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Quantitative Analysis of Deuterium in Zircaloy Using Double-Pulse Laser-Induced Breakdown Spectrometry (LIBS) and Helium Gas Plasma without a Sample Chamber

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ABSTRACT: A crucial safety measure to be strictly observed in the operation of heavy-water nuclear power plants is the mandatory regular inspection of the concentration of deuterium penetrated into the zircaloy fuel vessels. The existing standard method requires a tedious, destructive, and costly sample preparation process involving the removal of the remaining fuel in the vessel and melting away part of the zircaloy pipe. An alternative method of orthogonal dual-pulse laser-induced breakdown spectrometry (LIBS) is proposed by employing flowing atmospheric helium gas without the use of a sample chamber. The special setup of ps and ns laser systems, operated for the separate ablation of the sample target and the generation of helium gas plasma, respectively, with properly controlled relative timing, has succeeded in producing the desired sharp D I 656.10 nm emission line with effective suppression of the interfering H I 656.28 nm emission by operating the ps ablation laser at very low output energy of 26 mJ and 1 μ s ahead of the helium plasma generation. Under this optimal experimental condition, a linear calibration line is attained with practically zero intercept and a 20 μ g/g detection limit for D analysis of zircaloy sample while creating a crater only 10 μ m in diameter. Therefore, this method promises its potential application for the practical, in situ, and virtually nondestructive quantitative microarea analysis of D, thereby supporting the more-efficient operation and maintenance of heavy-water nuclear power plants. Furthermore, it will also meet the anticipated needs of future nuclear fusion power plants, as well as other important fields of application in the foreseeable future.

The worldwide demand for energy has continued to grow at an increasing pace. Meanwhile, the world is confronted with the problems of dwindling supply and increasing cost of fossil fuels, as well as the growing threat that their continued consumption is expected to pose to the global climate. The challenges to cope with those problems, among others, in the past, have led to a renaissance in the development of the nuclear power industry. Unfortunately, the nuclear reactor disaster induced by the devastating tsunami at the Fukushima Nuclear Power Station in Japan is making a significant dent in the further deployment of nuclear power plants worldwide.

Nevertheless, this is likely to be temporary in nature, as the initial socio-political reaction is bound to subside with time, especially when the continued improvement of reactor technology can be demonstrated to offer much safer operation of the new generation nuclear power plants. Besides, the large and unique advantages offered by nuclear energy, which are (at

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least until the end of this decade) unmatched by the other alternative new energy sources, is difficult to ignore, in the face of pressing demand for large-scale and high-efficiency energy supplies.¹ It is also highly improbable that the existing nuclear power plants responsible for a large share of energy supply in some developed countries will be abandoned abruptly. It should also be noted that most of the more recently built reactors are of the improved versions, employing the heavy-water moderator instead of the older version of light-water reactors adopted in the Fukushima Nuclear Power Station. However, there is one important common problem that must be tackled for improving the efficiency of their operations, as described below.

In a light-water nuclear power station, the enriched uranium fuel is contained in zircaloy pipes immersed in a water tank. During the operation of the reactor, hot water reacts with the zircaloy surface to form zirconium oxide and hydrogen gas, which readily penetrates into and accumulates in the zircaloy pipe. The excessive presence of this trapped hydrogen is known to cause a certain type of structural damage, leading to reduced mechanical strength of the material and potentially endangering the operation of the power plants. Therefore, the hydrogen concentration in the zircaloy pipes must be examined periodically. A standard technique for detecting hydrogen in such a case involves the use of a gas detector and requires the melting of a portion of the zircaloy pipe in a carbon furnace after the special handling for the removal of the remaining fuel in the pipe. Thus, it is highly desirable to replace the existing time-consuming and destructive method by a more-practical and less-destructive one. A similar demand for improved deuterium (D) detection technique is to be expected for the heavy-water nuclear power plants.

