

# Manuscript for JKSUS

*by* Ali Khumaeni

---

**Submission date:** 17-Jan-2022 11:54AM (UTC+0700)

**Submission ID:** 1742809140

**File name:** 2\_Manuscript\_and\_figures\_WITHOUT\_AUTHOR\_FINAL\_2.docx (310.8K)

**Word count:** 4936

**Character count:** 26404

## Liquid analysis using metal powder-assisted laser induced breakdown spectroscopy (LIBS) utilizing a pulse CO<sub>2</sub> laser

### Abstract

Analysis of impurity and trace element in liquid is urgently needed in environment and industries. In this present work, new sampling technique in LIBS has been devised using metal coarse utilizing pulse CO<sub>2</sub> laser. Experimentally, a liquid and polluted liquid was dropped into a metal coarse powder. A pulse CO<sub>2</sub> laser (10.6  $\mu\text{m}$ , 200 ns) beam with a laser energy from 0.75 to 1.5 J was bombarded on a metal coarse to generate a plasma. The plasma contains elemental analytical lines obtained from the liquid material; the metal coarse itself is never ablated and only works to induce a plasma. By this present technique, identification of major and minor elements in liquid material target such as commercial milk liquid and multi-vitamin liquid has successfully be made. Furthermore, a quantitative analysis of impurity of Cr has been demonstrated, resulting in good precision and good sensitivity with limit of detection of approximately 2  $\mu\text{g/ml}$ . This developed technique is feasible to be utilized for examination of major, impurity, and trace elements in liquid and water.

**Keywords:** liquid analysis; metal coarse powder; LIBS; TEA CO<sub>2</sub> laser

## 1. INTRODUCTION

Analysis of impurity and trace metal elements is required in various fields including industries and environment. In food and herbal products such as tea, dry fruits, moringa, and shilajit, periodic analysis of impurity and poisonous elements are very important to control the quality of the products [1-4]. In environment, analysis of impurity and trace metals elements as contaminants in water is urgently needed to identify and ensure the pollution of the metal in the water [5-8]. In drinking water, analysis of impurity is really necessary to ensure the quality of water from its impurity. In industries such as food and drinking industries, analysis of liquid is very important to control the stability of main ingredient in commercial products [8-10]. In metal industries, analysis of metal liquid is made to ensure the quality of the metal product from the impurity, which may contain during the production process [11-13].

Many various techniques have been employed to analysis of water and liquid including ICP-OES, AAS, and XRF spectroscopy [14-18]. By using mentioned techniques, analysis of elements in liquid with high accuracy and responsiveness can be carried out. However, those methods require serious sample pretreatment, are labor intensive and therefore should be carried out off-site, and are high-cost instrument.

LIBS is a tremendous analytical technique for identification and analysis of elemental composition in various phase samples including liquids, solids, and gases [19-24]. In this tool, a pulse Nd:YAG laser is more often used as a source of energy to induce a luminous plasma, which emits atomic emission from the material target.

However, researchers most often apply LIBS for solid and gas targets rather than liquid samples. This is mainly due to the technical complication in the use of LIBS for analysis of liquid sample [25, 26]. To solve this issues, various sampling techniques have been developed such as liquid jets [27-29], using filters for liquid deposition [30], aerosol technique [31], and solid conversion [32, 33]. However, most developed techniques are still limited by low reproducibility and detection sensitivity. The disadvantages of LIBS for liquid analysis include fast plasma quenching due to the splashing and fluctuation of liquid [34-36]. Furthermore, it has been found the <sup>2</sup> limit of detection (LoD) of analyte is quiet high in the order of tens part per million (ppm). To overcome this problem, some researchers used metal nanoparticles mixed with the liquid sample to enhance the emission sensitivity [37]. The other improved sampling techniques in LIBS for analysis of liquid were developed by Jin Yu et al. utilizing surface-assisted thin film [38-40]. The results certified that the developed techniques can overcome the matrix effect from the sample targets and improve the limit of detection of the analytes.

In other direction, we have treated a pulse <sup>15</sup> transversely excited atmospheric (TEA) CO<sub>2</sub> laser for specific applications of LIBS including analysis of organic powder material [41] and aerosol or liquid analysis [42]. The results certified that LIBS using pulse TEA CO<sub>2</sub> laser can improve the LoD of analyte to few ppm level. Pulse CO<sub>2</sub> laser is entirely reasonable for examination of organic material, liquid and soft solid material because the laser has longer <sup>3</sup> wavelength (10.64 μm) and longer pulse duration (200 ns) than that of Nd:YAG laser (1.064 μm and 10 ns in wavelength and pulse duration), which is commonly used in LIBS. Therefore, the

TEA CO<sub>2</sub> laser has high absorbance in those material targets. Furthermore, by assisting a metal subtarget [43], plasma temperature can be enhanced increasing the effective dissociation and excitation of analyte in the sample, resulting higher detection limit. Recently we employed a new technique of pulse CO<sub>2</sub> LIBS by assisting metal coarse powder for sensitive metal impurity analysis of soil material [44]. The technique was utilized for quick assurance of poisonous metal elements of Hg, Pb, and Cr in loam soil with limit detections of around 0.7, 15, and 0.8 mg/kg, respectively.

In this present study, the technique of metal-coarse-powder-assisted CO<sub>2</sub> LIBS is used for the direct analysis of liquid material. To this end, few amounts of liquid was dropped and trapped into the coarse metal powder. The pulse CO<sub>2</sub> laser was subsequently bombarded into the metal coarse. Some liquid materials were employed including liquid commercial milk, liquid vitamin, and contaminated water. The emission reproducibility of analytes was examined and finally semi-quantitative analysis of impurity in contaminated water was demonstrated.

## 2. EXPERIMENTAL PROCEDURE

New setup of this work is schematically displayed in Fig. 1. The system consisted of high-energy pulse TEA CO<sub>2</sub> laser (a wavelength of 10.6 μm and pulse duration of 200 ns), a monochromator (Jobin-Yvon HRS-2, spectral resolution of 0.02 nm) with an optical multichannel analyzer system, and optical system including optical fiber, ZnSe lens, sample holder.

In this experiment, a pulse TEA CO<sub>2</sub> laser beam was focused by ZnSe lens (20 cm in focal length) on liquid materials, which are trapped in coarse metal powders to generate a breakdown plasma (Fig. 2). The laser beam was focused both on liquid and metal coarse. The focus point size of laser beam on the coarse metal powder was around 2 mm in diameter. The size of coarse metal powder varies from around 100-500  $\mu$ m. Ranging of laser energy used was from 0.75 to 1.5 J. The plasma emission spectra were produced from a monochromator. The gate width and gate delay of the optical multichannel analyzer were 10  $\mu$ s and 100  $\mu$ s, consecutively.

