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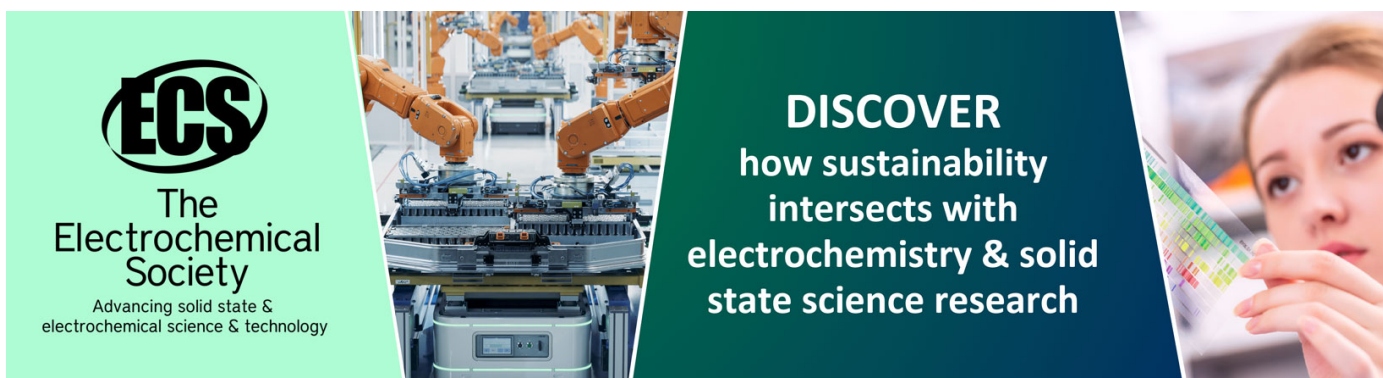
Study on Emission Spectral Lines of Iron, Fe in Laser-Induced Breakdown Spectroscopy (LIBS) on Soil Samples

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Study on Emission Spectral Lines of Iron, Fe in Laser-Induced Breakdown Spectroscopy (LIBS) on Soil Samples

Nasrullah Idris^{1*}, Kurnia Lahna¹, Fadhli¹, and Muliadi Ramli²

¹Department of Physics, Faculty of Mathematics and Natural Sciences, Syiah Kuala University, Jl. Syech Abdurrauf No. 3 Darussalam, 23111 Banda Aceh, Aceh, Indonesia

²Department of Chemistry, Faculty of Mathematics and Natural Sciences, Syiah Kuala University, Jl. Syech Abdurrauf No. 3 Darussalam, 23111 Banda Aceh, Aceh, Indonesia

^{a)}Corresponding author: nasrullah.idris@unsyiah.ac.id

Abstract. In this work, LIBS technique has been used for detection of heavy metal especially iron, Fe in soil sample. As there are a large number of emission spectral lines due to Fe and other constituents in soil, this study is intended to identify emission spectral lines of Fe and finally to find best fit emission spectral lines for carrying out a qualitative and quantitative analysis. LIBS apparatus used in this work consists of a laser system (Neodymium Yttrium Aluminum Garnet, Nd-YAG: Quanta Ray; LAB SERIES; 1,064 nm; 500 mJ; 8 ns) and an optical multichannel analyzer (OMA) system consisting of a spectrograph (McPherson model 2061; 1,000 mm focal length; f/8.6 Czerny-Turner) and an intensified charge coupled device (ICCD) 1024x256 pixels (Andor I*Star). The soil sample was collected from Banda Aceh city, Aceh, Indonesia. For spectral data acquisition, the soil sample has been prepared by a pressing machine in the form of pellet. The laser beam was focused using a high density lens (f=+150 mm) and irradiated on the surface of the pellet for generating luminous plasma under 1 atmosphere of air surrounding. The plasma emission was collected by an optical fiber and then sent to the optical multichannel analyzer (OMA) system for acquisition of the emission spectra. It was found that there are many Fe emission lines both atomic lines (Fe I) and ionic lines (Fe II) appeared in all detection windows in the wavelength regions, ranging from 200 nm to 1000 nm. The emission lines of Fe with strong intensities occurs together with emission lines due to other atoms such as Mg, Ca, and Si. Thus, the identification of emission lines from Fe is complicated by presence of many other lines due to other major and minor elements in soil. Considering the features of the detected emission lines, several emission spectral lines of Fe I (atomic emission line), especially Fe I 404.58 nm occurring at visible range are potential to be good candidate of analytical lines in relation to detection heavy metal pollution, Fe, in soil sample.

