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Arabian Journal of Chemistry

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1. **Draft manuskrip sebelum proses submission**

2. **Submission acknowledgment dari Arabian Journal of Chemistry (11 Juli 2021)**

webmail
FISIKA
universitas diponegoro

Ali Khumaeni <khumaeni@fisika.fsm.undip.ac.id>

Submission Confirmation
1 message

Arabian Journal of Chemistry <em@editorialmanager.com>   Sun, Jul 11, 2021 at 9:16 AM
Reply-To: Arabian Journal of Chemistry <awarthan@ksu.edu.sa>
To: Ali Khumaeni <khumaeni@fisika.fsm.undip.ac.id>

Dear Dr. Ali Khumaeni,

We have received your article "Analysis of sodium in steel surface using pulse CO2 laser-induced breakdown spectroscopy" for consideration for publication in Arabian Journal of Chemistry. Please be informed that by submitting the article to the journal, you agree to the payment of Open access charges of USD 1250 if your article has been accepted for publication.

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Kind regards,

Editorial Manager
Arabian Journal of Chemistry

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3. **Editor and reviewers' comments (21 Agustus 2021)**

webmail
FISIKA
universitas diponegoro

Ali Khumaeni <khumaeni@fisika.fsm.undip.ac.id>

Your Submission

Arabian Journal of Chemistry <em@editorialmanager.com>   Sat, Aug 21, 2021 at 5:49 PM
Reply-To: Arabian Journal of Chemistry <support@elsevier.com>
To: Ali Khumaeni <khumaeni@fisika.fsm.undip.ac.id>

Ms. Ref. No.: ARABJC-D-21-01158
Title: Analysis of sodium in steel surface using pulse CO2 laser-induced breakdown spectroscopy
Arabian Journal of Chemistry

Dear Dr. Ali Khumaeni,

The reviewers have commented on your above paper. They indicated that it is not acceptable for publication in its present form.

However, if you feel that you can suitably address the reviewers' comments (included below), I invite you to revise and resubmit your manuscript.

Please carefully address the issues raised in the comments.

If you are submitting a revised manuscript, please also:

a) outline each change made (point by point) as raised in the reviewer comments

   AND/OR

b) provide a suitable rebuttal to each reviewer comment not addressed

To submit your revision, please do the following:

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This takes you to the Author Main Menu.

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I look forward to receiving your revised manuscript.

Yours sincerely,

Abdulrahman A. Alwarthan, Ph.D.
Editor-in-Chief
Arabian Journal of Chemistry

Reviewers' comments:

Reviewer #1: In figure 1 a what is a Photon drug? Also in your description of the laser setup please include the beam diameter and the beam quality (M2) if possible.
In figyre 1b please label the pyrex tube.
In the results and discussion section please include the beam diameter and beam quality for the Nd:YAG laser system as well.
Please clarify the difference between the pyrex and the other container.
When discussing the defocused 18mm focal point, please clarify whether that is 18mm in front of the focal point or not.
Figure 5 what is the curve represented by the triangles? also the addition of error bars would help the reader determine the amount of variability of your measurements.

Figure 6, what do the error bars represent? one standard deviation or 95% confidence interval? or somethin else please specify.

Reviewer #2: Khumaeni et al. investigated the analysis of sodium in steel surface using pulse CO2 laser-induced breakdown spectroscopy. They compared the plasma spectra induced by Nd:YAG laser and CO2 laser, finding the CO2 laser is better than YAG laser for the analysis of sodium in steel surface. Some comments are as follows:

Abstract
The limit of detection of sodium in the metal surface was estimated to be 0.5 mg/l. "mg/l"? What unit is it?
The results certified that the present technique of LIBS using pulse TEA CO2 laser is much superior compared to the case of standard LIBS proven by an excellent emission spectrum of sodium with an optimum intensity and low noise and background emission. What is standard LIBS? Please show some references. LIBS is laser induced breakdown spectroscopy, what is "standard laser"?

INTRODUCTION
For "a pulse laser such crystal Nd:YAG laser is employed as an excitation and ionization source", why is Nd:YAG laser? Can't other lasers?
For "the metal itself is ablated and therefore the major and minor analytical lines associated with the sample disturbed the impurity and trace elemental lines", I think the factor should be the continuous emission, not other major and minor lines. And, the longer pulse duration will produce stronger continuous emission due to the plasma reheating.

EXPERIMENTAL PROCEDURE
For "laser energy was varied from 0.75 J to 1.5 J" and "a pulse TEA CO2 laser (Shibuya, 10.064 µm, 200 ns, 3 J" in abstract, why not use 3 J in the experiment?
How is the concentration of Na calibrated?
For "dropping 3 ml liquid droplet on the steel surface", is there extraction effect? If so, it is not the true concentration in the steel.
The gate delay time and gate width of OMA system was 10 and 100 µs, respectively. How is this gate optimized?

RESULTS AND DISCUSSION
The Nd:YAG laser energy was 83 mJ, the energy is far lower than that the energy of CO2 laser. If the Nd:YAG laser energy was increased to 1 J close to the energy of CO2 laser. The emission Na lines will be very high. The authors' experimental comparison is unfair.
For the correction curve, the data points are very few, and more data points should be required.

Reviewer #4: Analysis of sodium in steel surface using pulse CO2 laser-induced breakdown Spectroscopy

In this manuscript, authors have presented their study of Sodium detection on the steel surface by LIBS. They have compared performance of traditional LIBS with Nd:YAG laser and TEA CO2 LIBS, and claimed that the later one performed better. In my opinion, it does not have enough scientific novelty to publish it in a journal like Arabian Journal of Chemistry. Published literatures from the same authors group have already shown the advantages of TEA CO2 LIBS. The way they have presented traditional LIBS for Na detection in this manuscript is not convincing because Na is one of the easily detected analyte for LIBS. I would recommend submitting it to other journals which focus more on applications.
Here are the few comments if authors want to resubmit the manuscript elsewhere:
1.   Section: Introduction, Page 4, line 43 "Laser induced breakdown spectroscopy (LIBS) has become most popular technique…". Rewording is recommended, especially for the words "most popular". Need to be aware that all techniques have limitation so does LIBS.
2.   Section Introduction: page 4, line 50: May be typo: …laser such crystal Nd:YAG laser is employed as an excitation….
3.   Line 55: Due to its convenient and versatile tool as a spectroscopy technique… Correct the sentence.
4.   Page 5 line 38-50: "Therefore, this laser can produce large-volume luminous plasma and high plasma temperature….". Traditional LIBS has also high plasma temperature, what is the range of temperature authors mentioning here? Provide equation for the relation between laser wavelength and plasma absorption.
5.   Section: experimental procedure, Page 7, line 3, "The sample was placed in a chamber… kept constant at 1 atmosphere". Elaborate the reasoning for using the chamber and using the nitrogen gas.
6.   Section: results and discussion, page 7, Line 45: For standard LIBS, they have used 83 mJ of laser energy which is very high in general in LIBS experiment. How is this energy selected? Authors have mentioned that, "It is seen that completely no emission lines of neutral Na are detected in the spectrum." But looks like there are some unresolved emissions lines near 589 nm wavelength, which could be Na and may be affected by self-absorption. Explain it.
7.   Page 8, line 6 "…the background emission is also high…." what does this mean? Are you expecting low background emission at 1us Gate delay? From solid surface, background can be observed at 1us Gate delay, which is normal.

8.   Page 9, line 13-15 "The pulse TEA CO2 laser induced very unique characteristics compared to the case of pulse Nd:YAG laser, which generally applies in standard LIBS." Correct the sentence.

9.   Page 9, line 45-45, Bring self-absorption into discussion here?

10.   Conclusions: Reword the first sentence, "Sophisticated technique of laser-induced breakdown spectroscopy using pulse TEA CO2 laser has been employed for the identification and analysis of sodium impurity in the steel metal surface.

Reviewer #5:   Review

ARABJC-D-21-01158
Analysis of sodium in steel surface using pulse CO2 laser-induced
breakdown spectroscopy

The presented manuscript deals with a determination of sodium on the steel sheet surface with laser-induced breakdown spectroscopy (LIBS). In contrast to other LIBS analyses a TEA CO2 pulsed laser was used. The authors claim that the plasma from the CO2 laser is much larger, luminous and suppressing interfering iron lines in comparison with that from a Nd: YAG laser. Sodium determination is thus more sensitive. The topic can be of potential interest.

The manuscript structure is well-built but there are several important issues:

1) Some sentences should be re-written. The language requires correction.

2) There is the sodium concentration in mg/l also for the surface and LoD (p. 11). However, this information says nothing about the mg/cm2 of the steel sheet. Please recalculate the results.

3) Please give the dimensions of the stain made by the drop of the salty solution and a photo of the dried stain.

4) P. 6, Experimental Procedure: Was there a ring of concentrated deposit on the stain border (coffee ring effect)? How did you ensure the salt homogeneity on the surface?

5) You should also present craters photos to compare the ablated volumes from the CO2 and Nd: YAG lasers. You can estimate if the higher sodium signal is rather from the more ablated material or from the more efficient excitation.

6) For the CO2 laser you mention a higher plasma temperature but where and how did you measure this parameter? I think that a short comparison of T and electron number densities for the CO2 and Nd: YAG plasmas would be interesting. It is known that a higher T does not always mean a higher intensity of alkali metals lines. They can be easily ionized which means a decrease of the number of atoms. The intensity may therefore also decrease.

7) Concerning the interaction of NaCl with the steel material, is your experiment sufficiently representative? I mean e.g. sodium migration into the steel body during a longer time exposition in comparison with a quick drop and drying on the surface. And what about a chloride corrosion?

8) P. 7-8: "This indicated that the steel metal itself are also ablated when the Nd:YAG laser beam is directed and focused on the steel metal." - Please explain in context of the qu. 10).

9) P. 8: "However, when the steel sample does not contain sodium line on its surface, completely no emission lines of Na occur and only Fe emission lines appear as shown in Fig. 3(b)." - There may be sodium atoms on the surface, not sodium lines.

10) P. 8 and 10: "It should also be noticed that the ablation of steel metal itself happen during laser bombardment." - Do I understand well that you do not suppose the ablation of the sample body under certain conditions? Does the CO2 laser uniquely ablate only the surface sediment without spectral contamination by iron lines?

11) P. 9: "Physically, when the pulse laser is irradiated tight focus on a surface…" - I mean that the laser is pulsed and the sample is irradiated, not the laser.

12) P. 10, line 50: "...the steel metal containing 50 mg/kg sodium on its surface…" - Do you mean 50 mg/l in the dropped solution?
Optimization of the focusing - it would be nice to see on photos how the crater diameter and appearance changes with the focusing.

13) P. 11: In my opinion the calibration dependence is a quite typical LIBS curve, not excellent.
Please explain: "Each data plotted in the curve is average of three spectra.
Each spectra was taken by 20 shots laser bombardment and the data acquisition was
repeated 5 times under the condition that the laser beam was defocused at the
surface of steel sample." - 20 spectra were integrated on chip and this was repeated 3-times and the average point from 3 integrated intensities was depicted in the Fig. 6? If so where are the 5 replicates please?

