

Chemical warfare detection by LIBS

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Abstract

The detection of a chemical agent was demonstrated using a fully optical technique method. Indeed, the LIBS (Laser Induced Breakdown Spectroscopy) technique analyses surfaces in situ, in real time, without any contact or sample preparation. Remote analysis is also possible. LIBS simultaneously detect all elements, including fluorine, chlorine, phosphorous, sulphur and arsenic, traces elements characteristics of warfare agents. At first, specific LIBS experimental conditions are determined in order to detect these elements inside a thin organic film. Then a 1 g/m² of sarin simulant contamination was spread on various substrates, likely to exist in a public building. Fluorine and phosphorous elements were easily detected by LIBS. Besides, a portable LIBS instrumentation dedicated to contamination detection is developed in collaboration between CEA and IVEA SAS. First results obtained on chemical contamination detection with this instrumentation are reported ; several elements as fluorine, chlorine, phosphorous are already detected. Moreover, on site detection of uranium contamination down to 10 mg/m² is achieved with a portable LIBS system. Finally, rocks or alloys are successfully classified by LIBS analysis followed by chemometrics : PCA (Principal Component Analysis) or SIMCA (Soft Independent Modelling by Class Analogy) results are presented. These methods could similarly discriminate and identify a toxic molecular contamination on a substrate.

Keywords: chemical agents, contamination detection, LIBS, transportable instrument.

1 Introduction

Homeland security is of major concern for many states in the world. Worldwide brainstorming is done to look for the weak points in state security and define actions or instruments that could help in increasing security. In particular, optically based techniques are investigated to detect either warfare or industrial chemical agents. Optical systems are now compact and robust, and then can be transported on the crime scene or can make in situ measurement. In some cases, stand-off detection is implemented.

Laser Induced Breakdown spectroscopy is a simultaneous multielemental spectrometry technique, measuring light and heavy elements in the ppm range (parts per million) [1]. LIBS sounds attractive in case of remote, in situ, real time and even stand off applications [2]. Indeed no sample preparation is required, and nowadays transportable instruments are available, together with compact laser and spectrometer. Molecules identification is studied either through elemental detection and ratios estimation, or by statistical data processing methods applied to the spectra [3]. This paper presents the work performed at the French Atomic Energy Commission in collaboration with IVEA [4] to develop a portable LIBS system dedicated to the real time in situ detection of chemical warfare agents.

2 LIBS technique

Laser Induced Breakdown Spectroscopy (LIBS) analyzes the emission spectra of the plasma induced by focusing a nanosecond laser pulse onto the sample surface (figure 2.1). The laser pulse ablates pg of matter, vaporizes it and excites the vapor into a plasma. After cooling down, within a few hundreds of ns, the plasma emits elemental transitions. The UV visible emission is collected and analyzed by a spectrometer. The elemental composition is derived from the line positions, while the qualitative elemental composition is calculated from the line intensities. Quantitative measurement can be obtained by elemental calibration with etalons having a similar matrix, or by a calibration free data analysis. All the elements are detectable, either light or heavy, with a limit of detection varying from sub ppm (part per million) to percent depending on the element.

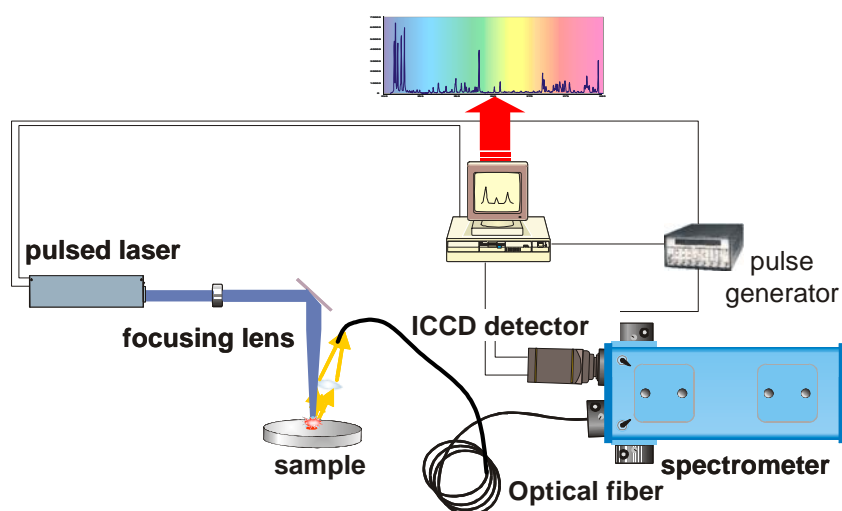


Figure 2.1: LIBS principle and set-up

3 LIBS experiment and results

A chemical warfare agent is an organic molecule containing a few non-metallic atoms, typically phosphorous, sulfur, chlorine, fluorine, arsenic. LIBS can detect these elements and their elemental ratios – for example fluorine over phosphorous. Detecting these data gives a fingerprint of a chemical warfare agent. In particular, phosphorous and fluorine - with an elemental ratio equal to one - is a specific measurement of the sarin molecule. A harmless sarin simulant is produced by mixing one mole of DMMP (dimethyl methylphosphonate) with one mole of 3-fluoroanisole. This simulant is a colorless liquid which can be deposited on a substrate.

