Technical note
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MAGELLAN™

The ultimate nanoparticle analyzer for water characterization

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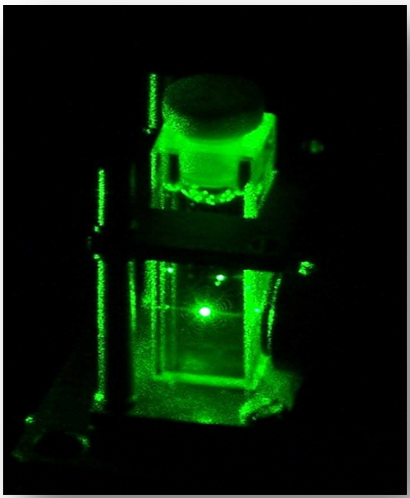
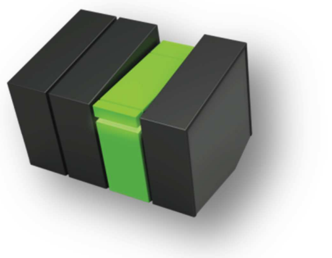
An insight on LIBD principle and performances



MAGELLAN^{TM}: THE ULTIMATE NANOPARTICLE ANALYZER FOR WATER CHARACTERIZATION

***Key Words**: MAGELLAN, Laser Induced Breakdown Detection (LIBD), nanoparticle trace size distribution & concentration, water analysis, membrane fouling, microorganism and biocolloid detection, filtration membranes, ultrafiltration, colloid migration.*

***Abstract:** This note presents the MAGELLAN^{TM} analyzer dedicated to nanoparticle traces detection for water analysis. Developed by CORDOUAN Technologies in collaboration with the Karlsruhe Institute of Technology (KIT), MAGELLAN is the very first and unique nanoparticle analyzer on the market based on an innovative technique called Laser Induced Breakdown Detection (LIBD). Its unprecedented sensitivity and resolution for measuring size and concentration of nanoparticle traces in water makes MAGELLAN the perfect tool for research and industrial applications. This note describes the basic principle of MAGELLAN and highlights some of its benefits and unique performances.*



INTRODUCTION

The increasing amounts of engineered nanoparticles and their many different uses from common consumer products to the most advanced applications cause a risk of spreading of such substances into the environment and in particular in water resources. Thus, it is becoming more and more important to suppliers and users of water for domestic and industrial applications to detect nanoparticles even at very low concentration. It will enable to prevent contamination and to evaluate their impact on the efficiency of the water treatment process (membrane fouling, membrane integrity, etc.) in water production. Today the testing is conducted within the production facility as quality assurance and in the water works during operation. Common integrity tests applied in water works include measurements of turbidity, spiking tests or air pressure tests [Gu]. These tests are able to detect defects of about 1 to 3µm but do not provide any information on membranes defects with sizes below 500nm and in particular in the range of viruses, which are about 20-30nm. Current commercial particle counters for water applications have some limitations in size and concentration sensitivity, and constraints of use like fixed flow rate, no pressure, etc., which make them inappropriate for such applications. Also normalization on water quality at a European and worldwide level is rapidly evolving to anticipate the thread of such nanoparticles spreading. In this context and to fulfill the demand for new and efficient characterization tools, CORDOUAN Technology has developed the MAGELLAN analyzer in partnership with the Institute for Nuclear Waste Disposal (INE) from the Karlsruhe Institute of Technology (KIT).

MAGELLAN MEASUREMENT PRINCIPLE

Most commercial instruments dedicated to the characterization of nanoparticle colloidal suspensions in transparent liquids like water are based on optical methods (i.e. dynamic light scattering, light obscuration, turbidimeter, particle tracking). However, in many cases these techniques are not sensitive enough to detect and characterize accurately the size and concentration of nanoparticles traces, in particular for particle size below 100nm and at sub-ppm concentrations. Also these techniques are usually inappropriate for online monitoring.

