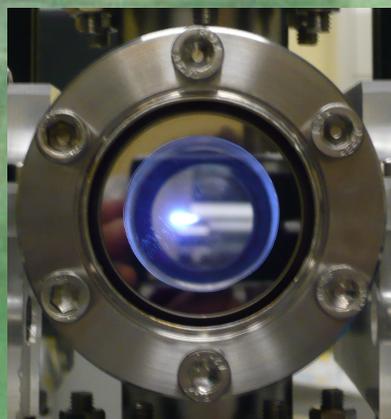




*Safe production and  
use of nanomaterials*

***Laser-Induced Breakdown  
Spectroscopy (LIBS):  
A possible tool for on-line  
monitoring and surveillance of  
nanoparticle production processes***



*Dissemination report  
September 2009  
DR—N°1312 200909-8*

Project ID NMP2-CT-2005-515843

An European Integrated Project Supported by through the Sixth Framework  
Programme if research and Technological Development



*Dissemination reports from Nanosafe2 project are designed to highlight and present in a simplified way the main results obtained in the studies carried out during this project. These reports mainly deal with one question which is of general concern for whom is interested by the safe production and use of nanomaterials. The full results are summarized in the corresponding Technical reports.*

**All the Dissemination reports and Technical reports are publicly available from Nanosafe2 project website: <http://www.nanosafe.org>**

## **Authors:**

Christophe Dutouquet  
E-mail: christophe.dutouquet@ineris.fr

Tanguy Amodeo  
E-mail: tanguy.amodeo@ineris.fr

Olivier Le Bihan  
E-mail: olivier.Le-Bihan@ineris.fr

Emeric Frejafon  
E-mail: emeric.frejafon@ineris.fr

## **European Community acknowledgement**

Nanosafe2 is supported by the European Community through the Sixth Framework Programme for Research and Technological Development with up to 7,0 M Euros (out of a total of 12,4 M Euros)

### *Disclaimer*

*This report reflects only the author's view. It may not in any circumstances be regarded as stating an official position of the author's employer nor of the European Community. In no case shall the author's employer, nor the Nanosafe 2 project Consortium as a whole, nor the European Community be liable for any physical or psychological injury or material or economic damage resulting from any use of the information contained therein.*

## On-line monitoring and surveillance of nanoparticle production processes: How?

Tracking nanoparticles for on-line monitoring of production processes or workplace surveillance requires their identification, the latter being based on one of their intrinsic properties such as elemental composition or shape. However, most of the currently available tools dedicated to nanoparticle metrology do not allow differentiating manufactured nanoparticles from those of background air, thereby rendering targeted nanoparticle detection arduous. Such problem may be addressed by chemically identifying nanoparticles. To achieve this goal, the LIBS (Laser-Induced breakdown Spectroscopy) technique was deemed as a potential candidate.

### How does LIBS work?

LIBS consists in focusing a powerful laser pulse on a material (solid, liquid, gas, aerosol, nanoparticle flow) whose elemental composition is to be determined. The strong heating of the sample at the focusing spot leads to the ignition of a hot and luminous transient ionized gas called plasma. Plasma light contains the signature of all the chemical elements the interrogated material is made of. This signature is read by sending the emitted light through a spectrometer equipped with a detector. The LIBS signal presents itself as an optical emission spectroscopy spectrum displaying lines corresponding to the detected elements.

