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To cite this article: Ali Khumaeni, Masahiko Tani, Kazuyoshi Kurihara, Kiichiro Kagawa & Hideaki Niki (2017): Coarse Metal Powder-Assisted pulsed CO₂ Laser-induced Breakdown Spectroscopy for the Direct Determination of Heavy Metals in Soil, Analytical Letters, DOI: [10.1080/00032719.2016.1254222](https://doi.org/10.1080/00032719.2016.1254222)

To link to this article: <http://dx.doi.org/10.1080/00032719.2016.1254222>



Accepted author version posted online: 04 May 2017.
Published online: 04 May 2017.



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

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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.

ARTICLE HISTORY

Received 11 July 2016
Accepted 25 October 2016

KEYWORDS

Carbon dioxide laser; heavy metals; laser-induced breakdown spectroscopy; soil

Introduction

The analysis of soil containing hazardous elements has become a subject of interest. The pollution of hazardous chemicals in soil from various sources has been found to cause harm 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 et al. 2003; Allen et al. 1995; Senesil et al. 1999; Zimmerman and Weindorf 2010). Thus, the analysis of contaminated soil prior to cultivating, constructing, or selling is necessary.

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

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Laser-induced breakdown spectroscopy (LIBS) is an increasingly popular technique for qualitative and quantitative elemental analysis of solids, liquids, and gases. This advantage has driven an interest in the application of LIBS for environmental analysis including soil and liquids (Cremers and Radziemski 2006).

Several papers have been reported applications of LIBS for soil (Srungaram et al. 2013; Yang et al. 2010; Jantzi and Almirall 2011; Hussain and Gondal 2008; Dell'Aglio et al. 2011; Popov, Colao, and Fantoni 2010). Characterization of pollution indices in soil was performed by Arab et al. (2015) using LIBS. Srungaram et al. (2013) used LIBS and spark-induced breakdown spectroscopy (SIBS) for the analysis of Hg in soil. The detection limits for Hg by LIBS and SIBS were 483 and 20 mg/kg, respectively. Popov, Colao, and Fantoni (2010) proposed a novel configuration of spatial confinement in LIBS for the analysis of soil. The limits of detection for As, Hg, and Pb were 30, 25, and 90 mg/kg, respectively (Popov, Colao, and Fantoni 2010). Liu et al. (2012) proposed LIBS assisted by a microwave, designated as microwave-assisted LIBS, for the enhancement of the sensitivity for soil analysis. The limit of detection for Cu in soil using this approach was 30 mg/kg (Liu et al. 2012). However, in standard LIBS, the soil is most often prepared as a pellet prior to laser irradiation. The most common source is a neodymium yttrium aluminum garnet (Nd:YAG) laser. In this case, insufficient atomization of the soil may be obtained and the sample preparation is time consuming. Furthermore, soil includes a complex matrix containing many elements including Al, Ca, Mg, and Fe, which have more than 100 peaks (Yang et al. 2010).

Instead of using a pulse Nd:YAG laser for LIBS, a pulse transversely excited atmospheric (TEA) CO₂ laser is more suitable for the direct analysis of soil. 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 soil and the plasma is initiated readily. Significant blow-off of the soil is suppressed. This method has been used for the analysis of soil for heavy metals using high-vacuum silicon grease binder and unique microstructured holes on a metal plate (Khumaeni et al. 2010b; Idris et al. 2007). Compared to standard LIBS, this approach offers higher sensitivity.

Here a novel LIBS protocol is reported utilizing a TEA CO₂ laser for excitation. Fine particles of soil were trapped into a coarse iron powder (diameter from 1 to 3 mm) by efficient mixing. The iron traps the soil to induce a high-temperature plasma. The fine particles of soil were effectively dissociated and excited in the plasma. The detection limits for heavy metals in soil were significantly reduced compared to standard LIBS methodology.