As reported previously,² it is indeed possible to improve the hydrogen (H) detection method by means of some modification of the laser-induced plasma spectroscopy (LIPS), which was first introduced by Brech and Cross in 1962.³ This method was later developed into the celebrated technique of laser-induced breakdown spectroscopy (LIBS) by Radziemski et al.,⁴ which has become a widely adopted modern tool for rapid spectrochemical analysis in industry and research laboratories.⁵ Using low-pressure (5 Torr) ambient helium gas,⁶ we have demonstrated the detection of the sharp H I 656.28 nm and D I 656.10 nm emission lines from the zircaloy sample, overcoming the long-standing problems of the Stark broadening effect and intensity diminution due to the time mismatch effects, which are commonly encountered in the standard operation of LIBS conducted with ambient air at atmospheric pressure. It is worth recalling that the time mismatch effect refers to the premature passage of the ablated atoms before the shock wave formation, thereby missing out on the shock-wave-induced thermal excitation process. This was suggested to be responsible for the weak intensity observed in the emission of very light and fast-moving atoms such as H and D.² Taking advantage of the previous result, suggesting the role of the metastable excited state of He in the low-pressure plasma,² those disturbing effects were effectively eliminated by the appropriately delayed and prolonged detection of the H atomic emission. It was proposed that, during this delayed detection period, the measured H emission, instead of arising from the conventional hot plasma excitation, was mainly the result of the so-called helium-assisted excitation (HAE) process in the sufficiently cooled plasma via the Penning-like ionization process proposed previously.⁷ This suggested excitation

mechanism was further expanded with detailed energy-level diagram of He and the energy transfer processes in a most recent study of other atomic emission enhancements.⁸ However, those results were all achieved with low-pressure (5–10 Torr) ambient helium gas. This implies the need for a vacuum pump for the preparation of the sample chamber, which is unwieldy for the need of rapid and frequent inspections. In a most recent experiment, the need for a low-pressure environment was circumvented by employing atmospheric-pressure helium gas and an additional surface water precleaning procedure,⁹ which also succeeded in producing the nice linear calibration line that was needed for quantitative analysis. Nevertheless, the use of a bulky sample chamber in this and all previous cases has virtually prevented its application to in situ D detection of zircaloy vessel immersed in the water tank. Therefore, further improvement of the experimental method specifically addressed to overcoming this hurdle is badly needed to support the efficient operation and maintenance of the heavy-water nuclear reactor.

It should be added that the importance of developing a practical, in situ, rapid detection of D can hardly be overemphasized. The benefits of its realization goes beyond just meeting the urgent needs of the existing as well as other heavy-water nuclear power plants to be launched in the immediate future. No less importantly, it will also fulfill the anticipated crucial needs when the current nuclear fission power technology will be replaced eventually by the fusion power technology, which offers safer, cleaner, and more-efficient power production process with long-term sustainability and much smaller amounts of long-lived nuclear wastes, compared to nuclear fission processes. In the thermonuclear fusion reactor, one of the two fuel components used is the deuterium, which is chemically bonded in the solid LiD compound. Therefore, the deuterium analysis of this material is a matter of necessity. Furthermore, deuterium in its gas phase is readily adsorbed by certain metals and can be subsequently released via a simple heating process when needed for use. These metal pieces can be easily transported in disguise for concealed purposes. A practical and reliable D detection method can play an important role in deterring and preventing nuclear terrorism, as well as other illegal abuses of the potentially dangerous and lethal material.

In this work, we have developed a modified version of the conventional double-pulse (DP) LIBS technique employing two laser systems in an orthogonal configuration, which has been widely used for the studies of increasing the emission intensity. The results of those studies have generally demonstrated intensity enhancements with various degrees of enhancement, depending on the sample and ambient gas used,^{10–23} as well as the chosen gas pressure.^{24,25} Specifically, in the preablation DP experiments, the observed intensity enhancement effect was commonly attributed to the rarefied gas condition created by the preablation laser pulse, which led to a more-effective ablation process.^{10,11} In the present experiment, a major technical modification is introduced by employing flowing helium gas at atmospheric pressure without the use of a sample chamber. In this setup, the He atoms in their relatively long-lived metastable excited state are produced in the helium gas breakdown plasma generated in front of the sample, while the sample is separately ablated to release the D atoms into the region of the helium plasma where they are excited by the HAE process. It is found that this method has produced a D emission line of very narrow spectral width,

