Rapid identification of impurity in the material surface using mesh-assisted laser-induced plasma technique utilizing pulse CO\textsubscript{2} laser

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Abstract. Impurity analysis in the material surface urgently required in various fields such as material sciences and industries. In this research, a new technique was devised based on a pulse CO\textsubscript{2} laser. Technically, the surface of the alminate material as a material target was covered by a metal mesh. To induce a big-size plasma, the pulse CO\textsubscript{2} laser was directed to the metal mesh at an inclining degree of 30\textdegree by a ZnSe lens. Using this present technique, some impurities including potassium and calcium in the surface of the alminate sample can be detected with the limit of detection of 10 and 5 mg/kg, respectively.

1. Introduction
Recently, impurity analysis in the surface of the material has become an important subject especially in the field of industries [1]. In the semiconductor industry, the impurity placed in the material surface can influence the characteristics of electricity [2-5]. Also, the contamination can significantly suppress the quality of material products. Therefore, rapid and periodic analysis of impurity is urgently needed.

Atomic emission spectroscopy based on a pulse laser (laser-induced plasma spectroscopy) has been widely used as a spectrochemical method to identify elements in various materials including liquid, solid, and gases [6-7]. In LIPS, a pulse laser of Nd:YAG is commonly employed as an energy source to induce a luminous plasma on the surface of the material. Ablated materials produce the plasma from the sample target. This plasma contains fine particles, molecules, elements, ions, and electrons from the goal. By using an emission spectrometer, the elements from the ablated material can easily be detected. LIPS method has some benefits, namely rapid analysis of elements can be made; no tedious sample preparation is needed, and experimental equipment is much cheaper. The technique has been applied in many fields including environment, geology, and industries. In industries, the method can be used for rapid detection of impurity in real products. However, the LIPS method cannot be easily applied to impurity analysis on the surface of material because the ablation of material happens when the laser was focused on material surface.

On the contrary, a pulse CO\textsubscript{2} laser is very convenient for impurity analysis on the material solid surface [8]. By controlling the laser power density on the material surface, no ablation of material happens because the laser power density is much lower compared to the power density of the material itself. In this present technique, we developed a new sampling device for analysis of impurity on solid material target utilizing a pulsed TEA CO\textsubscript{2} laser. To control the laser fluence and enhance the plasma emission, a metal mesh was employed. The mesh tightly covered the material surface. Furthermore, to generate a big plasma, the laser beam was irradiated on the surface of metal mesh with a laser beam
inclining degree of 30°. Using this present technique of metal mesh, the emission intensity of impurity deposited on the material surface increased compared to the method without a metal mesh.

2. Experimental procedure
The setup of experiment used in this study is illustrated in Fig. 1(a).

![Setup of experiment](image)

**Figure 1** (a) the setup of experiment, (b) new sampling device in this research.

A pulse transversely excited atmospheric (TEA) CO₂ laser (10.64 μm) was directed and focused to the material surface at the degree of inclination of 30° by a ZnSe lens as illustrated in Fig. 1(b). The laser energy was 1500 mJ, and the duration of laser pulse duration was 200 ns. The gas plasma emission was then sent into an optical multichannel analyzer (OMA) system (ATAGO Macs-320) via optical fiber. Gating delay time and gate width of the OMA systems were 10 us and 100 us, respectively.

The sample used in this research was an almite solid sample (Al₂O₃). A sample chamber with a dimension of 12 cm x 12 cm x 12 cm was used for the sample evacuation. In the chamber, helium gas (99.999 %) was flowed for 4 liter per minute. The gas pressure inside the chamber was 1 atm.

To enhance impurity emission intensity, a metal mesh made of stainless-steel wires was used to tightly cover the surface of material. The metal mesh functions to initiate a gas plasma produced just above the mesh. Furthermore, the metal mesh can also retard the laser beam path, which arrives on a material surface and therefore reducing laser energy.