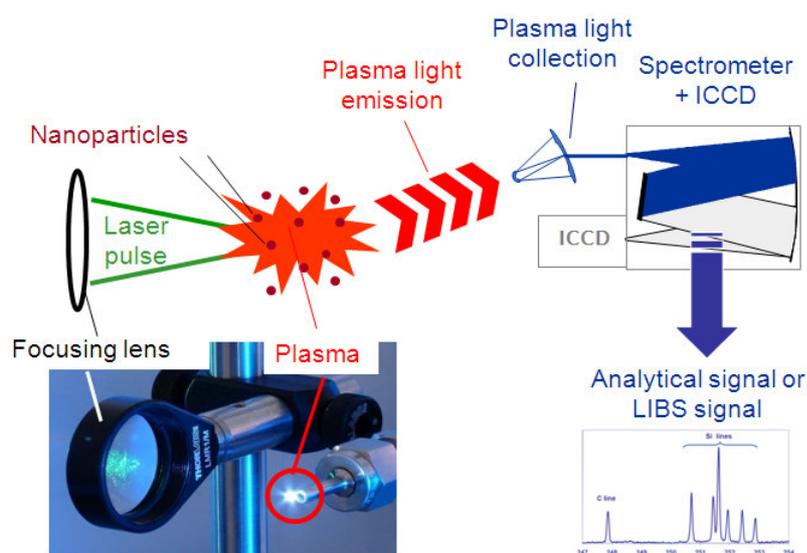


Illustration of the basic principle of LIBS

LIBS displays advantages of great interest for industrial applications. Detection of all the elements is possible at various pressure conditions. In addition, samples do not need preliminary preparation making LIBS eligible for on-line monitoring. It is a multielemental analysis technique with simultaneous detection of all the elements contained in the sample. Being all optical, it is not intrusive requiring only optical access to the sample and thus allowing in-situ measurements. LIBS is potentially fast and suitable for real-time monitoring, its speed depending on the number of laser shots required to obtain reliable results. Remote or stand-off analyses are even possible, as needed. These qualities make LIBS a promising analytical chemistry method intended to be operated at industrial sites as illustrated below.

### LIBS technique presents many advantages for on-line monitoring and workplace surveillance of nanoparticle production processes



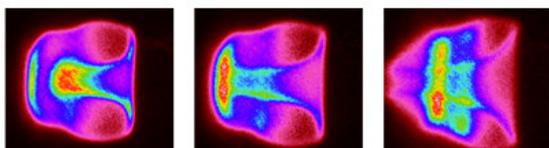
- ✓ No sample preparation required
- ✓ Non intrusive (**All optical technique**)
- ✓ **Rapid** analysis
- ✓ Remote / Stand-off detection possible
- ✓ Analysis at various pressure conditions

- ➔ Allows **in-situ** and **real time** monitoring while the nanoparticle production process is being operated
- ➔ **Safety** for the personnel
- ➔ Wide range of **on-site** applications

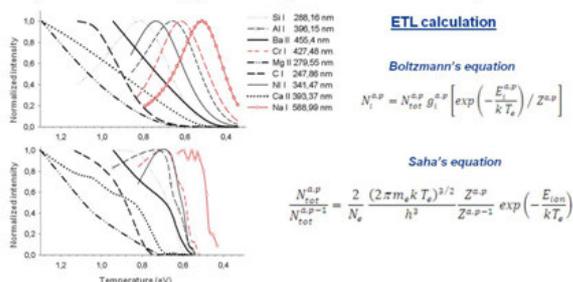
## Preliminary studies: LIBS signal optimization

Preliminary investigations aiming at studying the dependency of the LIBS signal on various experimental parameters such as laser energy, laser wavelength and background gas were carried out. Spatio-temporally resolved plasma imagery and spectroscopic measurements coupled with theoretical considerations helped optimizing the LIBS system dedicated to nanoparticle detection.