The MAGELLAN works on a completely innovative and disruptive approach called Laser Induced Breakdown Detection (LIBD) [Ja]. Basically the technique consists in focusing a pulsed laser beam into the liquid sample to be analyzed. When the local pulse energy density is high enough, when a particle crosses the beam section in the focal area, the light-matter interaction breaks the atomic links by a multi photon process and creates plasma. Since solid matter has a lower plasma threshold than water and liquids in general, it is possible to detect the plasma generated by solid nanoparticles in suspension before breaking down water molecules. That is basically how MAGELLAN works; its principle is depicted in Figure 1 (left).

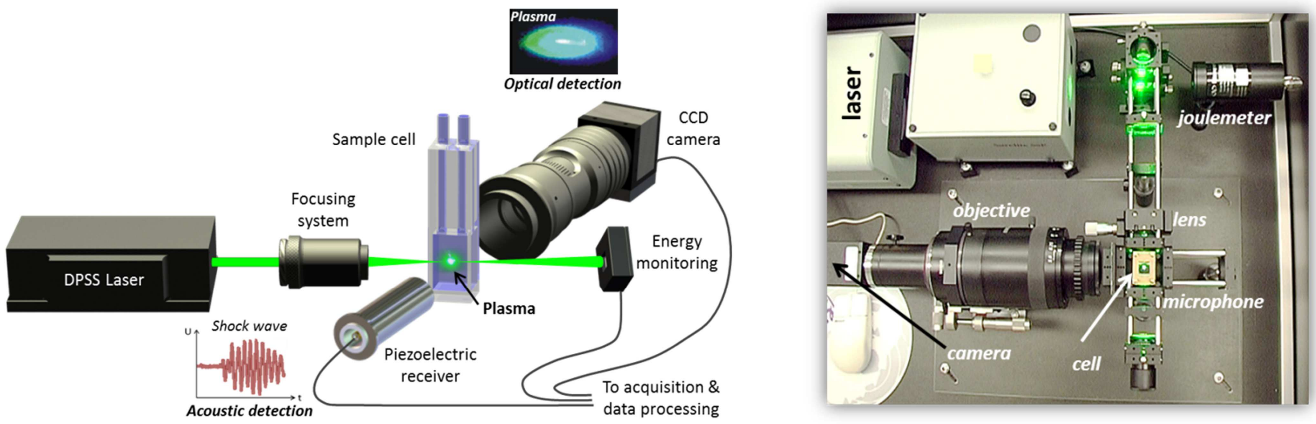


Figure 1: LIBD measurement principle (left) and corresponding laboratory setup (right)

As shown in Figure 1, a typical LIBD setup comprises a stable pulsed nanosecond laser, typically (but not restrictively) a frequency doubled Nd:YAG laser emitting at 532nm. The energy of the pulses is adjusted automatically thanks to a variable attenuator and recorded by an energy detector. The laser beam is focused into a sample cell (Quartz) by a set of AR coated optical lenses (typical beam diameter at focus is <10µm). The sample cell is maintained securely in a fixed position with respect to the beam focus thanks to a dedicated sample cell holder. A beam dump system is usually placed after the cell to block the unabsorbed beam. The plasma events are detected in the cell in two different and complementary ways: the first and simplest one is the acoustic method where an acoustic sensor (piezoelectric transducer) is connected to the sample cell and the plasma is detected by the acoustic wave emitted during the plasma expansion into the liquid. The second detection method is an optical one where a CCD camera is equipped with a magnification objective to record the axial distribution of the successive plasma events in the focus area (Rayleigh zone). The size and concentration of colloids can then be determined in a statistical way thanks to a preliminary calibration made with colloids standards (latex) of known size and concentrations.

