

A COMPACT TEA CO<sub>2</sub> LASER FOR FIELD-BASED  
SPECTROCHEMICAL ANALYSIS OF GEOLOGICAL SAMPLES

Wagini R.<sup>\*</sup>, K. Kagawa<sup>\*\*</sup>

A compact capacitor-transfer TEA CO<sub>2</sub> laser of 180 mJ output energy and 50 ns pulse duration in half width was designed and constructed for field use. This laser is suitable for laser microprobe spectrochemical analysis on geological and mining samples. Experiments show that the use of helium as a surrounding gas suppresses the continuous emission spectrum of the plasma, thus increasing the S/N ratio. Using glass as standard samples, the minimum detectable concentrations are estimated with Zn neutral line and F ionic line to be 60 ppm and 500 ppm, respectively.

KEYWORDS : lasers (compact TEA CO<sub>2</sub>), field-based analysis, laser microprobe analysis

#### Introduction

The method of laser microprobe spectrochemical analysis (LMSA) was first introduced by Brech<sup>1</sup> in 1962. Since then, many improvements have been made, mainly to increase the stability of the laser output and reproducibility of the sample removal process<sup>2-4</sup>. In addition to this, efforts have also been made to improve the detection system of the emission spectrum by employing photomultipliers or OMA (optical multichannel analyser) systems. In general, high-power solid-state lasers, such as ruby and Nd lasers, have been used in LMSA, and almost all of the instruments employed in the LMSA were designed for application in the laboratory, but not for removal to the field.

Recently, an analytical method of laser induced breakdown

---

<sup>\*</sup> Jurusan Fisika FMIPA UGH

<sup>\*\*</sup> Department of Physics, Faculty of Education, University of Fukui, Japan

spectroscopy (LIBS) was presented by Cramers and his co-workers<sup>5-6</sup>. This method offered the possibility of field-based rapid analysis. They used a Nd: YAG laser (45-475 mJ, 15 ns) with the OMA as a detection system.

We believe that the TEA CO<sub>2</sub> laser has great potential for field-based rapid analysis on geological or mining samples for two reasons. First, a compact version of the TEA CO<sub>2</sub> laser can be constructed, and secondly, geological samples show high absorbance at the wavelength of the CO<sub>2</sub> laser radiation (10.6 μm). This leads to highly effective plasma generation. The emission spectrochemical analysis using the laser plasma induced by the bombardment of the TEA CO<sub>2</sub> laser was first attempted by Gibson et al<sup>7</sup> on Ge samples. They used a CO<sub>2</sub> laser pulse with 280 mJ output energy and 350 ns pulse duration. The bombardment was made at a reduced pressure in order to decrease the continuous emission spectrum. Conversely, Kagawa et al<sup>8,9</sup> have shown that 'Laser-induced Shock Wave Plasma' is produced by the bombardment of a highpower TEA CO<sub>2</sub> laser with short pulse duration (500 mJ, 100 ns) provided that the pressure of the surrounding gas is reduced to around 1 torr. In their experiments, they used a commercial TEA CO<sub>2</sub> laser designed for laser marking applications. They proved that the shock wave plasma has characteristics favourable to spectrochemical analysis. In particular, it has been noted that the background emission intensity of the plasma is relatively low, and there is a good linear relationship between the atomic line emission intensity and the concentration of the elements.

This paper presents a compact TEA CO<sub>2</sub> laser which was designed for field-based spectrochemical analysis on the geological samples. The small size, low cost, and narrow pulse duration are advantages when compared with the ordinary TEA CO<sub>2</sub> laser. In this experiment, emission spectrochemical analysis was made under 1 atmospheric pressure in order to accommodate the laser's application to field-based rapid analysis. The method of time resolved emission

spectroscopy was employed in order to reduce the signal generated by the continuous emission spectrum of the plasma.

### Laser System

Figure 1 shows the cross-section of the compact TEA CO<sub>2</sub> laser. It basically consists of a capacitor-transfer discharge circuit. The dimension of the laser system are 400 mm x 250 mm x 200 mm. The length and the separation of the main electrodes are 150 mm and 20 mm, respectively. The optical cavity is composed of a concave gold mirror with a curvature of 10 m and a coated ZnSe reflecting flat mirror (70 % reflection). The pre-ionization electrodes are arranged on both sides of the main electrodes, and the discharge of the pre-ionization is made just before the main discharge, thus making the main discharge uniform. Six ceramic capacitors (Murata, 2 nF, 40 kV) are used as energy-storing elements and 25 kV is supplied through a compact high voltage power source, in which a neon-transformer is used with a double rectification circuit. The laser was operated at 5 Hz under the flowing gas mixtures (He 82%, CO<sub>2</sub> 8%, N<sub>2</sub> 8%, CO 2%) at the rate of 0.5 litre min<sup>-1</sup>. Two small fans were set inside the laser chamber for gas circulation. The beam cross-section obtained from the compact TEA CO<sub>2</sub> laser is 18 mm x 7 mm.

