Analysis of liquid sodium purity by laser-induced breakdown spectroscopy. Modeling and correction of signal fluctuation prior to quantitation of trace elements

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ABSTRACT

Liquid sodium is used as coolant in sodium-cooled fast nuclear reactors. Among many parameters to monitor to ensure the safe operation of the reactor, the coolant chemical purity is a relevant indicator of several undesirable situations, like corrosion of structural materials or sodium contamination, which may release different elements in the coolant. Several techniques have already been implemented to measure the sodium purity, but their response time is long and not suited for continuous monitoring. Therefore, as a complement to them, laser-induced breakdown spectroscopy (LIBS) is considered as a promising technique for real-time analysis of the coolant purity. In this paper we report on the first LIBS quantitative measurements performed in liquid sodium at 150 °C. Calibration curves were traced for lead and indium using the standard addition method. Important intensity drifts and fluctuations were observed, mostly due to pressure variations in the sodium oven. Background subtraction and/or normalization was used to compensate for those intensity fluctuations. To describe the effect of these corrections on the analytical signal noise, a simple model was proposed and its results were found to satisfactorily fit the experimental data. Using this approach, the best detection limits were obtained for the background-subtracted and normalized data, and were found to be 6 ppm for lead and 5 ppm for indium.

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1. Introduction

The sodium fast nuclear reactors (SFR) are being evaluated in France as a generation IV system, as they benefit from the largest technological experience and are considered as one of the most promising systems. The roadmap is set in for the design, construction and operation of a prototype reactor, called ASTRID, in the 2020 decade.

Among the large number of parameters to monitor to ensure the safe operation of the reactor, the coolant chemical purity is a relevant indicator, not only to maintain the coolant fluidity for heat-transfer purposes and to avoid pipe plugging, but also to detect phenomena like corrosion of structural materials by oxygen, contamination of the liquid metal (e.g. due to an air ingress), or even fuel clad failures. Each of these events may release in the sodium different elements such as oxygen, corrosion products (Fe, Cr, Ni or Mn) or fission products [1]. Monitoring the concentration of these elements in the coolant is then a way to limit to a minimum and to detect those undesirable situations.

In the French SFRs Phénix and SuperPhénix, the sodium purity was measured using plugging indicators and sodium samples (Tastena concept). Plugging indicators are based on the variation of impurities solubility with temperature [2]. The measurement is robust but not chemically selective, slow when the sodium purity is high, and it was found complex to interpret by the operator. Tastena measurements consist in sampling a few grams of liquid sodium, dissolving the sample and making a complete chemical analysis using standard laboratory techniques (e.g. ICP). The main limitation of this second measurement is that it is performed only a few times per cycle, most often during a reactor shut-down.

These techniques have been proved to be rather efficient for the operation of built reactors, and a large operating feedback was acquired on them. Yet the monitoring of the liquid sodium chemistry remains challenging. An ideal instrumentation should be implementable on-line, able to operate in severe conditions of high temperature and chemically reductive liquid sodium, and specific to chemical species present at the trace level. This may be useful to the reactor's operation in order to allow faster diagnostics of any chemical deviations and to propose corrective actions.

Therefore, as a complement to plugging indicators and Tastena sampling, there is an opportunity for innovative techniques that would give lower limits of detection, faster analysis, provide redundancy for safety related instrumentation, and be less complex compared to existing systems. In particular, real time measurements may have a strong interest to continuously monitor the coolant purity and to detect

potential drifts of the target elements concentration. The laser-induced breakdown spectroscopy (LIBS) technique is developed at CEA for that purpose. In LIBS, a pulsed laser is focalized onto the sample surface. The resulting laser ablation leads to the formation of a plasma. The spectroscopic analysis of the plasma emission allows to measure the sample elemental composition.

As an all-optical technique, LIBS is well suited to remote or on-line analysis in hostile conditions [3,4]. For that reason, it has found several applications in nuclear environment, where radioactivity [5], high temperature [6], presence of highly corrosive media [7] or weak accessibility to the sample [8] strongly limit the choice of analytical techniques.

In this paper, LIBS was used to analyze the chemical purity of liquid sodium, with the objective to detect in real-time a possible drift of the metallic impurities concentration in the primary cooling circuit. As a first step, our work consisted in characterizing this approach and in estimating the measurement sensitivity for two model elements highly soluble in liquid sodium: lead and indium [9]. Acquisition parameters were optimized to lower as much as possible their detection limits, and calibration curves were obtained using the standard addition method. Strong signal drifts and variations were observed. Different approaches were tested to model them and to normalize the analytical signal in order to improve the calibration.