1. Introduction

Iron, Fe is actually essential in soil since it is generally considered as micronutrient for plant growth [1]. Iron deficiency causes chlorosis and a reduced rate of the growth plants [2]. However, it turns into toxicity in excess. The excessive Fe in soil would be exposed to the grown plant, accumulating Fe in the plant tissues at high concentration causing many kinds of metabolic disorders of plants [3-6]. In general, iron concentrations in soils range from 0.2% to 55% (20,000 to 550,000 mg/kg) [7] and the concentrations can vary differently by regions, even within localized areas, due to soil types and the presence of other natural and anthropogenic sources. On average, common concentration of iron in soil including agriculture soil is about 4%. Therefore, periodical analysis of Fe content in soil is very important for both assuring iron concentration meets the essentiality and hinders the toxicity.



Tsunami is one source altering significantly chemical composition the impacted soil including heavy metal elements such as Fe as it brings very large volume of water and various materials including sediment from the sea into the impacted land. The giant Indian Ocean tsunami, Aceh 26 December 2004 have not only brought about deadliest, catastrophic effect to human being and living things, but it have also caused severe environmental problems, including erosion and pollution of the impacted land, water source and surface water due to the sea water and the contaminated sediment and other material depositions [8-10].

Analytical studies conducted on sediment samples taken from the tsunami impacted coastal region of Thailand and Banda Aceh, Indonesia after the giant tsunami found that concentration of salts and heavy metals in the tsunami-impacted sand and soil was highly elevated [8-10]. This condition is persistent even 1.5 years and 3.5 years after the tsunami [10]. Therefore, detection of heavy metal including Fe in the tsunami-impacted soil is very important. Nowadays various laboratory tools such as Fourier transform infrared (FTIR) spectroscopy, X-Ray Diffraction (XRD) spectroscopy and atomic absorption spectroscopy (AAS) has been used for soil analysis. However, these conventional techniques are impractical considering number of sample and disability for in situ analysis. Therefore, it is required to develop a fast, efficient and effective analytical tool. A new technique analytical tool, namely laser induced breakdown spectroscopy (LIBS) has emerged, a future super star analytical tool, promising unequivocally advantages such as very efficient and effective nondestructive analysis [11]. This technique based on using laser to generate luminous plasma as optical emission source for detection and analysis spectrochemically the constituent of the questioned samples. In previous study, a transversely excited atmospheric pressure (TEA) carbon dioxide (CO₂) laser, LIBS technique has succeed to detect heavy metal in soil [12]. This result promises a similar succeed analysis for Fe in soil. In this work, LIBS technique has been used to detect Fe in soil sample. However, referring to atomic spectra database, there are many emission spectral lines of Fe appear in the wavelength range of 200-1000 nm [13]. Therefore, prior to application LIBS technique to detect and analyze iron, Fe in the tsunami-impacted soil, at first the LIBS study will be made on agriculture soil samples from the region which is not affected by the tsunami, the tsunami-unimpacted soil, to detect and identify Fe emission spectral lines and finally conclude the best analytical lines for carrying out a qualitative and quantitative analysis.

2. Experimental Setup

Basic LIBS experimental setup used in this work is similar to that used in previous study elsewhere [14]. The LIBS system consists a Nd-YAG laser (Quanta Ray; LAB SERIES; $\lambda=1,064$ nm; $E=500$ mJ, $\Delta t=8$ ns, $f=10$ Hz) as plasma excitation source, a lens of +250 mm for focusing laser beam, an optical fiber for collecting and delivering plasma emission, and an optical multichannel analyzer (OMA) system as optical detector of the plasma emission. The OMA system composes of a spectrograph (McPherson model 2061; 1,000 mm focal length; $f/8.6$ Czerny-Turner) and ICCD having 1024x256 pixels (Andor I*Star), 26-mm square (960 x 256 active pixels). The laser beam energy was measured by a joulemeter (Duo watt-joule meter). The energy can be varied in the range from 1 mJ to 500mJ/pulse. In the whole experiment, the laser beam energy was made constant at 68 mJ.