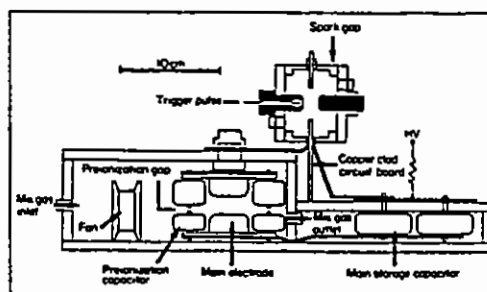


Fig. 1. Cross-sectional view of the compact TEA CO<sub>2</sub> laser system

Figure 2 shows the pressure dependence of the laser energy of the compact TEA CO<sub>2</sub> laser. It can be seen that the maximum energy



of 180 mJ can be extracted at 1020 torr. At pressure higher than 1020 torr, the laser energy decreases and the relative standard deviation of the laser energy increases. The optimum gas pressure condition of 1020 torr was used through this experiment.

Figure 3 shows the pulse form of the laser radiation. This signal was detected using a photodrag detector (Rofin 7410). It is seen that the half-width of the laser pulse is approximately 50 ns, and the rise time of the laser pulse is as short as only a few nanoseconds. Menyuk and Moulton<sup>10</sup> reported a high repetition rate mini TEA CO<sub>2</sub> laser with an output energy of 60 mJ and a pulse duration of 100 ns half width. It is believed that the short duration in our compact TEA CO<sub>2</sub> laser is due to the low overall inductance in the discharge circuit, and also due to the resonator geometry<sup>11</sup>.

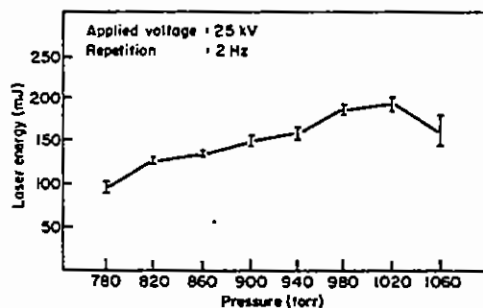


Fig. 2. Pressure dependence of the laser output energy

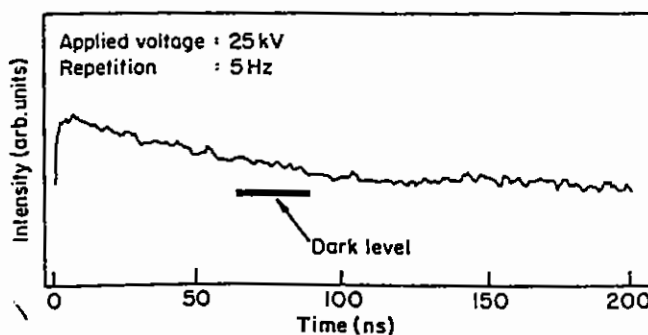


Fig. 3. Pulse form of the compact TEA CO<sub>2</sub> laser

It was proved experimentally that this laser is very effective in producing the 'Laser-induced Shock Wave Plasma'. In fact, this laser generates a large plasma as compared with the plasma that was produced using a commercial TEA CO<sub>2</sub> laser under the same pulse energy and the same pressure of the surrounding gas.

### Spectrochemical applications

Figure 4 shows the set-up used in this experiment. The laser radiation was focused by a Ge lens ( $f = 100$  mm) through a ZnSe window onto the surface of the sample in the chamber. The flow of the surrounding gas in the chamber was regulated at a pressure of 1 atm. The radiation of the laser-induced plasma was observed at a right angle to the laser beam using an imaging quartz lens ( $f = 150$  mm). The electrical signal from the photomultiplier (Hamamatsu R-1104, load resistance of  $500 \Omega$ ) attached to a monochromator (Nikon P-150,  $f = 250$  mm), was fed into a 100 GHz sampling oscilloscope (Iwatsu SAS 601B). The trigger signal of the sampling oscilloscope was generated using another photomultiplier (Hamamatsu R-331) in combination with a UV filter. The plasma light emitting from 3 mm above the surface of the sample was sent into the monochromator. When the time-resolved emission spectrum was taken, the time axis of the sampling scope was fixed at a desired time and the wavelength of the monochromator was scanned with a scanning speed of  $45 \text{ nm min}^{-1}$ . The signal from the sampling scope was memorized by a digital storage scope (Kikusui, DSS 6522) and sent to a personal computer (NEC, PC-9801 F). It was observed that the emission intensity of the plasma remained almost constant for about 2 minutes after the initiation of the bombardment when the sample is homogeneous.