a) THE ACOUSTIC DETECTION METHOD

With the acoustic approach (the one implemented in the MAGELLAN system), the laser energy is scanned from zero up to the plasma threshold of ultrapure water with optimized energy incremental steps; for each step, the laser shoots a fixed number of pulses (typically between 500 to 2000) at 100Hz repetition rate and in the same time the number of induced plasma detected is recorded by a high speed acquisition card, each plasma event corresponding to a breakdown in the liquid. For each pulse energy, a BreakDown Probability (BDP) value is calculated by:

$$BDP = \frac{Number\ of\ breakdown}{Number\ of\ laser\ pulses} \qquad (1)$$

BDP depends on several parameters: the local energy fluence, the size and the concentration of the nanoparticles. BDP varies from 0 (no breakdown) to 1 (100% of breakdown). The plot of BDP versus pulse energy gives a measurement curve like the ones shown in Figure 2 (left) with a typical S shape. The S curve is characterized by two parameters: its energy threshold (inflexion point in the beginning of the curve from which BDP starts to increase) and its slope. The breakdown threshold depends on the particle size only: the bigger the particle size, the lower the threshold. The slope of the S curve is related to the colloidal concentration: the higher the particle concentration, the higher the slope. Fitting the S curve with calibration data allows then to determine the size distribution and the absolute concentration of the colloid traces in the solution.

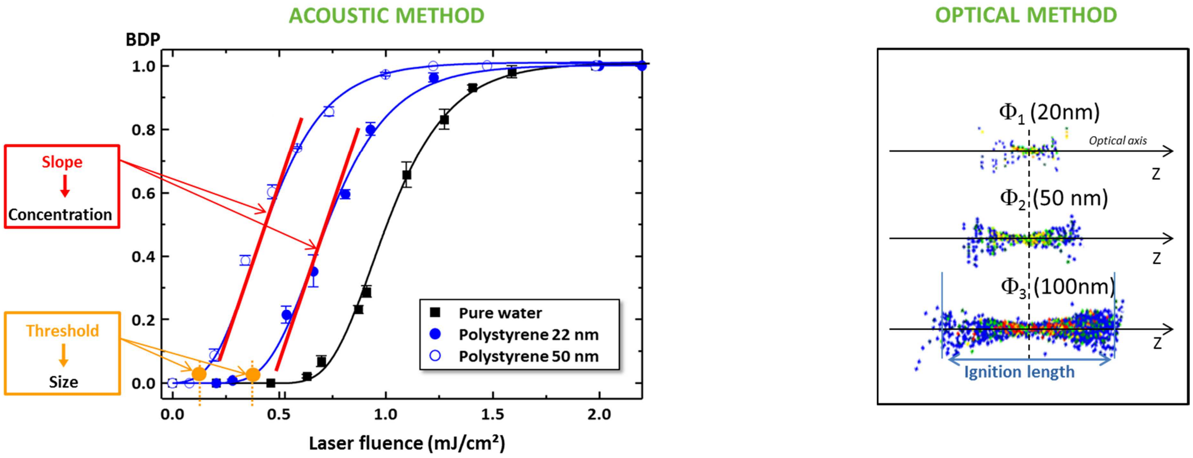


Figure 2: Acoustic method (left), BreakDown Probability as a function of particle size and laser pulse energy for pure water, 22nm and 50nm latex colloidal suspensions; Optical method (right), plasma spatial distribution versus colloid average diameter.

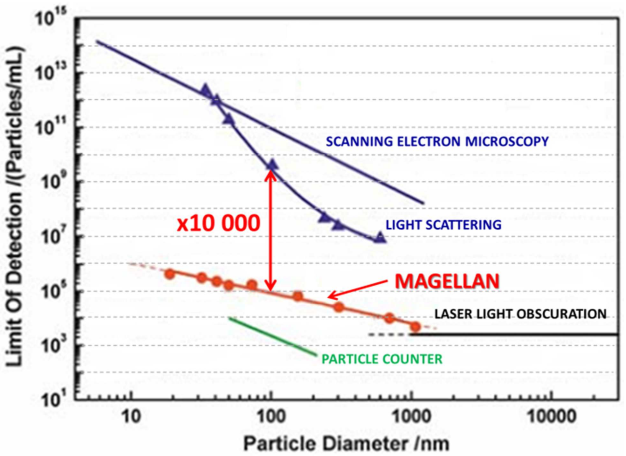
Thus thanks to this statistical approach, the size and absolute number of nanoparticles can be derived from the recorded signal within 10 to 30 minutes depending on the water content and the level of accuracy required.