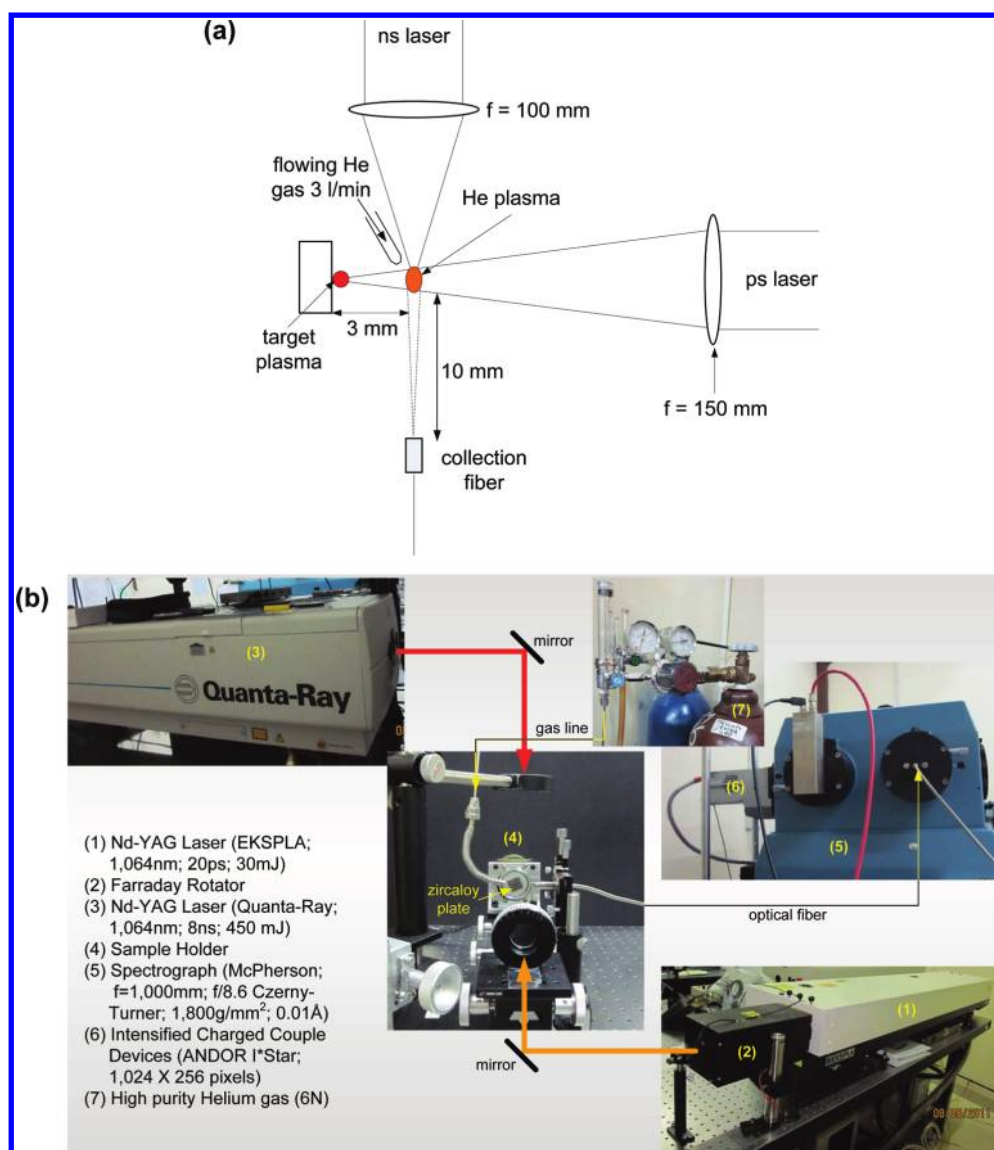


Figure 1. (a) Schematic diagram and (b) photographic display of the experimental setup used in this study.

practically free from the interfering emission of H dissociated from the water molecule. It also eliminates the need for a vacuum chamber, hence promising its potential application for in situ analysis. Finally, our result further shows that the excellent D emission spectrum can be obtained by avoiding the use of a large ablation energy, hence preventing the formation of undesirably large crater sizes on the sample surface.

EXPERIMENTAL PROCEDURE

Figure 1a is the schematic layout of the experimental setup, with its full photographic picture given in Figure 1b. The system employs two orthogonally configured ns and ps Nd:YAG lasers without the presence of a sample chamber. A constant flow of helium gas at atmospheric pressure (Air Liquid, 6N) was maintained in front of the sample target, using a stainless steel tube at a fixed flow rate of 3 L/min, which was determined as the lowest flow rate needed to flush out the pre-existing surrounding air and to ensure the appearance of the detected orange He emission. Both laser systems were operated in the Q-switched mode with a repetition rate of 10 Hz, but in a certain time sequence, as explained below. The ns laser

operating at its fundamental wavelength of 1064 nm and a fixed energy of 80 mJ was focused onto a spot within the flowing helium gas to generate a helium plasma ~ 3 mm in front of the target. The second laser, which was also operated at its fundamental wavelength of 1064 nm, produced 20-ps (ps laser) pulses of 26 mJ for the ablation of the solid target with a certain time difference (τ) between the two laser shots. It should be stressed that the employment of the ps laser pulses has made it possible to perform the effective ablation of the sample with a considerably lower energy of 26 mJ, compared to those applied in previous experiments (~ 100 mJ).⁹ The relative timing between the two laser irradiations was varied to explore the optimal experimental result. The emission spectra of the ablated atoms were collected by an optical fiber with its entrance end positioned in front of the sample and fixed at a distance of 1 cm sidewise from the helium plasma. Thus, only emission taking place in the region facing the fiber end was detected. The other end of the optical fiber was connected to the detection system, which consisted of a spectrograph (McPherson, model 2061, $f = 100$ cm, Czerny Turner configuration) and an optical multichannel analyzer (OMA)