First effort concentrates on fluorine detection simultaneously with phosphorous, as a molecular fingerprint of the chemical species. As halogen atoms are not easily detected by LIBS due to their high excited energy levels and ionization potentials, LIBS experimental parameters are carefully selected to succeed in observing fluorine. A high laser irradiance is required, about 10 GW/cm^2 [5]. Furthermore, literature shows that helium atmosphere can raise the halogen lines by decreasing the continuum level [6]. The most intense fluorine lines show up at 685 nm, while the phosphorous intense visible lines emerge at 253-255 nm. A UV laser beam (266 nm, Nd:YAG 4th harmonic) is selected in order to couple efficiently the laser into the colorless micrometric contamination film. Actually, longer laser wavelengths tend to penetrate deeper in the sample, emphasizing the substrate contribution to the LIBS signal ; however, good results are also obtained with double pulse IR systems, the first pulse creates the plasma which is heated again by the second one [6].

This experiment should simulate an in-situ measurement. The simulant mixture is deposited with a micropipette on various substrates coming from a public building (figure 3.1): white and grey mural ceramics, an aluminum garbage can, a road sign and a glass frame. Those samples are dirty, have different colors, rugosities, elemental compositions, therefore represent a daily life public environment. Film thickness is about a few micrometers but tends to evaporate rapidly.



Figure 3.1 : Samples composed of ceramics, glass, aluminum and a road sign.

The five simulant contaminated samples are qualitatively analyzed by LIBS; LIBS fluorine and phosphorous spectra are recorded for each sample. The elemental transitions are simultaneously observed, unambiguously in case of four over the five samples: white and grey ceramics, the aluminum and glass samples (see figure 3.2). Some road sign fluorine lines are interfered, probably with iron, chromium and titanium lines. The spectral window recorded is too narrow to identify clearly these interferences. A specific spectra treatment should be elaborated to interpret clearly the spectra.

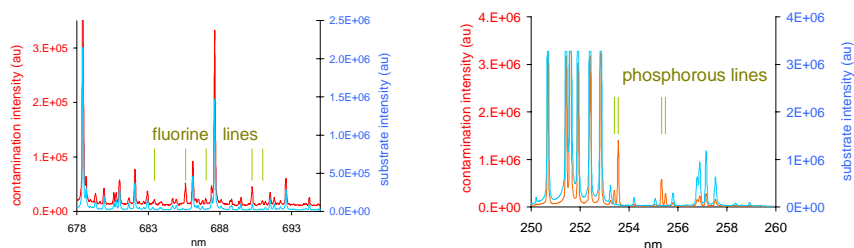


Figure 3.2 : Simultaneous LIBS spectra of fluorine and phosphorous lines obtained from a

Experiments are currently continued with LIBS systems having a hand held analyzer head detector. Preliminary results obtained on chemical contamination are quite promising. On the following paragraph, the hand held detector is presented with recent results obtained on nuclear contamination analysis.

4 LIBS contamination detection by a portable device

Regarding its easy to use and fast analysis capability, LIBS can be a useful technique to detect contaminated surfaces inside nuclear hot cells. A compact and light LIBS head has so been developed by CEA and the French IVEA company for this application (Figure 4.1). This set-up is made of two parts connected to each other by two few meters long optical fibers. The first part includes the laser beam unit, the spectrometer, the computer which controls the acquisition and enables to analyze the spectra. The second one, called the optical head, focuses the laser beam from the optical fiber onto the target, and collects the plasma emission back to the spectrometer through the second optical fiber. This system was used to obtain quantitative measurements of lanthanides simulating contaminated surfaces. Very good sensitivity was obtained, with limits of detection as low as 10 pg or 100 $\mu\text{g}/\text{cm}^2$, in case of Sr deposited on steel sample, or 10 mg/cm^2 in 30 s in case of uranium deposited on painted concrete [8].

Another portable detector is also developed, with a small laser positioned inside the head detector, allowing a greater laser irradiance on the sample. Such an irradiance will be useful to detect elements as F or Cl.



Figure 4.1: Hand held LIBS detector

5 LIBS for identification of materials and substances

A LIBS signal consists in spectral data, each element, atom or ion, being characterized by its own emission lines, whose intensity depends on the plasma characteristics. Specific data processing has then to be performed to extract pertinent analytical information. This can be performed by means of multivariate spectra treatments, particularly suited for LIBS data which are highly multidimensional and contain a large amount of information. Chemometrics methods based on Principal Components Analysis (PCA) and on variants of PCA, as SIMCA (Soft Independent Modeling by Class Analogy) can be used for that purpose [9].