14) Figures
1a) - nice drawing but the microplasma should not cover the whole sample.
2-7 - the lines should be thinner, not smooth (only straight lines connecting points)
5 - What does mean the green line and what does the right y-axis?
5, 6, 7 - axes description is very small, please enlarge
6 - You state on p. 6: "Samples used in this work were 304 steel samples containing various
concentrations of Na on their surface, namely 10, 20, 40, 50, and 100 mg/l." Nevertheless, there are c = 250 - 2500 mg/l in Fig. 6. Please explain and correct.
What do mean the error bars? Where is the equation of the line and R2? The intercept of the depicted line is not zero

- please compare with the statement in Abstract and correct.
I mean that this manuscript should be revised thoroughly before it can be considered for publication.

Reviewer #6: The manuscript proposes the quantitative measurement of sodium in steel samples by laser-induced breakdown spectroscopy (LIBS) using pulse transversely excited atmospheric CO_2 laser. According to the authors, the importance of measure sodium is due to the fact of this element reduces the strength of the material.
Some specific comment about the manuscript:
1.   "analysis of sodium" should be replaced by "determination of sodium" or "quantification of sodium" since sodium is the analyte. The term "analysis" should be used for sample, e.g. "analysis of steel".
2.   As solid samples has been analysed, LoD should be presented in "% (m/m)" or "mg/g" instead of mg/L. This is strongly reccomended also because Figure 6 shows Na concentration in % in calibration curve.
3.   Figure 6: equation and R2 shoul be shown e discussed.
4.   Besides the proposal is the analysis of solid steel samples, Na solution was deposited onto the sample to make the calibration. It is known however that the behaviour of the analyte in solid sample and in solution is not similar, causing interference.
5.   How LoD was calculated?
6.   The accuracy of the method shoul be checked by analysing reference material or using another well stablished method like ICP OES.
7.   Page 4, lines 52-57: "The Na-deposited steel was then placed on a microwave oven for 5 minutes with a temperature of 100 for drying and depositing the NaCl liquid on the steel surface." Steel was dried in the microwave oven? How it is possible?

Reviewer #9: The paper submitted by Khumaeni et al. investigates the possibility of the determination of sodium on the steel surface by using CO_2 LIBS. Liquid sodium and highly concentrated sodium chloride solutions induced corrosion on different types of steel, so the relevant study presented here could be of interest not only for scientists but also for industrial purposes. However, there are some unclear statements in the manuscript.
(1) In my opinion it would be useful to emphasize more clearly what is new and significant in this paper. The introduction is focused on the effect of liquid Na and yet NaCl solutions were used for the sample preparation. Also, the introduction needs to be reorganized and written. The research progress is not sufficiently elaborated, and the novelty of the work is not sufficiently clear, it should be highlighted.
(2) Sample preparation for the calibration is not clear. NaCl solution was dropped on the steel sample and dried in the microwave. What was the diameter of the resulting film? Was it evenly spread and how did it affect the RSD of the emission line of Na?
(3) Since analyzed Na comes from deposed NaCl solution on the surface of a metal, it cannot be classified as analysis of Na in steel. This analysis can be associated with surface-assisted LIBS. SALIBS allows the deposition of a thin homogeneous film of the liquid sample on a metallic surface that can greatly improve the analytical performance. The metallic surface is expected to contribute to increasing the temperature and the density of the plasma and, consequently, the better overall sensitivity of the method is achieved. A different approach for the preparation of the calibration set should be investigated. Furthermore, investigation of the effect of the Na on the surface hardness might be an interesting addition to this manuscript.

Reviewer #10: This paper is on some experimental work of rather good quality, but it is very poorly structured and in parts rather confusing.

The confusion begins with the opening statement in the abstract:

Analysis of sodium in metal samples is very necessary because the existence of
sodium can reduce the strength of the material.

This implies determination of Na in the bulk metal. For steel, this is totally irrelevant, since Na contamination in the metallurgical process is no problem. Reading further in the introduction, it becomes clear that it is actually surface contamination of Na on steels that is the object of this study. This analytical need of is confined to steel material of reactor coolers using liquid Na, which is a rather rare application of steel. Both the abstract and the introduction must clarify this.

Another confusing term is "standard LIBS". There is no such term defined, here it is clear that the authors mean LIBS using a Nd:YAG laser. Please remove all "standard LIBS" from the text and just state in the introduction that this laser type is the most commonly used in LIBS. It is sufficient to write this once, not repeat it in several places of the text!

The paper is then very badly structured, with large parts of the "Results and discussion" actually belonging to the introduction and experimental procedure sections. The beginning of the "Results and discussion" section up to page 8 line 26 is essentially all "Experimental procedure". There is also plenty of redundant information/repetition. Here is an example:

Page 5, lines 33 - 50.
This is because the pulse TEA CO_2 laser has much longer
wavelength of 10.64 µm and longer pulse duration of 200 ns compared to the
Nd:YAG laser case. Therefore, this laser can produce large-volume luminous
plasma and high plasma temperature. It is known that longer laser wavelength
strongly related to the absorption coefficient of luminous plasma because the
plasma absorption coefficient is proportionally related to the inverse square of the
frequency of laser light. Namely, the longer the laser wavelength, the higher the
plasma absorption that results in large-volume of plasma.

Page 9 lines 35- 50:
It should be emphasized that the plasma absorption for the TEA
CO_2 laser is much higher compared to the case of the Nd:YAG laser because the
coefficient of plasma absorption is proportional to the inverse square of the
frequency of laser light. Also, the pulse duration of the TEA CO_2 laser is much
longer about 20 times compared to the Nd:YAG laser case. Therefore, the energy
from the CO_2 laser is most often absorbed by the luminous plasma, resulting large
volume and high-temperature plasma.

Specific comments on the results:

Line 47: Why use the unit mg/l for "concentration on the surface"? The proper unit should be mass/area (e.g. mg/m2),
which is how you normally measure surface contamination. I believe these numbers instead represent the
mass/volume of the liquid solutions used to deposit Na on the surface. Please clarify! This also goes for Fig. 6, where
the unit on the x-axis is just %. Percent of what? The mass fraction of the top surface layer? If so, how can this be
defined?

The Nd:YAG LIBS spectra in Fig. 2 - 3 are truly appalling, and definitively not typical of what you can achieve with
such a system. Have you identified any of the Fe lines claimed to overlap the Na lines in this spectrum without any
clear line structure?

Finally, the paper lacks any comparison with the performance of alternative analytical techniques. It is stated that the
results obtained are "much superior" to Nd:YAG LIBS, but no number for the DL of such a system is given (should be
from a system that performs properly). Also there is a complete lack of comparison with other optical emission
techniques, e.g. spark OES and Glow Discharge (GD) OES. A bit of research on what these techniques can
accomplish is required.

4. **Balasan komentar Editor dan Reviewers**

Ms. Ref. No.: ARABJC-D-21-01158
Title: Analysis of sodium in steel surface using pulse CO2 laser-induced breakdown spectroscopy

Dear Abdulrahman A. Alwarthan, Ph.D.
        Editor in Chief, Arabian Journal of Chemistry

Thank you very much for reviewing our paper entitled "Analysis of sodium in steel surface using pulse CO2 laser-induced breakdown spectroscopy", which we have submitted to Arabian Journal of Chemistry.

We have completely read your letter and feel happy that our manuscript is suitable for publication in Arabian Journal of Chemistry after appropriate revisions.

In this letter, we would like to respond the comments from reviewers as below. Considering the comments from reviewers, we have made a final revision in our manuscript. The revision parts are shown in the revised manuscript using red letter.

We would like to thank you very much for your kindness.

Best regards
Ali Khumaeni et al.

Reviewer #1

Reviewer point #1: In figure 1 a what is a Photon drug? Also in your description of the laser setup please include the beam diameter and the beam quality (M2) if possible.

Author response #1: in our experimental setup, a digital delay system (SRS DG535) was used to set a gate delay time and gate width of OMA system during data acquisition. For triggering a digital delay system, a small part of laser beam was used by sending the laser beam via a photon-drag. We have included this explanation in the section of Experimental Procedure.

Reviewer point #2: In figure 1b please label the pyrex tube.

Author response #2: We have revised the figure following your suggestion as shown in Fig. 1(b).

Reviewer point #3: In the results and discussion section please include the beam diameter and beam quality for the Nd:YAG laser system as well.

Author response #3: the beam diameter and beam divergence are 3 mm and less than 1 mrad. We have added this information in the revised manuscript.

Reviewer point #4: Please clarify the difference between the pyrex and the other container.

Author response #4: The Pyrex was used as a container of sample during data acquisition. This is because the Pyrex is overwhelmingly available in local market and has a good quality glass material compared to other glass tube. We have included this explanation in the revised manuscript.

Reviewer point #5: When discussing the defocused 18mm focal point, please clarify whether that is 18mm in front of the focal point or not.

Author response #5: It should be mentioned that the defocused 18 mm focal point means that the laser is focused at 18 mm in front of the focal point. We have included this explanation in the final revised manuscript.

Reviewer point #6: Figure 5 what is the curve represented by the triangles? also the addition of error bars would help the reader determine the amount of variability of your measurements.

Author response #6: The curve indicated by triangle represents the intensity ratio between emission lines of Na I 588.9 nm and Na I 589.5 nm. We have revised the figure as in the final revised manuscript.

Reviewer point #7: Figure 6, what do the error bars represent? one standard deviation or 95% confidence interval? or something else please specify.

Author response #7: The error bar shown in Fig. 6 represents standard deviation. We have this explanation in the revised manuscript.

Reviewer #2

Reviewer point #1: Abstract, The limit of detection of sodium in the metal surface was estimated to be 0.5 mg/l. "mg/l"? What unit is it?

Author response #1: We have revised the unit from mg/l to mg/kg as in the revised manuscript.

Reviewer point #2: The results certified that the present technique of LIBS using pulse TEA CO2 laser is much superior compared to the case of standard LIBS proven by an excellent emission spectrum of sodium with an optimum intensity and low noise and background emission. What is standard LIBS? Please show some references. LIBS is laser induced breakdown spectroscopy, what is "standard laser"?

Author response #2: Standard LIBS is laser-induced breakdown spectroscopy using Nd:YAG laser as an energy source. The Nd:YAG laser is one of laser type commonly used as an energy source in LIBS. To avoid misunderstanding, we removed the term standard LIBS and changed to Nd:YAG LIBS.

Reviewer point #3: Introduction, For "a pulse laser such crystal Nd:YAG laser is employed as an excitation and ionization source", why is Nd:YAG laser? Can't other lasers?

Author response #3:in LIBS, an Nd:YAG laser is commonly used as an energy source to induce a plasma in/on material target. The Nd:YAG laser is generally used because it includes solid state laser and commercially available in the market with a compact, reliable, and easy way to produce a plasma. Furthermore, the Nd:YAG laser can produce a high peak power and low beam divergence enable a plasma to be readily generated from any kinds of samples such as solid, liquid, and gas.

The other types of pulse laser can also be used as an energy source for plasma generation in LIBS such as excimer laser, CO_2 laser, microchip laser, Ti:sapphire: femtosecond laser, and fiber laser.

Reviewer point #4: Introduction, For "the metal itself is ablated and therefore the major and minor analytical lines associated with the sample disturbed the impurity and trace elemental lines", I think the factor should be the continuous emission, not other major and minor lines. And, the longer pulse duration will produce stronger continuous emission due to the plasma reheating.