(Andor ICCD, 256×1024 pixels). The OMA system was set at a fixed gate delay of $4 \mu\text{s}$ after formation of the helium plasma, with a gate width of $50 \mu\text{s}$ to yield the time-integrated intensities covering the subsequent emission lifetime. The above timing of the detection was chosen to coincide roughly with the HAE excitation process in the helium plasma. This delayed excitation process, as mentioned earlier, effectively alleviates or even eliminates the time mismatch and Stark broadening problems, giving rise to the clearly resolved emission lines of H and D.

The main targets employed in this experiment consist of a set of zircaloy-4 samples, composed of 98.23 wt % Zr, 1.45 wt % tin, 0.21 wt % iron, 0.1 wt % chromium, and 0.01 wt % hafnium. These samples were prepared using the standard process, which involved a prolonged high-temperature and low-pressure doping technique. The resulting concentrations of deuterium impurity (60, 170, 540, 700, 900, and $1700 \mu\text{g/g}$) were determined via gas chromatography (GC). All of the samples have a cross-sectional area of $10 \text{ mm} \times 10 \text{ mm}$ and a thickness of 1 mm.

RESULTS AND DISCUSSION

As mentioned earlier, the ambient helium gas plays a central role in overcoming the time mismatch and Stark broadening effects.⁷ These effects are known to degrade the otherwise excellent performance of standard LIBS operation when applied to the analysis of light elements such as H and D. Since it is also expected to play a crucial role in this study, it is desirable to verify and demonstrate the expected favorable effect in the present experimental environment. To this end, a copper plate was used as the target, because it has bright green emission lines, in clear contrast to the orange emission line of He. Figure 2a shows the plasma generated in flowing helium gas at 1 atm by the first Nd:YAG laser, with a pulse width of 8 ns and an energy of 80 mJ. The dominant orange color of the plasma is attributed to the He I 587.6 nm emission, with its measured lifetime of $\sim 20 \mu\text{s}$. Meanwhile, no sign of the red H emission was observed, confirming the absence of water molecules in the flowing helium gas. The white and bright color displayed by the rest of the plasma is the result of its overexposure due to the strong continuum background emission. The same feature appears in Figure 2c. Figure 2b shows the small copper plasma generated by the ps Nd:YAG laser with a much-lower energy of 26 mJ without irradiation of the helium gas with the ns laser, hence the disappearance of the orange color. The green color observed at the tip of the plasma shows the combined contributions of the Cu I 510.5 nm, Cu I 515.3 nm, and Cu I 521.8 nm emission lines. The same emission lines originating from the Cu atoms moving slightly behind the tip (slightly decelerated) are mostly drowned by the intense continuum plasma emission. The relatively faint orange color appearing at the other part of the plasma indicates He emission due to the concurrent excitation of the He atoms by the laser-induced gas breakdown effect at the sample surface. Figure 2c shows the result obtained when the two laser systems were activated with a $3\text{-}\mu\text{s}$ time lag for the ps laser. The green-colored Cu emission appearing in front of the helium gas plasma has become even more pronounced in this figure, compared to that observed in Figure 2b. This clearly demonstrates the effective contribution of the HAE mechanism in the presence of the helium plasma. It is also interesting to note that the appearance of the relatively extended area of Cu emission is compensated by the corresponding shrinkage of the helium gas plasma. This may