The soil samples used in this work was taken in an agriculture region. The region is the tsunami un-impacted zone in Aceh Besar Regency, Aceh, Indonesia. The collected samples has been prepared in such that the samples are free from leafs, root and other organic matters. The soil sample was pressed into the form of pellet using a hydraulic pressing apparatus with a force of 10 ton. The dimension of pellet is 20 mm in diameter with thickness of 3mm. The soil pellet was fixed on a sample holder placed in a chamber. The ambient gas in the chamber actually can be vacuumed and then exchanged with different kind of gas. The pressure of the ambient gas can be adjusted. However, this experiment was carried out under air surrounding gas at 1 atmosphere. The sample chamber was attached on a movable x-y platform controlled with a stepping motor.

For producing plasma, the laser beam was focused using the lens (+250 mm) onto the pellet surface. The spot size of the focused laser beam is about 300 μ m, resulting in a power density of around 1 GW/cm². The sample was rotated during data acquisition to assure new position for each acquisition. The emission from the plasma was collected and delivered by using an optical fiber bundle to the entrance slit of the monochromator (spectrograph). Optical signal has been detected from the exit slit of the monochromator using intensified charge coupled device (ICCD) camera of the OMA system for detecting and acquiring emission spectral lines. During data acquisition, the OMA system was run under 1800 groove/mm grating mode having a useful wavelength window of about 12 nm. Gate delay and gate width of the OMA system were set at 3 μ s and 50 μ s, respectively during data acquisition.

3. Results and Discussion

In order to carry out a qualitative and quantitative analysis using LIBS, the first step is identification elements through assignment of the emission spectral lines of the elements. Identification and confirmation of an emission spectral line requires knowledge, experience and skill [15]. Thus, in order to detect and make a qualitative and quantitative analysis of Fe in soil sample, we should have strategy or procedures, namely knowing about (1) major and minor elements in the soil sample, (2) relative intensities of the emission spectral lines from reference/database wavelength tables, (3) the ionization stage of the emission spectral lines of the element, (4) the specific experimental conditions, and (5) observation of multiple strong emission spectral lines [15]. Thus, it is really crucial step to find ionization stage and relative intensities of the emission lines from reference/database to know strong emission lines before starting detection and assignment of any emission lines.

It well known that main constituents of soil are Si, Fe, Ca, Al, Ti, Mg, Na, Sr, etc. Inspection on atomic spectra database [13] revealed that there are 14310 atomic (Fe I) and ionic (Fe II) emission spectral lines in the wavelength range from 200 nm-1000 nm with relative intensities vary extremely from 1 (the lowest) till 2510000 (the highest). Although our final goal is to find best fit Fe emission line for carrying out qualitative and quantitative analysis, however we face a problem of dealing with such number of emission spectral lines. Therefore, considering the procedure of identifying element mentioned above, we then decided to narrow the interest emission lines, namely at first to work simply on the emission lines having very strong relative intensities (≥ 1000000). In this case, there are 27 emission lines consisting of 20 atomic emission lines (Fe I) and 7 ionic emission lines (Fe II), as displayed in Table 1. It can be seen that the strongest emission line is Fe atomic line, Fe I 374.55 nm, having relative intensity of 2510000. In general, based on the tabulated relative emission intensities of the emission lines, which are extremely strong as compared to the lowest relative emission intensity, namely 1, it is expected all the tabulated emission lines could be detected. Excitation energy of the emission lines are also shown in Table 1.

Table 1. List of strong emission lines of Fe (relative intensity ≥ 1000000) extracted from reference database [13].

