Laser-Induced Breakdown Spectroscopy (LIBS) for on-line monitoring and workplace surveillance of nanoparticle production processes

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ABSTRACT

Research studies up to technical optimisations were realized on laser / plasma / particle interactions in order to further achieve LIBS measurements with optimum efficiency. Polydisperse and monodisperse flows of salt and metallic particles with sizes ranging from 40 nm up to few µm produced by two different particle generators were introduced inside a cell where they were vaporized by the laser induced plasma for LIBS analysis purposes. Time-resolved emission spectroscopy measurements were carried out and the influence on the LIBS signal of parameters such as chemical nature of particles, their concentration, laser wavelength, laser energy, kind of background gas was investigated. Then, calibration curves and limit of detection have been investigated for a wide range of metallic particles (Ti, Al, Cu) [1,2]. These results allowed to make a first assessment of LIBS potentialities for manufactured nanoparticle detection in workplace.

Keywords: LIBS, laser, plasma, spectroscopy, on-line monitoring, workplace surveillance, nanoparticles,

1 INTODUCTION

Today, nanotechnology is a growing field of research and nanoparticle-based material production is expected to soar in years to come. With the emergence of nanoparticle-based materials, concerns regarding health and safety have been brought to the fore.

Little is known yet about potential health effects nanoparticles might induce. Due to their small sizes, nanoparticles are more likely to get past biological barriers and penetrate much deeper into organs (e.g. the lungs) than their micrometric counterparts. Inhalation, ingestion and skin absorption are possible ways of penetration through the human body. The potential dangers of the engineered nanoparticles stem from their unique physical and chemical properties conferring them specific properties in the way they interact with biological systems. Nanoparticle characteristics such as chemical composition, surface area, solubility may influence toxicity [3].

In consequence, there is a matter of urgency to assess the risks associated to nanoparticle exposure. Though research is still currently under way to secure nanoparticle production processes, the risk of accidental release is not to be neglected. Thus, there is an urgent need for the manufacturers to have at their command a tool enabling leak detection in-situ and in real time so as to protect workers from potential exposure. Several reports and articles [4] have emphasized the lack of appropriate metrology tools for workplace surveillance. At present time, several expensive and sophisticated off-line systems exist such as microscopic techniques (STEM, STM or PEEM) giving structural information that can be combined with electron and X-ray diffraction for information on compositions (RHEED, LEED, XRD). There are also in-situ spectroscopy (ATR, Raman, GD-OES) or X-rays photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), photoelectron emission spectroscopy and photon correlation spectroscopy (PCS) but most of them suffer of high detection limit and might depend on nanoparticle shape or size.

Consequently, there is currently no device that directly measures worker exposure to, and the toxicity of, engineered nanoparticles, with monitoring being limited to expensive laboratory analysis of ambient air. As a consequence, most of the available tools 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.

2 LIBS PRINCIPLE

LIBS measurements consist in focusing a powerful laser pulse on a material which elemental composition is to be determined. At the focus spot, the matter whatever its state be (solid, liquid, gas, aerosol) is strongly heated resulting thereby in the generation of a hot and luminous ionized gas called plasma. Elemental composition of the irradiated target is then determined through plasma analysis by optical emission spectroscopy.

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.

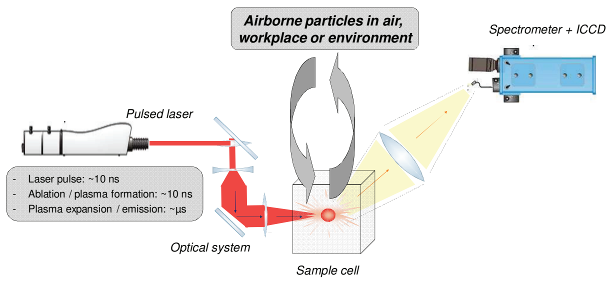

Figure 1 : description of the LIBS principle, case of nanoparticle detection in air.

These qualities are advantages over other techniques as the LIBS analyzer is intended to be operated on the production sites: no sample preparation required, in-situ and real time detection and survey for a wide range of on-site application.

3 RESULTS

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 (a TSI atomizer and a PALAS spark generator) 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). So far, concentrations such as 4 milligrams per cubic meter for fine TiO_2 corresponding to the respirable fraction for a long term exposure limit (8-hour reference period) are advised for worker protection (see table 1, exposure limits values).