The samples examined in this study were liquid commercial milk, which were overwhelmingly obtainable in the market. The other targets included commercial Ca and Mg vitamins, phosphoric acid, sodium chloride solution, KNO<sub>3</sub> solution and polluted water containing Cr at various concentrations of 10, 20, 40, and 200  $\mu$ g/ml. During experiments, 350 mg coarse metal powders were set in a hole (diameter of 10 mm) made in an acrylic plastic plate (thickness of 8 mm), on which the copper plate was tightly attached in the tight contact of the back of acrylic; the copper plate functions to keep the coarse metal powder from falling down during laser bombardment. Subsequently, 3 ml liquid sample was homogeneously dropped into the metal coarse and finally covered by stainless steel mesh with a diameter of 0.1 mm and a lattice constant of 0.4 mm, which was set in close contact on the front side of the metal coarse. The steel mesh functions to cover and keep the metal powder from the blow-off of coarse during laser bombardment. It ought to be referenced that during data acquisition, the mesh was not damaged and ablated because the ablation threshold of the mesh material is higher than laser power

density on the mesh due to the plasma shielding effect [44]. The samples were then settled in a chamber (120 mm and 100 mm in a diameter and a height, respectively). Inside the chamber can be filled by with various surrounding gases including air, N<sub>2</sub>, and He. In this present work, He gas (purity of 99.999%) was drifted in the metal chamber during the data acquisition. The rate of gas flowing was 3 liters per minute and the inside of the chamber pressure was set at 1 atmosphere; the helium plasma provided lower background emission compared to the use of a nitrogen gas and air.

### 3. RESULTS AND DISCUSSION

At initial, we examine that the metal coarse powder only functions to initiate a breakdown plasma and is not ablated by the laser bombardment. To this end, coarse metal powders without any samples were tested. Figure 3 shows emission spectrum ranging at the wavelength of 640 nm to 680 nm obtained from the coarse metal powder target. The laser energy used was 0.75 J. Hydrogen line at 656.3 nm and He at 667.8 nm occur very clear with very sharp and high-intensities and low background emission. The H line is assumed originating from H<sub>2</sub>O, which is still deposited and trapped in the metal coarse powder, while the He line comes from He gas flowed in the metal chamber during experiments. It should be noticed that no Fe emission lines identified in the spectrum. In this region, the Fe line has a wavelength at around 657 nm as reported here [45]. We also confirmed that even though the gate delay time of spectrometer was opened from 1  $\mu$ s, it is still no Fe line was identified in this spectrum region. This indicated that no ablation happened

from the coarse metal powder. The metal powder <sup>6</sup> only functions to initiate and induce a breakdown plasma. The plasma generation mechanism by assisting coarse metal powders is assumed follows: once the pulse CO<sub>2</sub> laser beam falls on coarse metal powder, only electrons escape from the coarse metal by multiphoton absorption process. Those free electrons accelerate in the laser light electrical field, inducing a chain gas ionization and generating an early breakdown <sup>2</sup> plasma. The plasma then absorbs incident laser beam by inverse bremsstrahlung. The plasma <sup>1</sup> absorption is much stronger for the CO<sub>2</sub> laser than the case of pulse Nd:YAG laser because the coefficient of plasma absorption is proportional to the square of the laser wavelength, thus most of the <sup>7</sup> CO<sub>2</sub> laser energy is absorbed by the breakdown plasma. Furthermore, coarse metal itself is not ablated by the CO<sub>2</sub> laser with a laser <sup>2</sup> energy of 1.5 J and focusing point of lens of 200 mm. This result is similar with our previous work [43], namely when pulse TEA CO<sub>2</sub> laser was directed and focused <sup>2</sup> on a metal powder or metal plate, no ablation happens from the metal and only high-intensity breakdown plasma occurs. Therefore, identification of elements from the liquid sample by using coarse metal powders assisted LIBS can be made without any interference of emission lines from the metal powder itself. The technique of coarse metal powder is then used to examination of elemental composition in liquid sample target.

Prior to liquid elemental analysis, we examined the plasma temperature generated by the present technique. For this purpose, we used Boltzmann distribution technique applying the ratio of two neutral lines of Cu at 510.5 nm and 521.8 nm obtained from the CuSO<sub>4</sub> powder mixed with iron coarse powder; these



techniques have been presented in our previous papers [44]. Figure 4 displays the plasma temperature profile corresponding to plasma lifetime. The temperature has long lifetime and has a peak of around 7000 K at 1  $\mu$ s and finally slightly decreases up to around 6500 K at 30  $\mu$ s. This temperature profile is almost the same pattern with our previous work of metal-assisted LIBS using pulse TEA CO<sub>2</sub> laser [43]. Namely, the lifetime of plasma emission is quiet long and the plasma temperature slightly decreases with the plasma lifetime. This sophisticated phenomenon is never happened for the Nd:YAG LIBS where the plasma lifetime is quiet short up to around 10  $\mu$ s. Therefore, with long lifetime of plasma emission and quiet high plasma temperature, atoms can effectively be excited in the plasma region, resulting in sensitivity increment.

Analysis of major elements in commercial liquid product was then made using our present technique. First, we used liquid commercial milk containing Ca at a concentration of 1000  $\mu$ g/ml. It is known that Ca is a primary source of nutrition and is to bolster the bone strength of human being and contains at high concentration in the milk liquid. Ionic Ca lines at 393.3 nm and 396.8 nm obviously appear with high intensity as shown in Fig. 5(a). Moreover, Al lines at 394.1 nm and 396.1 nm are faintly detected near Ca lines. Using the ionic Ca II 393.3 nm, the LoD of Ca was estimated to be 8  $\mu$ g/ml. The other liquid samples used were two liquid vitamins contain Ca and Mg with concentrations of 6.8% and 3%, respectively. The emission spectra of Ca and Mg from the liquid vitamins are displayed in Figs. 5(b) and (c), respectively. It can clearly be seen that for Ca emission spectrum, high ionic Ca intensities at 393.3 nm and 396.8 nm occur

obviously together with He line at 388.8 nm. For Mg spectrum shown in Fig. 5(c), Some Mg lines including neutral Mg at 285.3 nm and ionic Mg at 279.2 nm and 281.3 nm appear with quiet high intensities. The other liquid sample was phosphoric acid containing P at a concentration of 30 mg/kg. Phosphor is a macronutrient, which is used a plant to store and use energy including for the process of photosynthesis. Figure 5(d) shows emission spectrum of P obtained from the phosphoric acid liquid. It can be seen that the neutral P lines clearly occur with high intensity at the wavelengths of 253.6 nm and 255.3 nm. Also, no emission lines of Fe appear in the wavelength of around 250 nm, whereas the Fe has many emission lines in this region. This certified that the iron coarse powder is not ablated during data acquisition of liquid sample. Based on the result, it confirmed that the present technique of metal coarse-assisted LIBS is successfully used for the analysis of major elements in liquid sample.

The present technique was further examined to perform analysis of delicate elements in liquid. First, the technique is employed to identification of chlorine. It is known that the analysis of chlorine is very required in building construction to ensure durability of constructions and structural safety. However, Cl analysis is very delicate to be conducted using the standard LIBS technique because Cl has quiet high ionization energy, resulting in low detection sensitivity. Chlorine emission spectrum from the sodium chloride solution is shown in Fig. 6. Three analytical lines of neutral Cl at 833.3 nm, 837.6 nm, and 842.8 nm clearly occur. Identification was further made in nitrogen from the  $\text{KNO}_3$  solution. Total nitrogen analysis was important in environmental and agricultural fields. Nitrogen is one of

essential elements needed for plant growth. Thus, periodical inspection of nitrogen in water and liquid is very required to control the content of nitrogen in water. Figure 7 shows the nitrogen spectrum from the  $\text{KNO}_3$  solution. Neutral N emission lines at around 742 nm were clearly detected together with unknown emission lines.