Author response #4: Some factors disturb the analytical lines including continuous emission contributed from the Bremsstrahlung effect and recombination effect. Based on our experiment for analysis of soft sample and liquid samples using Nd:YAG laser utilizing the metal subtarget technique, metal subtarget such as iron or alloy itself will ablate and therefore the major and minor elements from the metal subtarget disturbed the impurity elemental lines because the iron or alloy have many emission lines in the region of UV and visible wavelengths.

We have included the explanation including your suggestion in the revised manuscript.

Reviewer point #6: Experimental procedure, For "laser energy was varied from 0.75 J to 1.5 J" and "a pulse TEA CO2 laser (Shibuya, 10.064 μm, 200 ns, 3 J" in abstract, why not use 3 J in the experiment?

Author response #6: In the experiment, we used laser energy varied from 0.75 J to 1.5 J and not maximum laser energy of 3 J. This is because the laser energies of 0.75 J to 1.5 J have been already enough to induce a large volume gas plasma, as an excitation source of sodium atoms, without any damage or ablation of steel metal. When the laser energy was increased to 3 J, the plasma is very large and is high temperature. However, the steel metal itself is ablated by the laser bombardment and many iron emission lines occur and disturb the sodium analytical lines. Furthermore, the high-temperature plasma also produce continuous emission lines contributed from the Bremsstrahlung effect and recombination process takes place in the plasma region.

Reviewer point #7: Experimental procedure, how is the concentration of Na calibrated?

Author response #7: The prepared samples are being tested in standard analytical laboratory by using ICP technique to reconfirm its concentration.

Reviewer point #8: Experimental procedure, For "dropping 3 ml liquid droplet on the steel surface", is there extraction effect? If so, it is not the true concentration in the steel.

Author response #8: The concentrations of Na mentioned in the manuscript is true concentration after confirming by the ICP technique, which is commonly used as a standard analytical technique of atomic emission spectroscopy.

Reviewer point #9: The gate delay time and gate width of OMA system was 10 and 100 μs, respectively. How is this gate optimized?

Author response #9: For plasma emission studies, a delay time and gate width of OMA system was selected at 10 μs and 100 μs, respectively. This is because in laser plasma induced by a pulse TEA CO_2 laser (10.64 um, 200 ns, 1500 mJ), the best spectral quality, namely narrow full width at half-maximum (FWHM) and optimum signal to noise (S/N) ratio with low background continuum emission is obtained at around 10 μs. Below 10 μs, the FWHM is still quiet wide and background continuum is still high. The background continuum emission, which is produced by Bremsstrahlung effect (free-free) and recombination (free-bound transition), has long lifetime up to around 10 μs compared to that of plasma emission produced by Nd:YAG laser, which has background continuum emission up to around 1 μs. In laser-induced breakdown spectroscopy (LIBS), FWHM of emission line, S/N ratio, and background emission determine the spectral quality and thus influence the sensitivity. Therefore, the delay time of OMA system was set at 10 micro second to remove the background emission.

Reviewer point #10: The Nd:YAG laser energy was 83 mJ, the energy is far lower than that the energy of CO2 laser. If the Nd:YAG laser energy was increased to 1 J close to the energy

of CO2 laser. The emission Na lines will be very high. The authors' experimental comparison is unfair.

Author response #10: Based on our experiment using quartz and ZnSe lenses with a focal length of 100 mm, the optimum laser energy used was around 100 mJ. More than 100 mJ, the background continuum emission produced has long lifetime and disturbed the analytical lines, and thus, signal to noise ratio (S/N ratio), signal to background ratio (S/B ratio), and full width half maximum of analytical lines which influence the sensitivity, decrease with the increasing laser energy more than 100 mJ. Therefore, in LIBS experiments using Nd:YAG laser, most scientists use laser energy of around 100 mJ to produce a breakdown plasma as an excitation source.

However, for TEA CO_2 laser, based on our experiment, the optimum emission intensity of analytical lines in various kinds of samples is obtained at laser energy of around 1 J. If the laser energy is set more than 1.5 J, the plasma has high temperature and high density, resulting in wider FWHM and increasing background continuum emission.

Reviewer point #11: For the correction curve, the data points are very few, and more data points should be required.

Author response #11: We have added the data points in the curve and showed the standard deviation each data point plotted as shown in Fig. 6.

Reviewer #4

Reviewer point #1: In this manuscript, authors have presented their study of Sodium detection on the steel surface by LIBS. They have compared performance of traditional LIBS with Nd:YAG laser and TEA CO2 LIBS, and claimed that the later one performed better. In my opinion, it does not have enough scientific novelty to publish it in a journal like Arabian Journal of Chemistry.

Author response #1: Identification of impurity on material sample surface using pulse TEA CO_2 laser is very unique and not common in LIBS, which is most often used an Nd:YAG laser as an energy source. Based on our experience, a pulse TEA CO_2 laser can effectively be used for surface analysis of metal because no ablation of metal materials happens by controlling the power density of CO_2 laser beam on metal surface. This present study has high novelty because we propose that some parameters should be considered for the surface analysis including focusing defocusing laser beam and clean environment of sample from the other impurity. Furthermore, we also made a comparative study on LIBS using pulse Nd:YAG laser, which is commonly used in conventional LIBS, and other spectroscopic technique of inductively coupled plasma atomic emission spectroscopy. We have included this additional explanation in the revised manuscript.

Reviewer point #2: Section Introduction: page 4, line 50: May be typo: …laser such crystal Nd:YAG laser is employed as an excitation….

Author response #2: We have revised the sentence as follow, a pulse Nd:YAG laser is employed as an energy source to induce a breakdown plasma on the material target.

Reviewer point #3: Section: Introduction, Page 4, line 43 "Laser induced breakdown spectroscopy (LIBS) has become most popular technique…". Rewording is recommended, especially for the words "most popular". Need to be aware that all techniques have limitation so does LIBS.

Author response #3: We have changed the sentence to be "Laser induced breakdown spectroscopy (LIBS) has become an established analytical atomic spectroscopy technique for rapid and in-situ analysis in various kinds of samples including liquid, solid, and gas without complicated preparation"

Reviewer point #4: Line 55: Due to its convenient and versatile tool as a spectroscopy technique… Correct the sentence.

Author response #4: We have changed the sentence to be "Due to its simple sample preparation and its ability to analyze simultaneously several elements…"

Reviewer point #5: Page 5 line 38-50: "Therefore, this laser can produce large-volume luminous plasma and high plasma temperature….". Traditional LIBS has also high plasma temperature, what is the range of temperature authors mentioning here? Provide equation for the relation between laser wavelength and plasma absorption.

Author response #5: TEA CO₂ LIBS can produce a plasma with a temperature almost the same with traditional LIBS using Nd:YAG laser, namely around 10000 K at initial stage (10 ns to 1 μs) and around 5000 K at later stage around 3-10 μs. We have revised the sentence to be "this laser can produce large-volume luminous plasma…" We have also added below explanation in the revised manuscript.

The TEA CO₂ laser can produce large volume plasma compared to Nd:YAG laser because the TEA CO₂ laser has longer wavelength or lower frequency (10 times lower than the fundamental Nd:YAG case). Gibson et al. reported the plasma shielding effect is much more serious for pulsed CO₂ laser because the absorption coefficient, K, due to the free-free transition of electrons can be expressed as

$$K = N/\omega^2\tau$$

where N is a density of electron in the initial plasma, ω is a frequency of the laser light, and τ is a function of the electron temperature. As is known from the equation, with decreasing the frequency of the laser light the absorption coefficient increases. Therefore, when we use TEA CO₂ laser for plasma generation, the shielding effect becomes conspicuous because of its low frequency (long wavelength).

Reviewer point #6: Section: experimental procedure, Page 7, line 3, "The sample was placed in a chamber… kept constant at 1 atmosphere". Elaborate the reasoning for using the chamber and using the nitrogen gas.

Author response #6: During data acquisition, the sample was placed in a chamber and a nitrogen gas was flowed in the chamber, in which the pressure was kept constant at 1 atmosphere. This condition was made to avoid other element impurity from the ambient air disturbing the analytical emission lines. Based on our experiment, when an experiment was made at ambient air without any chamber, the sodium impurity deposited in the ambient air disturbs the analytical lines. Therefore, to ensure the emission lines really come from the sample, the sample was placed in the chamber with nitrogen flowing gas at 1 atmosphere.

We have included above explanation in the revised manuscript.

Reviewer point #7: Section: results and discussion, page 7, Line 45: For standard LIBS, they have used 83 mJ of laser energy which is very high in general in LIBS experiment. How is this energy selected? Authors have mentioned that, "It is seen that completely no emission lines of neutral Na are detected in the spectrum." But looks like there are some unresolved emissions lines near 589 nm wavelength, which could be Na and may be affected by self-absorption. Explain it.

Author response #7: The Nd:YAG laser energy of 83 mJ was selected in this study because based on our experiment, optimum emission intensity of sodium with lower background emission intensity was obtained using 83 mJ laser energy. Furthermore, when we reduce the

laser energy, the intensity of Na also decreases. Otherwise, when the laser energy was increased, the intensity of sodium also increases with increasing background emission.

Regarding some unresolved emissions lines near 589 nm wavelength, after we enlarged the spectrum, there are no emission lines, but they are noise, which comes from the spectrograph.

Reviewer point #8: Page 8, line 6 "…the background emission is also high…." what does this mean? Are you expecting low background emission at 1us Gate delay? From solid surface, background can be observed at 1us Gate delay, which is normal.

Author response #1:The statement can be explained as follow: In some solid surface (not metal sample), gate delay time set at 1 μs has already reduced the background emission (continuous emission) contributed from the Bremsstrahlung effect and free-bound transition, while for the case of solid metal sample such as steel sample, gating time set at 1 μs still results in high background emission because the plasma induced in the metal surface has still high temperature even at later stage of 1 μs of plasma emission. We have added some explanation in the revised manuscript.

Reviewer point #9: Page 9, line 13-15 "The pulse TEA CO2 laser induced very unique characteristics compared to the case of pulse Nd:YAG laser, which generally applies in standard LIBS." Correct the sentence.

Author response #9: We have changed the sentence as follow: as compared to an Nd:YAG laser case, a unique phenomenon takes place in the plasma generation using the pulse TEA CO_2 laser due to their specific characteristics of long wavelength (10.6 um) and long pulse duration (200 ns)

Reviewer point #10: Page 9, line 45-45, Bring self-absorption into discussion here?

Author response #10: It should be mentioned that the plasma absorption mentioned in the sentence is significantly difference from the self-absorption commonly happened in LIBS. Self-absorption is the effect where the light emitted by an element in a LIBS plasma is absorbed by that element in another part of the plasma. This effect happens from emission lines originating from direct resonant transition involving the ground state and for high concentrations of the analyte atoms. For plasma absorption in LIBS using TEA CO_2 laser, when the initial plasma has already produced by CO_2 laser beam focused on the metal target, the laser pulse itself still exists due to the long pulse duration of around 200 ns. Therefore, the initial plasma absorbs the remaining laser energy of laser pulse, resulting in large volume and high-temperature plasma.

