Atomic emission spectrometric analysis of steel and glass using a TEA CO2 laser-induced shock wave plasma

メタデータ	言語: English 出版者: 公開日: 2008-01-28 キーワード (Ja): キーワード (En): 作成者: KAGAWA, Kiichiro, HATTORI, Hiroyuki, ISHIKANE, Masuo, UEDA, Masahiro, HENDRIK, KURNIAWAN メールアドレス: 所属:
URL	http://hdl.handle.net/10098/1443

Atomic emission spectrometric analysis of steel and glass using a TEA CO_2 laser-induced shock wave plasma

Kiichiro Kagawa [a,*], Hiroyuki Hattori [a], Masuo Ishikane [a], Masahiro Ueda [a],
Hendrik Kurniawan [b]

[a] *Faculty of Education, Fukui University, Fukui 910, Japan*
[b] *Spectroscopy Laboratory, Graduate Faculty for Opto-electronic and Laser Application, University of Indonesia, 4 Salemba Raya, Jakarta 10430, Indonesia*

Abstract

The shock wave plasma induced by the bombardment of laser light coming from a commercial TEA CO_2 laser has been used for the direct elemental analysis of solid samples. By using standard low-alloy steel samples, it is demonstrated that there is a linear relationship between the Cr content and the emission intensity, using an internal standard method. A background equivalent concentration for the Mg 383.8 nm emission line is found to be as low as about 0.005% in glass samples.

Keywords: Laser ablation analysis; Shock wave plasma; TEA-CO_2 laser

1. Introduction

Development of new techniques for direct analysis of solid samples without pretreatment has been ardently demanded in many fields, scientific and industrial. General methods for the direct analysis of solid samples are the spark-discharge method, the Grimm-discharge method and x-ray fluorescence spectrometry. The disadvantage of the spark-discharge and Grimm-discharge methods is the limitation of the analysis only to metal samples. X-ray fluorescence spectrometry cannot be applied to light elements such as Be and B. Another method for the direct analysis of solid samples is laser ablation atomic emission spectrometric analysis (LAESA) [1–3]. Advantages of LAESA are that both metallic and non-metallic samples are analyzed and the light elements can also be detected.

In normal LAESA, high power solid state lasers, such as ruby and Nd, are used and laser light is focused under atmospheric pressure. In the case of Q-switched laser bombardment, plasma generation takes place with a strong continuum emission spectrum due to the high density plasma. This makes it difficult to obtain highly sensitive analysis. Furthermore, strong self-absorption occurs because the heated plasma is surrounded by a sheath of cool atoms. These problems have been overcome to some extent by separating the evaporation and excitation stage. Commercial equipment is available in which the sample target is vaporized by a laser beam from a normal oscillation laser and the excitation is made by a spark discharge in terms of auxiliary electrodes placed above the surface of the target. However, there are still some difficulties in precision and sensitivity. Therefore, LAESA has mainly been used for qualitative analysis of solid samples.

Another possible method for separating the evaporation and excitation stages in LAESA is to employ the laser-induced shock wave. Basov et al. [4] proved for the first time the generation of laser-induced shock wave plasma with the use of a high-power laser pulse (6 J, 15 ns) under lower ambient gas pressures (2 Torr). Hughes [5] reviewed these experiments concerning the laser-induced shock wave plasma. However, all these experiments were made only from the view point of high-temperature hydrodynamics, and no report has been made by other researchers on the application of the laser-induced shock wave plasma to spectrometric analysis.

