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1. Draft manuskrip sebelum proses submission
2. Submission acknowledgment dari Analytical Letters (11 Juli 2016)
3. Editor and reviewers' comments (15 Agustus 2016)
4. Balasan komentar Editor dan Reviewers
5. Paper setelah proses revisi mempertimbangkan masukan Editor dan Reviewers
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1. Draft manuskrip sebelum proses submission

**Metal coarse powder-assisted pulse CO₂ laser-induced gas
plasma spectroscopy for the direct analysis of heavy metals in
soils**

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Abstract

A novel method of laser-induced plasma spectroscopy utilizing a pulse transversely excited atmospheric (TEA) CO₂ laser has been developed for the high-sensitivity direct analysis of heavy metals in soil. Metal coarse powder was used to trap the soil powder sample and generate a gas plasma. When a pulsed TEA CO₂ laser (10.6 μm, 1.5 J, 200 ns) was irradiated on the metal coarse powder, in which the soil powder was trapped, a high-temperature and long-lifetime gas plasma was produced. Fine particles of soil sample was dissociated and excited in the gas plasma region. Nice linear calibration curve of Hg in loam soil was made. The method has been employed to rapid detection of various heavy metals including Cr, Pb, and Hg in loam soil. Detection limits of Cr, Pb, and Hg were approximately 0.8, 15, and 0.7 mg/kg, respectively.

Keywords: laser-induced breakdown spectroscopy; LIBS; Heavy metal detection; Soil analysis; TEA CO₂ laser

1. Introduction

The analysis of soil containing hazardous elements has become a subject of great interest. The pollution of hazardous chemicals in soil, coming from various sources, has been found to cause harms to humans. Soil contamination is a sensitive issue, related to increasing public environmental and security awareness, dealing with land ownership transfer and utilization, such as for farming, building construction, and real estate businesses (Nicholson 2003; Allen 1995; Senesil 1999; Zimmermen 2010). Thus, the analysis of soil contamination prior to cultivating, constructing, or selling is really necessary.

Several methods have been applied to perform soil analysis such as X-ray fluorescence spectrometry (XRF), atomic absorption spectroscopy (AAS), inductively coupled plasma mass spectrometry (ICP-MS), and inductively coupled plasma atomic emission spectrometry (ICP-AES) (Bings 2010; Gauglitz 2003; Beckhoff 2006). Those methods offered high precision and high sensitivity for the purpose of quantitative analysis. However, the methods require delicate sample pretreatment, time consuming, and are labor intensive. Therefore, the methods do not appropriate for rapid and in- situ monitoring of the heavy metals in soils (Srungaram 2013).

Laser-induced breakdown (LIBS) has recently become an increasingly popular technique for qualitative and quantitative elemental analysis of various samples in

different phase such as solids, liquids, and gases. This advantage has largely driven an interest in application of LIBS to environmental sample analysis such as soil and liquids (Cremers 2006).

Several works have been devoted to the applications of LIBS to soil analysis (Srungaram 2013; Yang 2010; Jantzi 2011; Hussain 2008; Dell'Aglio 2011; Popov 2010). Characterization of pollution indices in soil has been made by Arab et al. using laser-induced breakdown spectroscopy (Arab 2015). Srungaram et al. applied LIBS and spark-induced breakdown spectroscopy (SIBS) for the analysis of Hg in soil (Srungaram 2013). The detection limit for the Hg by using LIBS and SIBS were 483 and 20 mg/kg, respectively. Popov et al. proposed a new configuration of spatial confinement in LIBS for the analysis of soil. The detection limit of heavy metals including As, Hg, and Pb were 30, 25, and 90 mg/kg, respectively (Popov 2010). Liu et al. proposed LIBS assisted by a microwave (microwave-assisted laser-induced breakdown spectroscopy/MA-LIBS) for the enhancement of sensitivity in soil analysis. The detection limit of Cu in soil by using the proposed method was 30 mg/kg (Liu 2012). However, it should be mentioned that in a standard LIBS technique, the soil sample is most often prepared into a pellet prior to laser irradiation generally by using neodymium yttrium aluminium garnet (Nd:YAG) laser. Based on our experimental results, the insufficient atomization of the soil sample still cannot be

resolved and this technique is also time consuming. Furthermore, the soil includes complex matrix containing a host of elements including Al, Ca, Mg, and Fe, which had more than a hundred peaks (Yang 2010).

On contrary to the standard LIBS technique above, we found that a transversely excited atmospheric (TEA) CO₂ laser is suitable to the analysis of soil sample. Due to the long wavelength and long pulse duration (10.64 μm in wavelength, 200 ns in pulse duration), the TEA CO₂ laser has high absorbance in the soil sample and the plasma can be initiated more easily and the serious blow-off of the soil can effectively be suppressed. This method has been applied to the analysis of soil containing various heavy metals by using high-vacuum silicon grease binder and unique microstructured holes made on a metal plate (Khumaeni 2010; Idris 2007). Compared to the standard LIBS method, the developed method has higher sensitivity of analytical detection.

To significantly reduce the detection limit of heavy metals in the soil, a novel method of the LIBS by utilizing a TEA CO₂ laser was proposed. In this method, fine particles of soil powder are trapped into the metal coarse powder with a diameter of around 1-3 mm by mixing the soil powder with the metal coarse powder. The iron particles function to trap the soil powder and induce a high-temperature gas plasma. The fine particles of soil powder are effectively dissociated and excited in the gas plasma region. The detection limit of heavy metals in soil can be significantly reduced

and much lower compared to the results of standard LIBS, SIBS, and MA-LIBS.

2. Experimental procedure

A schematic diagram of the experimental procedure used in this study is shown in Fig.1(a). A TEA CO₂ laser (Shibuya SQ 2000, energy of 3 J, wavelength of 10.6 μm, pulse duration of 200 ns) was employed as an energy source. The laser beam was focused by a ZnSe lens ($f = 200$ mm) onto a sample surface through a ZnSe window. The laser energy was fixed at 1.5 J by setting an aperture in the path of laser beam. The spot size of the laser beam in the sample surface was 2 mm x 2 mm, which resulted in a power density of 0.18 GW/cm² for energy of 1.5 J.

The samples used in this study were standard loam soil containing heavy metals of Cr, Pb and Hg. Prior to laser irradiation, 50 mg soil sample were homogeneously mixed with 350 mg metal coarse powder (volume ration 1:1) so that the soil is effectively trapped in the coarse powder (metal coarse powder, 99%, Soekawa chemicals). The metal coarse powder-mixed soil was then placed into a small hole with a diameter of 10 mm made of plastic acrylic with a thickness of 8 mm, on which the copper plate was attached in the tight contact of the backside of the acrylic. The diameter and depth of the hole are 10 mm and 8 mm, respectively. To suppress the blow-off of the soil and induce a high-temperature gas plasma, a metal mesh made of

stainless steel wires (lattice constants of 0.4 mm and the wires of 0.1 mm in diameter) was placed in tight contact on the front side of the mixed soil samples. It should be stressed that the metal mesh itself is never damaged and ablated during the laser irradiations because the power density of the laser beam impinging on the metal mesh is lower than the ablation threshold of the metal mesh due to the fact that most part of laser energy is absorbed by the strong gas breakdown plasma (plasma shielding effect) (Khumaeni 2010; Khumaeni 2011). For semi quantitative analysis of soil sample, the standard loam soils containing various concentrations of Hg (10, 50, 500, and 1000 mg/kg) were employed. The samples were placed in a metal chamber with dimensions of 12 cm x 12 cm x 12 cm, which was filled with helium gas. In this experiment, the pressure of the surrounding gas in the chamber was set at 1 atmosphere. The flowing rate of gas was 3 liters per minute (Lpm). It should be mentioned that the plasma induced in the He gas has lower background emission compared to the case of plasma in N₂ gas. The gas also functions to suppress the breakdown plasma induced by fine soil particles in the path of laser beam.