Reviewer point #11: Conclusions: Reword the first sentence, "Sophisticated technique of laser-induced breakdown spectroscopy using pulse TEA CO2 laser has been employed for the identification and analysis of sodium impurity in the steel metal surface.

Author response #11: We have changed the sentence as follow: Laser-induced breakdown spectroscopy using pulse TEA CO_2 laser has been employed for the identification and analysis of sodium impurity in the steel metal surface.

Reviewer #5

Reviewer point #1: The presented manuscript deals with a determination of sodium on the steel sheet surface with laser-induced breakdown spectroscopy (LIBS). In contrast to other LIBS analyses a TEA CO2 pulsed laser was used. The authors claim that the plasma from the CO2 laser is much larger, luminous and suppressing interfering iron lines in comparison with that from a Nd: YAG laser. Sodium determination is thus more sensitive. The topic can be of potential interest.

Author response #1: Thank you very much for your kind positive response that our work has potential interest for publication in Arabian Journal of Chemistry.

Reviewer point #2: Some sentences should be re-written. The language requires correction.

Author response #2: We have revised the manuscript and grammatical error in the manuscript. Also, we asked a professional company to check the grammar of our revised manuscript.

Reviewer point #3: There is the sodium concentration in mg/l also for the surface and LoD (p. 11). However, this information says nothing about the mg/cm2 of the steel sheet. Please recalculate the results.

Author response #3:We have revised the units of concentration. Based on the prepared samples being tested in standard analytical laboratory using ICP technique to reconfirm its concentration, the unit of sodium concentration is mg/kg. Based on our calculation, for Na concentration of 50 mg/kg on the surface of material target, it corresponds to 0.06 mg/cm^2.

Reviewer point #4: Please give the dimensions of the stain made by the drop of the salty solution.

Author response #4: The dimension of stain of salty solution produced on the steel surface was 10 mm in diameter. We have included this explanation in the revised manuscript.

Reviewer point #5: P. 6, Experimental Procedure: Was there a ring of concentrated deposit on the stain border (coffee ring effect)? How did you ensure the salt homogeneity on the surface?

Author response #5: We estimated the homogeneity on the surface by the emission spectrum obtained from the stain. When we made a laser bombardment at the different places in the stains, the intensity of the sodium emission lines is almost the same. The laser bombardment was most often made inside the stain border.

Reviewer point #6: You should also present craters photos to compare the ablated volumes from the CO2 and Nd: YAG lasers. You can estimate if the higher sodium signal is rather from the more ablated material or from the more efficient excitation.

Author response #6: From the sample after laser bombardment, we obtained the dimension of crater obtained from the Nd:YAG laser and TEA CO$_2$ laser. For the Nd:YAG laser case, the crater size is around 400 μm in diameter and around 10 μm in depth. For the CO$_2$ laser case, the crater size is around 1,3 mm in diameter and around 5 μm in depth. Based on this data,

we obtained that the higher sodium emission intensity in the case of TEA CO$_2$ laser is from the more ablated material of sodium contaminant deposited on the steel surface.

Reviewer point #7: Concerning the interaction of NaCl with the steel material, is your experiment sufficiently representative? I mean e.g. sodium migration into the steel body during a longer time exposition in comparison with a quick drop and drying on the surface. And what about a chloride corrosion?

Author response #7: In liquid sodium-cooled fast reactor, the interaction between stainless steel used as a fuel cladding pipe and Na causes corrosion. Mainly sodium causes the corrosion, not chloride, which is also common cause corrosion. Thus, it is important to investigate the sodium concentration deposited on the steel surface. Our experimental procedure is sufficiently representative for depositing the sodium contaminant in the surface of steel target.

Reviewer point #8: P. 7-8: "This indicated that the steel metal itself are also ablated when the Nd:YAG laser beam is directed and focused on the steel metal." - Please explain in context of the qu. 10).

Author response #8: Our purpose is to perform quantification of sodium contaminant in the surface of steel material. Ablation of steel material contributes to the emission lines of iron in the spectrum and therefore disturbing the sodium analytical lines. Therefore, we intentionally look for the sampling technique of LIBS to suppress the ablation of steel material by using pulse CO$_2$ laser as an energy source of LIBS.

Reviewer point #9: P. 8: "However, when the steel sample does not contain sodium line on its surface, completely no emission lines of Na occur and only Fe emission lines appear as shown in Fig. 3(b)." - There may be sodium atoms on the surface, not sodium lines.

Author response #9: We made a mistake, we have changed sodium line to sodium atoms as shown in the revised manuscript.

Reviewer point #10: P. 8 and 10: "It should also be noticed that the ablation of steel metal itself happen during laser bombardment." - Do I understand well that you do not suppose the ablation of the sample body under certain conditions? Does the CO2 laser uniquely ablate only the surface sediment without spectral contamination by iron lines?

Author response #10: We confirmed that the TEA CO$_2$ laser beam only ablates the surface sediment and does not ablate the steel itself. This was proved by examining the emission spectrum from initial plasma (100 ns) to later stage (30 μs) that no iron emission lines are identified in the spectrum. Furthermore, based on our many previous works, when we control the power density of TEA CO$_2$ beam on the surface metal plate such as Cu, Ni, and steel sheets used as subtargets, we did not detect the elements from the metal subtargets and only elements from the samples placed in the surface of metal subtargets are identified.

Reviewer point #11: P. 9: "Physically, when the pulse laser is irradiated tight focus on a surface…" - I mean that the laser is pulsed and the sample is irradiated, not the laser.

Author response #11: We have revised the sentence as follow: when a hard metal plate is irradiated tight focus by a pulse TEA CO₂ laser on its surface, electrons come out…

Reviewer point #12: P. 10, line 50: "...the steel metal containing 50 mg/kg sodium on its surface…" - Do you mean 50 mg/l in the dropped solution?

Author response #12: Yes, the steel metal containing 50 mg/kg sodium on its surface means 50 mg/l in the dropped solution.

Reviewer point #13: P. 11: In my opinion the calibration dependence is a quite typical LIBS curve, not excellent. Please explain: "Each data plotted in the curve is average of three spectra. Each spectra was taken by 20 shots laser bombardment and the data acquisition was repeated 5 times under the condition that the laser beam was defocused at the surface of steel sample." - 20 spectra were integrated on chip and this was repeated 3-times and the average point from 3 integrated intensities was depicted in the Fig. 6? If so where are the 5 replicates please?

Author response #13: We miswrote in the sentence, the data acquisition was repeated 5 times, not 3 times. We have changed the sentence in the revised manuscript. Each data plotted in the curve is average of five spectra. Each spectra was taken by 20 shots laser bombardment and the data acquisition was repeated 5 times under the condition that the laser beam was defocused at the surface of steel sample.

Reviewer point #14: Figures
1a) - nice drawing but the microplasma should not cover the whole sample.
2-7 - the lines should be thinner, not smooth (only straight lines connecting points)
5 - What does mean the green line and what does the right y-axis?
5, 6, 7 - axes description is very small, please enlarge
6 - You state on p. 6: "Samples used in this work were 304 steel samples containing various concentrations of Na on their surface, namely 10, 20, 40, 50, and 100 mg/l." Nevertheless, there are c = 250 - 2500 mg/l in Fig. 6. Please explain and correct.
What do mean the error bars? Where is the equation of the line and R2? The intercept of the depicted line is not zero - please compare with the statement in Abstract and correct.
I mean that this manuscript should be revised thoroughly before it can be considered for publication.

Author response #14:

1(a), We have revised the figure following your suggestion as shown in the revised manuscript.

2-7, We have revised the figures following your suggestion.

5, The green line is intensity ratio between Na I 588.9 nm and Na I 589.5 nm. We have revised the figure following your suggestion.

5,6,7, we have revised the figures following your suggestion.

6, we miswrote the x axis in Fig. 6. We have revised the figure as in the revised manuscript.

The error bars mean standard deviation obtained from the data acquisition repeated 5 times.

Reviewer #6

Reviewer point #1: The manuscript proposes the quantitative measurement of sodium in steel samples by laser-induced breakdown spectroscopy (LIBS) using pulse transversely excited atmospheric CO2 laser. According to the authors, the importance of measure sodium is due to the fact of this element reduces the strength of the material.

Author response #1: Thank you very much for your kind comments on our submitted manuscript.

Reviewer point #2: "analysis of sodium" should be replaced by "determination of sodium" or "quantification of sodium" since sodium is the analyte. The term "analysis" should be used for sample, e.g. "analysis of steel".
Author response #2: We have revised "analysis of sodium" to "quantification of sodium" following your suggestion.

Reviewer point #3: As solid samples has been analysed, LoD should be presented in "% (m/m)" or "mg/g" instead of mg/L. This is strongly reccomended also because Figure 6 shows Na concentration in % in calibration curve.

Author response #3: We have changed the unit using mg/kg as shown in the revised manuscript. We also made a mistake in axis-x of figure 6. We have changed the axis of Fig. 6.

Reviewer point #4: Figure 6: equation and R2 should be shown e discussed.

Author response #4: We have included equation and R^2 in Fig. 6. The explanation has also been added in the revised manuscript.

Reviewer point #5: Besides the proposal is the analysis of solid steel samples, Na solution was deposited onto the sample to make the calibration. It is known however that the behavior of the analyte in solid sample and in solution is not similar, causing interference.

Author response #5: In the present work, we do not make an analysis of solid steel sample. However, our work is to perform identification of sodium contaminant on the surface of the steel sample. We have changed the title and some sentences in the revised manuscript.

Reviewer point #6: How LoD was calculated?

Author response #6: Limit of detection was derived from the emission line of Na by multiplying three-time noise divided by emission intensity of sodium from the surface of steel metal. We have included this explanation in the revised manuscript.

Reviewer point #7: The accuracy of the method should be checked by analyzing reference material or using another well-established method like ICP OES.

Author response #7: We have made a comparative study for identification of sodium contaminant using ICP-OES technique as described in the revised manuscript.

Reviewer point #8: Page 4, lines 52-57: "The Na-deposited steel was then placed on a microwave oven for 5 minutes with a temperature of 100 for drying and depositing the NaCl liquid on the steel surface." Steel was dried in the microwave oven? How it is possible?

Author response #8: For making an impurity Na element deposited on the surface of steel sheet, 3 ml NaCl liquid was poured on the surface of the steel sheet. The steel sheet was then heated by microwave oven for 5 minutes so that the NaCl liquid was dried completely on the surface of the steel sheet.

Reviewer #9

Reviewer point #1: The paper submitted by Khumaeni et al. investigates the possibility of the determination of sodium on the steel surface by using CO2 LIBS. Liquid sodium and highly concentrated sodium chloride solutions induced corrosion on different types of steel, so the relevant study presented here could be of interest not only for scientists but also for industrial purposes.

Author response #1: Thank you very much for your kind positive comments.

Reviewer point #2: In my opinion it would be useful to emphasize more clearly what is new and significant in this paper. The introduction is focused on the effect of liquid Na and yet NaCl solutions were used for the sample preparation. Also, the introduction needs to be reorganized and written. The research progress is not sufficiently elaborated, and the novelty of the work is not sufficiently clear, it should be highlighted.