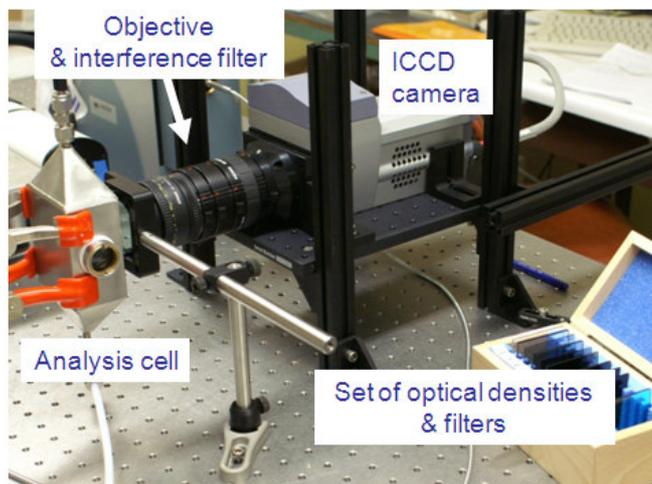
### Plasma imagery



### Spectroscopy and plasma theory



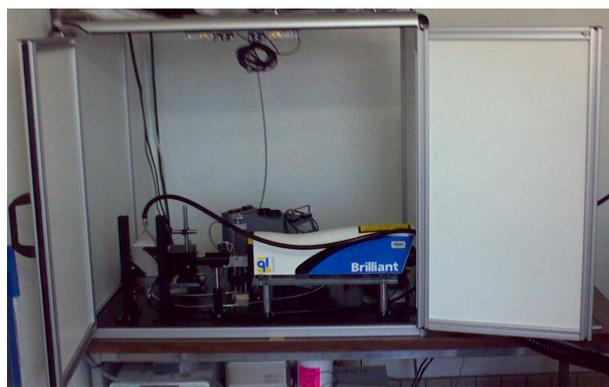
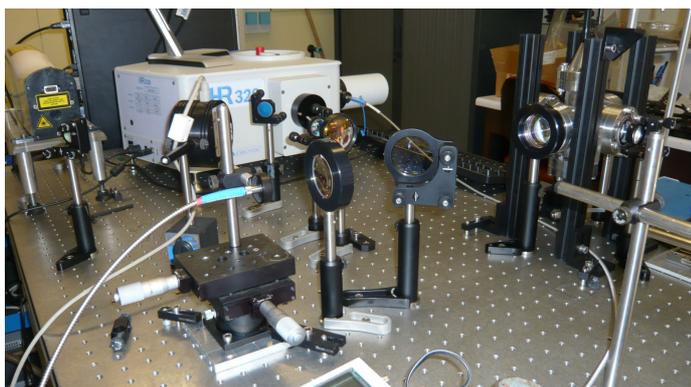
### Experimental set-up



Spatio-temporally resolved plasma imagery and spectroscopy coupled with theoretical considerations for LIBS measurements optimization

## From a laboratory set-up to a transportable prototype operated on-site

The LIBS optical bench was first set up in the laboratory. It was then turned into a transportable system for field measurement purposes. Developments are still currently under way to make it more compact.



From a laboratory set-up to a transportable prototype operated on-site

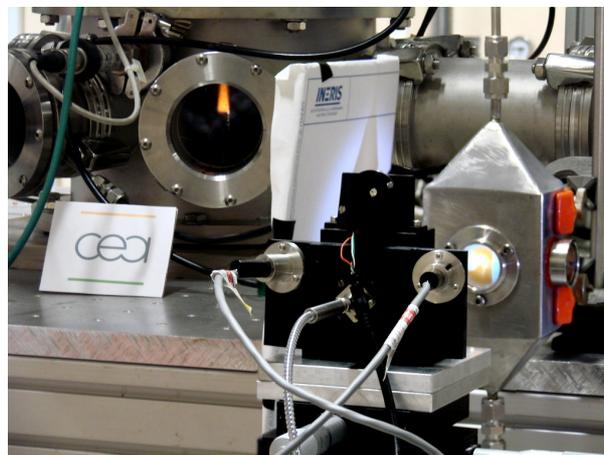
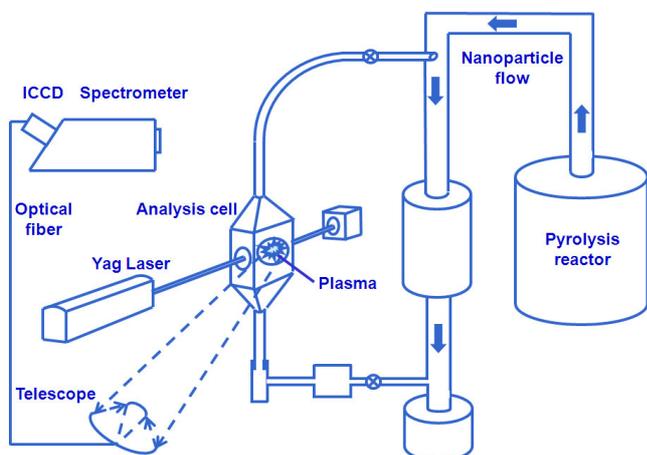