Taking advantages of the successful identification of major and delicate elements in various liquid samples, the present technique was further used to quantitative analysis of Cr in water. The accurate and rapid analysis of Cr as impurity in water is necessary in environmental and industrial fields. Figure 8 shows Cr spectrum from the tap water containing  $40 \mu\text{g/ml}$  Cr. Very clear and sharp Cr lines at 425.4 nm, 427.4 nm, and 428.9 nm are obtained with high emission intensities. Also, Ca I 422.6 nm emission lines exhibits in the spectrum; the Ca emission comes from the tap water. Before quantitative examination, the reproducibility of Cr intensity concerning a quantity of the laser shots was examined. For this purpose, the emission spectra were accumulated each 20 shots of laser bombardment using the same sample in Fig. 8. The emission intensities of Cr show a good reproducibility with the laser dependence (Fig. 9). The same tendency also occurs for Ca emission, namely its intensities almost the same with the laser shot dependence. This graph confirmed that the present procedure can be utilized to perform an investigation with a good precision proven by good reproducibility of emission intensity with laser shot dependence.

Finally, the metal coarse powder-assisted LIBS technique further was employed to perform analysis of Cr in tap water containing various concentrations of Cr. Figure 10 exhibits a calibration curve of Cr obtained from the tap water containing

various Cr concentrations. Good linearity calibration curve with an intercept zero has been successfully produced. To perform analysis with a good accuracy, Ca emission from the bulk was used as a standard element. Each points in the curve represents average of three spectra, which were obtained by 20 laser shots. The error was quiet low of around 5%. Finally LoD of Cr in tap water was evaluated using Cr I 425.4 nm. The LoD was estimated to be 2  $\mu\text{g/ml}$ ; the LoD was derived from the 3 times noise level divided detected emission intensity [46]. This result demonstrated that the present technique can be applied to perform direct analysis of Cr in water containing Cr at few  $\mu\text{g/ml}$  level. As reported and reviewed by Wang et al., various sample preparation techniques have been devised for analysis of liquid including microdroplet, surface-assisted LIBS, and quick-freeze procedure [47]. Those techniques generally attempt to overcome the chemical and physical matrix effect usually happens in LIBS experiment so that precision and high-sensitivity analysis can be realized. In this present work, we have successfully demonstrated that the unique and simple sample preparation of liquid analysis using the assist of coarse metal powder makes enable one to easier conduct analysis of liquid using LIBS with good precision and good sensitivity without tedious sample preparation.

#### 4. CONCLUSIONS

Developed technique utilizing metal coarse powder has been successfully demonstrated for an identification and analysis of Cr impurity in water. Besides, the present technique has also been employed to perform identification of major

and delicate elements in liquid material target such as commercial milk liquid and multi-vitamin liquid. Impurity analysis of Cr has been demonstrated, resulting in good precision and good sensitivity with LoD of approximately 2  $\mu\text{g/ml}$ . This present technique is possible to be employed for analysis of major, impurity, and trace elements in liquid and water without any tedious sample pretreatment.

#### **Acknowledgment**

This present work was financially supported by Institute for Research and Community Services Universitas Diponegoro under Research Grant of World Class Research Universitas Diponegoro, Contract No. 118-10/UN7.6.1/PP/2021.

#### **References**

1. R. K. Aldakheel, M. A. Gondal, M.A. Almessiere, S. Rehman, M.M. Nasr, Z. Alsalem, and F.A. Khan, Spectrochemical analysis using LIBS and ICP-OES techniques of herbal medicine (Tinnevelly Senna Leaves) and its anti-cancerous/antibacterial applications, *Arabian Journal of Chemistry* 14 12, 2021, 103451.
2. I. Rehan, M.A. Gondal, R.K. Aldakheel, M.A. Almessiere, K. Rehan, S. Khan, S. Sultana, and M.Z. Khan, Determination of nutritional and toxic metals in black tea leaves using calibration free LIBS and ICP:AES technique, *Arabian Journal for Science and Engineering*, 2021, <https://doi.org/10.1007/s13369-021-06233-y>.
3. R.K. Aldakheel, M.A. Gondal, H.N. Alsayed, M.A. Almessiere, M.M. Nasr, A.M. Shemsi, Rapid determination and quantification of nutritional and poisonous metals in vastly consumed ayurvedic herbal medicine (Rejuvenator Shilajit) by humans using three advanced analytical techniques, *Biological Trace Element Research*, 2021, <https://doi.org/10.1007/s12011-021-03014-4>.
4. I. Rehan, M.A. Gondal, M.A. Almessiere, R.A. Dakheel, K. Rehan, S. Sultana, M.A. Dastageer, Nutritional and toxic elemental analysis of dry fruits using laser-induced breakdown spectroscopy (LIBS) and inductively coupled plasma

atomic emission spectrometry (ICP-OES), *Saudi Journal of Biological Sciences*, 28 1, 2021, 408-416.

5. J. Xiao, L. Wang, L. Deng, and Z. Jin, Characteristics, sources, water quality and health risk assessment of trace elements in river water and well water in the Chinese Loess Plateau, *Science of The Total Environment* 650 2, 2009, 2004-2012.
6. M. Siepak and M. Sojka, Application of multivariate statistical approach to identify trace elements sources in surface waters: a case study of Kowalskie and Stare Miasto reservoirs, Poland, *Environmental Monitoring and Assessment* 189, 2017, 364 1-15.
7. J. Li, H. Yu, and Y Luan, Meta-analysis of the copper, zinc, and cadmium absorption capacities of aquatic plants in heavy metal-polluted water, *International Journal of Environmental Research and Public Health* 12 12, 2015, 14958-14973.
8. W-H Su and D-W. Sun, Mid-infrared MIR spectroscopy for quality analysis of liquid foods, *Food Engineering Reviews* 11, 2019, 142-158.
9. L. Wang, D-W. Sun, H. Pu, and J-H. Cheng, Quality analysis, classification, and authentication of liquid foods by near-infrared spectroscopy: A review of recent research developments, *Critical Reviews in Food Science and Nutrition* 57, 2107, 1524-1538.
10. F-G. C. Ekezie, D-W. Sun, J-H. Cheng, A review on recent advances in cold plasma technology for the food industry: Current applications and future trends, *Trends in Food Science and Technology* 69, 2017, 46-58.
11. C. DiGiovanni, X. Han, A. Powell, E. Biro, and N. Y. Zhou, Experimental and Numerical Analysis of Liquid Metal Embrittlement Crack Location, *Journal of Materials Engineering and Performance* 28, 2019, 2045-2052.
12. W. Zhang, C. Wang, R. Chen, W. Tian, S. Qiu, and G. H. Su, Preliminary design and thermal analysis of a liquid metal heat pipe radiator for TOPAZ-II power system, *Annals of Nuclear Energy* 97, 2016, 208-220.
13. S. W. Hudson, J. Craparo, R. D. Saro, and D. Apelian, Applications of Laser-Induced Breakdown Spectroscopy (LIBS) in Molten Metal Processing, *Metallurgical and Materials Transactions B* 48, 2017, 2731-2742.
14. A. T. Duarte, A. R. Borges, A. V. Zmozinski, M. B. Dessuy, B. Welz, J. B. de Andrade, M. G. R. Vale, 2016, Determination of lead in biomass and products of the pyrolysis process by direct solid or liquid sample analysis using HR-CS GF AAS, *Talanta* 146, 166-174.
15. F. C. Pinheiro, A. I. Barros, J. A. Nobrega, 2019, Evaluation of dilute-and-shoot procedure for determination of inorganic impurities in liquid pharmaceutical samples by ICP OES, *Microchemical Journal* 146, 948-956.

