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Viability study of using the Laser-Induced Breakdown Spectroscopy technique for radioactive waste detection at IPEN-CNEN/SP

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ABSTRACT

In this work a viability study to apply the Laser-Induced Breakdown Spectroscopy (LIBS) technique for radioactive waste characterization was developed using a high power q-switched Nd:YAG rod-Laser, operating at 1064 nm with 9 ns of pulse-width and pulse-to-pulse energy around 10 to 20 mJ. When applied in a non-radioactive deionized water sample, our methodology exhibits a good potential to spectroscopy detection of Hydrogen species with resolution around 0.035 nm at full width at half maximum (FWHM).

1. INTRODUCTION

Radioactive waste can be generated in a large number of processes related to nuclear field procedures and operation of nuclear installations. They arise in a wide range of compositions of radionuclides and in a great variety of physical states and chemical forms. To avoid accidents and for protection of the facilities, people and the environment, the International Atomic Energy Agency (IAEA) states a several safety rules to management the radioactive wastes to ensure its proper and adequate disposal [1].

The characterization of radioactive waste according to physical, chemical and radiological properties is the first step to establish a complete policy to implement a safe scheme in which it is handled and stored [2]. Nowadays this characterization is performed as usual: measuring the activity levels and concentration of waste using detectors and counters.

Just after characterization, the radioactive waste should be classified according to six different groups: exempt waste (EW), very short lived waste (VSLW), very low level waste (VLLW), low level waste (LLW), intermediate level waste (ILW) and the high level waste (HLW) [3]. Unfortunately to execute the waste characterization researchers, technicians and workers may be *in situ* with hand detectors close to the material and this fact contributes to increase the probability of contamination and radiation exposure resulting in human diseases or even death.

In this scenario the Laser characterization methodologies may be an alternative to traditional procedures within the nuclear field. An interesting technique is the Laser-Induced Breakdown Spectroscopy (LIBS) that has become recently a reliable method to perform analytical detection and spectroscopy characterization of several types of elements, with no complex sample setup and high remote sensing capability with fast analysis [4].

We report in this paper a study regarding LIBS technique viability to perform the characterization of radioactive wastes in the Centre for Lasers and Applications of the National Nuclear Energy Commission (CLA IPEN-CNEN/SP). This work has a preliminary background in remote sensing of non-radioactive elements instead radioactive wastes.

The LIBS set-up that we developed has been applicable to Uranium-238 characterization with success using U-238 in a form of solid-state pellets [5]. In this work we apply the technique in liquid-state elements, first working with deionized water to pursue Tritium isotope identification: a low level beta radioactive element whose detection is of concern to the Management of Radioactive Wastes (GRR) of IPEN since there is no an efficient method or procedure to track and identify it.

2. HYDROGEN ISOTOPES SPECTROSCOPY: TRITIUM

Tritium is the only radioactive isotope of Hydrogen. Its chemical and physical properties are essentially the same as ordinary Hydrogen. This isotope is frequently reported in the scientific literature as a fission product in nuclear weapons tests and in nuclear power reactors with a yield of 0.01% . It can be produced in nuclear reactors by neutron absorption of a litium-6 atom and also by thermal fission in the core of reactors. It has been used in medical field as a biological tracer and also for environment studies. From human health point of view, Tritium is hazard only if it is taken into the body since it decays by emitting a low-energy beta particle with no electromagnetic gamma radiation. The hazard is associated with cell damage in which may result in a cancer [6].

The spectroscopy of Tritium and others Hydrogen species is a complex problem to solve since that shift of spectroscopy transitions from Hydrogen Balmer-α lines are very close to the resolution limit of scientific instrumentation [7].

In the early times, the measurement method was carried out using electric discharges coupled to the sun with prisms, gratings and optical interferometry [8-9]. Others authors used some modern techniques like microwave, radiofrequency measures and magnetic resonance with atomic beams [10-12] in which results in a higher precision. The rapid development of Laser in the 1970s has lead to arise of other spectroscopy methods such as saturated absorption [13], two-photon Doppler-free spectroscopy [14-15] and frequency combs [16]. All these techniques have a complex experimental hardware and require extensive sample preparation.

Kireyev and his group [17] was the first to apply the Bohr effective mass theory to experimental investigation of the hyperfine structure (HFS) of Hydrogen species. Kibble, Rowley and Shawyer [18] using interferometry methods observed the experimental Tri-

tium transition lines. Garcia and Mack[19] in a parallel work to Erickson [20], applied the Quantum Electrodynamics for Spectroscopy of One-Electron atoms to enhance the results for Hydrogen species. Tate et. al. [21], using saturated absorption spectroscopy have achieved the best results regarding to Tritium and Deuterium lines in which nowadays are accepted in the scientific area and now its data has been used as reference in the NIST database [22].