The emission spectrum was obtained by using a high resolution monochromator (Jobin-Yvon HRS-2, $f = 640$ mm, 2400/mm, spectral resolution of 0.02 nm) attached with an OMA system (Lambda vision LVICCD 1012). The plasma radiation at 5 mm from the sample surface was imaged in a ratio of 1:1 onto the entrance slit of the

monochromator with the use of a quartz lens ($f= 70$ mm). The slit width and the slit height of the monochromator were set at $20\ \mu\text{m}$ and 1 mm, respectively. In all experiments using the TEA CO_2 laser the gate delay and gate width of OMA system were set at $10\ \mu\text{s}$ and $100\ \mu\text{s}$, consecutively.

3. Results and discussion

At initial, the lifetime of plasma emission induced by using this present method was examined. To this end, a copper sulfate (CuSO_4) powder was employed as a sample. Cu was used as the sample because the plasma temperature can easily be derived by the ratio of the emission intensity of Cu I 521.8 nm (excitation energy of 6.2 eV) to that of Cu I 510.5 nm (excitation energy of 3.8 eV), with the assumption of Boltzmann's distribution (Ramli 2008). Figure 2 shows how the emission intensities of Cu I 521.8 nm and Cu I 510.5 nm change with time after the TEA CO_2 laser bombardment on the metal coarse powder-trapped CuSO_4 powder. The gate width of the OMA system was set at $1\ \mu\text{s}$ and the laser energy was 750 mJ. It is seen that the emission intensity of Cu I 521.8 nm is much higher than the case of Cu I 510.5 nm. It should be noticed that the plasma emission keeps long lifetime of around $35\ \mu\text{s}$, which is much longer emission compared to the case of standard LIBS. The intensity of Cu I 521.8 nm steeply increases up to $10\ \mu\text{s}$ and decreases slowly to $35\ \mu\text{s}$. For the Cu I

510.5 nm, the intensity significantly increases to 6 μs , is almost stable to 15 μs , and finally decreases slowly to 35 μs . Both Cu lines have a peak at around 10 μs . With the assumption of Boltzmann's distribution, the plasma temperature can be estimated around 7500 K at 10 μs . The high-plasma temperature and long-lifetime of plasma emission produced by using a present method was then employed to the rapid detection of heavy metals in soil sample.

Figure 3 shows the emission spectrum of Cr taken from the loam soil containing 50 mg/kg of Cr. The gate delay time and gate width of the OMA system were 10 μs and 100 μs , respectively. The laser energy was 1500 mJ. High-intensity and sharp typical neutral emission lines of Cr at 425.4 nm and 427.4 nm clearly appears together with many spectral lines including Ca and Fe, which are major elements in soil. The Cr line at 428.9 nm overlapped with the other line can also be detected. It should be noted that compared to other previous work by using standard LIBS method (Dell'Aglio 2011), the result by using the present method has nice analytical performance proved by higher signal to noise ratio (S/N) intensity.

This result revealed that our present method of metal coarse powder-assisted laser-induced gas plasma spectroscopy can clearly be used to rapidly identify the heavy metals in the soil containing low concentration of the heavy metals. This analytical spectrum also confirmed that the sensitivity of analytical detection by

utilizing TEA CO₂ laser has been improved when the metal coarse powder was used to trap the soil powder.

As reported in our previous study by using microstructured holes on metal subtargets utilizing TEA CO₂ laser-induced gas plasma (Idris 2007), the detection limit of the Cr line is approximately 25 mg/kg. By using the present method, we still can clearly detect the emission lines even we use low concentration of Cr impurity of 50 mg/kg. The method developed in this study by utilizing the metal coarse powder to trap the soil particles and to induce high-temperature and long lifetime gas plasma is very sophisticated. It is considered that metal coarse powder gives significant influence in the excitation process in the gas plasma as illustrated in Fig. 4; When a TEA CO₂ laser beam was focused on metal coarse powder, in which soil particles are trapped, electrons are released from the powder due to a multiphoton absorption process. These electrons are accelerated to high energy in the low frequency electric field of the laser light, which induces the cascade ionization of the atoms in the gas and generate an initial gas plasma is produced. Once the initial plasma has been produced, the laser light is most often absorbed in the gas plasma by inverse bremsstrahlung via free-free transition. This absorption is much stronger for the TEA CO₂ laser than for the Nd:YAG laser as the plasma absorption coefficient is proportional to the inverse square of the frequency of the laser light. Furthermore, the

pulse duration of the TEA CO₂ laser is relatively long (200 ns), about 20 times longer than that of the Nd:YAG laser, which means that almost all the energy from the TEA CO₂ laser is absorbed by the gas plasma, resulting large volume and high temperature gas plasma. The fine soil particles trapped in the metal coarse powder were then effectively dissociated and excited in the gas plasma region.

Further experiment was carried to detect the other heavy metal in soil. For this purpose, a loam soil containing 750 mg/kg was used as a sample. Figure 5 shows the emission spectrum of Pb taken from the soil containing 750 mg/kg of Pb by using the present method. High-intensity emission line of Pb was clearly observed together with the other lines as major elements in soil. Again, we confirmed that the present method can easily be employed to identify the heavy metals in soil.

The present method was then adopted to study on analysis of soil samples containing various concentrations of mercury (Hg). As is known that mercury includes poisonous heavy metals, which is dangerous for human health. Figure 6 shows the emission spectrum of Hg taken from the loam soil containing 10 mg/kg of Hg. Clearly detected emission line of neutral Hg at 435.8 nm appears together with many Fe lines, as a major element in soil. It should be mentioned that for the case of standard LIBS method, it is difficult to detect the Hg at low concentration in soil. This is because the soil sample is difficult sample to be analyzed due to matrix effect,

namely the soil contains many major elements such as Al, Ca, Mg, and Fe that had more than a hundred peaks (Yang 2010). Those lines of major constituents easily interfere the expected analytical lines. It should also be noticed that quiet high background emission also occurs even the spectrum detection was set from 10 μ s. This indicated that the plasma temperature induced by using the present method is still high enough even at later stage of plasma emission.

Finally, a study of semi-quantitative analysis of soil samples containing different concentration of mercury was made. Nice linear calibration curve of Hg from soil sample has successfully been made as displayed in Fig. 7. For a standardization, the neutral emission lines of Fe at 436.7 nm, which is a major elements contained in soil, was employed. Non-intercept zero of calibration curve is might be because of the high background emission produced from the soil samples. The soil sample includes high matrix samples as described above. By using our present method, the detection limit of heavy metal elements for Cr, Pb, and Hg were 0.8, 15, and 0.7 mg/kg, respectively; the detection limit was derived by calculating what concentration of the signal yielded 3 times of the noise level is because the 3 times of the noise is clearly identified as a signal that can be distinguished from the noise (Ingle Jr 1988). It should be mentioned that those detection limits are much lower compared to the result in standard LIBS and SIBS methods presented in this paper (Popov 2010). Thus, this technique is

promising as a potential field screening tool for the direct analysis of soil sample in the field.

4. Conclusion

A direct analysis of soil sample with high sensitivity has been experimentally demonstrated using a pulsed TEA CO₂ laser by assisting metal coarse powders. The metal powder was employed to trap the soil particles and induce large-volume and high-temperature gas plasma. Fine particles of soil were effectively dissociated and excited in the gas plasma region. A semi-quantitative analysis of heavy elements in soil has been successfully made. Nice linear calibration curve of Hg in soil has been obtained. The limits of detection (LoD) of Cr, Pb, and Hg in soil were estimated to approximately 0.8, 15, and 0.7 mg/kg, respectively.

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Figure captions

Fig. 1 Experimental setup used in this work.