3. Results and discussion
Laser-induced plasma generation via the usage of a pulsed TEA CO₂ laser is particular, and it is excluded from the plasma generated by way of the Nd: YAG laser, mainly for the case of metal sample target. In the Nd:YAG laser case, once the laser beam turned into a metal target, the metal target become ablated, and the shock wave plasma was induced via the ablated materials [9-10]. The emission spectrum was then obtained from the produced plasma. For the TEA CO₂ laser case, once the laser beam impinged on the metal surface, no ablation of material happens, and only electrons come out of the surface of material because of multiphoton absorption. The electrons then accelerate and collide with the constituents in the surrounding gas to produce a luminous plasma. The plasma emission is then detected by using an atomic spectrometer to obtain an atomic emission spectrum. The plasma induced by the TEA CO₂ laser is useful to be applied as an excitation source.

At initial, identification of impurity on the material solid surface was done by using the present technique with the assist of a mesh and without a mesh. The material used in this study was a solidalbite sample (Al₂O₃). The almite sample contains an impurity of potassium (K) and calcium (Ca) with a concentration of around 200 and 500 part per million (ppm), respectively. Figure 2(a) displays emission line of potassium obtained from the almite sample using TEA CO₂ laser without a metal mesh. In this study, the laser beam was directly irradiated on the sample target at inclining degree of 30°. Sharp and high-intensity emission lines of K I 766.5 nm and K I 769.9 nm occurs with high background emission. By using the emission line of K at 766.5 nm, it was obtained that the limit of detection of K was around 10 mg/kg.

Furthermore, the oxygen line coming from the air surrounding gas appears at 777.7 nm. When the metal mesh was applied by placing the mesh at tight contact with a material surface as illustrated in Fig. 1(b), the total emission intensity of potassium increased at around 1.5 times (Fig. 2(b)) compared the result without the metal mesh (Fig. 2(a)). Furthermore, the emission intensity of oxygen also significantly increased at around two times. This result certified that the excitation process effectively happens inside the plasma region for the case with a mesh. It is assumed that with the mesh assistant, the plasma temperature increases as in the case of our previous report [10]. By increasing the temperature, the plasma constituents including atoms coming from the real target and atoms from the surrounding gas can effectively be excited, increasing the enhancement of emission intensity.
Figure 2 Emission spectrum of potassium as an impurity on the almite surface using the present technique (a) without a metal mesh and (b) with a metal mesh.

The role of laser shot repetition was then examined to get the optimum intensity of impurity on the material target (almite sample). Figure 3 displays the spectrum of potassium taken from the almid sample using the present technique with the assist of metal mesh. The number of laser shots was varied for five shots, ten shots, and 15 shots as displayed in Fig. 3(a), 3(b), and 3(c), respectively. As is seen, the increment of the number of laser shots reduced the emission intensity of potassium as shown in Figs. 3(a), 3(b), and 3(c). This is because with increasing the number of laser shots, the potassium as an impurity on material target was removed and ablated due to the laser bombardment. Therefore, it is better to use a lower number of laser shots for an analysis of impurity of the surface of material.
Figure 3 Emission spectra of potassium obtained by using the present technique with the different laser shots of (a) 5 Hz, (b) 10 Hz, and (c) 15 Hz.

Finally, identification of calcium on the surface of almite material was also conducted. Calcium is impurity on almost material because it is deposited in the air surrounding gas and therefore it is easily deposited on surface of the material. An emission spectrum of Ca deposited as an impurity on the almite surface is displayed in Fig. 4. The atomic emission line of Al at 394.6 nm and 396.1 nm occurs strongly near Ca lines. The Al lines are contributed to the material target of the almite sample (Al$_2$O$_3$). Double emission lines of ionic Ca are detected. The limit of detection of Ca was approximately 5 ppm. This result certified that the technique could be readily employed to the impurity analysis on the material surface.
Figure 4 Calcium emission spectrum with the number of laser shots of 5 Hz.

4. Conclusion
Identification of impurity on the surface of almite ($\text{Al}_2\text{O}_3$) material target was successfully conducted by using the inclining technique with the assist of metal mesh utilizing a pulsed CO$_2$ laser. In this research, a pulsed TEA CO$_2$ laser was irradiated on the almite material surface at the degree of inclination of 30° to induce a luminous plume. The metal mesh, functions to enhance the emission intensity. It has been found that the number of laser shots has an essential role in the emission intensity of the impurity spectrum. Namely, with the increment of the laser shots, the intensity of impurity emission decreased. The result concluded that the present technique could be employed to identify some contaminants including potassium and calcium deposited on the almite material surface.

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