In a series of studies, we have developed another LAESA method [6–15]. In our method, a laser beam with short pulse duration, such as N_2, excimer and TEA CO_2 laser beams, is employed and the pressure of the surrounding gas must be decreased to around 1 Torr. The laser induced plasma consists of two distinct regions. The first is a small area of plasma (called the primary plasma), which gives off intense continuous emission spectra for a short time just above the surface of the target. The other area (secondary plasma) expands with time around the primary plasma, emitting sharp atomic line spectra with low background signals. The shape of the secondary plasma is hemispherical when observed by the naked eye. The radius of the secondary plasma depends on the pulse energy of the laser and also on the pressure of the surrounding gas. The secondary plasma has characteristics quite suitable for emission spectrometric analysis. Especially, the low background emission intensity and the linear relationship between the emission line intensity and the content of the element are most advantageous. On the basis of the experiments using time-resolved spectroscopic study on the plasma induced by a TEA CO_2 laser and XeCl excimer laser, we have proposed a shock wave model to explain the mechanism in forming the secondary plasma, although the pulse energy of the laser is considerably lower than that employed in the experiments of Basov et al. [4]. We have called this analytical method laser-induced shock wave plasma spectrometry (LISPS).

In this paper, we report briefly on the practical application of LISPS using a TEA CO_2 laser as the exciting source. Gibson et al. [16] attempted for the first time the application of a TEA CO_2 laser to laser ablation emission spectrometric analysis. They determined Si in Ge samples under reduced pressure of the surrounding gas. However, it seems that their plasma is different in character from our shock wave plasma. The luminous region of their plasma was very small and the shape is not hemispherical. This is probably because in their case the pulse duration was rather long and the pulse energy was lower compared to our case.

The advantage of applying the TEA CO_2 laser as the source of the shock wave plasma are as follows:

(1) The TEA CO_2 laser is widely used industrially for marking processes and is commercially available. The laser operates with high power and with good shot-to-shot output stability. The running costs are very low.

(2) Since the photomultiplier tube is not sensitive at the wavelength of the TEA CO_2 laser light, there is no to care about stray laser light coming into the monochromator.

(3) Since the TEA CO_2 laser light has high absorbance on glass samples or rock samples, plasma generation takes place effectively with a low threshold pulse energy of the laser light.

2. Experimental

Fig. 1 shows the schematic representation of the experimental set-up used in this study. The TEA CO_2 laser used in this work is a Shibuya SQ-2000, which was developed and constructed by the Shibuya com-

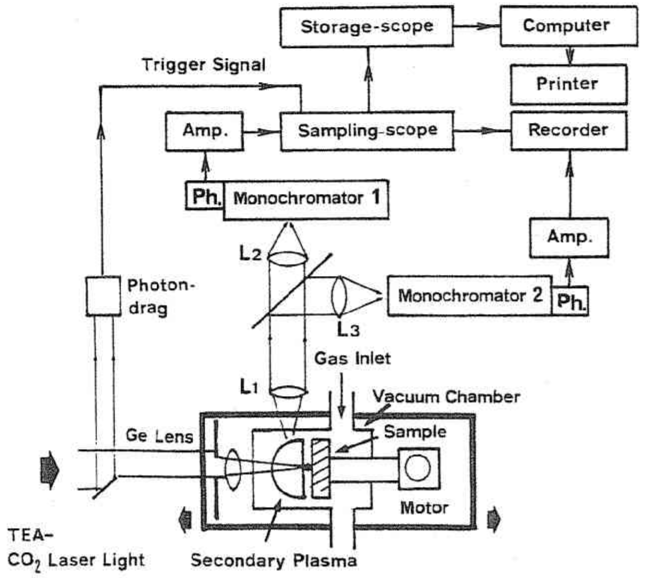

Fig. 1. Schematic representation of the experimental set-up used for emission spectrometric analysis using a TEA CO_2 laser-induced shock wave plasma.

pany for laser marking. The laser was operated at 5 Hz with characteristics of 3 J pulse energy, 100 ns pulse width in half and 30×30 mm beam area. The laser beam was transmitted through a ZnSe window and focused on the sample surface with a Ge lens of 100 mm focal length. The focused energy of the laser pulse was changed with variable apertures placed in front of the Ge lens. The pulse energy of 700 mJ was used for steel samples and 300 mJ for glass samples. The shot-to-shot fluctuation of the laser pulses was about 3%. The sample was set in a vacuum-tight metal chamber in which the pressure was regulated at 200 Pa with air.