Author response #2: We have made a revision following your suggestion as shown in the revised manuscript especially in the section of abstract, introduction, and results and discussion. We have also emphasized the novelty of the present work in introduction. In this present study, we propose some parameters that should be considered for the surface analysis including focusing defocusing laser beam and clean environment of sample from the other impurity. Furthermore, comparative study was also made this present work with LIBS using pulse Nd:YAG laser, which is commonly used in conventional LIBS, and other spectroscopic technique of inductively coupled plasma atomic emission spectroscopy (ICP-OES). A quantification of sodium contaminant in steel surface was successfully demonstrated using a pulse TEA CO₂ LIBS, resulting in an excellent linear calibration curve of Na as a surface contaminant in the steel sample.

Reviewer point #3: Sample preparation for the calibration is not clear. NaCl solution was dropped on the steel sample and dried in the microwave. What was the diameter of the resulting film? Was it evenly spread and how did it affect the RSD of the emission line of Na?

Author response #3: We have added more explanation about the sample preparation as in the revised manuscript. The diameter of resulting film is around 10 mm. The sodium contaminant spreads on the steel surface quiet homogeneous proven by that almost the same intensity of sodium was obtained when laser bombardment was made at the different places in the film

Reviewer point #4: Since analyzed Na comes from deposed NaCl solution on the surface of a metal, it cannot be classified as analysis of Na in steel. This analysis can be associated with surface-assisted LIBS. SALIBS allows the deposition of a thin homogeneous film of the liquid sample on a metallic surface that can greatly improve the analytical performance. The metallic surface is expected to contribute to increasing the temperature and the density of the plasma and, consequently, the better overall sensitivity of the method is achieved. A different approach for the preparation of the calibration set should be investigated. Furthermore, investigation of the effect of the Na on the surface hardness might be an interesting addition to this manuscript.

Author response #4: We have made a revision that our study is not analysis of Na in steel, but the study focuses on the identification and quantification of sodium contaminant in steel surface. We have also added some published papers in the references about surface-assisted LIBS. The investigation of the effect of the Na on the surface hardness will be studied in the near future.

Reviewer #10

Reviewer point #1: This paper is on some experimental work of rather good quality, but it is very poorly structured and in parts rather confusing. The confusion begins with the opening statement in the abstract:
Analysis of sodium in metal samples is very necessary because the existence of sodium can reduce the strength of the material.

Author response #1: We have revised the structure of paper including the grammar by professional company. We have also revised the abstract

Reviewer point #2: This implies determination of Na in the bulk metal. For steel, this is totally irrelevant, since Na contamination in the metallurgical process is no problem. Reading further in the introduction, it becomes clear that it is actually surface contamination of Na on steels that is the object of this study. This analytical need of is confined to steel material of reactor coolers using liquid Na, which is a rather rare application of steel. Both the abstract and the introduction must clarify this.

Author response #2: We have made a revised manuscript especially in the abstract and introduction. As you mentioned that this work is about surface contamination of Na on steel surface.

Reviewer point #3: Another confusing term is "standard LIBS". There is no such term defined, here it is clear that the authors mean LIBS using a Nd:YAG laser. Please remove all "standard LIBS" from the text and just state in the introduction that this laser type is the most commonly used in LIBS. It is sufficient to write this once, not repeat it in several places of the text!

Author response #3: Thank you very much for your kind suggestion. We have removed all term "standard LIBS" and changed to "Nd:YAG LIBS" from the text and just state in the introduction that the Nd:YAG laser type is most commonly used in LIBS.

Reviewer point #4: The paper is then very badly structured, with large parts of the "Results and discussion" actually belonging to the introduction and experimental procedure sections. The beginning of the "Results and discussion" section up to page 8 line 26 is essentially all "Experimental procedure". There is also plenty of redundant information/repetition. Here is an example:

Page 5, lines 33 - 50.
This is because the pulse TEA CO2 laser has much longer wavelength of 10.64 μm and longer pulse duration of 200 ns compared to the Nd:YAG laser case. Therefore, this laser can produce large-volume luminous plasma and high plasma temperature. It is known that longer laser wavelength strongly related to the absorption coefficient of luminous plasma because the plasma absorption coefficient is proportionally related to the inverse square of the frequency of laser light. Namely, the longer the laser wavelength, the higher the

plasma absorption that results in large-volume of plasma.

Author response #4: We have moved some parts of the Results and Discussion to Introduction and Experimental Procedure following your suggestion. Also, we have removed some redundant explanation as above.

Reviewer point #5: Page 9 lines 35- 50:
It should be emphasized that the plasma absorption for the TEA
CO2 laser is much higher compared to the case of the Nd:YAG laser because the coefficient of plasma absorption is proportional to the inverse square of the frequency of laser light. Also, the pulse duration of the TEA CO2 laser is much longer about 20 times compared to the Nd:YAG laser case. Therefore, the energy from the CO2 laser is most often absorbed by the luminous plasma, resulting large volume and high-temperature plasma.

Author response #5: We have removed this part because it has been explained in page 5 line 33-50 as in the submitted manuscript.

Reviewer point #6: Why use the unit mg/l for "concentration on the surface"? The proper unit should be mass/area (e.g. mg/m2), which is how you normally measure surface contamination. I believe these numbers instead represent the mass/volume of the liquid solutions used to deposit Na on the surface. Please clarify! This also goes for Fig. 6, where the unit on the x-axis is just %. Percent of what? The mass fraction of the top surface layer? If so, how can this be defined?

Author response #6: We have revised the units of concentration. Based on the prepared samples being tested in standard analytical laboratory using ICP technique to reconfirm its concentration, the unit of sodium concentration is mg/kg. Based on our calculation, for Na concentration of 50 mg/kg on the surface of material target, it corresponds to 0.06 mg/cm^2.

In Fig. 6, we have made a mistake in X axis of submitted manuscript. We have revised the X-axis as in the revised manuscript.

Reviewer point #7: Line 47:
The Nd:YAG LIBS spectra in Fig. 2 - 3 are truly appalling, and definitely not typical of what you can achieve with such a system. Have you identified any of the Fe lines claimed to overlap the Na lines in this spectrum without any clear line structure?

Author response #7: We have confirmed by experiments using our OMA system (OMA ATAGO Macs 320), which consists of 0.32 m focal length spectrograph with a grating of 1200 groves/mm, that Figs 2 and 3 are the optimum spectra obtained. Emission lines of Fe does not overlap with the sodium lines around 588 and 589 nm. The Fe emission lines appear in the spectrum at the wavelength of around 570-580 nm. We have revised the sentence as in the revised manuscript.

Reviewer point #8: Finally, the paper lacks any comparison with the performance of alternative analytical techniques. It is stated that the results obtained are "much superior" to Nd:YAG LIBS, but no number for the DL of such a system is given (should be from a system that performs properly). Also there is a complete lack of comparison with other optical emission techniques, e.g. spark OES and Glow Discharge (GD) OES. A bit of research on what these techniques can accomplish is required.

Author response #8: In the manuscript, we made a comparative study between present TEA CO_2 LIBS and Nd:YAG LIBS. Furthermore, we have also added additional data of sodium contamination using ICP-OES as in the revised manuscript.

5. **Paper setelah proses revisi mempertimbangkan masukan Editor dan Reviewers**

Quantification of sodium contaminant in steel surface using pulse CO₂ laser-induced breakdown spectroscopy

Ali Khumaeni,[1] Wahyu Setia Budi,[1] Koo Hendrik Kurniawan,[2] Ken-Ichi Fukumoto,[3] Kazuyoshi Kurihara,[4] and Kiichiro Kagawa[5]

[1]*Department of Physics, Faculty of Science and Mathematics, Diponegoro University, Jl. Prof. H. Soedarto, S.H., Tembalang, Semarang 50275, Indonesia*
[2]*Maju Makmur Mandiri Research Center, Jl. Srengseng Raya 40, Kembangan, Jakarta Barat, Indonesia*
[3]*Research Institute of Nuclear Engineering, University of Fukui, 1-2-4, Kanawa, Tsuruga, Fukui, 914-0055 Japan*
[4]*Department of Physics, Faculty of Education, University of Fukui, Bunkyo 3-9-1, Fukui, 910-8507, Japan*
[5]*Fukui Science Academy, Takagi Chuo, Fukui, Japan*

*) Corresponding author: khumaeni@fisika.fsm.undip.ac.id

Abstract

Corrosion is a main reason of in-core damage accidents in liquid sodium-cooled fast reactors, especially fuel cladding pipe damage accidents. It is urgently required to investigate what kind of compound was produced as a corrosion product after interaction between stainless steel and sodium in Fast Breeder Reactor (FBR). In this work, identification and quantification of sodium contaminant in the surface of steel material has been conducted using laser-induced breakdown spectroscopy utilizing specific characteristics of pulse transversely excited atmospheric CO_2 laser. Experimentally, a pulse TEA CO_2 laser (Shibuya, 10.64 µm, 200 ns) beam was directed and bombarded onto the sodium contaminant deposited on the surface of stainless steel. An excellent emission spectrum of sodium from the sodium contaminant was obtained without any disturbance of analytical lines from the steel metal itself. A quantification of sodium contaminant in the steel surface has been successfully made proven by a linear calibration curve obtained from the steel metal containing various concentrations of sodium. The limit of detection of sodium in the metal surface was estimated to be 0.5 mg/kg. Also, a comparative study of sodium analysis was qualitatively made by using LIBS utilizing pulse Nd:YAG laser. The results certified that the present technique of TEA CO_2 LIBS is much better compared to the case of Nd:YAG LIBS proven by an excellent emission spectrum of sodium with an optimum intensity and low noise and background emission.

Keywords: Sodium analysis; steel sample; LIBS; TEA CO_2 laser; Nd:YAG laser

I. INTRODUCTION

In Fast breeder reactor (FBR), corrosion is a main reason of in-core damage accidents in liquid sodium-cooled fast reactors, especially fuel cladding pipe damage accidents. Thus, it is important to investigate what kind of compound was produced as a corrosion product after interaction between stainless steel and sodium (Na) [1-3]. In fast reactors, the cladding and internal structures are made of steel, so the chemical reaction and coexistence of Na with stainless steel is an important issue [4-7]. When Na reaction products that are formed on spent fuel rods and in-core structural components are found during the visual inspection, it is necessary to perform a quasi-non-destructive inspection to analyze the products. The problem of fuel roads and internal structures deposited with Na in fast reactors should be discussed with utilization of analytical spectroscopy for diagnostic technology for maintenance in FBR.

Some spectroscopic methods have been introduced for identification of impurity contaminants deposited in the surface of metal material. Sodium ionization detector has been developed and employed in liquid metal cooled fast breeder reactor [8-9]. The other techniques include differential pressure detector, ionization chamber, and contact leak detector [10-11]. However, they need tedious sample pretreatment and require great deal work.

Laser induced breakdown spectroscopy (LIBS) has become an established analytical atomic spectroscopy technique for rapid and in-situ analysis in various kinds of samples including liquid, solid, and gas without complicated preparation [12-16]. In LIBS, a pulse laser Nd:YAG laser is commonly employed as an energy

source to induce a breakdown plasma in/on the material target. Due to its simple preparation and its ability to analyze simultaneously several elements in the material target, LIBS has been applied as analytical technique in various major fields such as medical, environmental, and industrial fields [17-21]. Some researchers used surface-assisted LIBS technique for liquid analysis […]. However, the LIBS technique cannot easily be employed to identification of contaminant deposited on the metal surface having spectral analytical lines such as iron and metal alloy [22]. This is because when the laser beam directly irradiated on those metal surface, the metal itself is ablated and therefore the major and minor analytical lines associated with the metal disturbed the impurity and trace elemental lines, reducing the sensitivity of the technique. The other factor is continuous background emission contributed from the Bremsstrahlung and recombination effects [12]. Thus, limit of detection (LoD) of contaminants is still high.

