**Figure 3.** Absorption coefficients of trimethylbenzene

Figure 4. Absorption coefficients of n-heptane

Observing the figures 2,3,4 is possible assume that :

- The CO_2 laser source is able to produce the absorption spectra that are clearly different and constitute the finger-prints of the TIM/TIC used for the experiments;

- The absorption of the pure substance is almost always higher than the one of substance+air it means that the presence of air provoke a decrease in the absorption coefficient. The behaviour of the spectra is almost the same.

3.2 Discussion of data elaborated with multivariate analysis

Figure 5 shows the scores plot of the first two principal component of the PCA model built with the dataset related to several replicas of 5 different compounds in air:

- Allylic alcohol

- Benzene

- Chlorobenzene

- Methanol

- Piperidine

It is interesting to observe that the different volatile compounds are clearly separated confirming the potentiality of the proposed approach as method to distinguish the different compounds. These

discrimination capabilities is further confirmed by the k-NN classification model that obtains a perfect discrimination score for all the 5 classes with leave 5 out cross validation procedure[33].
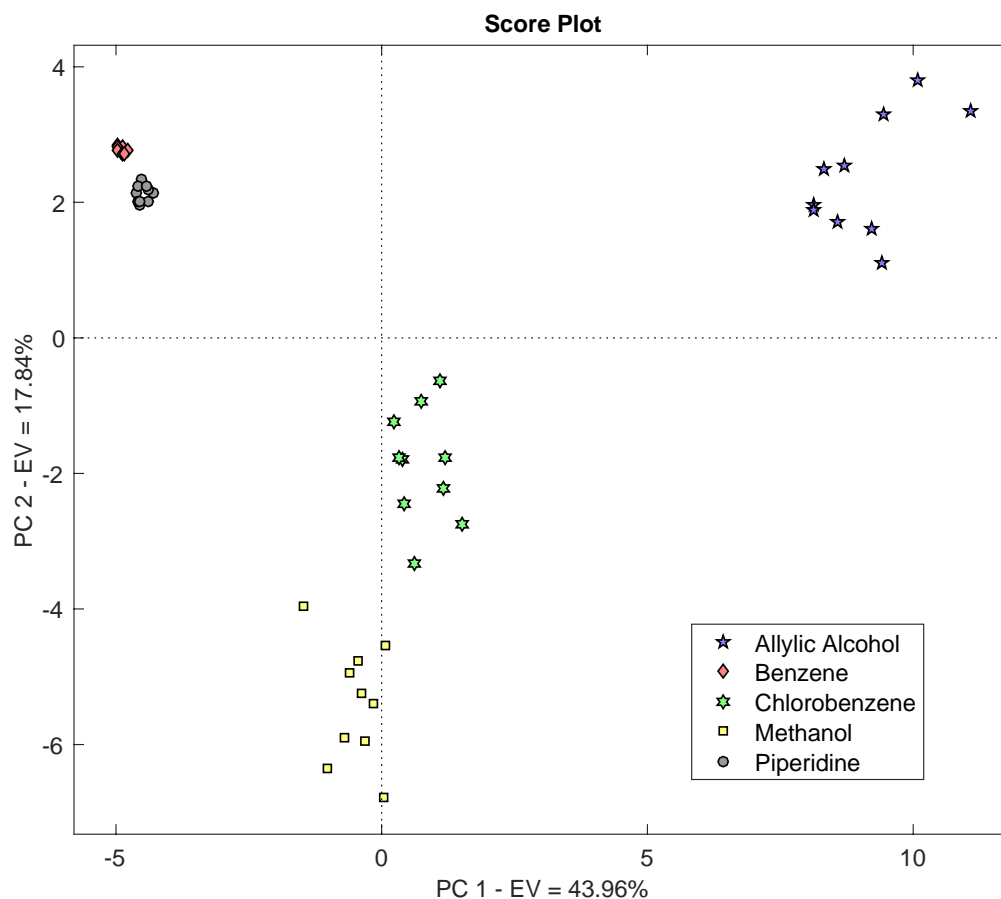

Figure 5. Scores plot of the PCA model built with dataset related to the five measured compounds

4. Conclusions

During the last fifteen years, the authors have demonstrated that laser-based optical techniques can enable a continuous, and quasi real-time, monitoring of particulate and of the CAs, in air for medium-long distances. In particular, the capability of LIDAR systems to detect CAs for the early warning phase and that of the DIAL systems could be used to identify at short-medium range some CAs, so the usefulness of those systems to support (once that the test in field will be done) decision making. The risks of chemical contaminations can be relevant also in healthcare settings and in a number of industrial plants; therefore, it is necessary to guarantee, in all these environments, a continuum monitoring to reduce the probabilities and the magnitude of harmful events. Once that the absorption spectra are obtained it has been necessary find a way to identify the substances starting from the data matrix. The method applied based on PCA and the K-NN classification method allow the identification of all the substances, it means that once prepared a database with all the absorption spectra of the substances it will be possible pass to the identification phase through the mentioned approach. The authors have demonstrated that the use of optical techniques could be a viable solution with a an experiment aimed at identifying five different volatile compounds in air showing promising results. The challenges for the future are: to optimize the systems reducing the dimensions and the

costs, while improving at same time the performances in terms of reduction of false alarms, to increase the robustness, the acquisition speed and the reliability during the acquisition and elaboration data phases.

Acknowledgements

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