Fig. 2 Emission intensity vs lifetime of Cu taken from the powdered Cu_2O_3

Fig. 3 Emission spectrum of Cr taken from the loam soil containing 50 mg/kg of Cr.

Fig. 4 Illustration of the excitation process in metal powder assisted laser-induced plasma.

Fig. 5. Emission spectrum of Pb taken from the loam soil containing 750 mg/kg of Pb.

Fig. 6. Emission spectrum of Hg taken from the loam soil containing 10 mg/kg of Hg.

Fig. 7. Calibration curve of Hg taken from the loam soil containing various concentration of Hg.

Figure 1

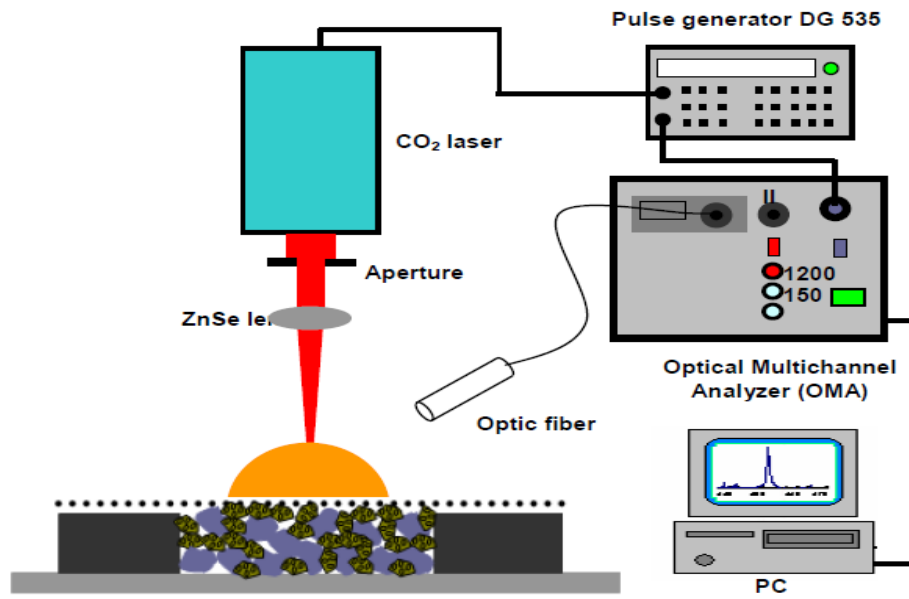


Fig. 2

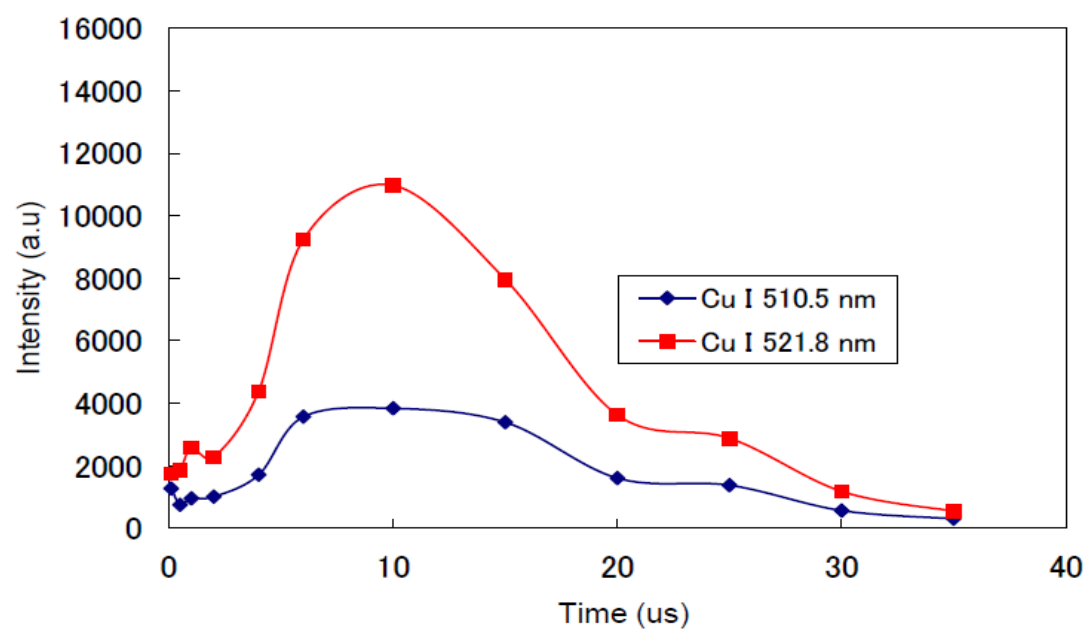


Figure 3

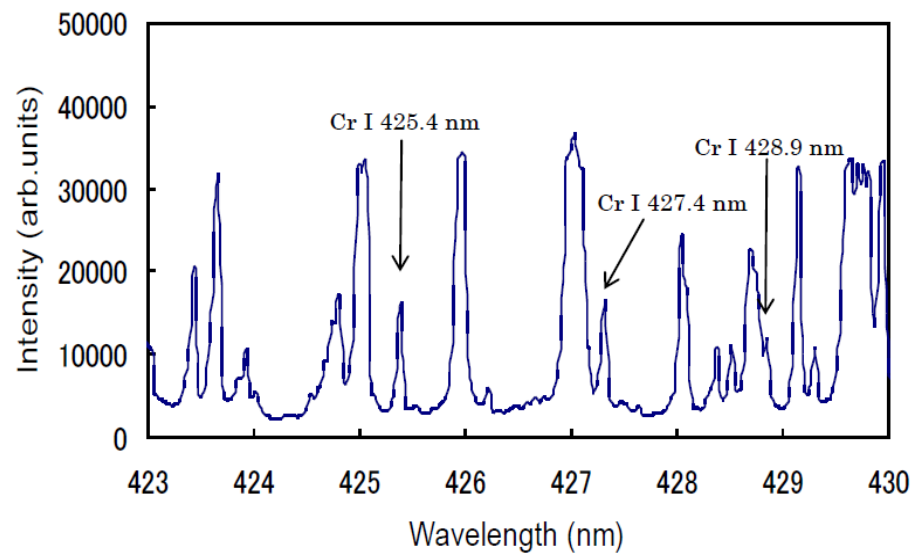


Figure 4

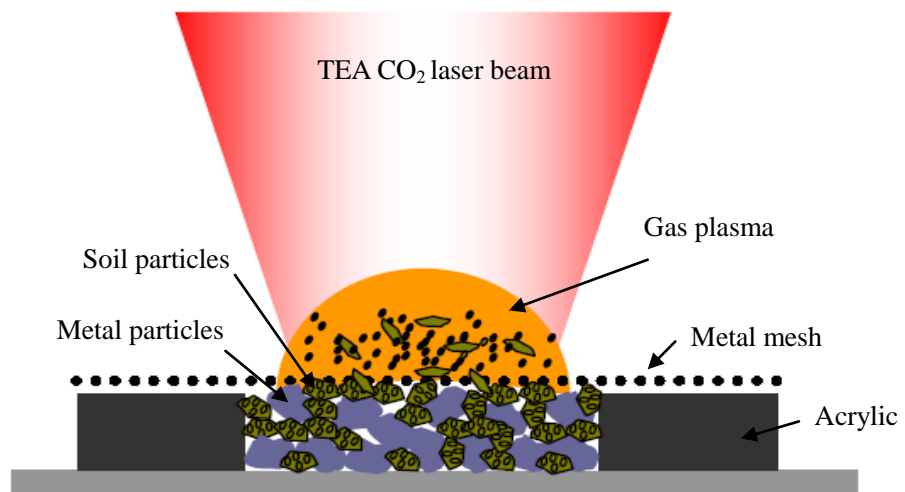


Figure 5

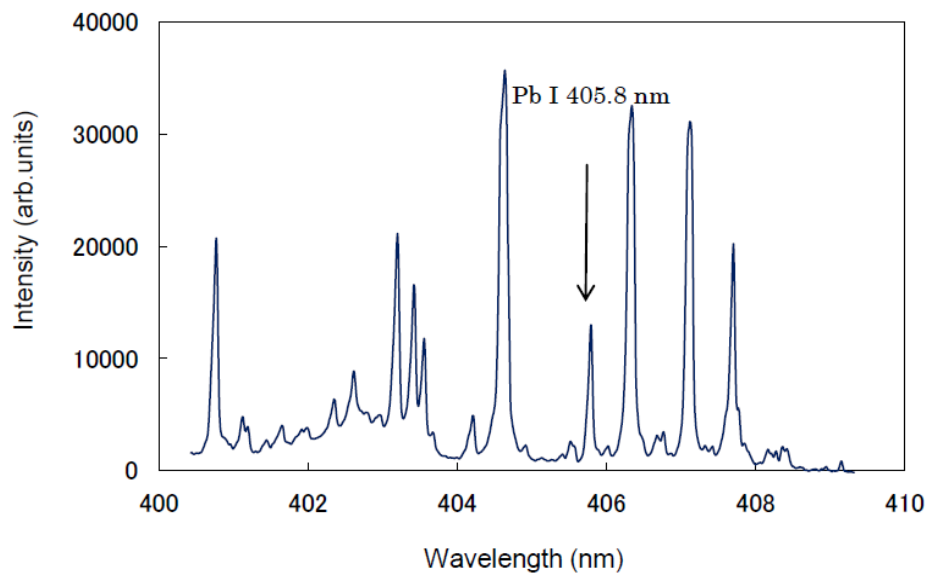


Figure 6

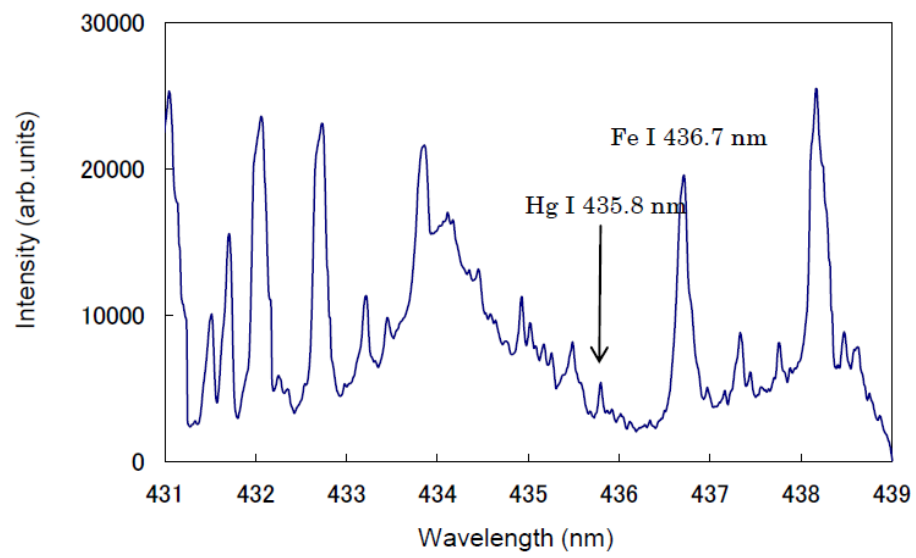
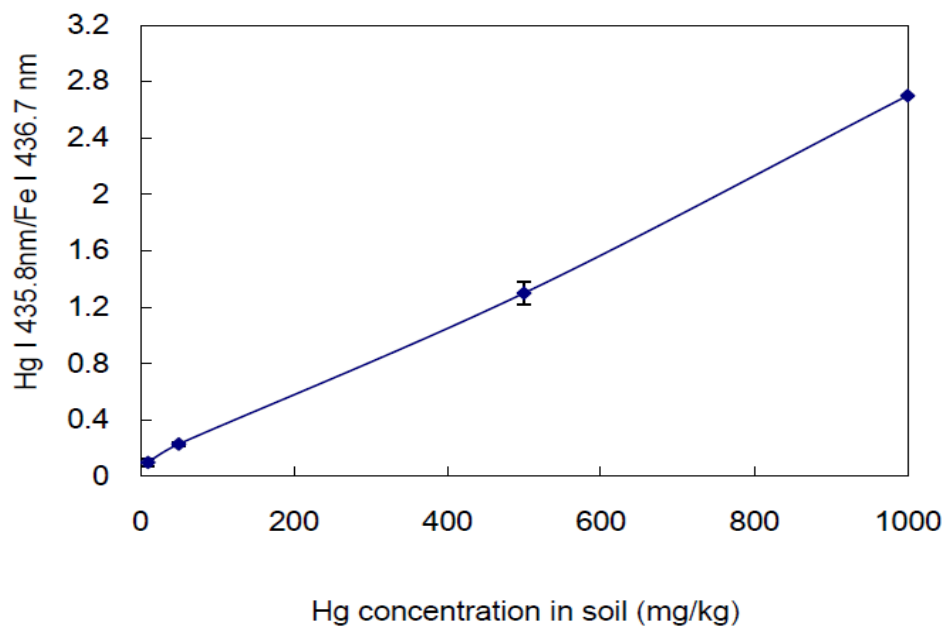


Figure 7



2. Submission acknowledgment dari Analytical Letters (11 Juli 2016)

Manuscript ID LANL-2016-0812 Submitted

Analytical Letters <onbehalfof+analyticalletters+analytchem.org@manuscriptcentral.com> Tue, Jul 12, 2016 at 5:02 AM
Reply-To: analyticalletters@analytchem.org
To: khumaeni@fisika.undip.ac.id

11-Jul-2016

Dear Dr. Khumaeni:

Your manuscript entitled "Metal coarse powder-assisted pulse CO2 laser-induced gas plasma spectroscopy for the direct analysis of heavy metals in soils" has been successfully submitted online and is presently being given full consideration for publication in Analytical Letters.

Your manuscript ID is LANL-2016-0812.

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Sincerely,