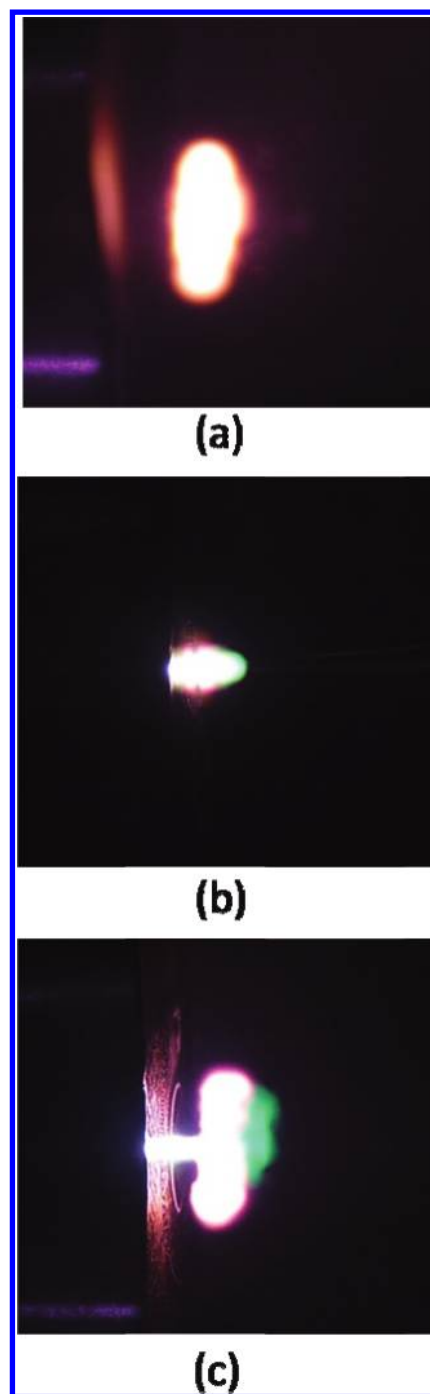


Figure 2. (a) Photograph of the plasma generated in flowing helium gas at 1 atm by the ns Nd:YAG laser with 8 ns pulses and 80 mJ energy; (b) the much-smaller copper plasma generated by the ps Nd:YAG laser with much narrower pulses of 20 ps and lower energy of 26 mJ without irradiation of the helium gas with the ns laser; and (c) the result obtained when both lasers were activated with $\tau = 3 \mu\text{s}$ time lag for the ps laser.

be interpreted as the result that a good part of the metastable-excited He atoms released their energies for the excitation of the Cu atoms, instead of giving them up in the form of photoemission. To proceed with the following experiment, it is important to recall that the effectiveness of the HAE process depends on the condition or the density of excited He atoms in the plasma as it rapidly expands and more away from its designated region with time. Besides, it is also affected by the

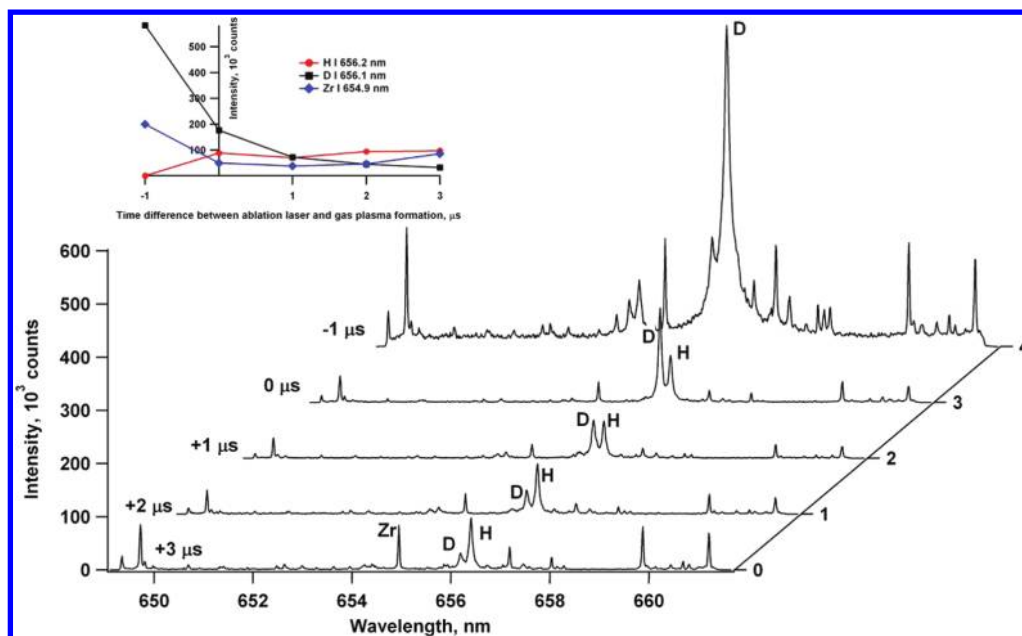


Figure 3. Emission spectra of a zircaloy plate containing 1700 $\mu\text{g/g}$ of D impurity measured for $\tau = -1, 0, 1, 2$, and $3 \mu\text{s}$ with 26 mJ ablation laser energy. The negative sign ($-$) indicates the case that the target ablation precedes the helium gas plasma formation, and the positive sign ($+$) denotes the opposite order of laser irradiations.

energy transfer efficiency taking place via the Penning collision-induced ionization process. This, in turn, is influenced by the relative speed or momentum of the ablated atoms, with respect to the excited He atoms. Consequently, the timing of the two laser operations and the ablation laser energy are important factors to be considered. We shall first investigate the effect of time difference between the two laser operations in the ensuing experiment.