In other direction, we have developed various unique sampling techniques of LIBS by utilizing a pulse transversely excited atmospheric CO_2 laser [23-25]. We noticed that compared to Nd:YAG laser that is usually used in conventional LIBS, a pulse transversely excited atmospheric TEA CO_2 laser is much convenient for spectrochemical analysis in specific materials such as powder sample and soft solid material. The TEA CO_2 laser can produce large volume plasma compared to Nd:YAG laser because the TEA CO_2 laser has longer wavelength or lower frequency (10 times lower than the fundamental Nd:YAG case) and longer pulse duration. Gibson et al. reported the plasma shielding effect is much more serious

for pulsed CO_2 laser because the absorption coefficient, K, due to the free-free transition of electrons can be expressed as

$$K= N/\omega^2\tau \qquad (1)$$

(where N is a density of electron in the initial plasma, ω is a frequency of the laser light, and τ is a function of the electron temperature. As is known from the equation, with decreasing the frequency of the laser light the absorption coefficient increases. Therefore, when we use TEA CO_2 laser for plasma generation, the shielding effect becomes conspicuous because of its low frequency (long wavelength), resulting in large-volume plasma. We have successfully demonstrated the pulse TEA CO_2 laser-induced breakdown spectroscopy for various applications including powder analysis, softwood analysis, and surface analysis [25-28]. It should also be mentioned that when a pulse CO_2 laser beam is focused on metal surface such as Cu and Ni metal plates, intense luminous plasma is produced without any ablation of the metal [28-29]. The plasma constituent consists of elements from the surrounding gas and is not from the metal itself. This breakdown plasma is very favorable and effective as ionization and excitation sources of elements as reported in our previous work [30-32].

Taking advantages of this phenomenon, we applied a pulse TEA CO_2 laser-induced breakdown spectroscopy (TEA CO_2 LIBS) for identification and quantification of sodium contaminant in the surface of 304 stainless steel. In this present study, we propose some parameters that should be considered for the surface analysis including focusing defocusing laser beam and clean environment of sample from the other impurity. Furthermore, comparative study on this present

work was also made with LIBS using pulse Nd:YAG laser (Nd:YAG LIBS), which is commonly used in conventional LIBS, and other spectroscopic technique of inductively coupled plasma atomic emission spectroscopy (ICP-OES). A quantification of sodium contaminant in steel surface was successfully demonstrated using a pulse TEA CO_2 LIBS, resulting in an excellent linear calibration curve of Na.

EXPERIMENTAL PROCEDURE

Experimental setup used in this study is shown in Fig. 1(a). The pulse TEA CO_2 laser beam (Shibuya, 10.64 µm, 200 ns) was directed and focused by ZnSe lens with a focal length of 200 mm on a sample surface passing through ZnSe window to induce a breakdown plasma. During data acquisition, laser energy was varied from 0.75 J to 1.5 J by placing a metal aperture in the laser beam path. The beam size of laser on the sample surface was 2.25 mm^2 for the laser energy of 0.75 J.

Samples used in this work were 304 steel samples containing various concentrations of Na contaminant on their surface, namely 25, 50, 100, and 250 mg/kg. To produce Na contaminant on the steel surface, almost the same procedure with the previous experiment […] was carried out. For example, to produce Na contaminant at a concentration of 50 mg/kg, homogeneous dilution of 110 mg of NaCl in 1000 ml of tap water was made; tap water was used because Na particles can be deposited easily on the steel surface. 3 ml mixed Na water was then poured on the surface of the steel sheet. The steel sheet was then heated by microwave oven for 5 minutes so that the Na was dried completely on the surface of the steel sheet.

The dimension of Na film produced on the steel surface was 10 mm in diameter. The sample was placed in a chamber with a diameter and a height of 12 cm and 10 cm, respectively. During data acquisition, the sample was placed in a chamber and a nitrogen gas was flowed in the chamber, in which the pressure was kept constant at 1 atmosphere. This condition was made to avoid other element impurity from the ambient air disturbing the analytical emission lines. The flow rate of the gas was 4 liters per minute (Lpm).

A comparative study was also made using LIBS utilizing a Nd:YAG laser (1064 nm, 7 ns, 10 Hz, beam diameter of 3 mm, beam divergence less than 1 mrad). For Nd:YAG LIBS, the laser energy was at 83 mJ. This laser energy was selected because based on our experiment, optimum emission intensity of sodium with lower background emission intensity was obtained using 83 mJ laser energy. Furthermore, when we reduce the laser energy, the intensity of Na also decreases. Otherwise, when the laser energy was increased, the intensity of sodium also increases with increasing background emission. The Nd:YAG laser beam was directly focused by using a quartz lens (focal length of 100 mm) on the steel surface containing Na contaminant to produce a breakdown plasma.

The plasma emission obtained was then sent via optical fiber into the optical multichannel analyzer system (OMA ATAGO Macs 320), which consists of 0.32 m focal length spectrograph with a grating of 1200 groves/mm, a 1024 channel photodiode detector array, to obtain an emission spectrum of sodium from the steel surface. The gate delay time and gate width of OMA system was 10 and 100 μs, respectively. In our experimental setup, a digital delay system (SRS DG535) was

used to set a gate delay time and gate width of OMA system during data acquisition. For triggering a digital delay system, a small part of laser beam was used by sending the laser beam via a photon drug as shown in Fig. 1(a).

RESULTS AND DISCUSSION

First, we employed a LIBS using pulse Nd:YAG laser for identification of sodium contaminant on steel surface. The sample used was 304 steel metals without any cleaning on the steel surface. To examine the contamination of sodium from the atmosphere, which generally contains sodium, the steel was placed inside a Pyrex glass tube (Fig. 1(b)) and finally put inside the chamber, which was flowed by N_2 gas. The Pyrex was used as a container of sample during data acquisition because it is overwhelmingly available in local market and has a good quality glass material compared to other glass tube. Figure 2(a) shows emission spectrum obtained from the 304 steel sample placed inside the glass tube. It is seen that completely no emission lines of neutral Na at the wavelength of 588.9 nm and 589.6 nm are detected in the spectrum. However, some analytical lines at the wavelength of around 570-580 nm that are contributed from the steel surface are faintly detected. This indicated that the steel metal itself are also ablated when the Nd:YAG laser beam is directed and focused on the steel metal. Furthermore, the background emission is also high even the gate delay time was set at 1 μs; The background emission (continuous emission) is contributed from the Bremsstrahlung effect and free-bound transition. This is because the plasma induced in the metal surface has still high temperature even at later stage of 1 μs of plasma emission, resulting high

background emission. When the sample was placed inside the metal chamber without Pyrex glass tube, neutral Na emission lines at 588.9 nm and 589.6 nm are faintly occurred as shown in Fig. 2(b). This Na is contributed from the Na contaminant deposited in atmosphere, which still remains inside the chamber. This result certified that the use of Pyrex glass tube is very essential to avoid the sodium contaminant from the atmosphere. Therefore, in this work the glass tube was used during experimental data acquisition.

To convince that the Nd:YAG LIBS can be employed to identify sodium contaminant deposited in the steel surface, a steel metal containing sodium on its surface was used as a sample. Figure 3(a) show emission spectrum of Na taken from the 304 steel metal sample containing 10 mg/kg Na using Nd:YAG LIBS. High emission intensity of Na at 588.9 nm and 589.6 nm clearly occurs with quiet high background emission. Furthermore, many emission lines of Fe at around 570-580 nm appear which comes from the steel metal. However, when the steel sample does not contain sodium contaminant on its surface, completely no emission lines of Na occur and only Fe emission lines appear as shown in Fig. 3(b). It should also be noticed that the ablation of steel metal itself happen during laser bombardment. To overcome this issue, we proposed a pulse TEA CO_2 laser instead of Nd:YAG laser as an energy source to induce a luminous plasma on steel surface.

Prior to explaining experimental data, it is more desirable to shortly review the mechanism of plasma generation using pulse TEA CO_2 laser on metal surface as reported in our previous work [27,28, 32]. As compared to an Nd:YAG laser case, a unique phenomenon takes place in the plasma generation using the pulse TEA

CO_2 laser due to their specific characteristics of long wavelength (10.6 um) and long pulse duration (200 ns). Namely, large volume and high temperature plasma is readily produced. Physically, when a hard metal plate is irradiated tight focus by a pulse TEA CO_2 laser on its surface, electrons come out from the metal surface due to a multiphoton absorption process at the surface impinged by the laser beam. The electrons are subsequently accelerated by the electric field of laser light, which produce overwhelming ionization in the gas and finally initiates a luminous plasma. The plasma then absorbs the laser beam via free-free transition due the inverse Bremsstrahlung. It should also be mentioned that no ablation on the surface of metal plate occurs and only gas plasma is produced by the focusing of TEA CO_2 with laser energy of 1.5 J and focal length of ZnSe lens of 200 mm.

We then apply a pulse TEA CO_2 LIBS to obtain an emission spectrum from the steel surface containing Na contaminant. Figure 4(a) displays emission spectrum of sodium obtained from the same sample as in Fig. 3(a) using pulse TEA CO_2 LIBS. High emission intensity of neutral Na I 588.9 nm and Na I 589.6 nm is obtained with low background emission. Furthermore, completely no Fe lines are detected in the spectrum. This unique phenomenon only happens for the LIBS using pulse TEA CO_2 laser. Namely, when the pulse CO_2 laser was focused on a metal surface, by controlling its power density on the metal surface, no ablation from the metal surface happens and only ablation from the contaminant. Thus, no Fe lines from the steel metal occur in the spectrum. When the steel sample without any sodium contaminant was used, completely no sodium emission lines appear as shown in Fig. 4(b). It should be noticed that the emission profile of sodium lines is

much better for TEA CO_2 LIBS compared to the case of Nd:YAG LIBS. Namely, the emission lines of sodium have high intensity and low background and noise level.

Present technique of TEA CO_2 LIBS is then employed for quantification of sodium in the surface of steel metal. However, prior to this end, effect of focused laser beam to the emission intensity of sodium was examined. Figure 5 shows how the emission intensity of sodium taken from the steel metal containing 50 mg/kg sodium contaminant on its surface changes with the laser beam defocused. It is seen that the sodium intensity is very low at laser tight focus condition. The intensity then increases and attain a maximum with a laser beam defocus at 4 mm. With increasing the laser beam defocuses, the intensity decreased and finally almost stable up to 18 mm defocused. It should be mentioned that the defocused 18 mm focal point means that the laser is focused at 18 mm in front of the focal point. Based on this result, we used 4 mm beam defocused to obtain an optimum emission intensity of sodium from the steel surface containing Na contaminant.