16. A. Virgilio, D. Schiavo, J. A. Nobrega, and G. L. Donati, 2016, Evaluation of standard dilution analysis (SDA) of beverages and foodstuffs by ICP OES, *Journal of Analytical Atomic Spectrometry* 31, 1216-1222.
17. A. Limbeck, M. Bonta, and W. Nischkauer, 2017, Improvements in the direct analysis of advanced materials using ICP-based measurement techniques, *Journal of Analytical Atomic Spectrometry* 32, 212-232.
18. S. Zou, Z. Yuan, Q. Cheng, Z. Zhang, and J. Yang, 2018, Rapid in situ determination of heavy metal concentrations in polluted water via portable XRF: Using Cu and Pb as example, *Environmental Pollution* 243, 1325-1333.
19. D. F. Andrade, M. A. Speranca, and E. R. Pereira-Filho, 2017, Different sample preparation methods for the analysis of suspension fertilizers combining LIBS and liquid-to-solid matrix conversion: determination of essential and toxic elements, *Analytical Methods* 9, 5156-5164.
20. B. Sezer, G. Bilge, and I. H. Boyaci, 2017, Capabilities and limitations of LIBS in food analysis, *TrAC Trends in Analytical Chemistry* 97, 345-353.
21. D. Giron, T. Delgado, J. Ruiz, L. M. Cabalin, and J. J. Laserna, 2018, In-situ monitoring and characterization of airborne solid particles in the hostile environment of a steel industry using stand-off LIBS, *Measurement* 115, 1-10.
22. P. K. Tiwari, S. Awasthi, R. Kumar, R. K. Anand, P. K. Rai, and A. K. Rai, 2017, Rapid analysis of pharmaceutical drugs using LIBS coupled with multivariate analysis, *Laser in Medical Science* 33, 263-270.
23. S. Yao, L. Zhang, Y. Zhu, J. Wu, Z. Lu, and J. Lu, 2020, Evaluation of heavy metal element detection in municipal solid waste incineration fly ash based on LIBS sensor, *Waste Management* 102, 492-498.
24. S. Moncayo, S. Manzoor, J. D. Rosales, J. Anzano, and J. O. Caceres, 2017, Qualitative and quantitative analysis of milk for the detection of adulteration by Laser Induced Breakdown Spectroscopy (LIBS), *Food Chemistry* 232, 322-328.
25. L. Ripoll, J. Navarro-Gonzalez, S. Legnaioli, V. Palleschi, and M. Hidalgo, 2021, Evaluation of Thin Film Microextraction for trace elemental analysis of liquid samples using LIBS detection, *Talanta* 223, 121736.
26. X. Cama-Moncunill, M. Markiewicz-Keszycka, P. J. Cullen, C. Sullivan, M. P. Casado-Gavaldà, 2020, Direct analysis of calcium in liquid infant formula via laser-induced breakdown spectroscopy (LIBS), *Food Chemistry* 309, 125754.
27. K. Skocovska, J. Novotny, D. Prochazka, P. Porizka, K. Novotny, and J. Kaiser, 2016, Optimization of liquid jet system for laser-induced breakdown spectroscopy analysis, *Review of Scientific Instruments* 87, 043116.

28. R. Bhatt, D. Hartzler, J. Jain, and D. L. McIntyre, 2021, Determination of As, Hg, S, and Se in liquid jets by laser-based optical diagnostic technique, *Applied Physics B* 127, 8.
29. M. A. Aguirre, E. J. Salva, M. Hidalgo, and A. Canals, 2015, Dispersive liquid-liquid microextraction for metals enrichment: A useful strategy for improving sensitivity of laser-induced breakdown spectroscopy in liquid samples analysis, *Talanta* 131, 348-353.
30. X. Wang, Y. Wei, Q. Lin, J. Zhang, and Y. Duan, 2015, Simple, Fast Matrix Conversion and Membrane Separation Method for Ultrasensitive Metal Detection in Aqueous Samples by Laser-Induced Breakdown Spectroscopy, *Analytical Chemistry* 87, 5577-5583.
31. X. Yang, L. Guo, J. Li, R. Yi, Z. Hao, M. Shen, R. Zhou, K. Li, X. Li, Y. Lu, and X. Zeng, 2016, Laser-induced breakdown spectroscopy of liquid solutions: a comparative study on the forms of liquid surface and liquid aerosol, *Applied Optics* 55, 7406-7411.
32. D. M. Diaz Pace, C. A. D'Angelo, D. Bertucelli, and G. Bertucelli, 2006, Analysis of heavy metals in liquids using Laser Induced Breakdown Spectroscopy by liquid-to-solid matrix conversion, *Spectrochimica Acta Part B: Atomic Spectroscopy* 61, 929-933.
33. Q. Lin, Z. Wei, H. Guo, S. Wang, G. Guo, Z. Zhang, and Y. Duan, 2017, Highly concentrated, ring-shaped phase conversion laser-induced breakdown spectroscopy technology for liquid sample analysis, *Applied Optics* 56, 5092-5098.
34. P. Yaroshchuk, R. J. S. Morrison, D. Body, B. L. Chadwick, 2005, Quantitative determination of wear metals in engine oils using LIBS: The use of paper substrates and a comparison between single- and double-pulse LIBS, *Spectrochimica Acta Part B: Atomic Spectroscopy* 60, 1482-1485.
35. P. Fichet, M. Tabarant, B. Sale, and C. Gautier, 2006, Comparisons between LIBS and ICP/OES, *Analytical and Bioanalytical Chemistry* 385, 338-344.
36. F. Tognoni, V. Palleschi, M. Corsi, and G. Cristoforetti, 2002, Quantitative micro-analysis by laser-induced breakdown spectroscopy: a review of the experimental approaches, *Spectrochimica Acta Part B: Atomic Spectroscopy* 57, 1115-1130.
37. M. Dell'Aglio, R. Alrifai, and A.D. Giacomo, Nanoparticle enhanced laser induced breakdown spectroscopy (NELIBS), a first review, *Spectrochimica Acta Part B: Atomic Spectroscopy* 148, 2018, 105-112.
38. Y. Tian, H.C. Cheung, R. Zheng, Q. Ma, Y. Chen, N. Delepine-Gilon, and J. Yu, Elemental analysis of powders with surface-assisted thin film laser-induced breakdown spectroscopy, *Spectrochimica Acta Part B: Atomic Spectroscopy* 124, 2016, 16-24.