To provide an internal standard method for the emission spectrometric analysis, two monochromators were used. The image of the secondary plasma was formed on the entrance slit of two monochromators (M1, M2) with the aid of quartz lenses (L1, L2, L3), with a focal length of 150 mm, and a beam splitter. The radiation of the secondary plasma 7 mm above the surface of the sample was sent into the entrance slits of the monochromators. The position of the entrance slits was set carefully so that the same region of the secondary plasma could be observed by the two monochromators. The adjustment was guaranteed by observing the linear correlation between the two signals, which were measured with different photomultiplier tubes attached to the two monochromators, on one emission line of the host element of the sample. The slit width of the monochromator M1 (Jobin Yvon HRS-2) was usually set at 30 μm, and that of M2 (Nikon P-250) was set at 25 μm. The slit height of both monochromators was set at 15 mm. In order to adjust the intensity level of the emission lines to be measured, a filter of known transmittance was placed in front of the monochromators as needed.

The intensity of the atomic emission lines was measured by means of a time-integrated method. For this purpose, a high resistance of 50 kΩ was connected to a photomultiplier tube (Hamamatsu R331) which was attached to the monochromator M1. The electrical signal from the photomultiplier tube was sent into a sampling oscilloscope (Iwatsu, SAS 601-B), which has a similar function to a boxcar integrator. The trigger signal of the sampling oscilloscope was obtained from a part of the laser light using a photon drag detector (Instruments, 7410). The time axis of the sampling oscilloscope was fixed at 10 μs at which the signal reaches maximum intensity. The output signal of the sampling oscilloscope was fed into a two-pen chart recorder or into a computer after once stored in a digital storage scope (Kikusui, DSS 6522). The use of the sampling oscilloscope is very effective for improving the signal-to-noise (S/N) ratio in the measurement of the intensity of atomic emission lines because of its gate function. The output from the photomultiplier tube (Hamamatsu, R1104) attached to M2, which was used for monitoring the emission line intensity of the host element in the sample, was sent directly to the two-pen chart recorder after passing through a time-integrated circuit.

The standard samples used for quantitative analysis were of low-alloy steel (JSS 150, Iron and Steel Institute of Japan).

3. Results and discussion

3.1. Application to steel samples

We have already reported that by the use of the LISPS method emission spectrometric analysis can successfully be made on steel samples using a N_2 laser (6 mJ) [8] or XeCl excimer laser (50 mJ) [15]. In those experiments the samples were rotated at ca. 1 rpm under repeated bombardments of the laser pulses (5 Hz) to produce a groove with a diameter of ca. 1 cm, which made the shape and the emission intensity of the secondary plasma almost constant for about 1 h. However, in the case of the TEA CO_2 laser, the same technique cannot be employed because the secondary plasma fluctuates in size and in emission intensity. This is probably due to lack of power density of TEA CO_2 laser light on the surface of the steel samples. The spot size of the focused beam of the TEA CO_2 laser is ca. 0.5 mm in diameter and the estimated laser power density is 3.6×10^9 W/cm^2; in contrast, the diameter is <100 μm for the N_2 laser and the laser power density is about 10^{11} W/cm^2. In order to overcome this fluctuation problem, laser bombardment was performed with the sample held in a fixed position, without rotating. By this method the fluctuation of the secondary plasma can be decreased remarkably.