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Analytical Letters Editorial Office
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3. Editor and reviewers' comments (15 Agustus 2016)

Analytical Letters - Decision on Manuscript ID LANL-2016-0812

1 message

Analytical Letters

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Mon, Aug 15, 2016 at 8:56 AM

Reply-To: analyticalletters@analytchem.org

To: khumaeni@fisika.undip.ac.id

14-Aug-2016

Dear Dr. Khumaeni:

Your manuscript entitled "Metal coarse powder-assisted pulse CO2 laser-induced gas plasma spectroscopy for the direct analysis of heavy metals in soils" which you submitted to Analytical Letters, has been reviewed. The reviewer comments are included at the bottom of this letter.

I regret to inform you that the reviewers have raised serious concerns, and therefore your paper cannot be accepted for publication in Analytical Letters. However since the reviewers do find some merit in the paper, I would be willing to reconsider if you wish to undertake major revisions and re-submit, addressing the referees' concerns.

Please note that resubmitting your manuscript does not guarantee eventual acceptance, and that your resubmission will be subject to re-review before a decision is rendered.

You will be unable to make your revisions on the originally submitted version of your manuscript. Instead, revise your manuscript using a word processing program and save it on your computer. Please provide a separate letter explaining how you addressed each of the referee and editor comments on a point by point basis.

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I look forward to a resubmission.