No	Wavelength (nm)	Relative Intensity (a. u.)	Excitation Energy (eV)	No	Wavelength (nm)	Relative Intensity (a. u.)	Excitation Energy (eV)
1	Fe II 234.34	1000000	5.28	15	Fe I 373.33	1000000	3.32
2	Fe II 238.20	1800000	5.20	16	Fe I 374.55	2510000	3.31
3	Fe II 239.56	1500000	5.18	17	Fe I 374.58	1100000	3.31
4	Fe II 240.48	1100000	5.15	18	Fe I 374.82	1910000	3.30
5	Fe II 259.93	1000000	4.76	19	Fe I 374.94	1150000	3.31
6	Fe II 273.95	1000000	4.53	20	Fe I 382.44	1000000	3.24
7	Fe II 275.57	1100000	4.50	21	Fe I 385.63	1100000	3.21
8	Fe I 344.06	1350000	3.60	22	Fe I 387.85	1290000	3.20
9	Fe I 344.09	1290000	3.60	23	Fe I 389.97	1070000	3.18
10	Fe I 347.54	1200000	3.57	24	Fe I 392.29	1000000	3.16
11	Fe I 349.05	1320000	3.55	25	Fe I 393.02	1150000	3.16
12	Fe I 363.14	1150000	3.42	26	Fe I 404.58	1000000	3.06
13	Fe I 370.55	1290000	3.34	27	Fe I 526.95	1020000	2.36
14	Fe I 372.25	1290000	3.33				

Figure 1 exhibits emission spectra taken from plasma produced on the soil sample. The measurement window was centered at the wavelength of 373 nm. The emission spectra contain high density of emission lines. These lines are due to Fe and other constituents of soil. Using the above mentioned procedures [15], emission lines due to Fe in this wavelength region were able to be identified. It can be seen clearly that there are many Fe emission lines can be found in the spectra with strong intensities, namely Fe I 370.55 nm, Fe I 372.25 nm, Fe I 373.33 nm, Fe I 374.55 nm, Fe I 374.58 nm, Fe I 374.82 nm, Fe I 374.94 nm. The emission lines of Fe I 374.55 nm and Fe I 374.58 nm are not resolved since their separation very narrow, only 0.03 nm, thus the two lines are heavily overlap. The measured intensity of

Fe I 374.55 nm line is very strong in comparison with the other lines (Fe I 370.55 nm, Fe I 372.25 nm, Fe I 373.33 nm) just as expected from the database. While Fe I 374.94 nm shows significantly higher emission intensity as compared to the other Fe lines even though, based on the reference database, its relative intensity is actually lower than that of Fe I 374.55 nm. This is probably due to interference from other constituent emission line. However, in general the detected wavelengths and the measured emission intensities of the emission lines are in good coincidence with that of the database.