39. J.S. Xiu, V. Motto-Ros, G. Panczer, R.E. Zheng, J. Yu, Feasibility of wear analysis in oils with ppm and sub-ppm sensitivity using laser-induced breakdown spectroscopy of thin oil layer on metallic target, *Spectrochimica Acta Part B: Atomic Spectroscopy* 91, 2014, 24-30.
40. J.S. Xiu, X.S. Bai, E. Negre, V. Motto-Ros, J. Yu, Indirect laser-induced breakdown spectroscopy of transparent thin gel layer for sensitive trace element detection, *Applied Physics Letters* 102, 2013, 244101.
41. A. Khumaeni, H. Niki, Y. Deguchi, K. Kurihara, K. Kagawa, and Y. I. Lee, 2009, Analysis of organic powder samples by using the metal-assisted subtarget effect in a Transversely-Excited Atmospheric (TEA) CO<sub>2</sub> laser-induced he gas plasma at 1 atm, *Journal of The Korean Physical Society* 55, 2441-2446.
42. A. Khumaeni, K. Kurihara, Z. S. Lie, K. Kagawa, and Y. I. Lee, 2014, Analysis of sodium aerosol using transversely excited atmospheric CO<sub>2</sub> laser-induced gas plasma spectroscopy, *Current Applied Physics* 14, 451-454.
43. A. Khumaeni, Z. S. Lie, H. Niki, K. H. Kurniawan, E. Tjoeng, Y. I. Lee, K. Kurihara, Y. Deguchi, and K. Kagawa, 2011, Direct analysis of powder samples using transversely excited atmospheric CO<sub>2</sub> laser-induced gas plasma at 1 atm, *Analytical and Bioanalytical Chemistry* 400, 3279-3287.
44. A. Khumaeni, M. Tani, K. Kurihara, K. Kagawa, and H. Niki, 2017, Coarse Metal Powder-Assisted pulsed CO<sub>2</sub> Laser-induced Breakdown Spectroscopy for the Direct Determination of Heavy Metals in Soil, *Analytical Letters* 50, 1992-1999.
45. J. Mammosser, S. Ahmed, and K. Macha, Large-volume resonant microwave discharge for plasma cleaning of a Cebaf 5-Cell SRF cavity, *Proceedings of IPA C2012, New Orleans, Louisiana, USA*.
46. J. D. Ingle Jr. and S. R. Crouch, 1988, *Spectrochemical Analysis*, Prentice Hall, New Jersey.
47. Z. Wang, M.S. Afgan, W. Gu, Y. Song, Y. Wang, Z. Hou, W. Song, Z. Li, Recent advances in laser-induced breakdown spectroscopy quantification: from fundamental understanding to data processing, *TrAC Trends in Analytical Chemistry* 143, 2021, 116385.

### Figure captions

Figure 1 Experimental setup used in this work.

Figure 2 Illustration of metal coarse supported induced plasma.

Figure 3 Emission spectrum obtained from the coarse metal powder only without any liquid sample.

Figure 4 Plasma temperature at various plasma lifetime

Figure 5 Emission spectra obtained from (a) the commercial liquid milk containing  $1000 \mu\text{g/ml}$  Ca, (b) the commercial liquid vitamin containing 6.8% Mg, (c) the commercial liquid vitamin containing 3% Mg, and (d) the Phosphoric acid liquid.

Figure 6 Emission spectrum obtained from the NaCl solution

Figure 7 Emission spectrum obtained from the  $\text{KNO}_3$  solution.

Figure 8 Emission spectrum of Cr taken from the tap water containing  $40 \mu\text{g/ml}$  Cr.

Figure 9 The reproducibility of emission intensities of Cr with respect to the number of laser shots.

Figure 10 Calibration curve of Cr taken from the tap water containing various concentrations of Cr.