Sincerely,

Dr. David Butcher
Editor in Chief, Analytical Letters
Western Carolina University
david.butcher@analytchem.org

Referee(s)' Comments to Author:

Referee: 1

Comments:

1. Figure 3 isn't very clear. The peaks are not smooth enough.
2. In figure 7, the linear calibration curve of Hg only contains 4 samples, and the difference of Hg concentrations are too large

Novelty of the Work: This paper has certain innovation. Mercury in soil samples was detected by LIBS using a pulsed TEA CO2 laser assisted with metal coarse powders. The result of this paper hasn't been reported in other papers

Significance of the Work: The LOD of mercury is 0.7mg/kg which meets the requirement of the detection of mercury in soil. It could be used for direct analysis of soil samples

Technical Merit of the Work: The LODs of Cr and Hg are low

Presentation of the Work: This paper has a clear structure and smooth expression

Other Specific Comments: No

Editor's Comments to Authors:

1. Our journal uses software to compare the text of submitted manuscripts to previously published papers. The software observed considerable overlap in your manuscript with your previously published paper listed below. It will be necessary to completely rewrite the overlapping text to eliminate the overlap, cite the previous paper in the revised manuscript, and explain the significance of the new work compared to the published results.

Ali Khumaeni, PhD. Dissertation, Study on Laser-Induced Gas Plasma Using TEA CO₂ Laser for Atomic Emission Spectroscopy.

2. The English in the manuscript is not of publication quality and requires major improvement. Please carefully proofread and spellcheck the document to eliminate errors in the use of English. Please do not use the first person in the manuscript; instead use the passive voice. Please do not use all capital letters for the names of vendors; only the first letter should be capitalized. Please ensure that the text is all of the same font size. Please do not capitalize the names of analytical methods. Please do not use all capital letters for the names of instrument vendors or their products. Please do not capitalize the names of chemicals. Please note there should be the space between numerals and units; e.g., 6h should be 6 h. The manuscript should be written in complete sentences; lists of information should be avoided. The manuscript should be double spaced in a standard 12 point font.

3. Please eliminate non-standard acronyms from the manuscript such as OMA. Instead please refer to these by their full names. It will be necessary to address this matter in the text, in the tables, and in the figures.

4. Please remove the numerals before the headings and subheadings.

5. Please identify the corresponding author and provide his/her mailing address, telephone number, and email address directly after the complete list of authors and affiliations.

6. The references are not in the proper format for the journal. Please note that there should be a comma (,) between the last name and initials of the first author in the list of citations.

7. Please delete Figure 7.

8. Please resubmit the manuscript in final form for publication. Please do not highlight changes using bold, colored, or shaded text.

4. Balasan komentar Editor dan Reviewers

To Dr. David Butcher
Editor in Chief, Analytical Letters

Dear Dr. David Butcher

We would like to resubmit a final revised manuscript entitled "Metal coarse powder-assisted pulse CO₂ laser-induced gas plasma spectroscopy for the direct analysis of heavy metals in soils" to Analytical Letters. Also, we would like to respond and answer the comments from Editor and Reviewer as written below. We are so sorry to revise the manuscript very long.

Thank you very much for your kindness.

Best regards
Ali Khumaeni
Department of Physics
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Dear: Editor, Analytical Letters

We would like to answer your comments as below,

1. Regarding the overlapping text of our present manuscript with the previous paper, we have rewritten the overlapping text to eliminate the overlap. We also included the previous paper (Ali Khumaeni, PhD. Dissertation, Study on Laser-Induced Gas Plasma Using TEA CO₂ Laser for Atomic Emission Spectroscopy) in the revised final manuscript.
2. We have revised English grammar in the manuscript. We also followed your suggestion not to use the first person in the manuscript, all capital letters for the names of vendors, capital letters in the names of analytical methods, capital letters in the names of chemicals.
3. Regarding non-standard acronyms, we have rewritten by their full names such as OMA to be optical multichannel analyzer.
4. We have removed the numerals before headings and subheadings as shown in the revised final manuscript
5. We have added information about corresponding author including mailing address, telephone number, and email address.
6. Regarding the format of references, we have revised the format following your suggestion.
7. Regarding Fig. 7, we have removed it from the manuscript.

Dear: Reviewer

Thank you very much for reviewing our submitted paper entitled “Metal coarse powder-assisted pulse CO₂ laser-induced gas plasma spectroscopy for the direct analysis of heavy metals in soils”.

We have completely read your comments and feel happy for your positive evaluation that our manuscript has certain novelty and good presentation.

Considering your comments, we have **made a revision in our manuscript and will answer as below,**

1. Regarding Fig. 3 (the peak are not smooth enough), we have revised the figure to be very clear figure by an experiment.
2. Regarding Fig. 7 (calibration curve), we have removed the figures as suggested by Editor.

5. Paper setelah proses revisi mempertimbangkan masukan Editor dan Reviewers

**Coarse metal powder-assisted pulse CO₂ laser-induced
breakdown spectroscopy for the direct determination of heavy
metals in soils**

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Abstract

A novel method of laser-induced plasma spectroscopy utilizing a pulse transversely excited atmospheric (TEA) CO₂ laser has been developed for the high-sensitivity analysis of heavy metals in soil. Metal coarse powder was used to trap the soil powder and to assist a luminous plasma generation. When a pulsed TEA CO₂ laser (10.6 μm, 1.5 J, 200 ns) was irradiated on the metal coarse powder, in which the soil powder was trapped, a high-temperature and long-lifetime luminous plasma was induced. Fine particles of soil sample were dissociated and excited in the plasma region. The method has been used for rapid detection of various heavy metals including Cr, Pb, and Hg in loam soil. The limit of detection of Cr, Pb, and Hg was approximately 0.8, 15, and 0.7 mg/kg, respectively.

Keywords: laser-induced breakdown spectroscopy; LIBS; Heavy metal detection; Soil analysis; TEA CO₂ laser

Introduction

The analysis of soil containing hazardous elements has become a subject of great interest. The pollution of hazardous chemicals in soil from various sources has been found to cause harms to humans. Soil contamination is a sensitive issue, related to increasing public environmental and security awareness, dealing with land ownership transfer and utilization, such as for farming, building construction, and real estate businesses (Nicholson 2003; Allen 1995; Senesil 1999; Zimmermen 2010). Thus, the analysis of contaminated soil prior to cultivating, constructing, or selling is really necessary.

Various methods such as X-ray fluorescence spectrometry, atomic absorption spectroscopy, inductively coupled plasma mass spectrometry, and inductively coupled plasma atomic emission spectrometry have been used to perform soil analyses (Bings 2010; Gauglitz 2003; Beckhoff 2006). Those methods ensured high precision and high sensitivity for the purpose of quantitative analysis. However, the methods require delicate sample pretreatment and are labor intensive. Therefore, the methods do not appropriate for rapid and in-situ monitoring of the heavy metals in soils (Srungaram 2013).

Laser-induced breakdown (LIBS) has recently become an increasingly popular technique for qualitative and quantitative elemental analysis of various samples in

different phase such as solids, liquids, and gases. This advantage has largely driven an interest in application of LIBS to environmental sample analysis such as soil and liquids (Cremers 2006).

Several works have been devoted to the applications of LIBS to soil analysis (Srungaram 2013; Yang 2010; Jantzi 2011; Hussain 2008; Dell’Aglia 2011; Popov 2010). Characterization of pollution indices in soil has been made by Arab et al. using laser-induced breakdown spectroscopy (Arab 2015). Srungaram et al. applied LIBS and spark-induced breakdown spectroscopy (SIBS) for the analysis of Hg in soil (Srungaram 2013). The detection limit for the Hg by using LIBS and SIBS were 483 and 20 mg/kg, respectively. Popov et al. proposed a new configuration of spatial confinement in LIBS for the analysis of soil. The limit of detection (LoD) of heavy metals including As, Hg, and Pb was 30, 25, and 90 mg/kg, respectively (Popov 2010). Liu et al. proposed LIBS assisted by a microwave (microwave-assisted laser-induced breakdown spectroscopy) for the enhancement of sensitivity in soil analysis. The LoD of Cu in soil by using the proposed method was 30 mg/kg (Liu 2012). However, it should be noted that in a standard LIBS technique, the soil sample is most often prepared into a pellet prior to laser irradiation generally by using neodymium yttrium aluminium garnet (Nd:YAG) laser. In this case, the insufficient atomization of the soil sample still cannot be resolved and this technique is also time consuming.