**A compact LIBS system intended to be operated on-site was designed and put to the test for both purposes:**

- ➔ On-line monitoring
- ➔ Workplace surveillance

## LIBS applied to on-line process monitoring

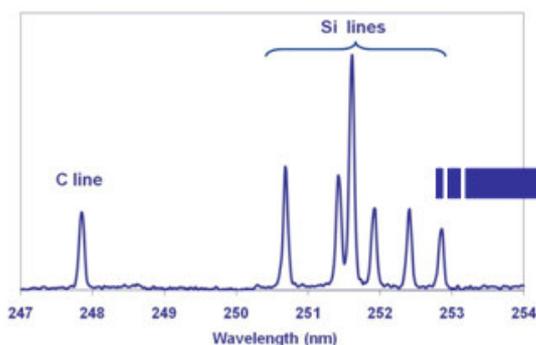
The LIBS system was integrated into a laser pyrolysis unit (CEA Saclay) producing SiC<sub>x</sub> composite nanoparticles. Though laser pyrolysis is a reliable process, stoichiometry variation may occur in the course of production. Part of the nanoparticle flow was therefore diverted from the main production duct and directed towards the LIBS cell for LIBS measurement purposes. Stoichiometry was inferred using calculations involving Si and C atomic line ratios obtained with experimental LIBS spectra.



LIBS system integration into the laser pyrolysis production unit (left) and implementation of the LIBS cell for on-line industrial measurements (right)

The results were found in good accordance with expected SiC<sub>x</sub> composite nanoparticle stoichiometry. However, stoichiometry determination proved to be quite sensitive to certain experimental parameters. Additional experiments are needed to consolidate these promising results.

This application is an appropriate illustration of the advantageous LIBS features presented above. This all-optical technique allows monitoring without disrupting the process, rendering possible direct chemical analysis on-line and in real time.



COMPOUND	EXPECTED STOICHIOMETRY	MEASURED STOICHIOMETRY
SiC	1	1.2
SiC <sub>2</sub>	2	1.8
SiC <sub>4</sub>	4	3.7
SiC <sub>8</sub>	8	8.2

LIBS spectrum displaying carbon and silicon lines (left) and a table comparing expected and measured stoichiometry (right)



- ➔ LIBS potentially well suited for on-line monitoring of nanoparticle production processes
- ➔ LIBS easily implemented on industrial sites
- ➔ Additional experiments should consolidate these results

## **LIBS applied to workplace surveillance: current detection limits**

*Polydisperse flows of nanoparticles of various elemental compositions with median and maximum sizes inferior to 100 and 300 nm respectively produced using two different nanoparticle generators were introduced in the LIBS cell for detection limit determination. The LIBS results were expressed in terms of mass concentration, thereby facilitating comparison with exposure limit values issued by HSL (Health and Safety Laboratory, UK) or INRS (French Institute for Health and Safety at Work, France). Most LIBS response signals were found below the occupational threshold limit values.*

*However, no specific regulation has hitherto been enforced regarding exposure to nanoparticles. As a consequence, these will probably be lowered in the near future. If so, direct LIBS measurement in the ambient air may be compromised for very low mass concentration levels.*

*However, an alternative approach based on substrate enrichment with nanoparticles prior to LIBS measurement may significantly improve detection limits. Enriched substrates could be interrogated at regular time intervals, in accordance with that needed for chronic risk assessment, thereby potentially meeting the future needs for workplace surveillance.*