Experimental

The experimental setup used in this study is shown in Figure 1. A pulsed TEA CO₂ laser (Shibuya SQ 2000, energy of 3 J, wavelength of 10.6 μm, pulse duration of 200 ns) was used as the excitation source. The laser beam was focused on a surface by a ZnSe lens (focal length of 200 mm). The laser energy was set at 1.5 J using an aperture in the path of laser beam. The spot size of the laser beam on the surface was 2 × 2 mm², which resulted in a power density of 0.18 GW/cm².

The samples were standard loam soil containing Cr, Pb, and Hg. The soil of 50 mg was homogeneously mixed with 350 mg of coarse metal powder (Soekawa Chemicals, 99%) at a

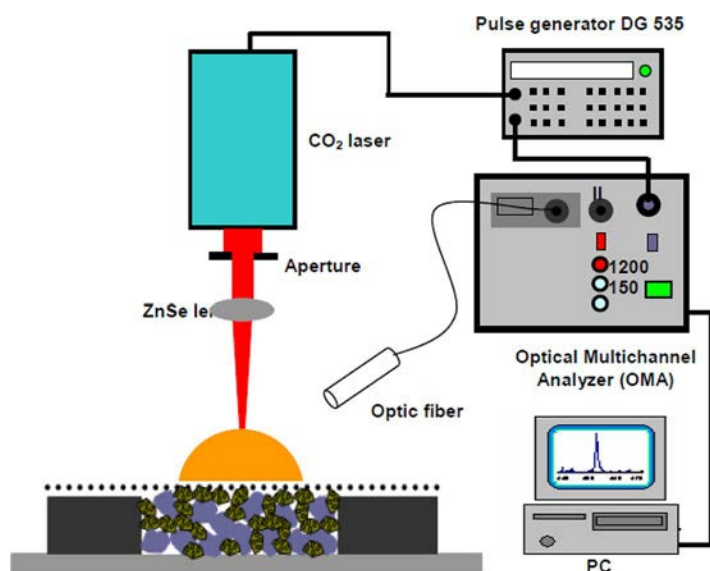


Figure 1. Instrumental setup in this work.

volume ratio of 1:1. The pretreated soil was then placed in a 10-mm small hole in acrylic with a thickness of 8 mm. The copper plate was attached in the tight contact of the back of the acrylic. The diameter and depth of the hole were 10 and 8 mm. To suppress the blow-off of the soil and to induce a high-temperature plasma, stainless steel mesh (0.4 mm lattice constant and 0.1 mm diameter) was placed in tight contact on the front side of the mixed soil. During the laser excitation, the mesh was not damaged because the power density of the laser beam on the metal was below the ablation threshold of this material by the plasma shielding effect (Khumaeni et al. 2010a; Khumaeni et al. 2011).

The samples were placed in a metal chamber with dimensions of $12 \times 12 \times 12 \text{ cm}^3$ filled with helium gas (99.999%). The flow rate of gas was 3 L/min. The pressure in the chamber was 1 atmosphere. The helium plasma provided lower background emission compared to the use of a nitrogen plasma. The gas also suppressed the breakdown induced by soil in the laser beam. A high-resolution monochromator (Jobin-Yvon HRS-2, focal length of 640 mm, 2400/mm, spectral resolution of 0.02 nm) with an optical multichannel analyzer system (Lambda Vision 1012) was used to collect the emission. The gate width and gate delay of the optical multichannel analyzer were 10 and 100 μs , consecutively. The plasma emission was imaged on the entrance slit of the monochromator using a quartz lens with a focal length of 70 mm.

Results and discussion

The lifetime of plasma emission was characterized. Powdered copper sulfate was used as a sample. The plasma temperature was derived from the emission lines of neutral Cu (Cu I) at 510.5 and 521.8 nm by the ratio of emission intensities of the former at 521.8 nm (excitation energy of 6.2 eV) to the latter at 510.5 nm (excitation energy of 3.8 eV) using Boltzmann's distribution (Ramli et al. 2008; Khumaeni 2013). Figure 2 shows how the