3. OUR EXPERIMENTAL SETUP TO PERFORM NON-RADIOACTIVE DEIONIZED WATER CHARACTERIZATION

Laser-induced breakdown spectroscopy (LIBS) is an atomic spectroscopic technique that employs a high power Laser as energy source in a non-invasive method. The high power pulse is focused to the surface of some sample inducing plasma generation due the high energy deposited in the tissue. The breakdown plasma is collected by some optical arrangement and then, the atomic spectrum is analysed by a computer.

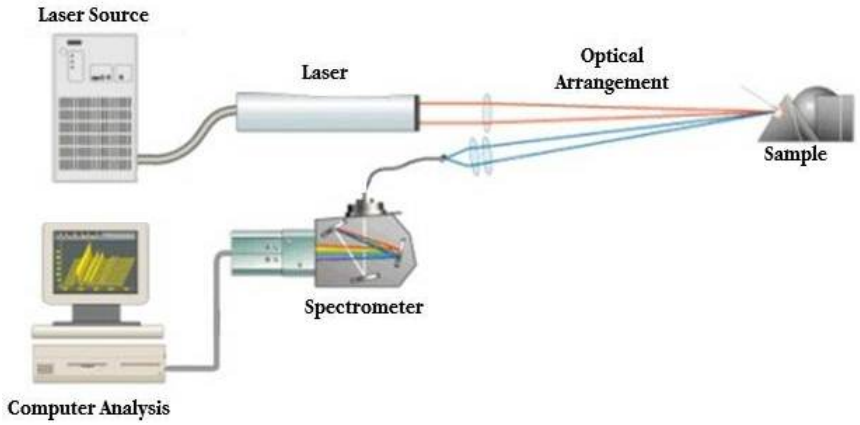

Figure 1: The conventional LIBS setup.

When focused close to the sample surface, the Laser pulse generates high density plasma (number of electrons $>> 10^{14} cm^{-3}$). In a short time period, the samples plasma expands at supersonic velocities and cools down [23]. After this point, the characteristic atomic emission lines from the sample can be observed using a fiber-coupled to a resolution spectrograph of 0.001 nm of resolution or in other cheap spectrometer-based with around 0.02 nm of resolution. These lines can then be used to perform detection and characterization of the ionized elements present in the plume of the plasma.

The Laser pulse must be specified before the experiment. In our work, we developed and applied a Nd:YAG q-switched rod-Laser, operating at 1064 nm with pulse time-width of 9 nanoseconds, 10 Hz of repetition rate with 20 mJ of pulse-to-pulse energy.

The optical glass bucket (quartz silica) with non-radioactive deionized water sample was placed into the optical arrangement with a mirror top coupled with 2 cm focal length lens to perpendicular incidence of beam and another lens (with 1.5 cm of focal length) arrangement to parallel beam incidence in the water in order to facilitate the plasma generation in the sample (see figure 2).

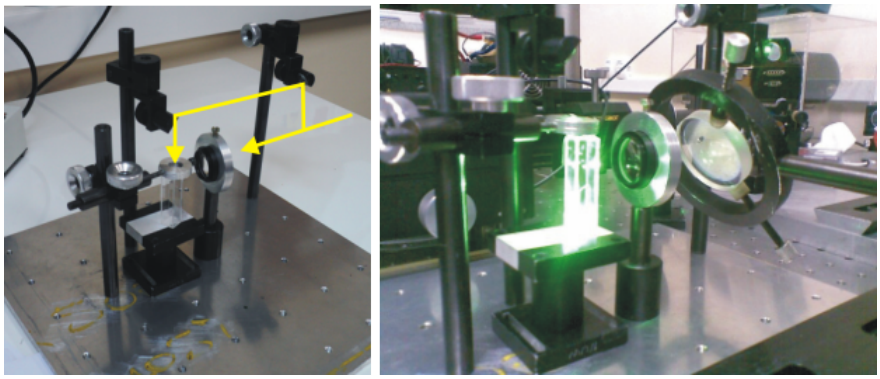

Figure 2: Experimental setup to execute non-radioactive deionized water characterization. In the left, we see the splitted beam to plasma generation in the sample. In the right the system working at 532 nm.