Fig. 2 shows the time-course of the intensity of the Cr 425.4 nm and Fe 406.4 nm emission lines, taken from one of the standard samples of low alloy steel containing 0.5% Cr in weight. The wavelength of mo-

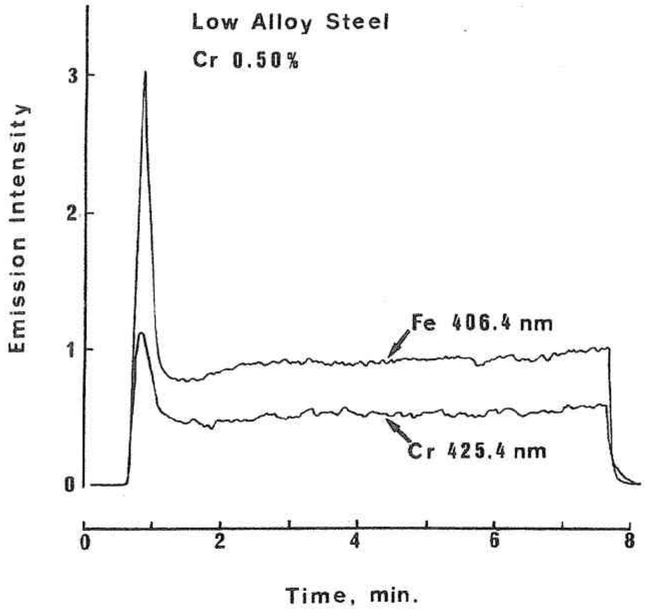

Fig. 2. Time course of the emission intensities of the Cr 425.4 nm and Fe 406.4 nm emission lines. Irradiation of laser light was made with the sample in a fixed position. The low-alloy standard steel sample contained 0.5 wt.% Cr.

nochromator 1 was fixed at 425.4 nm, and 406.4 nm for monochromator 2. The emission intensity reaches a maximum, after which it drastically decreases and finally is stabilized within about 1 min. At the beginning of the irradiation, the secondary plasma is about 2.5 cm in radius, which finally is decreased to ca. 1.5 cm. This phenomenon closely depends on the form and depth of the crater that is produced by the repeated bombardment by the laser. For convenience, in this paper the point at which emission intensity has the maximum value is called A and B stands for the plateau region.

It was observed that the intensity of the Cr emission line at A varies from experiment to experiment to some extent. The relative standard deviation (R.S.D.) of the intensity of the emission lines was obtained at A. As a result, the R.S.D. for Cr 425.4 nm was 9.8%, while that of the emission intensities of Cr 425.4 nm divided by the intensity of the Fe 406.4 nm emission line was 3.6%. Therefore, it can be said that quantitative analysis is possible at A provided that the internal standard method is used. It should be noted that this ratio is almost constant in region B. This implies that a constitution change does not take place in this sample during the successive bombardments on the same position of the sample. Therefore, region B can also be used for quantitative analysis.

In order to make calibration graphs from the results of the standard steel samples, the following preparation was made. A small block with dimensions of ca. 7×5×3 mm was cut out from each of six samples. The six pieces were arranged around the center of the disk. The disk was mounted in the chamber. Using the same method employed in the experiment in Fig. 2, the relative intensity of the Cr 425.4 nm line compared with that of the Fe 406.4 nm line was obtained in the two regions (A and B in Fig. 2) by changing the samples. Measurements were repeated three times on each sample by changing the position. In region B, the emission intensity was read out at five different randomly chosen points.

Fig. 3 shows the resultant analytical curves for Cr. Plot A was obtained at the peak signal and plot B in the plateau region. It should be noted that the plot is linear in both cases. Such a linear relationship was already observed in the TEA CO_2 laser-induced shock wave plasma in food samples on the emission intensity of Ca 422.67 nm [17]. In contrast, there is no linear relation-