2. Experimental setup and data acquisition

2.1. Description of the experimental setup

The sample consisted of 300 g of pure metallic sodium, contained in a hermetic oven topped with 3 optical windows. A heating system was used to heat the sodium at 150 °C, i.e. 52 °C above its melting point. The sodium sample was under an ultra-pure argon atmosphere representative of a sodium-cooled reactor. In order to protect the optical windows from possible projections of ablated matter and condensation of sodium vapor, argon was flushed below each of them with a controlled flow rate of 7 L/min.

We chose lead (Pb) and indium (In) as analytes since they are highly soluble in liquid sodium at 150 °C [9] and have emission lines in the UV–visible range [10]. Furthermore, their concentration was varied in the sample using the standard addition method [11]. Solid pieces of pure lead and indium were weighed and successively introduced in the oven. We assumed that both metals were totally dissolved and that the obtained mixture was homogeneous. These hypotheses were verified: after the experiments several samples were taken from the mixture and analyzed using ICP-AES, which showed the validity of our assumptions.

The experimental setup is shown in Fig. 1. A quadrupled Nd:YAG laser (266 nm, 5 ns pulse width, 20 Hz repetition rate) was used to ablate the sodium sample. It was chosen to perform LIBS ablation because liquid sodium absorbs more efficiently UV radiations. It could operate at 15 mJ maximum energy and was followed by an energy attenuator. The ablation beam was focused with normal incidence onto the liquid sodium surface using a convergent lens (focal length 1 m). The laser spot on liquid sodium had a diameter of 500 μm. The working irradiance was 1.3 GW/cm^2.

The LIBS signal was collected in the same direction as the ablation beam, using a telescope (working distance 950 mm), and sent to the detection system using an optical fiber (numerical aperture of 0.22 and core diameter of 910 μm). A Czerny–Turner monochromator (Acton SP2300i, 3600 grooves/mm) was used for the analysis of the LIBS signal. The entrance slit was 100 μm wide. The spectra were recorded using an Andor iStar ICCD (512 × 2048 pixels). This system had a resolution power $\frac{\lambda}{\Delta\lambda}$ of 3000 at 283 nm.

Four hundred laser shots were accumulated for each spectrum. For each standard addition, 100 replicas were successively acquired in about 30 min. Fig. 2 shows typical spectra, obtained using optimal acquisition parameters (see Section 2.2) for a concentration of 89 ppm of lead and 50 ppm of indium in liquid sodium. Atomic lines are visible above a continuum which can be attributed to Bremsstrahlung, radiative recombinations and in the case of Pb, the wing of a strong sodium line at 285.3 nm.

2.2. Optimization of acquisition parameters

The limit of detection (LoD) is linked to the continuum background noise, then to the signal to background noise ratio (SNR) [12]. To
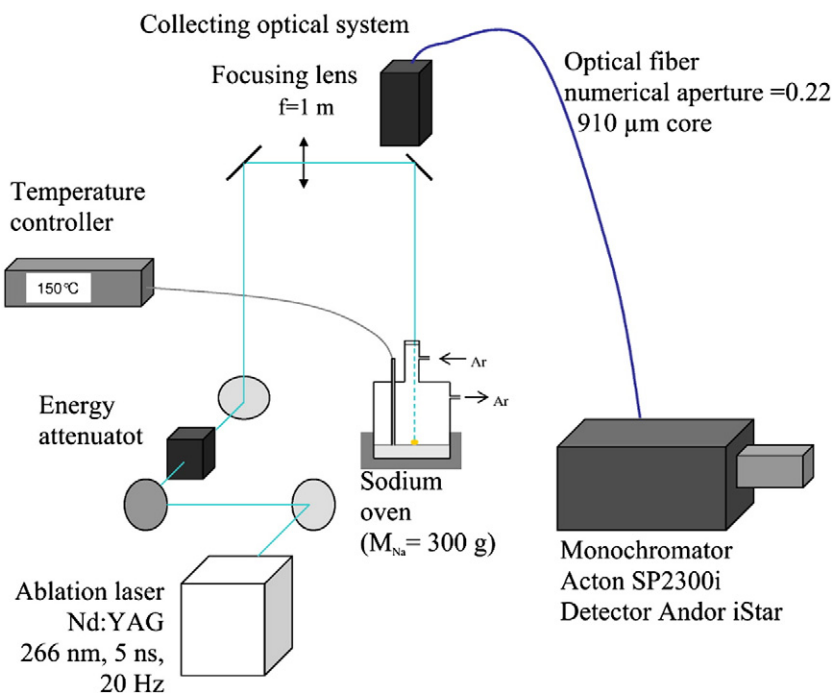

Fig. 1. Experimental setup.