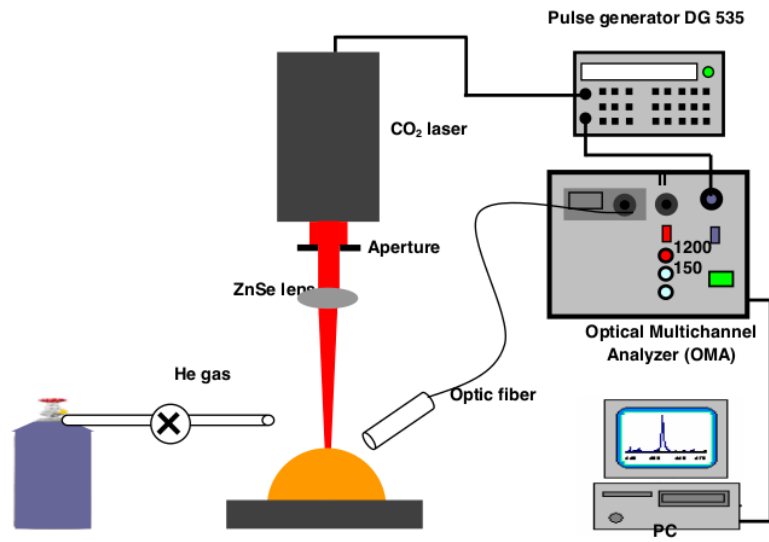


Figure 1

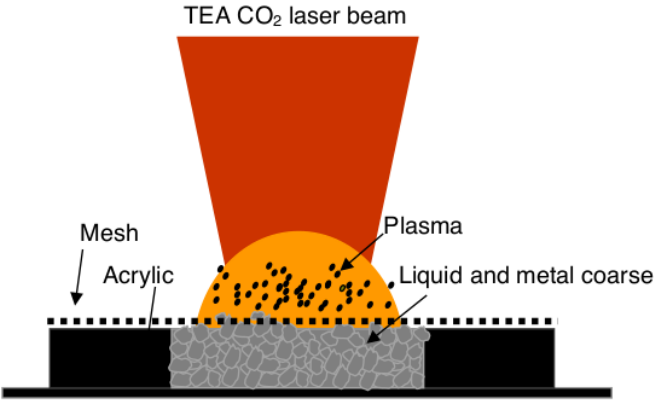


Figure 2

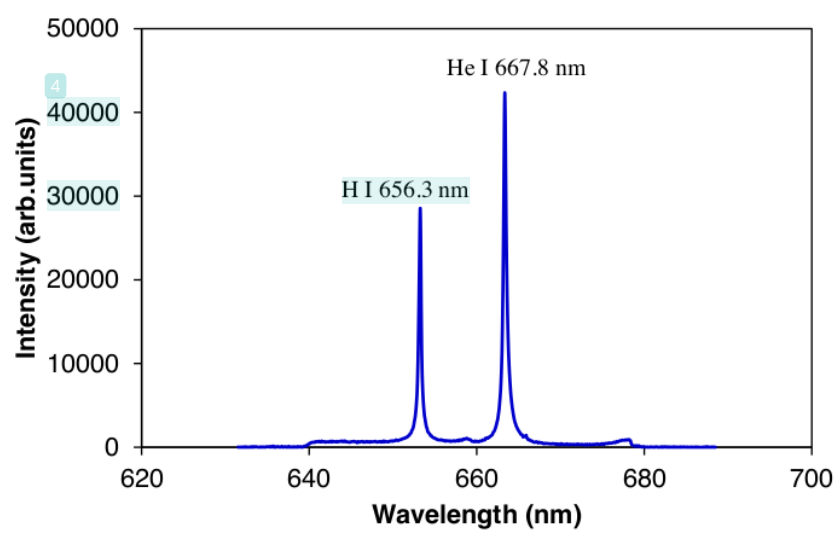


Figure 3

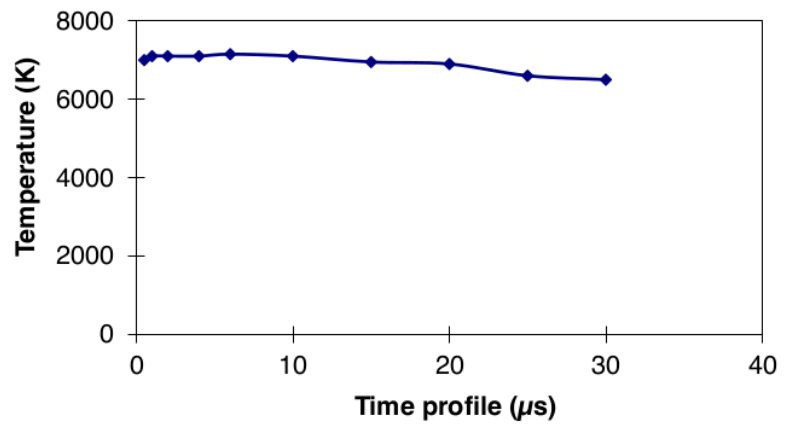
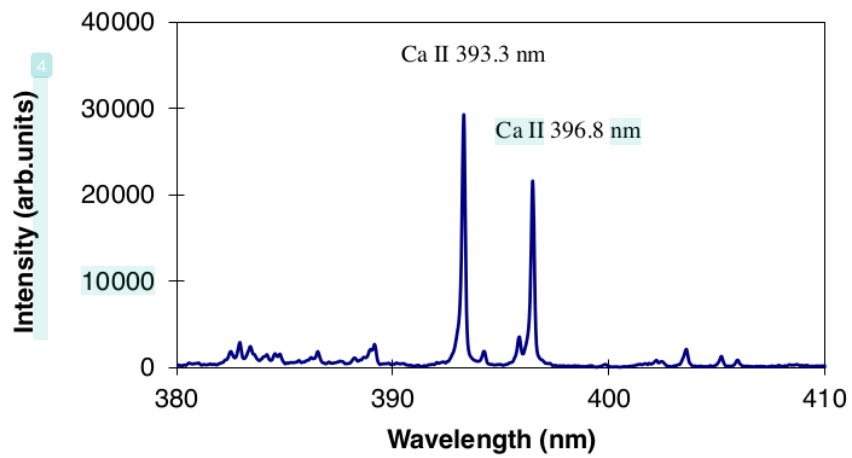
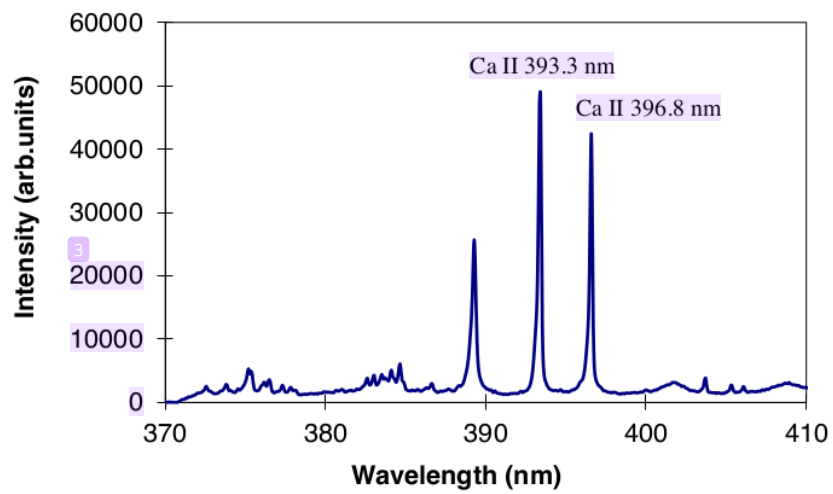


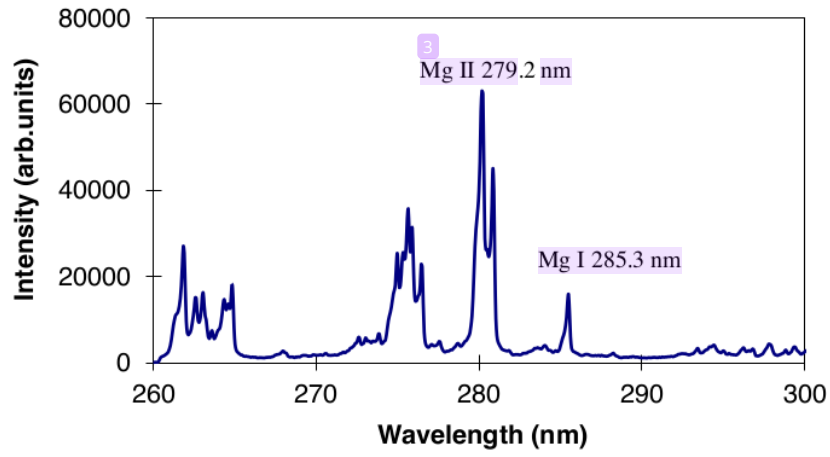
Figure 4



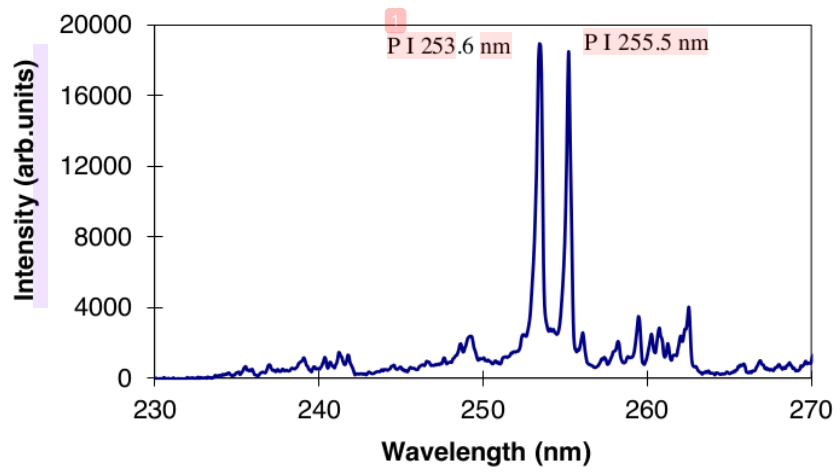
(a)



(b)



(c)



(d)