b) THE OPTICALDETECTION METHOD

The optical detection method uses a CCD camera to record the occurrence of plasma events and their spatial distribution along the optical axis (z-axis) in the focus area. This measurement is done at single fixed and predetermined laser pulse energy. For one measurement, the laser shoots a fixed number of pulses (typically between 5000 to 30000). At the end of the measurement cycle, the plasma events distribution along the optical axis (z-axis) is plotted (see Figure 2 (right)). The length of this distribution along the z-axis defines what is called the plasma ignition length which basically corresponds to the region of space along the optical axis in which 95% of the plasma events occur. The plasma ignition length is directly related to the average size of the nanoparticles and is obtained by fitting with calibration data. Nanoparticle absolute concentration is obtained by calculation of the BDP (see eq. (1)) and comparison with calibration data. Though faster than the acoustic detection method (because measurement is done at just one pulse energy), the optical detection is less accurate because it only gives an average size and no information is provided on the size distribution of the colloids

PERFORMANCES AND APPLICATIONS OF MAGELLAN

First real experimental demonstrations of LIBD technique were developed in the early 90's. Since that time many papers have been published which demonstrate the great capabilities of LIBD for nanoparticles traces characterization in various applications like for example: study about membrane fouling in water treatment process [Li], characterization of colloids in primary coolant of nuclear reactor system [Bo], study of radionuclides migration in aquifer, study of oxides and hydroxides characterization in natural surface and drinking waters [Ka, Bu1, Bu2], etc. It has been demonstrated that for the detection of traces of nanoparticles in water, LIBD overcomes the performances of existing techniques. As illustrated in Figure 3, LIBD offers one of the broadest particle size measurement range for nanoparticles characterization with a sensitivity 10 000 times superior to conventional light scattering techniques in the 10-100nm size range. Thus concentration as low as 10^4 particles/ml are accessible with LIBD which makes today LIBD certainly one of the most efficient technique for nanoparticle ultra-traces characterization in the sub-ppm (part per million) to ppt (part per trillion) concentration range.



SPECIFICATIONS	
Particle size range	10 – 1000nm
Concentration range	10^4 – 10^{11} part/mL
Accuracy	± 10% (depending on measurement time)
Calibration	Certified reference materials polystyrene (NIST) or customer reference
Sample preparation	None – Standard laboratory practices for ultra-trace sample analysis
Sample cell configuration	Static cell: 3.5ml Flow-through cell: up to 5 bars – 275µL
Measurement time	10 to 30min (for accurate size distribution)

Figure 3: (left) Detection limit comparison between MAGELLAN and other method, (right) MAGELLAN characteristics.

Despite its promises and potentialities, LIBD technique as always been confined until today into very few experts labs over the world because of its complexity and the size of experimental setups. The INE research lab from the KIT in Germany is one of the pioneering laboratories which masters LIBD for more than 20 years. The MAGELLAN product has been developed with their support and highly recognized expertise. To the best of our knowledge MAGELLAN is the very first and unique LIBD system brought to an industrialization and commercial stage, using up-to-date laser technology, optimized opto-mechanical layout and proprietary algorithm. In its current version the MAGELLAN system uses the acoustic detection method which is the best configuration for advanced applications with size distribution and absolute concentration capabilities. It is designed to be compact, transportable, robust, and easy to operate even in harsh environment like in water plants and outside the labs. It can also be operated online with filtration process, with various sample cell configurations and even under high pressure condition (up to 60bars with specific sample cell). All these characteristics are summarized in the table of Figure 3 (right).

CONCLUSION

Developed by CORDOUAN Technologies in collaboration with the KIT-INE, MAGELLAN is the very first and unique nanoparticle analyzer on the market based on a disruptive technique called LIBD. Its unprecedented sensitivity and resolution for measuring size and concentration of nanoparticle traces in water have no equivalent in the market. With its advanced capabilities, MAGELLAN is a very powerful and easy to use analysis tool for research and industry in water treatment, filtration and contamination applications.

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CONTACT

sales@cordouan-tech.com

Phone: +33 (0)556 158 045