The sample used for the following experiment is a zircaloy plate containing 1700 $\mu\text{g/g}$ deuterium. As mentioned earlier, the much-smaller mass of D, compared to that of Zr as the major component of the zircaloy host material must be taken into account, because of its influence on the optimal time difference (τ) to be explored in this experiment. Therefore, the emission spectra were measured for a number τ between the two different laser pulses. The result is presented in Figure 3 with the signal integrated over the time interval of 50 μs , starting from 4 μs after the generation of helium plasma. The general appearance of the strong H and D emission lines of relatively narrow width, as evidenced by their well-resolved spectral lines, are supposed to be largely the result of the use of helium ambient gas, which is expected to reduce the electron density in the gas breakdown plasma, because of the high ionization energy of He, and partly the result of the rarefied gas condition created by the preablation plasma and thereby increasing the effectiveness of the ablation process, as well as reducing the Stark broadening effect. Nevertheless, the important contribution of the role of HAE in this experimental setup can hardly be overlooked, as pointed out earlier, in connection with Figure 2c, and further explained throughout the ensuing discussion. Note that the negative sign ($-$) indicates the case that the target ablation precedes the helium gas plasma formation and the positive sign ($+$) denotes the opposite order of laser irradiations. The figure clearly shows the expected Zr and D emission lines along with the H emission line. However, the D emission detected with +3 μs time lag is very weak and was largely overshadowed by the presence of the

more-dominant H emission, which is supposed to have its origin in the dissociated water molecules deposited on the sample surface. The consistent improvement of D emission intensity was observed when τ was reduced to +2 μs , +1 μs , and 0 μs , successively. However, the maximum enhancement of D emission was observed when the zircaloy sample was ablated 1 μs ahead of the helium gas plasma generation (denoted by $\tau = -1 \mu\text{s}$).

The overall comparison of the intensity variations of H I 656.28 nm, D I 656.10 nm, and Zr I 654.9 nm emission lines, with respect to the time difference τ , is presented in the inset of Figure 3. Note that the intensity variations, with respect to τ in the positive and negative time regimes, are quite different and they deserve separate discussions as follows. In the positive τ regime, corresponding to the preablation operation, the variations generally are relatively mild. The observed slight intensity reduction of the Zr emission with the initial decrease of τ does not persist with further decreases in τ , while the H emission intensity remains practically unchanged over the entire range of time variation considered. In contrast, the D emission displays an interesting and visibly more steady rise (decline) of intensity with decreasing (increasing) τ . Note that the longer delay (larger positive τ) of the ablation simply implies the later excitation of the ablated atoms in the helium plasma. Since the amount of He atoms in their metastable excited states decreases with the flow of the helium gas and expansion of the plasma, lesser emission intensity of the ablated D will be detected in the fixed detection window. On the other hand, the simultaneously ablated Zr atoms were expected to move along more slowly with the subsequently generated shockwave and arrive later at the helium gas plasma, which has suffered from further depletion of the excited He atoms, in addition to partial blown off of the plasma by the shock wave, rendering the HAE process much less effective. For the lightest and fastest-moving H atoms, the probability of collision-induced Penning-like energy transfer process is supposed to be

lower, hence also resulting in low emission intensity as Zr emission.