Figure 5



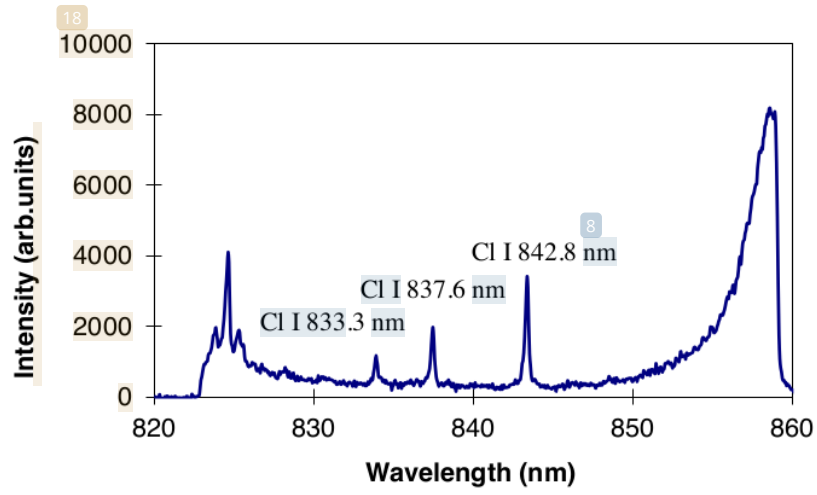


Figure 6

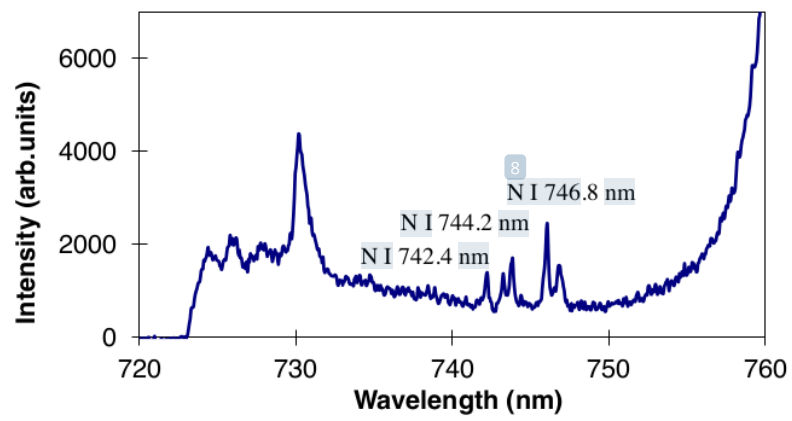


Figure 7

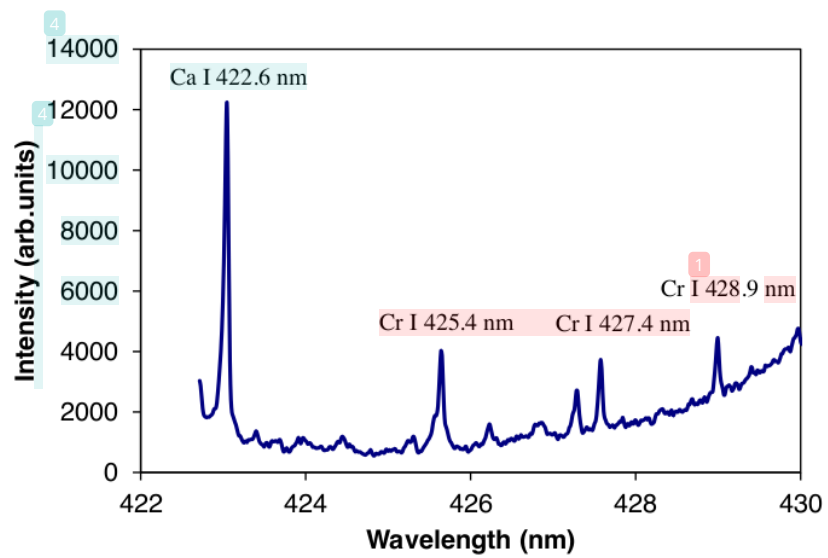


Figure 8

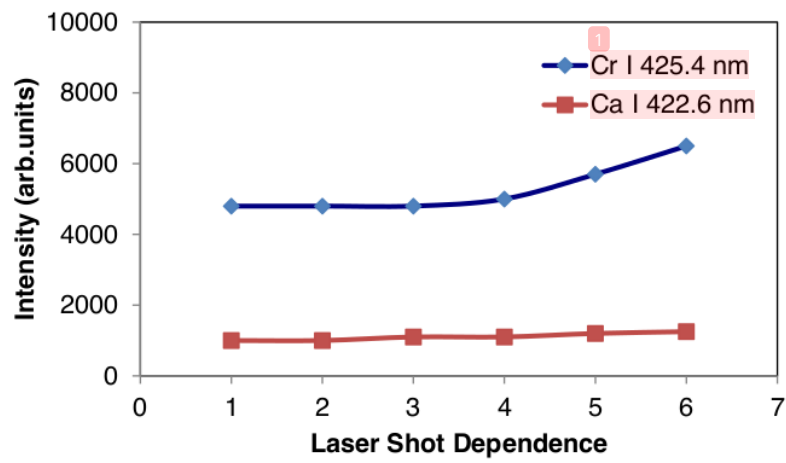


Figure 9

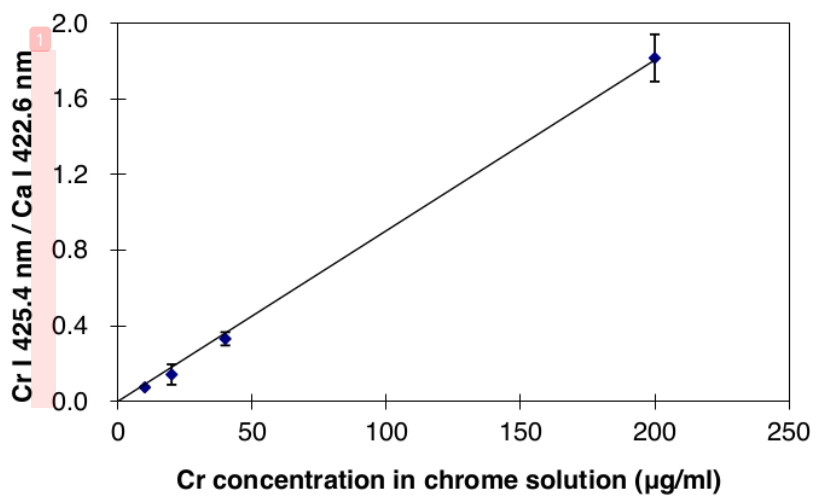


Figure 10

# Manuscript for JKUS

## ORIGINALITY REPORT

18%

SIMILARITY INDEX

10%

INTERNET SOURCES

17%

PUBLICATIONS

3%

STUDENT PAPERS

## PRIMARY SOURCES

1	<a href="http://hdl.handle.net">hdl.handle.net</a> Internet Source	5%
2	Ali Khumaeni, Wahyu Setia Budi, Koo Hendrik Kurniawan, Ken-Ichi Fukumoto, Kazuyoshi Kurihara, Kiichiro Kagawa. "Quantification of sodium contaminant on steel surfaces using pulse CO2 laser-induced breakdown spectroscopy", Arabian Journal of Chemistry, 2022 Publication	3%
3	Submitted to Universitas Diponegoro Student Paper	2%
4	Ali, Khumaeni. "Study on Laser-Induced Gas Plasma Using TEA CO2 Laser for Atomic Emission Spectroscopy", University of Fukui, 2013. Publication	1%
5	Ali Khumaeni, Asep Yoyo Wardaya, Hideaki Niki, Kiichiro Kagawa. "Rapid identification of elements in liquid by using pulse carbon	1%

dioxide laser-induced plasma spectroscopy",  
AIP Publishing, 2018

Publication

6

Ali Khumaeni, Asep Yoyo Wardaya, Wahyu Setia Budi. " Identification of elements in liquid-immersed particles by pulse CO laser-induced breakdown spectroscopy ", Journal of Physics: Conference Series, 2019

Publication

1 %

7

Koo Hendrik Kurniawan, May On Tjia, Kiichiro Kagawa. "Review of Laser-Induced Plasma, Its Mechanism, and Application to Quantitative Analysis of Hydrogen and Deuterium", Applied Spectroscopy Reviews, 2013

Publication

1 %

8

[www.atomtrace.com](http://www.atomtrace.com)

Internet Source

<1 %

9

A. Khumaeni, W.S. Budi, A.Y. Wardaya, R. Hedwig, K. H. Kurniawan. "ELEMENTAL CHARACTERIZATION OF HUMAN BLOOD USING LASER-INDUCED BREAKDOWN SPECTROSCOPY UTILIZING 355 NM Nd: YAG OPERATED AT REDUCED PRESSURE OF He GAS", Rasayan Journal of Chemistry, 2021