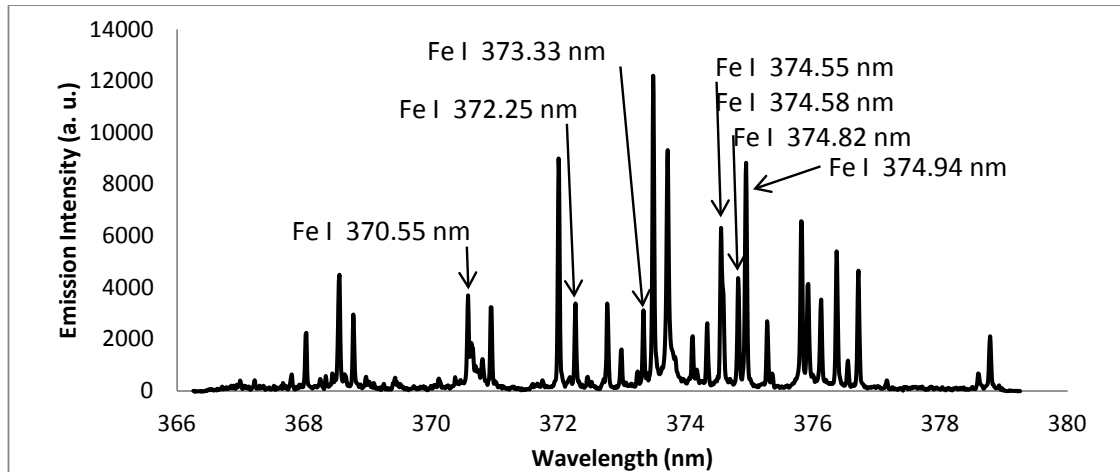


Figure 1. Emission spectra taken from plasma induced by irradiation of the focused Nd-YAG laser beam on the surface of the soil pellet sample under air surrounding gas at atmospheric pressure. The measurement window of the OMA system is centered at the wavelength of 373 nm. The soil sample was collected from agriculture region in Banda Aceh city, Aceh, Indonesia.

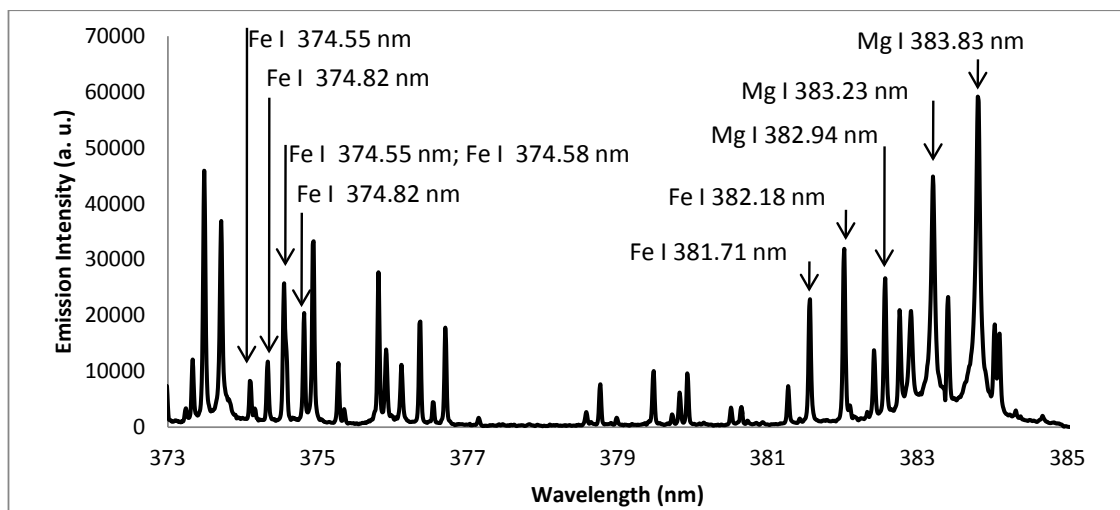


Figure 2. Emission spectra detected from the same soil sample under similar experimental conditions as for the Figure 1. The measurement window of the OMA system was shifted to a wavelength region centered at 379 nm.

Figure 2 displays emission spectra taken from the same soil sample under similar experimental condition as as for the Figure 1. The center of measurement window was shifted to 379 nm. At this wavelength region, the spectrum also contains high density of emission lines, especially on both sides of the spectrum. On the left part of the spectrum, the spectral lines are due to Fe atomic emission, the same as shown in Figure 1 since the detection window was shift only 6 nm from that of Figure 1. The other Fe I emission lines, namely Fe I 381.71 nm and Fe I 382.18 nm, can be found on the right part of the spectrum together with very strong Mg atomic emission lines (Mg I 382.94 nm, Mg I 383.23 nm, and Mg I 383.83 nm). The emission lines of Fe I 381.71 nm and Fe I 382.18 nm are not enlisted in Table 1

because their relative intensities are lower than those listed lines. Nevertheless after detailed examination on the wavelength database [13] the emission lines are confirmed due to Fe. Although their relative intensities lower compared to the strong emission line listed in Table 1, these emission lines appeared clearly with very strong intensities in the detected spectrum.