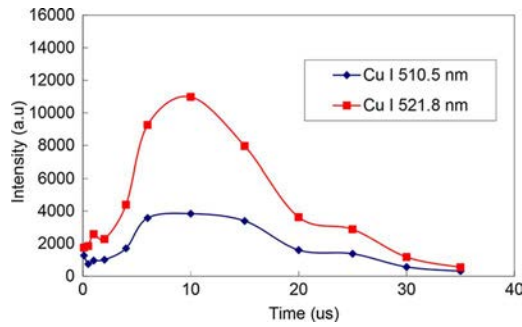


Figure 2. Emission intensity as a function of lifetime of copper from powdered copper sulfate.

emission intensities of Cu I 521.8 nm and Cu I 510.5 nm varied with time following the TEA CO₂ laser bombardment on the coarse metal CuSO₄ powder. The gate width was fixed at 1 μs. The emission intensity of the Cu I 521.8 nm line was much higher than at Cu I 510.5 nm. The plasma emission has a long lifetime of approximately 35 μs, which is longer compared to standard LIBS. The intensity of the Cu I 521.8 nm line increased up to 10 μs and decreased slowly to 35 μs. For the Cu I 510.5 nm line, the intensity significantly increased to 6 μs, was nearly constant to 15 μs, and decreased up to 35 μs. Both Cu lines had peaks at approximately 10 μs. Boltzmann's distribution was used to estimate the plasma temperature to be approximately 7500 K at 10 μs. The high-plasma temperature and long-lifetime of plasma emission produced were used for the rapid determination of heavy metals in soil.

Figure 3 shows the emission spectrum of Cr from the loam soil containing 50 mg/kg of Cr. High intensity and sharp typical neutral emission lines of Cr at 425.4 and 427.4 nm clearly appear with many other spectral lines, including Ca and Fe, two major elements in soil. The Cr line at 428.9 nm overlapped with other lines. Compared to previous work using a standard LIBS protocol (Dell'Aglio et al. 2011), the present method offers favorable analytical performance demonstrated by a higher signal-to-noise ratio intensity.

These results show that coarse metal powder-assisted laser-induced plasma spectroscopy may be used to rapidly identify heavy metals in the soil at low concentrations without elaborate sample pretreatment. This spectrum also confirmed that the sensitivity using TEA CO₂ laser was improved when the coarse metal powder was used to treat the soil.

As reported in a previous study using microstructured holes on metal targets using a TEA CO₂ laser-induced gas plasma (Idris et al. 2007), the detection limit for chromium

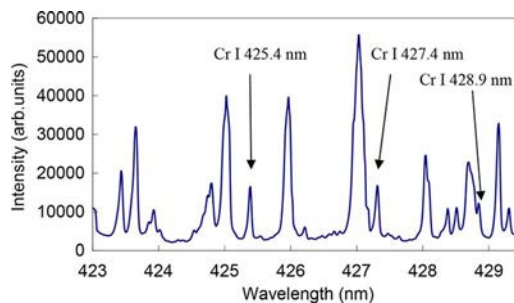


Figure 3. Emission spectrum of chromium from loam soil fortified with 50 mg/kg of the analyte.

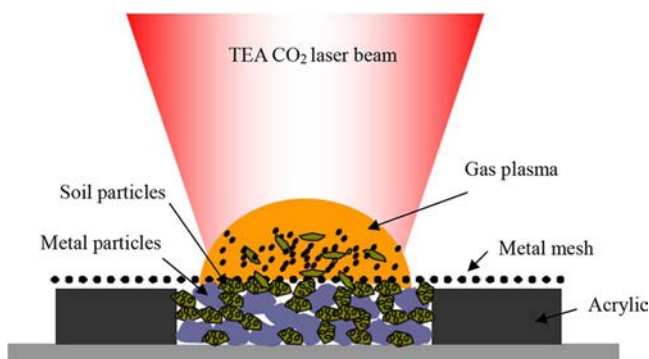


Figure 4. Illustration of the excitation processes that occur in the coarse metal powder-assisted laser-induced plasma.