Such analysis of LIBS spectra were successfully implemented by the CEA in the ChemCam project [10], to identify rocks at remote distance by LIBS, with rates of correct identification higher than 97%. Particular attention was paid to the robustness of the analysis, so as to minimize errors when unknown rocks are encountered [11]. Chemometrics was also used for studies related to the identification of aluminum alloys and to the determination of the geographical origin of yellow cake samples (Figure 5.1), yielding excellent rates of correct identification as well [12].

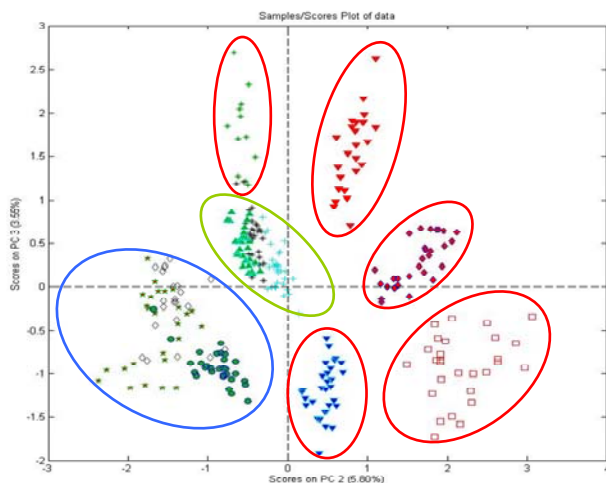


Figure 5.1: Classification of different yellow cake origins obtained after a first PCA.
The two clusters (blue and green circles) are resolved after a second PCA

6 Conclusion

First results show that LIBS is a promising technique for detection of hazardous contamination in the field, specially in public buildings. A fingerprint of chemical warfare agents is already measured by LIBS: the simultaneous phosphorous and fluorine detection in case of sarin. A micrometer thick contamination of a sarin simulant was successfully detected on 4 over 5 substrates that represent the material variety inside a public building ; substrate nature (ceramic, glass and metal) and the building dirt don't affect much the LIBS detection. Further work will focus on detection limit

estimation and improvement on optimizing the top surface layer signal versus the substrate signal. Besides, special effort will be put on compactness and robustness of the LIBS system, in collaboration with the start-up IVEA. At last, chemometrics methods, used to perform identification of complex substances will be developed to detect contamination among the substrate signal.

References

- [1] A.W. Miziolek, V. Palleschi, I. chechter. Laser Induced Breakdown Spectroscopy Fundamentals and Applications, Cambridge U. Press, 2006.
DA Cremers and LJ Radziemski. Handbook of laser-induced breakdown soectroscopy. Wiley 2006.
- [2] B. Sallé, P Mauchien and S. Maurice, Laser-induced Breakdown Spectroscopy in open-path configuration for yhe analysis of distant objects - review. Spectrochimica Acta B 62 (2007) 739-768
- [3] JL Gottfried & al., Appl. Spectrosc. 62 (2008) 353-363
- [4] www.ivea-solution.com
- [5] L. Dudragne , S. Morel, Ph Adam et J. Amouroux, "Analysis of polluted surfaces by time-resolved libs" N. Y. Acad. Sc. 891, pp 183-198 (1999)
- [6] L. St Onge & al., Spectrochim. Acta B **57** 1131-1140 (2002)
- [7] JL Gottfried & al., Discrimination of explosives residues on organic and inorganic substrates using laser-induced breakdown spectroscopy. Journal of Analytical Atomic Spectroscopy 2009, 24, pp. 288-296
- [8] JB Sirven & al., Analysis of uranium by LIBS : from lab to field. LIBS 2008
- [9] DL Massart, BGM Vandeginste, SN Deming, Y Michotte, L Kaufman. Chemometrics : a textbook. Elsevier Science Publishers B.V., 1988.
- [10] ChemCam is a part of the Mars Science Laboratory to be launched by NASA in 2009. It is devoted to remote analysis of rocks by Laser Induced Breakdown Spectroscopy. The development of the LIBS system is a French US collaboration (JPL, CNES, CEA)
- [11] JB Sirven, B. Sallé, P. Mauchien, J.-L. Lacour, S. Maurice and G. Manhès, Feasibility study of rock identification at the surface of Mars by remote laser-induced breakdown spectroscopy and three chemometric methods, J. Anal. At. Spectrom. 22. 1471–1480. 2007
- [12] JB Sirven & al., Towards the determination of the geographical origin of yellow cake samples by laser-induced breakdown spectroscopy and chemometrics. Journal of Analytical Atomic Spectroscopy. To be published 2009