In the negative τ region, corresponding to the post-ablation process, one observes more-sensitive and even drastic changes, with respect to τ variation in the intensities of all three emission lines. The conspicuously sharp increases in the D and Zr emission intensities with increasing negative τ are understood to be the result of a better-confined and more-concentrated helium plasma, which was generated in the presence of both D and Zr atoms. In the present case, the effect of depleted He atoms in their metastable excited states described previously is no longer operative, because the D and Zr atoms are already present before the formation of the helium gas plasma. The higher D emission intensity is most likely due to the more-effective energy transfer process for D, which is due to the smaller mass difference between D and He. No less remarkable is the sharp decline of the H emission intensity, resulting in practically vanishing intensity at $\tau = -1 \mu\text{s}$. This is both interesting and important. The unwanted H emission line, being so close to the D emission line, will inevitably interfere somewhat with the latter, even when they are well-resolved. This is undesirable for quantitative analysis, because of the presence of overlapping intensities between the two comparable emission lines, as indicated in the spectra of Figure 3 for $\tau > 0$. Therefore, the effective suppression of this notorious and long-standing ubiquitous effect in the observed spectrum without any precleaning process is indeed a remarkably significant result. We believe that this unexpected phenomena can be explained as follows. First, let us recall that the H emission is usually associated with the H atoms dissociated from the H_2O molecules in the ambient helium gas and those deposited on the sample surface. However, the first possibility is already largely ruled out, as we have explained in the discussion of Figure 2a. Focusing on the second possibility, it is important to recall that, being the lightest and, hence, the fastest-moving particles among the ablated atoms, a large part of them will have passed the designated gas plasma region when the plasma was formed. The earlier they were ablated, a greater number of them will miss out on the helium gas plasma.

In order to ascertain the most favorable experimental parameters, an additional measurement of the same sample were carried out for $\tau = -2 \mu\text{s}$ and beyond that. While the Zr emission became stronger, the D emission disappeared from the detected spectra. Apparently, the faster moving D atoms had moved out of the intended helium plasma region when the helium plasma was generated, leaving behind the much-heavier Zr atoms for the HAE process. This is consistent with the scenario described for the declining H emission, even with the smaller time difference. Given the larger D mass and, hence, its slower-moving speed, it is only natural that the disappearance of D emission occurred at a larger time difference between the earlier ablation and gas plasma generation processes.

The possibility of achieving the same or even better result with smaller ablation energy was examined by measuring the emission spectra of zircaloy sample containing $700 \mu\text{g/g}$ D impurity, applying ablation energies of 26 mJ and 12 mJ with the same time difference of $\tau = -1 \mu\text{s}$. The results are presented in Figures 4a and 4b, respectively. Figure 4a shows that the previous result is exactly reproduced from this sample, displaying the sharp emission line without the perceptible appearance of the H emission line when the same ablation energy of 26 mJ was used. On the other hand, almost equally strong D and H emission lines were found in the spectrum

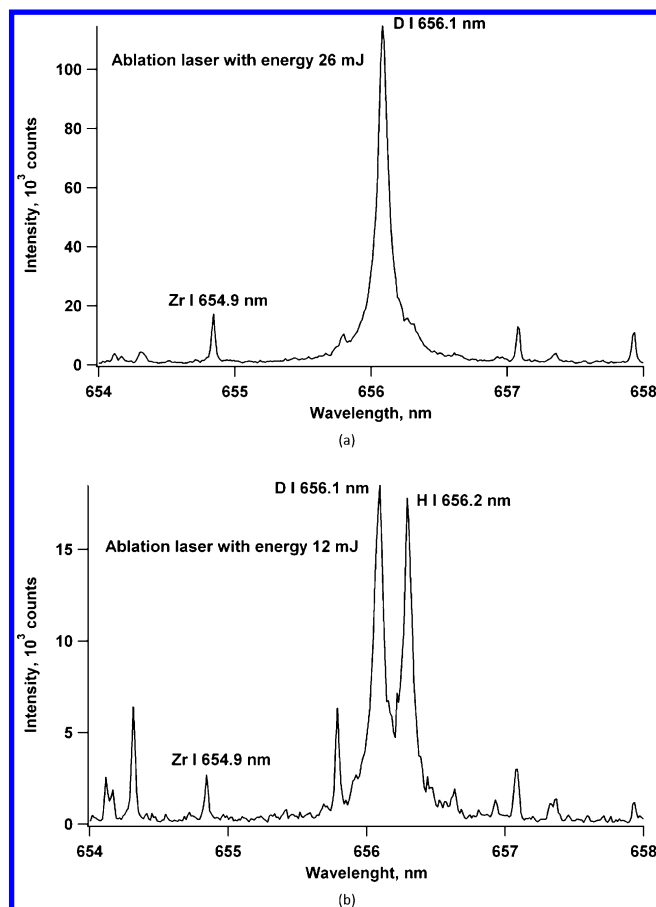


Figure 4. Emission spectra of a zircaloy plate containing $700 \mu\text{g/g}$ of D impurity obtained at different laser ablation energies ((a) 26 mJ, as in the previous case, and (b) 12 mJ, both measured with the same time difference ($\tau = -1 \mu\text{s}$)).

shown in Figure 4b when the ablation was conducted at the considerably lower energy of 12 mJ, which was originally conceived to explore the possibility of less-destructive detection. Apparently, at such a low ablation energy, the ablated H and D atoms are bound to move at lower speeds and, hence, overcome the time mismatch effect responsible for the absence of H emission in the former case, as explained earlier. Therefore, we have settled with the choice of an ablation energy of 26 mJ and $\tau = -1 \mu\text{s}$ as the most suitable operational parameters for the following experiment.