Element	Minimum concentration detected ( $\mu\text{g} / \text{m}^3$ )	Exposure limits ( $\mu\text{g} / \text{m}^3$ ) (8-hour exposure)	Substance
Al	560	4000	respirable dust
Ba	1.5	---	
Ca	10	4000	respirable
Cd	500	30	respirable dust
Cr	45	500	---
Cu	80	200 1000	fume dust
Fe	310	5000	fume
K	1.5	---	
Mg	10	4000	fume and respirable dust
Na	1.5	---	
Ni	250	100	---
Pd	160	---	---
Si	100	4000	respirable dust
Ti	430	4 000	respirable, $\text{TiO}_2$

*Current detection limits obtained by direct LIBS analysis of a nanoparticle flow of various elemental compositions in ambient air*



**LIBS potentially adapted for workplace surveillance:**

➔ **Direct measurement in the air suitable for leak detection**

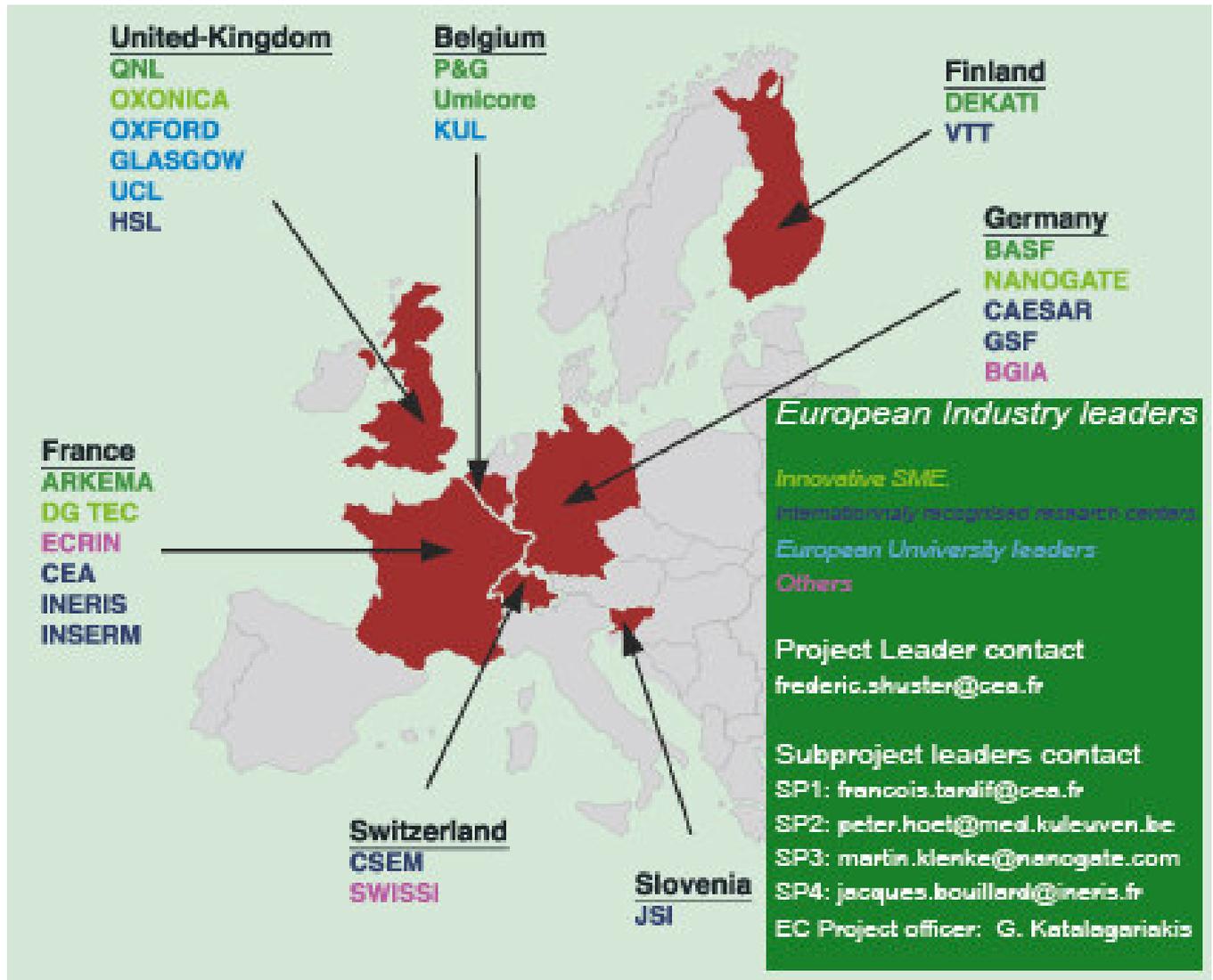
➔ **Collection on a substrate prior to LIBS interrogation more appropriate for chronic risk assessment**