Finally, a quantification of sodium contaminant on a steel surface was carried out using the TEA CO_2 LIBS. Figure 6 shows the calibration curve of sodium taken from the steel surface containing various concentrations of sodium. Each data plotted in the curve is average of five spectra. Each spectrum was taken by 20 shots laser bombardment and the data acquisition was repeated 5 times under the condition that the laser beam was defocused at the surface of steel sample. Excellent linear calibration curve was obtained between the intensity of sodium and its concentration in the steel surface with the determination coefficient R^2 of 0.98;

The error bar shown in Fig. 6 represents standard deviation. Thus, this technique is applicable to the practical quantitative analysis of sodium in the steel surface.

The technique was then used to identify sodium contaminant in the steel surface. Figure 7 shows emission spectrum of sodium contaminant obtained from the steel metal containing 50 mg/kg Na on its surface. Sodium lines at 588.9 nm and 589.6 nm are clearly detected with high emission intensity and low background emission. Un-identified line at around 572 nm occurs with a broaden and quit low intensity. The detection limit of sodium was estimated to be 0.5 mg/kg; the detection limit was derived from the emission line of Na by multiplying three time noise divided by emission intensity of sodium contaminant from the steel metal [33].

CONCLUSIONS

Laser-induced breakdown spectroscopy using pulse TEA CO_2 laser has been employed for the identification and quantification of sodium contaminant in the steel surface. Compared to the Nd:YAG LIBS, the present technique is superior. Namely, very nice emission spectrum of sodium without any disturbance of analytical lines from the steel bulk was successfully produced by using TEA CO_2 laser-induced breakdown spectroscopy, resulting in higher sensitivity. Excellent linear calibration curve of sodium obtained from the steel surface containing various concentrations of sodium was successfully made with an intercept zero. Limit detection of sodium is estimated to be 0.5 mg/kg. This present work is

potentially applicable to the practical quantitative analysis of sodium in the steel surface in metal industry and nuclear power reactors.

ACKNOWLEDGMENT

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Figure captions:

Figure 1. (a) Experimental setup used in this present work. (b) Illustration of steel sample containing sodium impurity placed in the pyrex glass.

Figure 2. Emission spectra obtained from the 304 steel sample taken by using Nd:YAG LIBS without NaCl on its surface placed (a) inside the glass tube, and (b) without the glass tube.

Figure 3 Emission spectrum taken by using Nd:YAG LIBS obtained from the 304 steel metal sample (a) containing 10 ppm Na, and (b) without Na.

Figure 4 Emission spectrum taken by using TEA CO_2 laser-induced breakdown spectrsocopy obtained from the 304 steel metal sample (a) containing 10 mg/kg Na, and (b) without Na.

Figure 5 Effect of laser beam defocused to the emission intensity of sodium.

Figure 6 Calibration curve of sodium taken from the steel 304 metal sample containing various concentration of Na on its surface.

Figure 7 Emission spectrum of Na taken from the steel 304 metal containing 50 mg/kg Na using the TEA CO_2 laser-induced breakdown spectroscopy

Figure 1
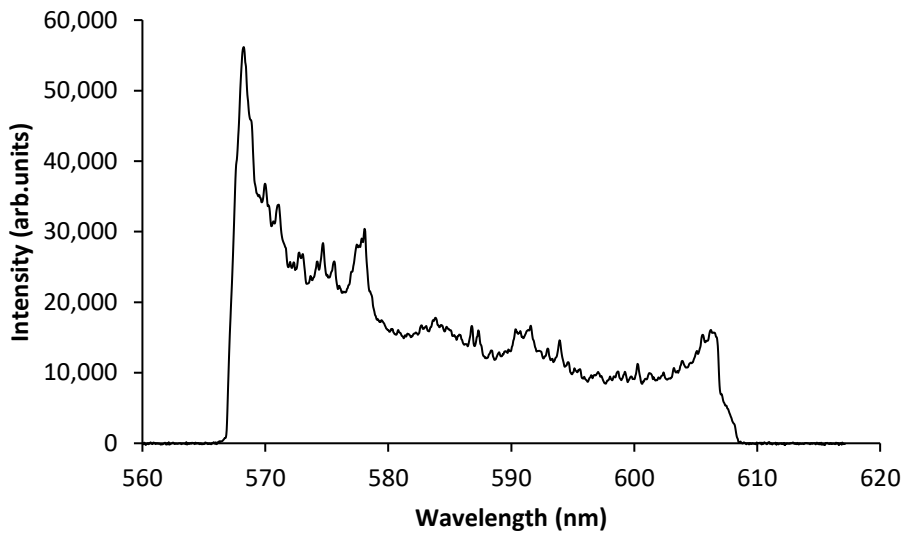Experimental setup used in this work
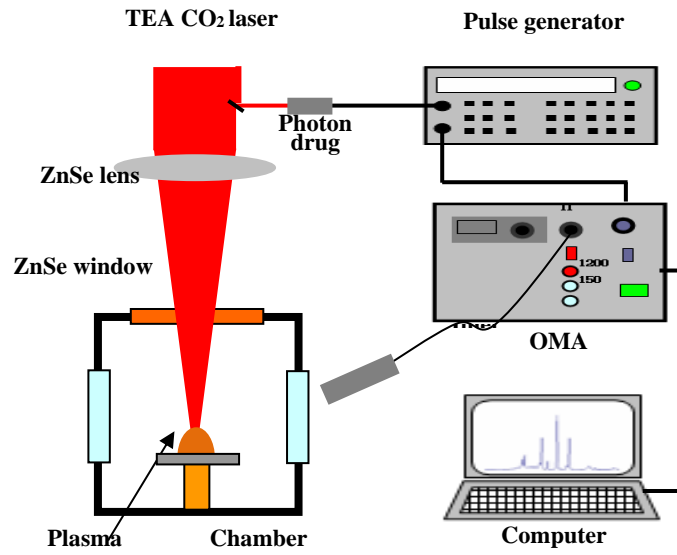
(a)
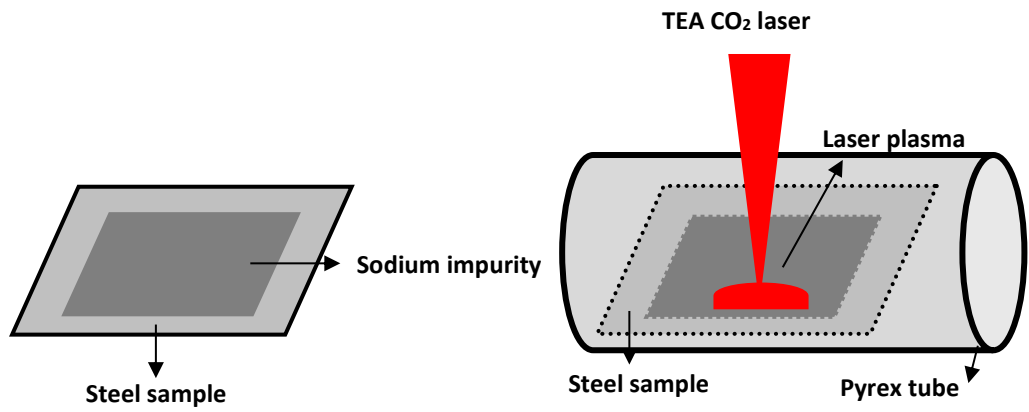
(b)

Figure 2
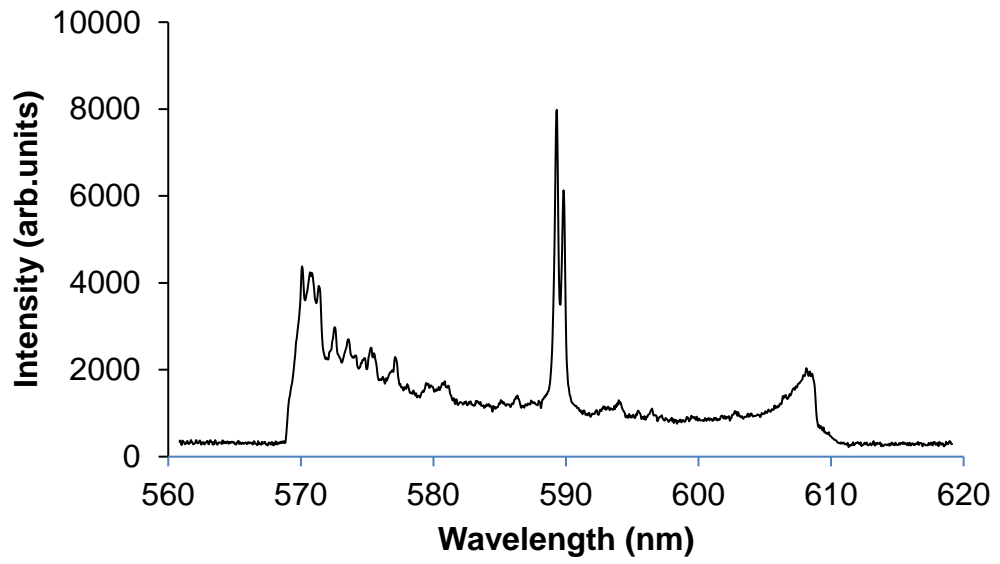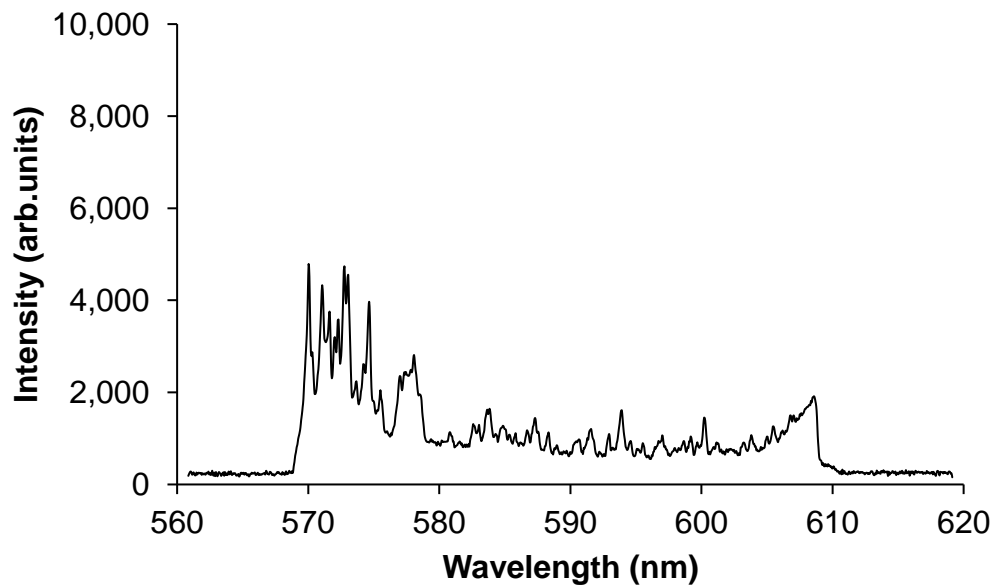Emission spectrum taken from the LIBS using pulse Nd:YAG laser
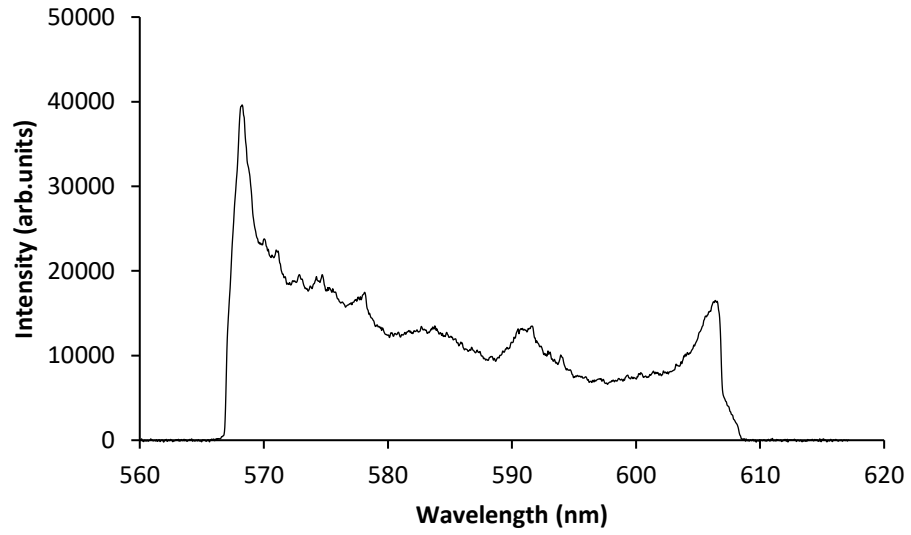
(a)