Publication

<1 %

10

Submitted to Syiah Kuala University

Student Paper

<1 %

11 A. Khumaeni, Z. S. Lie, K. H. Kurniawan, K. Kagawa. "Metal-Assisted Laser-Induced Gas Plasma for the Direct Analysis of Powder Using Pulse CO<sub>2</sub> Laser", Journal of Applied Spectroscopy, 2017  
Publication

---

12 [www.science.gov](http://www.science.gov)  
Internet Source

---

13 [www.tandfonline.com](http://www.tandfonline.com)  
Internet Source

---

14 Ali Khumaeni, Katsuaki Akaoka, Masabumi Miyabe, Ikuo Wakaida. "The role of metastable atoms in atomic excitation process of magnesium in microwave-assisted laser plasma", Optics Communications, 2021  
Publication

---

15 Sanja Zivkovic, Jelena Savovic, Miroslav Kuzmanovic, Jelena Petrovic, Milos Momcilovic. "Alternative analytical method for direct determination of Mn and Ba in peppermint tea based on laser induced breakdown spectroscopy", Microchemical Journal, 2018  
Publication

---

16 Zhijiang Chen, Hongkun Li, Ming Liu, Runhua Li. "Fast and sensitive trace metal analysis in aqueous solutions by laser-induced



breakdown spectroscopy using wood slice  
substrates", Spectrochimica Acta Part B:  
Atomic Spectroscopy, 2008

Publication

17

[aip.scitation.org](http://aip.scitation.org)

Internet Source

<1 %

18

[ikee.lib.auth.gr](http://ikee.lib.auth.gr)

Internet Source

<1 %

19

[www.eurekaselect.com](http://www.eurekaselect.com)

Internet Source

<1 %

20

Ali Khumaeni, Hideaki Niki, Ken-ichi Fukumoto, Yoji Deguchi, Kazuyoshi Kurihara, Kiichiro Kagawa, Yong Inn Lee. "A unique technique of laser-induced breakdown spectroscopy using transversely excited atmospheric CO<sub>2</sub> laser for the sensitive analysis of powder samples", Current Applied Physics, 2011

Publication

<1 %

21

Nasrullah Idris, Kurnia Lahna, Fadhli, Muliadi Ramli. "Study on Emission Spectral Lines of Iron, Fe in Laser-Induced Breakdown Spectroscopy (LIBS) on Soil Samples", Journal of Physics: Conference Series, 2017

Publication

<1 %

22

[link.springer.com](http://link.springer.com)

Internet Source

<1 %

23

Khumaeni, Ali, Zener Sukra Lie, Yong Inn Lee, Kazuyoshi Kurihara, Koo Hendrik Kurniawan, Ken-ichi Fukumoto, Kiichiro Kagawa, and Hideaki Niki. "Emission Characteristics of Ca and Mg Atoms in Gas Plasma Induced by the Bombardment of Transversely Excited Atmospheric CO<sub>2</sub> Laser at 1 atm", Japanese Journal of Applied Physics, 2012.

Publication

---

<1 %

24

Vasili Kiris, Jelena Savovic, Alena Nevar, Miroslav Kuzmanovic, Mikhail Nedelko, Dragan Rankovic, Nikolai Tarasenko. "Laser-induced breakdown spectroscopy analysis of water solutions deposited on PTFE surface: Influence of copper oxide nanoparticles and NELIBS effect", Spectrochimica Acta Part B: Atomic Spectroscopy, 2022

Publication

---

<1 %

25

Xinyan Yang, Lianbo Guo, Jiaming Li, Rongxing Yi et al. "Laser-induced breakdown spectroscopy of liquid solutions: a comparative study on the forms of liquid surface and liquid aerosol", Applied Optics, 2016

Publication

---

<1 %

---

Exclude quotes On

Exclude matches Off

Exclude bibliography On

# Manuscript for JKSUS

---

## GRADEMARK REPORT

---

FINAL GRADE

**/1**

GENERAL COMMENTS

**Instructor**

---

PAGE 1

---

PAGE 2

---

PAGE 3

---

PAGE 4

---

PAGE 5

---

PAGE 6

---

PAGE 7

---

PAGE 8

---

PAGE 9

---

PAGE 10

---

PAGE 11

---

PAGE 12

---

PAGE 13

---

PAGE 14

---

PAGE 15

---

PAGE 16

---

PAGE 17

---

PAGE 18

---

PAGE 19

---

PAGE 20

---

PAGE 21

---

PAGE 22

---

PAGE 23

---

PAGE 24

---

PAGE 25

---

PAGE 26

---

PAGE 27

---

PAGE 28

---

RUBRIC: SHORT ANSWER

---

**CLAIM/FOCUS**

State a clear claim/topic sentence and stay focused on supporting it.

---

**MEETS EXPECTATIONS** A precise claim/topic sentence based on the topic and/or source(s) is present. The response maintains a strong focus on developing the claim/topic sentence, thoroughly addressing the demands of the task.

**APPROACHES EXPECTATIONS** A claim/topic sentence based on the topic and/or source(s) is present, but it may not completely address the demands of the task, or the response does not maintain focus on developing it.

**DOESN'T MEET EXPECTATIONS** The claim/topic sentence is vague, unclear, or missing, and the response does not address the demands of the task.

**SUPPORT/EVID**

Provide evidence and explain how it supports the claim/topic sentence.

---

**MEETS EXPECTATIONS** The response includes sufficient, appropriate evidence to support the claim/topic sentence. Reasoning and understanding of the topic and/or source(s) are demonstrated by thorough explanations of the relationship between claims and support.

**APPROACHES EXPECTATIONS** The response presents some evidence to support the claim/topic sentence, but it may be insufficient or inappropriate. Some reasoning and understanding of the topic and/or source(s) are demonstrated, but attempts to explain the relationship between claims and support are inadequate.

**DOESN'T MEET EXPECTATIONS** Evidence is general or largely absent, and explanation of the relationship between claims and support is minimal.

**ORGANIZATION**

Present ideas in a logical structure that shows the relationships between ideas.

---

**MEETS EXPECTATIONS** An effective organizational structure enhances the reader's understanding of the information. The relationships between ideas are made clear with effective transitional phrases.

**APPROACHES EXPECTATIONS** An organizational structure is evident, but may not be fully developed or appropriate. Transitional phrases may be used but the relationships between ideas are somewhat unclear.

**DOESN'T MEET EXPECTATIONS** An organizational structure is largely absent and the relationships between ideas are unclear.

**LANGUAGE**

Communicate ideas using formal language and vocabulary specific to the topic.

---

MEETS EXPECTATIONS	The response has an established, formal style that is maintained throughout. Varied sentence structure, precise language, and domain-specific vocabulary are used to communicate ideas effectively. The response may stray from an objective tone at times, or have some errors that do not interfere with meaning.
APPROACHES EXPECTATIONS	The response attempts a formal style that may not be maintained throughout. Sentence structure is somewhat varied and some precise language and/or domain-specific vocabulary are used. The response contains some errors that may interfere with meaning.
DOESN'T MEET EXPECTATIONS	The response does not establish a formal style and ideas are unclear at times. There is little variety in sentence structure and language is general throughout. The response contains several errors that interfere with meaning.