Figure 5 shows the plasma observed when the laser light was focused on a CaCO<sub>3</sub> sample with air as the surrounding gas at a pressure of 1 atm.

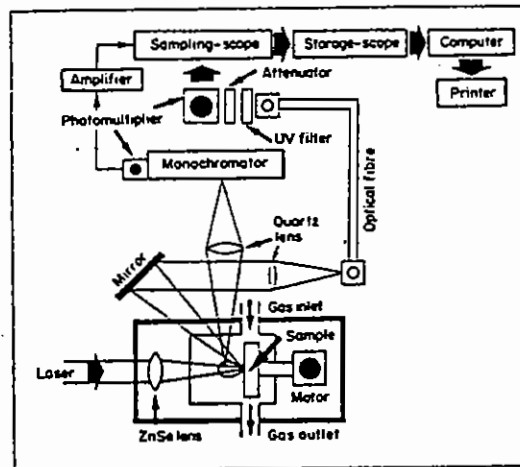


Fig. 4. Diagram of the experimental set-up

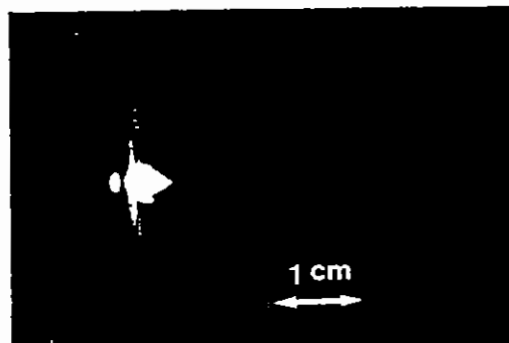


Fig.5 Photograph of the laser plasma using air as a surrounding gas. The sample is  $\text{CaCO}_3$

Figure 6 shows the time-resolved emission spectrum at different time delays after the laser pulse bombardment on  $\text{CaCO}_3$  : (a) using air as the surrounding gas; (b) argon; (c) helium. In the case of air as the surrounding gas, it is observed that at the

early time delay (1  $\mu$ s) a high background continuum dominates the spectrum. At 3  $\mu$ s, the background becomes low and definite atomic line spectra appear. At 7  $\mu$ s, the background emission becomes very low and the neutral calcium line (Ca I 4226 Å) appears clearly. No carbon ionic line was observed. With respect to the 'Laser-induced Shock Wave Plasma', the emission line due to the carbon ion (C II 4267 Å) could be plainly observed<sup>12</sup>. This is probably due to the difference in the excitation process of the plasma. In the case of argon surrounding gas, many argon ionic lines dominate the spectra in the early time delay, making the spectrum unsuitable for elemental analysis. Figure 6(c) shows the spectral in the helium surrounding gas. It is evident that even in the early time delay of 1  $\mu$ s, the background emission intensity level is low. Therefore, it is concluded that helium gas is most suitable as the surrounding gas. Furthermore, it should be noted that the strong emission line due to He I 3888 Å is observed in the early stage of the plasma formation, and decreases with time.