In the next experiment, a series of measurements were carried out on several zircaloy-4 samples prepared with different deuterium concentrations of 60, 170, 540, 700, and $900 \mu\text{g/g}$, which was prepared as described earlier. The measured D emission intensity is normalized by the particular Zr emission intensity appearing within the same spectral range in each case and plotted in Figure 5, with respect to the associated deuterium concentration. Each data point in this figure is the average of 50 data results produced by 50 successive laser shots on the same sample spot. This measurement was then repeated on five different spots of the same sample surface. The results of these measurements were found to be highly reproducible, implying the uniformity of the impurity D distribution in the sample. It is seen that the D impurity concentration and its associated emission intensity exhibit a clearly linear relationship with a practically zero intercept. For an estimation of the limit of detection (LOD) for

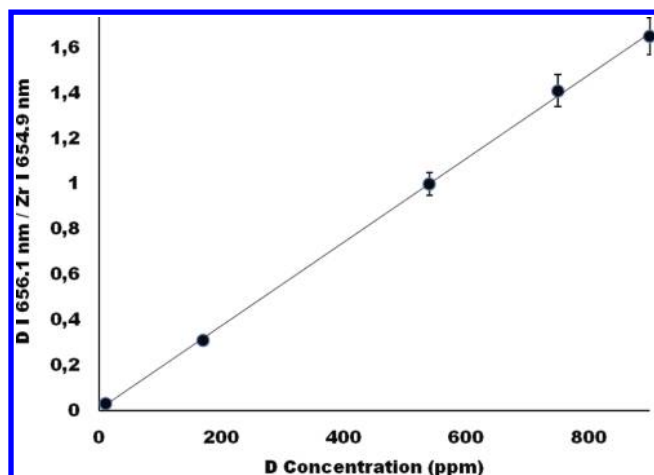


Figure 5. Relationship between the ratio of D I 656.10 nm/Zr I 654.9 nm and the D impurity concentration in a zircaloy sample.

D, the emission spectrum of a zircaloy-4 sample that contained 750 $\mu\text{g/g}$ D was used. The detection limit was estimated following the conventional criterium as a ratio of the signal against three times the noise level. The resulted LOD was determined to be $<20 \mu\text{g/g}$. This value is well below the tolerated threshold concentration of detrimental deuterium of 800 $\mu\text{g/g}$ in a zircaloy vessel used in a nuclear power plant. Taken together, the results described above have demonstrated the potential application of this technique for useful practical and sensitive, in situ, quantitative D analysis of zircaloy vessels used in heavy-water nuclear power plants.

Finally, it is important to stress that the actual realization of in situ application of this technique to zircaloy pipe inspection in the reactor will require the measurement to be conducted with the zircaloy pipes remaining in the heavy water, preferably without even disturbing the reactor operation. In other words, the challenges lying ahead for more-efficient operation and maintenance of the heavy-water reactor would be the development of in situ as well as in-service inspection of the D concentration in zircaloy pipes of the reactor. Works in this direction is being pursued. The result of its realization and application will be reported elsewhere.

CONCLUSION

The result of this study has shown that a method for practical quantitative D detection in zircaloy was successfully implemented by means of an orthogonal double-pulse laser-induced breakdown spectrometry (LIBS) technique, using a system of ps and ns lasers operated with a certain time difference (τ) and employing flowing helium gas at atmospheric pressure without being equipped with a sample chamber. It was demonstrated, specifically, that a strong and sharp D emission line was detected with $\tau = -1 \mu\text{s}$ and a laser ablation energy of 26 mJ, practically free from the interfering H I 656.28 nm spectral line. The experimental result further exhibits a linear calibration line with a zero intercept, as well as very low limit of detection (LOD) of 20 $\mu\text{g/g}$. The resulted average crater size $<10 \mu\text{m}$ in diameter may offer its application to virtually nondestructive analysis. The fact that these results were achieved without the use of a sample chamber has further made it promising for the further development of this technique and its application to practical regular in situ quantitative inspection of fuel vessels in heavy-water nuclear power plants. With further improvement of

its detection sensitivity, its application to geological study is to be expected in the foreseeable future, while in the long-term perspective, it is also expected to serve the needs of future nuclear fusion power plants.

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Notes

The authors declare no competing financial interest.

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