Furthermore, the soil includes complex matrix containing a host of elements including Al, Ca, Mg, and Fe, which had more than a hundred peaks (Yang 2010).

On contrary to the use of pulse Nd:YAG laser in LIBS technique, a pulse transversely excited atmospheric (TEA) CO₂ laser is much more suitable to the direct analysis of soil sample. Due to the long wavelength and long pulse duration (10.64 μm in wavelength, 200 ns in pulse duration), the TEA CO₂ laser has high absorbance in the soil sample and the plasma can be initiated readily and the serious blow-off of the soil can be effectively suppressed. This method has been applied to the analysis of soil containing various heavy metals by using high-vacuum silicon grease binder and unique micro-structured holes made on a metal plate (Khumaeni 2010; Idris 2007). Compared to the standard LIBS method, the developed method has higher sensitivity of analytical detection.

To suppress the LoD of heavy metals in the soil, a novel method of the LIBS by utilizing a TEA CO₂ laser was proposed. In this method, fine particles of soil powder were trapped into the metal coarse powder with a diameter of around 1-3 mm by mixing the soil powder with the metal coarse powder. The iron particles function to trap the soil powder and induce a high-temperature gas plasma. The fine particles of soil powder were effectively dissociated and excited in the gas plasma region. The LoD of heavy metals in soil can be significantly reduced and much lower compared to

the results of standard LIBS, SIBS, and MA-LIBS.

Experimental procedure

The basic setup used in this study is shown in Fig. 1(a). A pulse TEA CO₂ laser (Shibuya SQ 2000, energy of 3 J, wavelength of 10.6 μm, pulse duration of 200 ns) was used as an optical source. The laser beam was directed and focused onto a sample surface by a ZnSe lens (focal length of 200 mm) via a ZnSe window. During the experiment, the laser energy was set at 1.5 J by setting an aperture in the path of laser beam. The spot size of the laser beam in the sample surface was 2 x 2 mm², which resulted in a power density of 0.18 GW/cm² for laser energy of 1.5 J.

The samples used in this study were standard loam soil containing heavy metals of Cr , Pb and Hg. A simple sample pretreatment was made prior to experiment. 50 mg soil powder was homogeneously mixed with 350 mg metal coarse powder (volume ration 1:1) so that the soil is effectively trapped in the coarse powder (metal coarse powder, 99 %, Soekawa chemicals). The metal coarse powder-mixed soil was then placed into a small hole (diameter of 10 mm) made of plastic acrylic with a thickness of 8 mm, on which the copper plate was attached in the tight contact of the backside of the acrylic. The diameter and depth of the hole were 10 mm and 8 mm, respectively. To suppress the blow-off of the soil powder and to induce a

high-temperature gas plasma, a metal mesh made of stainless steel wires (lattice constants of 0.4 mm and the wires of 0.1 mm in diameter) was placed in tight contact on the front side of the mixed soil samples. It should be noted that during the laser irradiations, the mesh is never damaged and ablated because the power density of the laser beam impinging on the metal mesh is lower than the ablation threshold of the metal mesh due to the fact that most part of laser energy is absorbed by the strong gas breakdown plasma (plasma shielding effect) (Khumaeni 2010; Khumaeni 2011).

During the experiment, the samples were placed in a metal chamber with dimensions of 12 cm x 12 cm x 12 cm, which was filled with pure helium gas (99.999%). The flowing rate of gas was 3 liters per minute (Lpm). The pressure in the chamber was 1 atmosphere. It should be noted that the plasma induced in the He gas has lower background emission compared to the case of plasma in N₂ gas. The gas also functions to suppress the breakdown plasma induced by fine soil particles in the path of laser beam. A high resolution monochromator (Jobin-Yvon HRS-2, f= 640 mm, 2400/mm, spectral resolution of 0.02 nm) attached with an optical multichannel analyzer system (Lambda vision 1012) was used to obtain the emission spectrum; the gate width and gate delay time of optical multichannel analyzer were 10 μs and 100 μs, consecutively. The plasma emission was imaged onto the entrance slit of the monochromator using quartz lens with a focal length of 70 mm.

Results and discussion

First, the lifetime of plasma emission induced by using this present method was examined. To this end, a copper sulfate (CuSO_4) powder was employed as a sample. The plasma temperature can be readily derived from the emission lines of neutral Cu (Cu I) at 510.5 nm and 521.8 nm by the ratio of the emission intensity of Cu I 521.8 nm (excitation energy of 6.2 eV) to that of Cu I 510.5 nm (excitation energy of 3.8 eV), with the assumption of Boltzmann's distribution (Ramli 2008; Khumaeni 2013). Figure 2 shows how the emission intensities of Cu I 521.8 nm and Cu I 510.5 nm change with time after the TEA CO_2 laser bombardment on the metal coarse powder-trapped CuSO_4 powder. The gate width of the OMA system was set at 1 μs . It is seen that the emission intensity of Cu I 521.8 nm is much higher than the case of Cu I 510.5 nm. It should be noticed that the plasma emission keeps long lifetime of around 35 μs , which is much longer compared to the case of standard LIBS. The intensity of Cu I 521.8 nm steeply increases up to 10 μs and decreases slowly to 35 μs . For the Cu I 510.5 nm, the intensity significantly increases to 6 μs , is almost stable to 15 μs , and finally decreases slowly to 35 μs . Both Cu lines have a peak at around 10 μs . With the assumption of Boltzmann's distribution, the plasma temperature can be estimated around 7500 K at 10 μs . The high-plasma temperature and long-lifetime of

plasma emission produced by using a present method was then employed to the rapid detection of heavy metals in soil sample.

Figure 3 shows the emission spectrum of Cr taken from the loam soil containing 50 mg/kg of Cr. High-intensity and sharp typical neutral emission lines of Cr at 425.4 nm and 427.4 nm clearly appears together with many spectral lines including Ca and Fe, which are major elements in soil. The Cr line at 428.9 nm overlapped with the other line can also be detected. It should be noted that compared to other previous work by using standard LIBS method (Dell'Aglio 2011), the result by using the present method has nice analytical performance proved by higher signal to noise ratio (S/N) intensity.

This result revealed that the present method of metal coarse powder-assisted laser-induced gas plasma spectroscopy can clearly be used to rapidly identify the heavy metals in the soil containing low concentration of the heavy metals without delicate sample pretreatment. This analytical spectrum also confirmed that the sensitivity of analytical detection by utilizing TEA CO₂ laser has been improved when the metal coarse powder was used to trap the soil powder.

As reported in the previous study by using microstructured holes on metal subtargets utilizing TEA CO₂ laser-induced gas plasma (Idris 2007), the detection limit of the Cr line was approximately 25 mg/kg. By using the present method, we

still can clearly detect the emission lines even we use low concentration of Cr impurity of 50 mg/kg. The method developed in this study by utilizing the metal coarse powder to trap the soil particles and to induce high-temperature and long lifetime gas plasma is very sophisticated. It is considered that metal coarse powder gives significant influence in the excitation process in the gas plasma as illustrated in Fig. 4; When a TEA CO₂ laser beam was focused on metal coarse powders, in which soil particles are trapped, electrons are detached from the metal powder due to a multiphoton absorption process. The electron are then accelerated in the low frequency electric field of the laser light, which generates the cascade ionization of the atoms in the gas and an initial gas plasma is produced. The laser light is most often absorbed in the gas plasma by inverse Bremsstrahlung via free-free transition, resulting in large volume and high-temperature gas plasma. This absorption is much stronger for the TEA CO₂ laser than for the Nd:YAG laser because the plasma absorption coefficient is proportional to the inverse square of the frequency of the laser light. Furthermore, the pulse duration of the TEA CO₂ laser is relatively long (200 ns), about 20 times longer than that of the Nd:YAG laser, which means that almost all the energy from the TEA CO₂ laser is absorbed by the gas plasma. The fine soil particles trapped in the metal coarse powder were then effectively dissociated and excited in the gas plasma region.