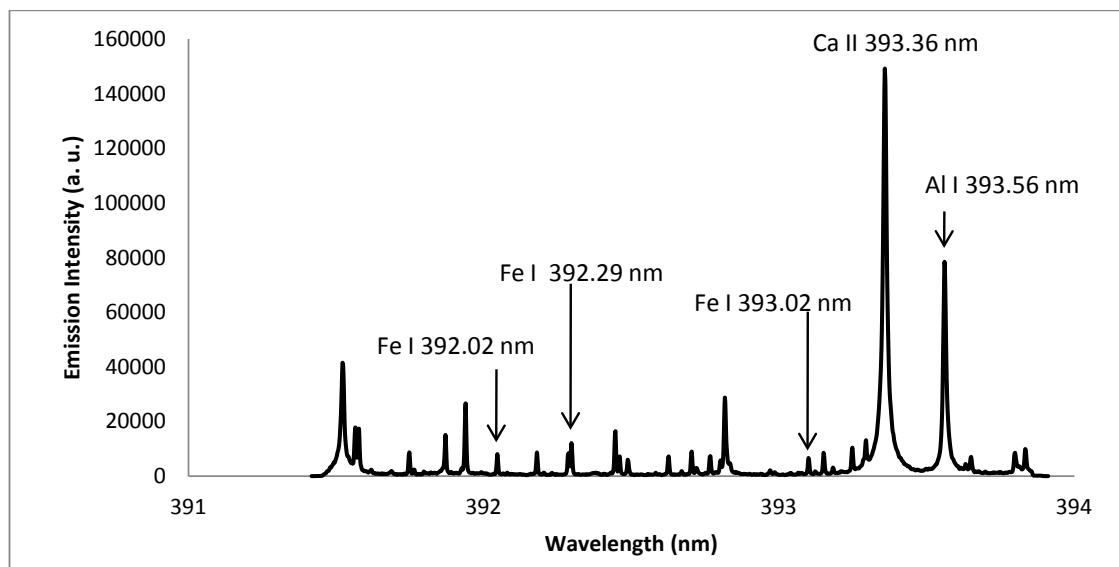


Figure 3. The emission spectra taken from the same plasma using the detection window of the OMA system set at center wavelength of 390 nm.

Next measurement was made on the same sample and experimental conditions by shifting spectral measurement to a detection window centered at the wavelength of 390 nm. Figure 3 presents the detected emission spectra in the wavelength region. It can be seen spectral lines due to atomic emission (Fe I), namely Fe I 392.02 nm, Fe I 392.29 nm, and Fe I 393.02 nm. In the measured spectra, intensities of the emission lines seem superficially weak. However, a careful inspection on the spectra figures out that their intensities are actually very strong, similar to that of Fe emission lines appeared in Figures 1 and 2. This is caused by the presence of the very strong emission line of Ca ionic emission (Ca II 393.36 nm), having about 10 times higher emission intensity, dominating the emission spectra at the region. In the spectrum, along with Fe and Ca lines, emission lines due to Al (Al I 393.56 nm) also occurs with strong emission intensity as soil contains Ca and Al as minor constituents. Figure 4 demonstrates emission spectra measured from the plasma when the spectral window was shifted further to the wavelength region centered at 405 nm. It can be found clearly several Fe atomic lines namely Fe I 400.52 nm, Fe I 404.58 nm, Fe I 406.35 nm and Fe I 407.17 nm. As shown in Table 1, the strongest Fe emission line in this wavelength region is Fe I 404.58 nm and it just coincides with the detected spectra displaying Fe I 404.58 nm as the line with highest emission intensity. The other Fe lines (Fe I 400.52 nm, Fe I 406.35 nm and Fe I 407.17 nm), even though not listed in the wavelength table above, Table 1, since their relative intensities are lower than 1000000, were confirmed as the correct assignment after detailed inspection on the wavelength database [13].