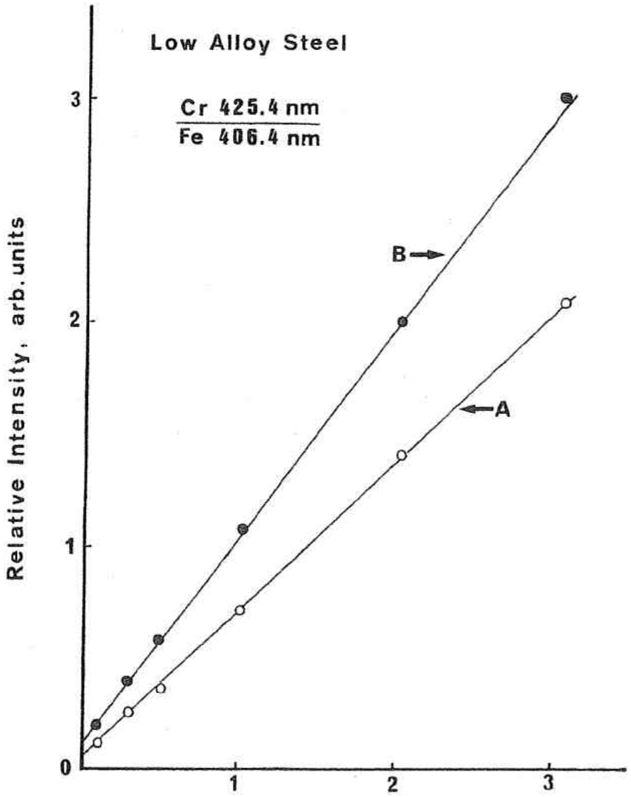

Fig. 3. Plot of the relative intensity of the Cr 425.4 nm line to that of the Fe 406.4 nm line against the Cr content of low-alloy standard steel samples. Curve A was obtained from the peak intensity and B from the plateau region.

ship for conventional LAESA, owing to the self-absorption taking place as resonance transitions in Cr atoms [18]. In the present case self-absorption is negligible. This probably arises because the secondary plasma has a thin shell structure seemingly like the inductively coupled plasma (ICP). This shell structure has already been proved in our previous experiments using a time-resolved spectroscopic technique [10,11,15]. As shown in Fig. 3, the slopes of the lines are different, probably because the temperature of the secondary plasma is different. The excitation energy of the Cr 425.4 nm line is 2.9 eV and that of the Fe 406.4 nm line is 4.6 eV. Different plasma temperature will give different intensity ratios.

From the intercepts of the lines on the ordinate in Fig. 3, the background equivalent concentration (BEC) was estimated to be ca. 0.06%. This value is high, but the BEC can be reduced by a factor of 10 or more by means of setting the entrance slit of the monochromator 12 mm from the sample surface. The BEC in the TEA CO_2 laser-induced shock wave plasma is higher than that for excimer laser-induced shock wave plasma. We already proved in the experiment using XeCl excimer laser that the BEC of the Cr 425.4 nm is as low as 0.0012% in the same low-alloy steel sample [15].

The calibration graph for Ni in the standard sample of the low-alloy steel is linear up to at least 4% Ni. The Ni emission intensity was less stable for Cr. This problem was solved by the use of helium (3000 Pa) as the surrounding gas; the emission intensity was read in the plateau region.

Measurements were also made on standard samples of high-speed steels. In contrast to the low-alloy steels, some problems were observed. In particular, it is surprising that emission lines due to W atoms could not be detected in spite of the fact that the sample contained ca. 10% of tungsten, and the emission lines for Fe are very strong; only in a limited region near the primary plasma could the emission of W be observed. In contrast, even for LISPS using a N_2 laser (pulse energy of 6 mJ) a good calibration for the W 400.9 nm emission line was obtained for high-speed steel samples [8]. It seems likely that the differences arise because in high-speed steel samples selective vaporization takes place because the boiling point of high-speed steels is higher than that of low-alloy steels. It is assumed that the vaporization of W atoms is delayed compared to the Fe atoms. As proposed in previous papers, a secondary plasma is produced through the adiabatic compression due to the atoms gushing from the primary plasma at supersonic speed [12,14,15]. Therefore, atoms are excited in the limited, thin-shell regions just behind the shock waves. If W atoms are delayed by the selective vaporization, the atoms cannot reach the excitation region and emission does not take place. However, such selective vaporization becomes negligible when the pulse duration is sufficiently short and the power density on the surface of the sample is sufficiently high. This is the case for the N_2 and XeCl excimer laser.