Further experiment was carried to detect the other heavy metal in soil. For this purpose, a loam soil containing 750 mg/kg was used as a sample. Figure 5 shows the emission spectrum of Pb taken from the soil containing 750 mg/kg of Pb by using the present method. High-intensity emission line of Pb was clearly observed together with the other lines as major elements in soil. The result confirmed that the present method can be effectively employed to identify the heavy metals in soil.

The present method was then adapted to study on analysis of soil sample containing mercury (Hg). It is known that mercury includes poisonous heavy metals, which is dangerous for human health. Figure 6 shows the emission spectrum of Hg obtained from the loam soil containing 10 mg/kg of Hg. Clearly detected emission line of neutral Hg (Hg I) at 435.8 nm appears together with many emission lines of Fe, as a major element in soil. It should be noted that for the case of standard LIBS method, it is difficult to detect the Hg at low concentration in soil. This is because the soil sample is difficult sample to be analyzed due to matrix effect, namely the soil contains many major elements such as Al, Ca, Mg, and Fe that had more than a hundred peaks (Yang 2010). Those lines of major constituents easily interfere the expected analytical lines. It should also be noticed that quiet high background emission also occurs even the spectrum detection was set from 10 μ s. This indicated that the plasma temperature is still high enough even at later stage of plasma emission.

By using the present method, the detection limit of heavy metal elements for Cr, Pb, and Hg were 0.8, 15, and 0.7 mg/kg, respectively; the detection limit was derived by calculating what concentration of the signal yielded 3 times of the noise level is because the 3 times of the noise is clearly identified as a signal that can be distinguished from the noise (Ingle Jr 1988). It should be noted that those detection limits are much lower compared to the result in standard LIBS and SIBS methods presented in this paper (Popov 2010). Thus, this technique is promising as a potential field screening tool for the direct analysis of soil sample in the field.

Conclusion

A direct and rapid analysis of soil sample with high sensitivity has been experimentally demonstrated using a pulsed TEA CO₂ laser by assisting metal coarse powders. The metal powder was employed to trap the soil particles and to induce large-volume and high-temperature gas plasma. Fine particles of soil were effectively dissociated and excited in the gas plasma region. A semi-quantitative analysis of heavy elements in soil has been successfully made. The limits of detection (LoD) of Cr, Pb, and Hg in soil were approximately 0.8, 15, and 0.7 mg/kg, respectively.

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Figure captions

Fig. 1 Experimental setup used in this work

Fig. 2 Emission intensity Vs lifetime of Cu obtained from the powdered Cu_2O_3

Fig. 3 Emission spectrum of Cr obtained from the loam soil containing 50 mg/kg of

Cr

Fig. 4 Illustration of the excitation process in metal powder-assisted laser-induced plasma.

Fig. 5. Emission spectrum of Pb obtained from the loam soil containing 750 mg/kg of

Pb

Fig. 6. Emission spectrum of Hg obtained from the loam soil containing 10 mg/kg of