In order to evaluate the limits of detection, the nanoparticle sizes and total mass concentrations were lowered until detection was no longer possible. Experimental parameters as energy, laser wavelength, time delay, gate width and number of accumulation were optimized for each element.
As major results, polydisperse nanoparticles with diameter smaller than 300 nm were detected leading to a detection limit corresponding to an estimated mass ranging from a few micrograms per cubic meters (Sodium) to few tens (copper) up to a few hundreds (aluminum) of microgram per cubic meters. The repeatability assessed during these measurements was found to be no more than 25 % for the whole campaign of experiments.
Monodisperse particles of sodium and copper with diameter ranging from 40 nm to few µm have been generated in order to prove that LIBS intensity is linear as a function of mass concentration indicating that no particular particle size effects take place under our experimental conditions, namely considering particles smaller than 2,5 µm which is in accordance with the inhalable fraction.
Thus, most LIBS response signals were found below the occupational threshold limit values. However, one could argue that these exposure limits might be revised downwards in the near future as they were not specifically released for nanoparticles.
No specific regulation has hitherto been enforced regarding exposure to nanoparticles. As a consequence, these will probably be lowered in the near future.

Materials	LIBS Detection limit (µg/m^3)	Exposure Limit Values (µg/m^3)	Guideline EU-OSHA « Nano : 0,066 »
Al	250	4000	264
Cu	50	1000	66
Ti	280	4000	264
Ca	10	4000	264
Mg	10	4000	264
Cd	300	30	1,98
Cr	45	500	33
Fe	200	5000	330
Ni	250	100	6,6
Si	100	4000	264

Table 1 : LIBS detection limits for some nanomaterials, actual associated occupational exposure limits and an example of future occupational exposure limits guidelines dedicated to nanoparticles (EU-OSHA)

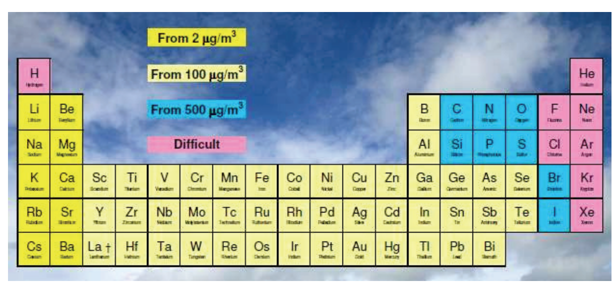

Table 2 : overview of LIBS expected detection limits for all elements

The above tables show detection limits obtained for some compounds, actual exposure limit and an extrapolation to future exposure limit assuming that specific surface is the key parameter in term of toxicity assessment.

4 CONCLUSION AND PERSPECTIVES

The results obtained by INERIS show a strong improvement of the continuous monitoring of aerosol containing engineered nano and ultra-fine particles. The

sensitivity and detection limits are below the actual recommended level in the micro range and could be compatible with future « nano » legislation.
This is a first and very important step towards legislation and effective control of airborne particles concentrations in air, workplaces and environment.

CILAS & INERIS join forces to make this innovative technology available for nano-community faced with exposure risk. Thanks to a collaborative program, we are working on a commercially available instrument.

The major advantages of this product are the following:
-Multi element detection
-Continuous measurement in real time of the concentration
-Distinction between the background natural NP & engineered NP
-Easy to use, reliable, affordable

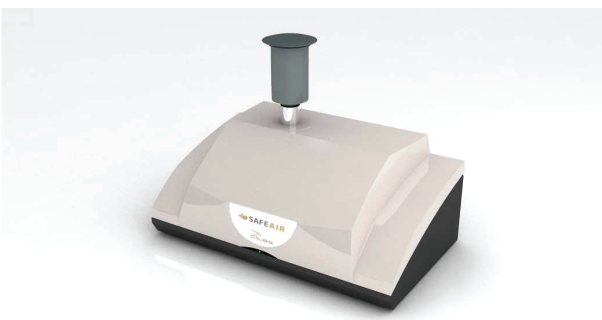

Figure 2: Safe-Air, description of the 'airborne real time selective particle detector'

REFERENCES

[1] 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

[2] 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 64 (2009) 1141–1152

[3] Approaches to safe nanotechnology: an information exchange with NIOSH, version 1.1, July 2006

[4] A. Franco, S.F. Hansen, S.I. Olsen, L. Butti, Limits and prospects of the "incremental approach" and the European legislation on the management of risks related to nanomaterials, Regulatory Toxicology and Pharmacology 48 (2007) 171-183

[5] List of approved workplace exposure limits (as consolidated with amendments October 2007), EH40/2005 Workplace exposure limits, Health and Safety Laboratory (HSL)

[6] Valeurs limites d'exposition professionnelle aux agents chimiques en France, ED984 june 2008, INRS (Institut National de Recherche et de Sécurité, French Institute for Health and Safety at work, France)