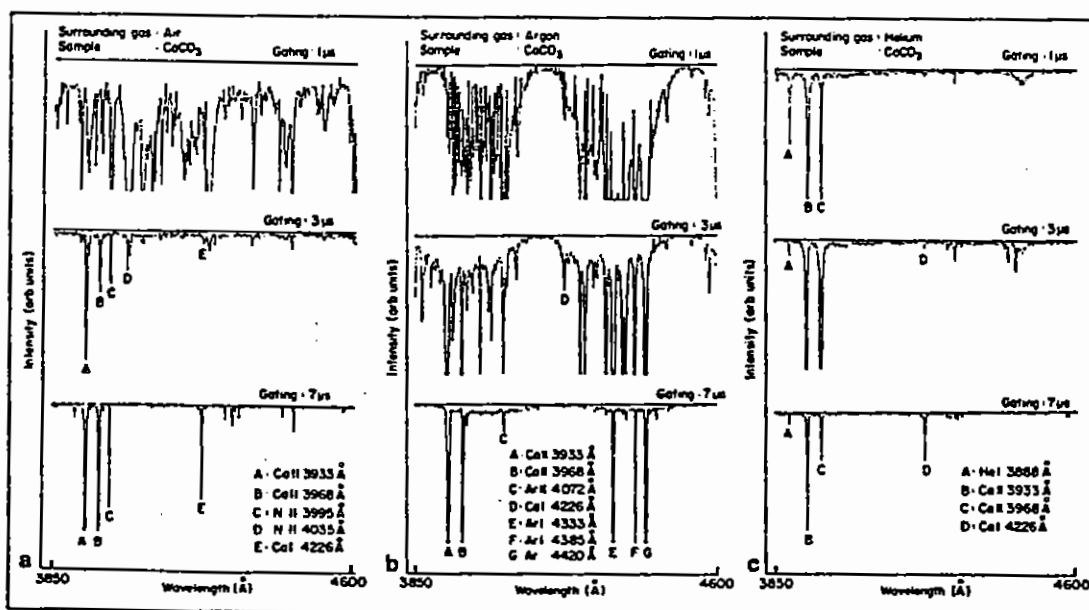


Fig. 6 Time-resolved emission spectrum of the  $\text{CaCO}_3$  in (a) air, (b) argon, and (c) helium

Figure 7 shows the comparison of the time-integrated emission spectrum on three kinds of surrounding gas, air, argon and helium. It is seen that helium also provides a low background signal, even in this detection method. This results gives rise to the possibility that this simple means of emission spectrochemical analysis can be used without employing the time-resolved detection

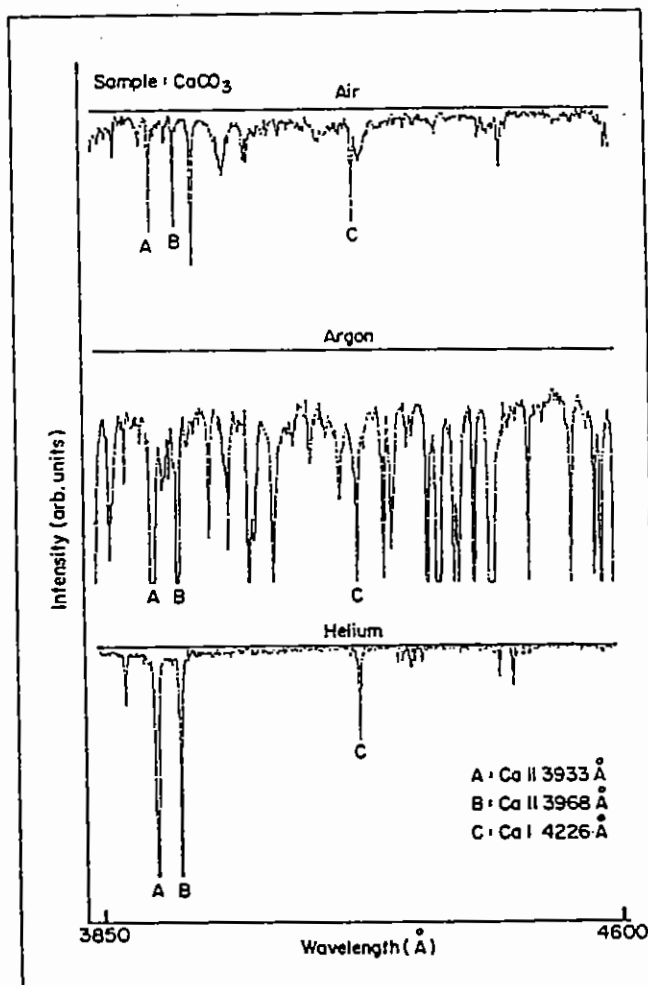


Fig.7. Time-integrated emission spectrum of the  $\text{CaCO}_3$  in different surrounding gases.



method.

Figure 8 shows the results of semiquantitative analysis using a standard glass sample. In this case, helium was used as the surrounding gas and the time axis of the sampling scope was set at 5  $\mu$ s. Glass sample no 1 contains 3.36% calcium, 0,07% magnesium, 1.07% fluorine and other elements, whereas glass sample no 2 contains 9.51% calcium, 4.08% magnesium and no fluorine. By comparing the Ca I 4226 A emission intensity, we obtained a good correlation between the Ca concentration and the emission intensity. From the spectrum, we can also find the fluorine ionic line, which is usually very difficult to detect because of the high-lying electronic energy levels. The appearance of the fluorine ionic line proves that helium atmospheric plasma has a temperature high enough to ionize the fluorine atoms.