Hg

Figure 1

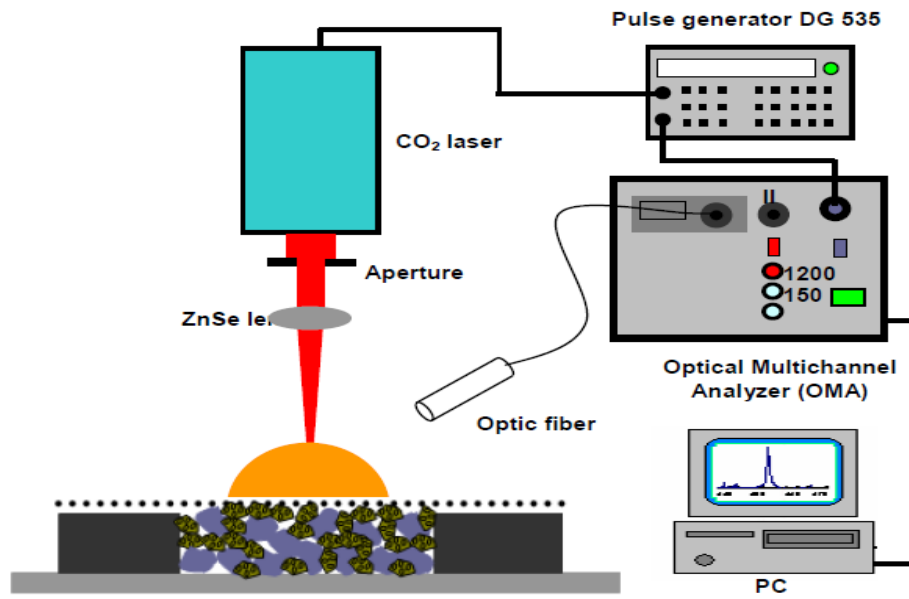


Fig. 2

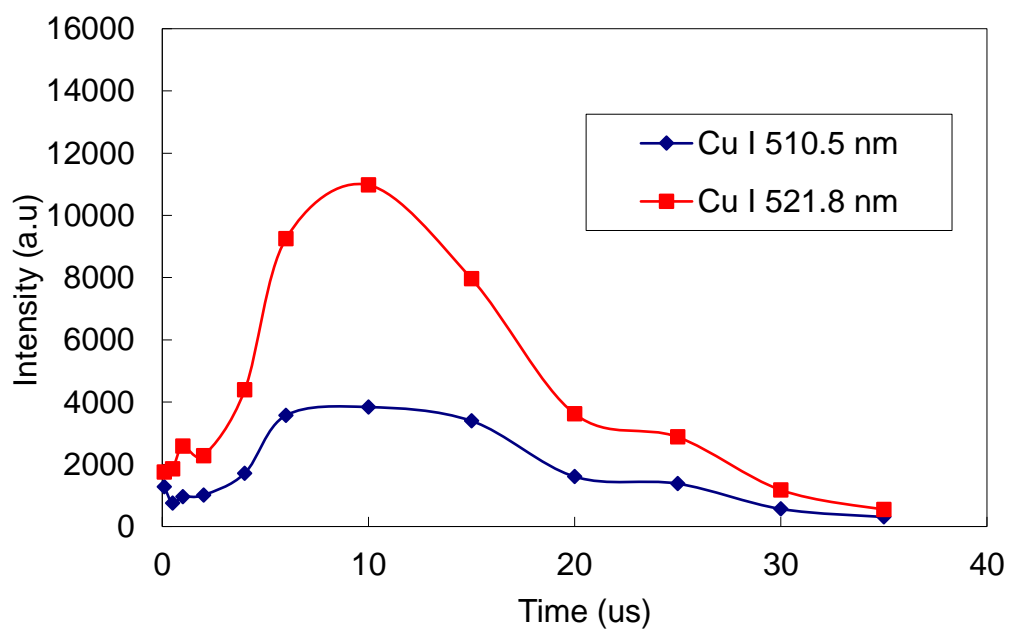


Figure 3

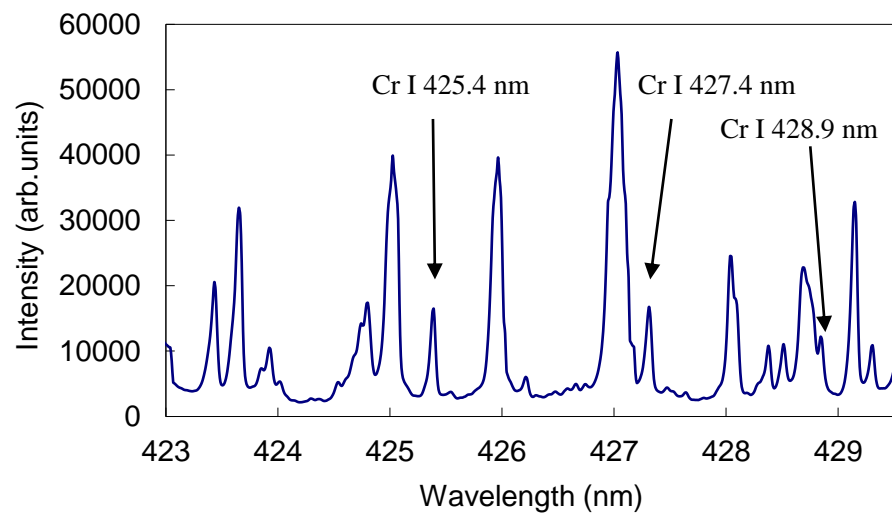


Figure 4

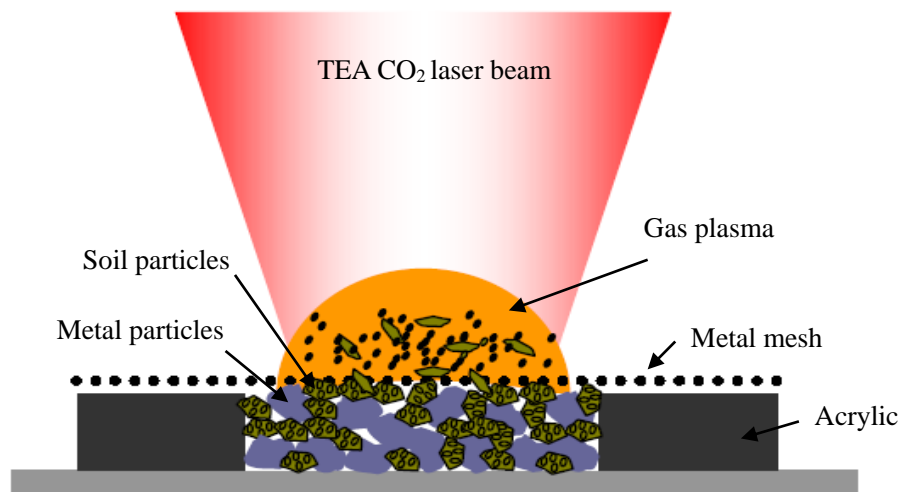


Figure 5

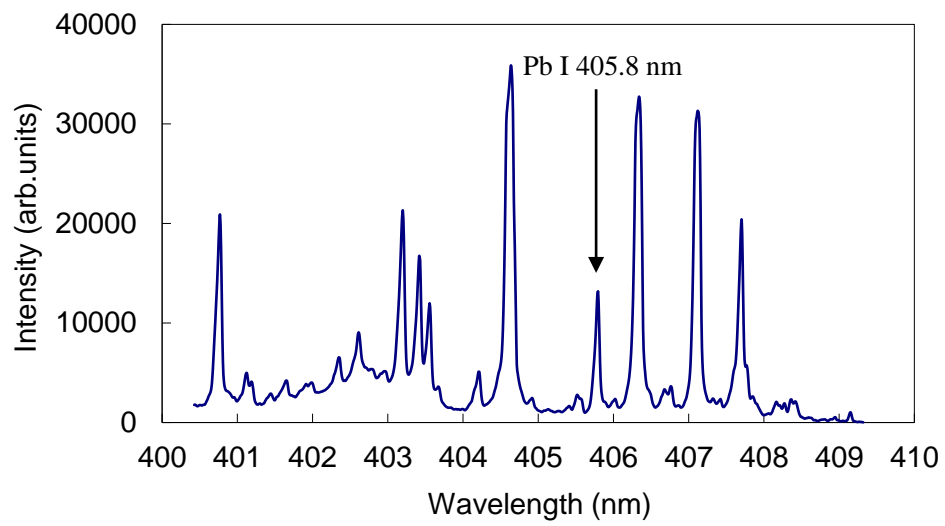
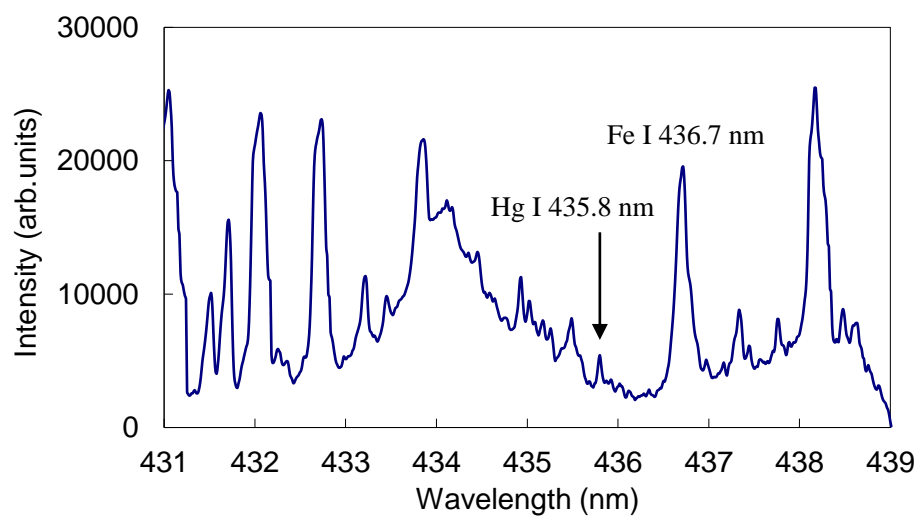


Figure 6



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Tue, Oct 25, 2016 at 12:50 PM

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To: khumaeni@fisika.undip.ac.id

25-Oct-2016

Dear Dr. Khumaeni:

Your manuscript entitled "Metal coarse powder-assisted pulse CO2 laser-induced plasma spectroscopy for the direct analysis of heavy metals in soils" **has been successfully submitted online** and is presently being given full consideration for publication in Analytical Letters.

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Wed, Oct 26, 2016 at 4:00 AM

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Ref: Coarse Metal Powder Assisted Pulsed CO2 Laser-Induced Breakdown Spectroscopy for the Direct Determination of Heavy Metals in Soil

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9. Bukti publikasi (31 Juli 2019)

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ATOMIC SPECTROSCOPY

Coarse Metal Powder-Assisted pulsed CO₂ Laser-induced Breakdown Spectroscopy for the Direct Determination of Heavy Metals in Soil

Ali Khumaeni , Masahiko Tani, Kazuyoshi Kurihara, Kiichiro Kagawa & Hideaki Niki

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ABSTRACT

A novel method of laser-induced plasma spectroscopy utilizing a pulsed transversely excited atmospheric CO₂ laser has been developed for the high-sensitivity determination of heavy metals in soil. A coarse metal powder was used to trap the soil and to assist with plasma generation. When the CO₂ laser (10.6 μm, 1.5 J, 200 ns) was irradiated on the metal and soil powder, a high-temperature and long-lifetime luminous plasma was induced. Fine particles of soil were dissociated and were excited in the plasma region. The method was used for the rapid determination of Cr, Pb, and Hg in loam. The limits of detection for Cr, Pb, and Hg

were approximately 0.8, 15, and 0.7 mg/kg, respectively.

Q KEYWORDS: Carbon dioxide laser heavy metals laser-induced breakdown spectroscopy soil

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