An optical fiber of 200 μm was placed near to the optical bucket to retrieve plasma signal. We used the *OceanOptics* spectrometer (HR2000 with resolution of 0.035 nm) to 200-700 nm wavelength range coupled to a computer for analyze the results.

4. RESULTS

Some preliminary spectral study was carried out in order to find an adequate spectral window for detection of Hydrogen-ionized lines from water plasma. We perform the alignment of our system and collected a several plasma spectra. The plasma was generated directly from water vapor in which has a pinkish aspect due the Hydrogen transitions.

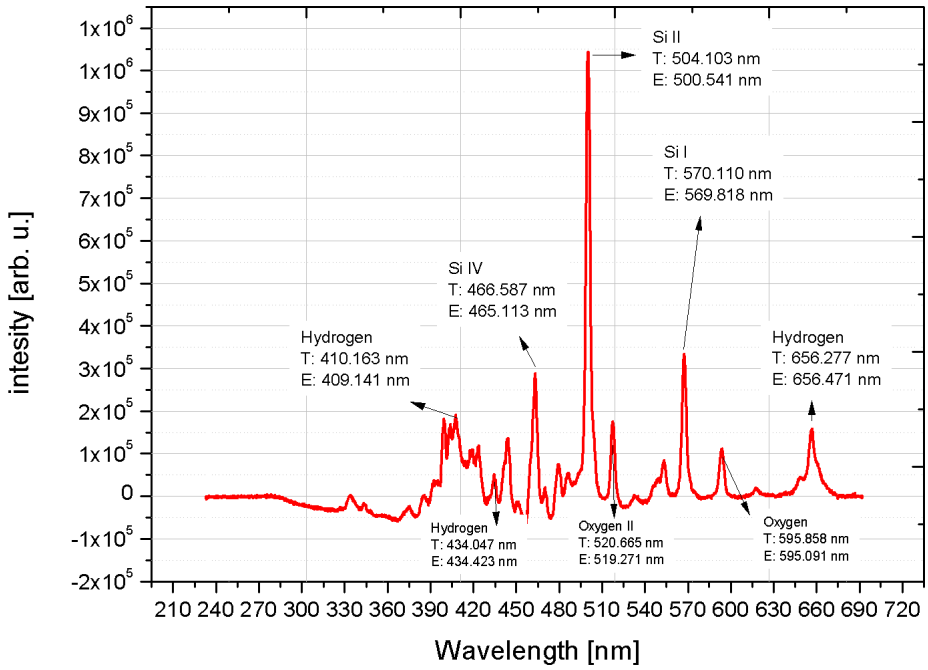

Figure 3: Deionized water plasma spectrum achieved using the LIBS instrumentation.

Figure 3 shows the net emission of deionized water plasma from approximately 10 pulses

shots with 10-20 mJ of energy, each on focalized in the same target of water in the isolated optical bucket. Due the light coupling in the optical glass the emission lines of Silica also were observed. We removed a baseline for continuous emission using the data software Origin 8 and due this fact the emission figure has a few negative values in the intensity y-axis.

The emission lines were identified using the NIST database and its values are noted by letter "T" in the figure. The letter "E" refers to experimental data value for correspondent wavelength with 0.035 nm (at FWHM) optical instrumentation precision. A set of ten spectra was used to build the net emission showed. Just the intensity changed signal-by-signal in our experiments.

5. DISCUSSION

From NIST database, the most evidenced Hydrogen line (2s-3p transition) is the 656.277 nm in which we obtain with LIBS instrumentation the value 656.471(35) nm. A very good result regarding to a cheap and compact system in a real-time detection. Our result has just 0.029% deviation from the NIST value.

In the NIST database the Tritium 2s-3p transition has the wavelength value in the 656.035 nm: a shift of **0.243 nm** of same Hydrogen transition. It may indicate that our LIBS system has the necessary resolution to perform the Tritium characterization in real-time with fair remote sensing capability than others techniques aforementioned.

The figure 3 presents peaks corresponding to Oxygen emission, but cannot state whether this emission is due directly the water plasma because we observed some problems of light coupling in the bucket (and the quartz glass is an oxide). Another two Hydrogen transitions were observed: 2p-6s in the 410.163 nm and 2p-5d corresponding to 434.047 nm. In both cases, we also have achieved a good precision.

6. CONCLUSION

We showed that our system installed and configured at Centre for Lasers and Applications has the necessary resolution to identify liquid-phase elements in non-radioactive form and this fact may indicated that the LIBS system has also a reasonable potential and can be used in the nuclear field as mechanism of radioactive waste characterization of elements in which the detection mechanism remains unsolved.

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