was approximately 25 mg/kg. The present method allows the determination of Cr at 50 mg/kg in soil. The reported method utilizing the coarse metal powder to trap soil and to induce a high temperature and long lifetime gas plasma is sophisticated. The metal coarse powder is presumed to influence the excitation process in the plasma as illustrated in Figure 4. When the TEA CO₂ laser beam was focused on the coarse metal–soil powder, electrons were removed from the metal due to multiphoton absorption. The electrons were then accelerated in the low-frequency electric field of the laser beam, which generates cascade ionization of the atoms and a plasma is produced. The laser light is frequently absorbed in the plasma by inverse Bremsstrahlung through free–free transitions, resulting in a large volume and high-temperature plasma. This absorption is stronger for the TEA CO₂ laser than for the Nd:YAG laser because the plasma absorption coefficient is proportional to the inverse square of frequency of the laser light. Furthermore, the pulse duration of the TEA CO₂ laser is relatively long (200 ns), approximately 20 times longer than for 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 trapped in the coarse metal was then dissociated and excited in the plasma.

Additional measurements were performed to determine other heavy metals in soil. A loam soil containing 750 mg/kg of the analytes was used as a sample. Figure 5 shows the emission spectrum of lead from soil fortified with 750 mg/kg Pb by the present method. A high-intensity lead emission line was observed along with lines from the major elements

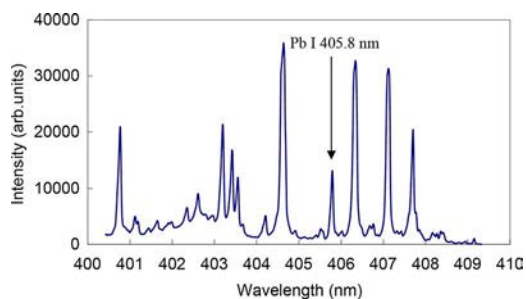


Figure 5. Emission spectrum of lead obtained from loam soil fortified with 750 mg/kg of the analyte.

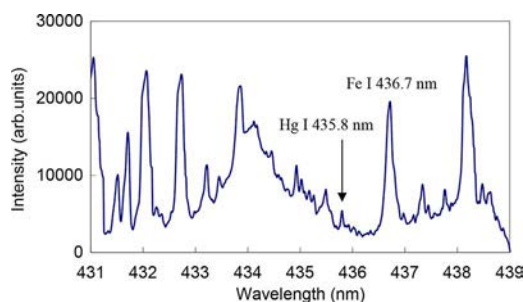


Figure 6. Emission spectrum of mercury obtained from loam soil fortified with 10 mg/kg of the analyte.

in soil. This result showed that the present approach is suitable for the identification of heavy metals in soil.

The present method was then used to analyze soil containing mercury, a poisonous heavy metal that is dangerous for human health. Figure 6 shows the emission spectrum of Hg obtained from the loam fortified with 10 mg/kg of this element. An emission line of neutral Hg (Hg I) at 435.8 nm appears together with many emission lines from Fe, a major element in soil. It is difficult to determine mercury at low concentrations in soil by standard LIBS protocols because soil contains major elements such as Al, Ca, Mg, and Fe that produce more than 100 peaks (Yang et al. 2010). Those lines from the major constituents may interfere with the analytical measurements for mercury. A high background emission was present even when the detection was set to 10 μ s, showing that the plasma temperature was high even at later stages of plasma emission. The detection limits for Cr, Pb, and Hg were 0.8, 15, and 0.7 mg/kg, respectively, by the reported approach. The detection limits were established based on the concentration that yielded three times the noise (Ingle and Crouch 1988). These reported detection limits are lower compared to the results obtained using standard LIBS and SIBS protocols (Popov, Colao, and Fantoni 2010). Thus, this technique is promising for field screening for the direct analysis of soil.

Conclusion

A direct and rapid analysis of soil with high sensitivity has been demonstrated using a pulsed TEA CO₂ laser using a coarse metal powder for sample preparation. The metal powder was used to trap the soil and to produce a large, high-temperature plasma. The fine soil was dissociated and excited in the plasma. Semiquantitative analysis of heavy elements in soil was performed. The limits of detection for chromium, lead, and mercury in soil were 0.8, 15, and 0.7 mg/kg, respectively.

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