Nanosafe2 brings together twenty five partners from seven different countries of the European Union, mainly small, medium and large enterprises and public research laboratories. The project is supported through the Sixth Framework Programme for Research and technological Development and addresses the thematic priority 3.4.3.2-1: Hazard reduction in production plant and storage sites. The project has started in April 2005 and will end in March 2009.

Nanosafe2 main objective is to develop risk assessment and management for secure industrial production of nanoparticles. It focuses on four areas: detection and characterisation techniques, Health hazard assessment, Development of secure industrial production systems and safe applications, Societal and environmental aspects.

## Partners



<http://www.nanosafe.org>

For further information, contact Dr Christophe Dutouquet (email: [Christophe.dutouquet@ineris.fr](mailto:Christophe.dutouquet@ineris.fr)) or Dr Emeric Frejafon ([emeric.frejafon@ineris.fr](mailto:emeric.frejafon@ineris.fr))

*References (Article published or to be published):*

T. Amodeo, C. Dutouquet, F. Tenegal, B. Guizard, H. Maskrot, O. Le Bihan, E. Frejafon, On-line monitoring of composite nanoparticles synthesized in a pre-industrial laser pyrolysis reactor using Laser-Induced Breakdown Spectroscopy, *Spectrochimica. Acta, Part B* 63 (2008) 1183-1190

T. Amodeo, C. Dutouquet, O. Le Bihan, M. Attoui and E. Frejafon, On-line determination of nanometric and sub-micrometric particle physicochemical characteristics using spectral imaging-aided Laser-Induced Breakdown Spectroscopy coupled with a Scanning Mobility Particle Sizer, *Spectrochimica Acta Part B*, accepted for publication 30 July 2009

# **Laser-Induced Breakdown Spectroscopy (LIBS): A possible tool for on-line monitoring and surveillance of nanoparticle production processes**

September 2009

---

## **LIBS technique presents many advantages for on-line monitoring and workplace surveillance of nanoparticle production processes**



- ✓ **No sample preparation required**
  - ✓ **Non intrusive (All optical technique)**
  - ✓ **Rapid analysis**
  - ✓ **Remote/stand-off detection possible**
  - ✓ **Analysis under various pressure conditions**
- ➔ **allows in-situ and real time monitoring while the nanoparticle production process is being operated**
  - ➔ **Safety for the personnel**
  - ➔ **wide range of on-site applications**



---

**A compact LIBS system intended to be operated on-site was designed and put to the test for both purposes:**

- ➔ **On-line monitoring of a nanoparticle production process**
- ➔ **Workplace surveillance**



---

**➔ LIBS potentially well suited for on-line monitoring of composite nanoparticle stoichiometry while the production process is being operated**

- ➔ **LIBS easily implemented on industrial sites**
- ➔ **Additional experiments should consolidate these results**



---

**LIBS potentially adapted for workplace surveillance:**

- ➔ **Direct measurement in the air suitable for leak detection**
- ➔ **Collection on a substrate prior to LIBS interrogation more appropriate for chronic risk assessment**