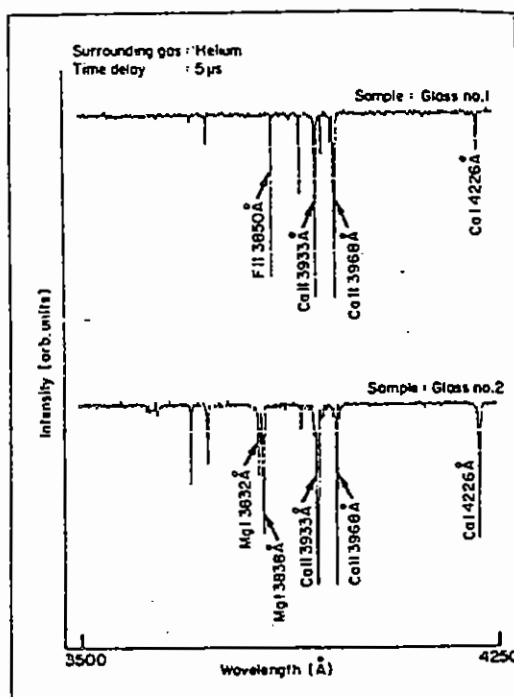


Fig. 8. Time-resolved emission spectrum of glass samples in surrounding helium for semi-quantitative analysis.

Another interesting fact that supports the high temperature plasma in the helium surrounding gas is obtained by observing the crater form. In the case of the helium surrounding gas, no molten material was observed around the crater, thus proving that effective vaporization takes place due to high temperature plasma. In contrast to this, in argon and air, a wall of molten material was observed around the crater, indicating that the plasma temperature is relatively low and a considerable part of the sample has been ejected as liquid, or in a recondensed form.

Using these standard glass samples, the minimum detectable concentrations of Zn I 4810 A and F II 3850 A were estimated to be about 60 ppm and 500 ppm, respectively.

#### Conclusion

Using a compact TEA CO<sub>2</sub> laser (180 mJ, 50 ns), it has been demonstrated that a rapid semiquantitative analysis can be successfully made when helium gas is used as a surrounding gas. This analytical method holds great potential for use in the field-based analysis of geological and mining samples. On the basis of our experiments, it is expected that if the OMA system for detecting the emission spectrum is employed, the time needed for analysis will be drastically reduced.

#### Acknowledgement

This work was partly supported by a Grant-in-Aid for scientific research priority areas. Shock Wave Research, from the Ministry of Education, Science and Culture of Japan.

#### References

- Brech, F. 'Optical microemission stimulated by a ruby laser'.  
Appl Spectrosc, 16, (1962) 59

- Iida, Y. 'Effects of atmosphere on laser vaporization and excitation processes of solid samples'. *Spectrochim Acta*, 45B, (1990) 1353-1367
- Piepmeyer, E. H., Osten, D. E. 'Atmospheric influences on Q-switched laser sampling and resulting plumes', *Appl Spectrosc*, 25, (1971) 642-652.
- Scott, R. H., Strasheim, A. 'Laser induced plasma for analytical spectroscopy'. *Spectrochim Acta*, 25B, (1970) 311-332
- Cremers, D.A. 'The analysis of metals at a distance using laser-induced breakdown spectroscopy'. *Appl Spectrosc*, 41, (1987) 572-579
- Cremers, D.A., Radziemski, L.J. 'Detection of chlorine and fluorine in air by laser-induced breakdown spectrometry'. *Anal Chem*, 55, (1983) 1252-1256
- Gibson, A.F., Houghes, T.P., Ireland, C.L.M. 'CO<sub>2</sub> laser generation of plasma for spectroscopy and spectrochemical analysis'. *J Phys D*, 4, (1971) 1527-1534
- Kagawa, K., Manda, T., Ueda, M., Li, Zhaozhi 'Blast wave generation by the bombardment of TEA CO<sub>2</sub> laser at low pressures'. *J Spectrosc Soc Japan*, 40, (1991) 150-154
- Kagawa, K., Kurniawan, H. 'Blast wave generation by the bombardment of TEA CO<sub>2</sub> laser at low density'. *Proceeding of the International Shock Wave Workshop*. Chiba, Japan (1991)
- Menyuk, N., Moulton, P.E., 'Development of a highrepetition rate mini-TEA CO<sub>2</sub> laser'. *Rev Sci Instrum*, 51, (1980) 216-220
- Baker, C., Dyer, P.E., Tait, B.L. 'Design of a compact high prf TEA CO<sub>2</sub> laser and performance under multimode and single mode conditions'. *J Phys E Sci Instrum*, 14, (1981) 1167-1170
- Kurniawan, H., Kobayashi, T., Nakajima, S., Kagawa, K. 'Correlation between front speed and explosion energy of the blast wave induced by a TEA CO<sub>2</sub> laser'. *Japan J Appl Phys*. (1992) in press