As observed above, the spectra detected at different wavelength regions from soil sample consist of high density of emission lines, especially Figures 1 and 2. After applying the above mentioned identifying procedures, we have able to assign the emission lines of Fe as shown in Figures 1, 2, 3, dan 4. For quantitative analysis, intensity of interest lines and set of lines are useful. The interested line should be free from interference of other lines (overlap), well isolated from other emission lines. The emission lines should also have high signal to background (S/B) ratio[15]. A careful examination on the emission lines of Fe displayed in Figures 1, 2, 3, and 4 found that the wavelength measurement region centered at 405 nm (Figure 4) is best spectral window for detecting Fe emission lines. This is because the detected emission spectra, in general the intensities of the emission lines are very strong in this spectral window. This strong emission intensity is especially observed for emission lines of Fe I 400.52 nm, Fe I 404.58 nm, Fe I 406.35 nm and Fe I 407.17 nm. The detected background emission intensity is relatively low, resulting in good signal to background (S/B) ratio in the spectral region. Moreover, in this wavelength

region, the emission lines are clean, well isolated from other emission lines. The strongest Fe emission line in this wavelength region is Fe I 404.58 nm, leading this line to be best candidate as analytical line for detecting and making a qualitative and quantitative analysis of Fe. Along with Fe atomic lines, strong and well isolated lines due to Ti (Ti 398.98 nm and Ti I 399.86 nm) can be observed. In addition, Mn atomic triplet lines also appear in the detected spectrum. These lines (Ti and Mn) especially the triplet Mn could be used to confirm and calibrate the assignment of the emission lines of Fe in the wavelength region.

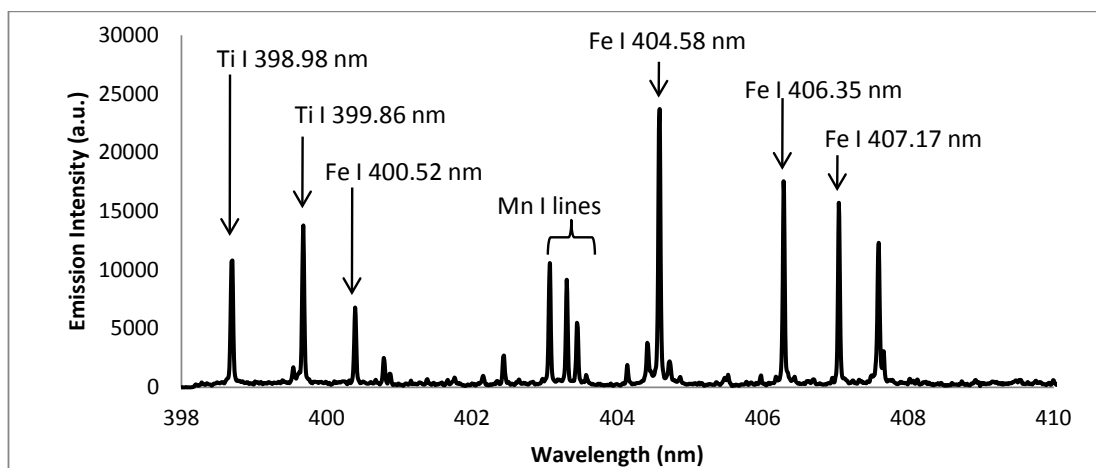


Figure 4. The spectra of the plasma emission detected using the spectral window of the OMA system centered at the wavelength of 405 nm.

4. Conclusion

The Fe emission lines with strong intensities can clearly be detected at various wavelength ranges especially the theoretically strongest atomic line of Fe I 374.55 nm appeared in the spectral windows centered at 373 nm or 376 nm. However, the strongest line Fe I 374.55 nm is not resolved well from Fe I 374.58 nm emission line since their separation is only about 0.03 nm. Profiles of the emission intensities of the detected Fe lines are in a good agreement with that of reference/database where the lines with high relative intensities in the database were found to display high intensities in the measured spectra and vice versa. A number of emission lines such as Fe I 392.02 nm and Fe I 392.29 nm are not well isolated. Several emission lines such as Fe I 374.94 nm probably overlap with other lines (interference), since its measured intensity profile is different from that of the database. Considering the spectral windows examined in this work, the spectral window centered at 405 nm is the best spectral window for detecting Fe emission lines as this region displays only several Fe emission lines featuring high emission intensities, well isolated, and high S/B ratio. The atomic emission line of Fe I 404.58 nm is the best line for detection and making a qualitative and quantitative analysis of Fe in soil sample as will be conducted in our near future work.

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