(b)

Figure 3
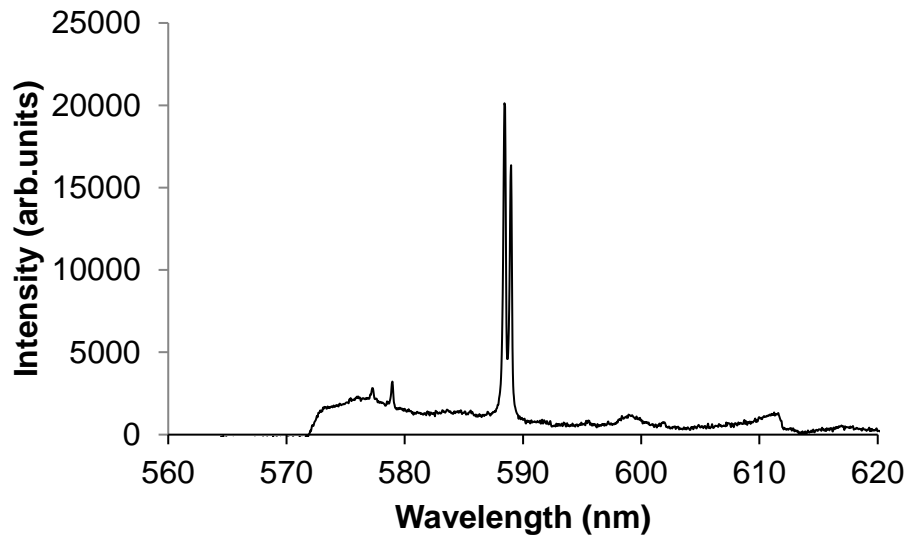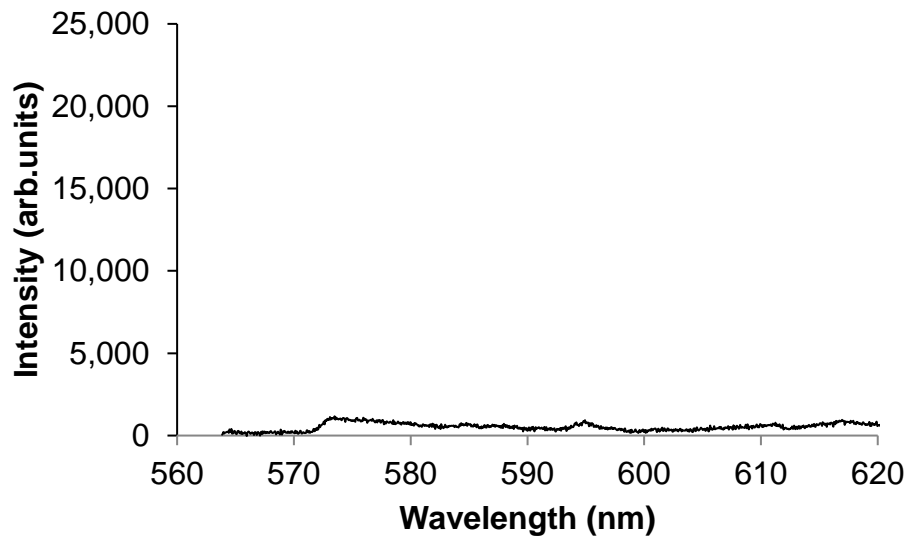Emission spectrum of Na taken by using LIBS utilizing pulse Nd:YAG laser

(a)

(b)

Figure 4
Emission spectrum of Na taken by using pulse TEA CO_2 laser-induced breakdown
spectroscopy

(a)

(b)

Figure 5

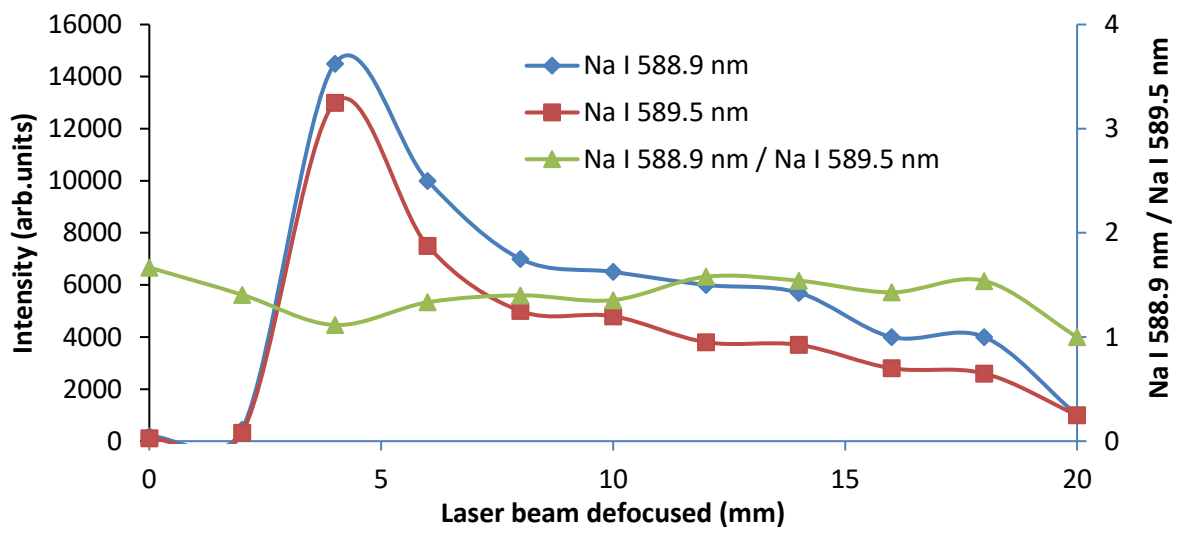Effect of laser beam defocus on the sample target

Figure 6

Calibration curve of sodium taken from the steel 304 metal sample containing various concentration of Na on its surface
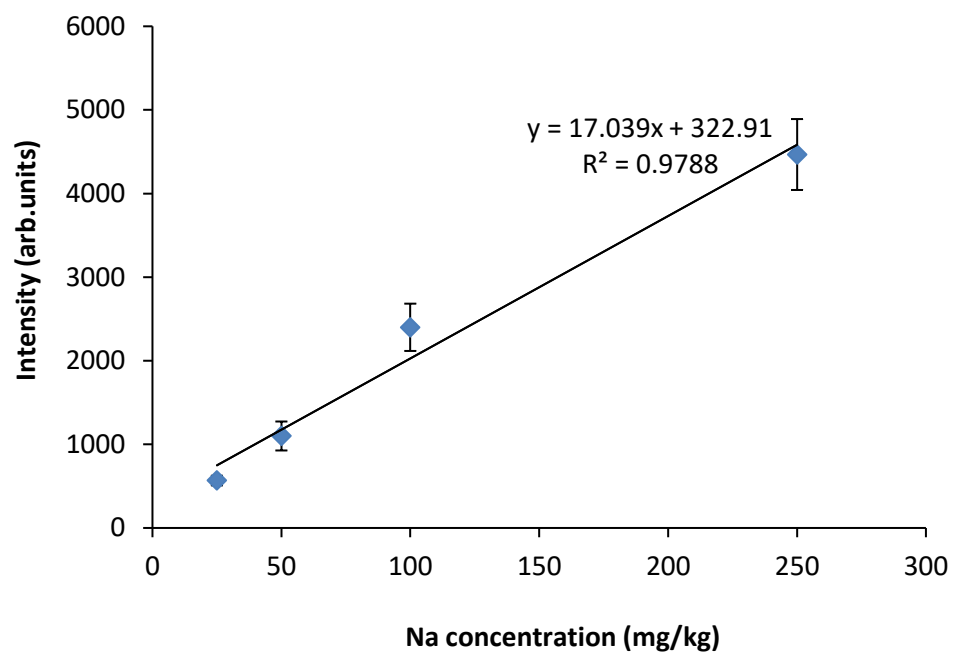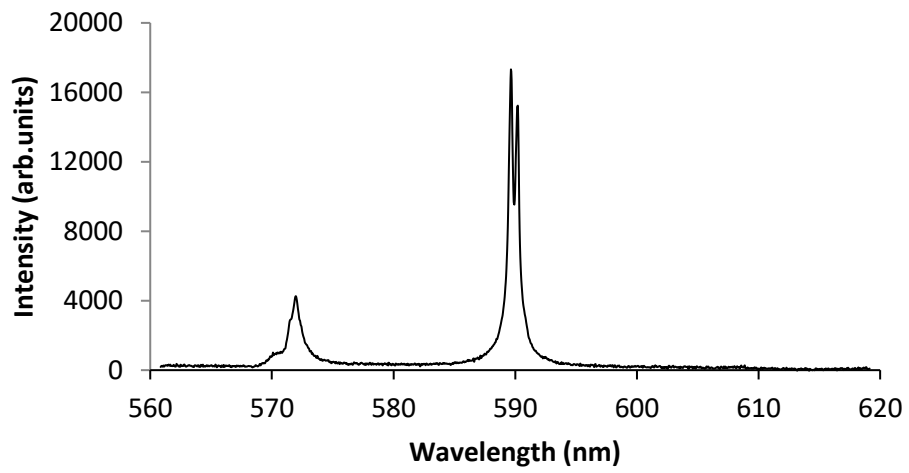
Figure 7

Emission spectrum of Na taken from the steel 304 metal containing 50 ppm Na using the TEA CO_2 laser-induced breakdown spectroscopy

6. **Acknowledgment dari jurnal setelah mengirim balasan (2 Oktober 2021)**

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Last night the proof of our accepted manuscript to the Arabian Journal of Chemistry came. If you do not mind, could you read the proof for confirmation? I have also read the proof and no change is made from my side. Thank you very much for your kindness.

Best regards
Ali Khumaeni
[Quoted text hidden]

9. **Notifikasi publikasi dari Arabian Journal of Chemistry (29 Oktober 2021)**

webmail
FISIKA
universitas diponegoro

Ali Khumaeni <khumaeni@fisika.fsm.undip.ac.id>

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