3.2. Application to glass samples

The LISPS method using a TEA CO_2 laser is especially suitable for glass samples. One advantage is the low threshold energy of plasma production. A very stable secondary plasma was produced under the successive bombardment of the laser light even when the sample was rotated. Another advantage of applying the TEA CO_2 laser is that a glass sample never emits fluorescence during irradiation. In contrast, for UV lasers such as the N_2 and XeCl excimer lasers, a glass sample fluoresces, thus raising the background level in the spectral measurement.

Fig. 4a shows the qualitative spectral profile obtained on the glass sample containing about a few percent of boron. In order to obtain this spectrum, the wavelength of the monochromator was scanned at 15 nm/min in the wavelength range from 245 to 258 nm and the signal from the sampling oscilloscope was fed into a digital storage oscilloscope (sweep time of 5 s/div). One spectrum was taken in 50 s. The measurements were repeated thrice and the signals were averaged in the computer. The sample was rotated at 1 rpm during the laser irradiation. The pulse energy of the laser was fixed at 300 mJ. Fig. 4b shows the result obtained from ordinary transparent glass containing no boron. Comparing these two spectra, it is seen that boron can easily be detected. This method has considerable promise for the rapid quantitative analysis of such light elements.

Fig. 4c shows how the emission intensity of the secondary plasma is stable for a glass sample. In this case the wavelength of the monochromator was fixed at 251.9 nm, one of the strong emission lines of Si. It should be noted that this curve is almost constant with little signal fluctuation, though it was obtained directly

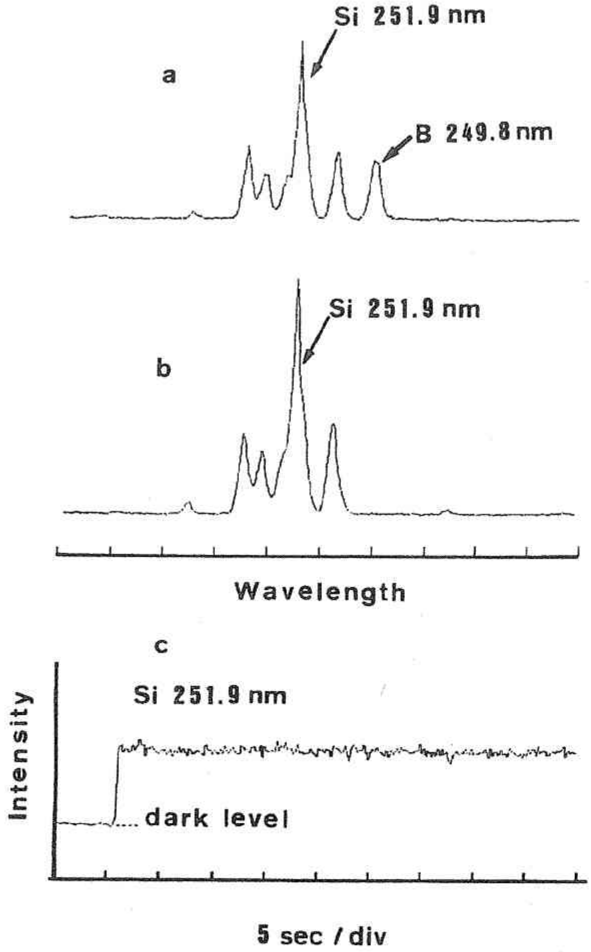

Fig. 4. Emission spectra obtained on the glass sample. (a) Glass containing a few percent of boron, (b) glass containing no boron. (c) Time variation of the emission intensity of the Si 251.9 nm line obtained in glass samples. Samples were rotated at 1 rpm under repeated irradiation of the TEA CO_2 laser with 5 Hz.

from the output of the sampling oscilloscope without passing through any smoothing circuit. This good stability of emission intensity endorses the possibility of high precision analysis.

In order to estimate the attainable detection limit due to this LISPS method, a glass sample containing 3% Mg was used. By comparing the emission intensity of the Mg 383.8 nm line with the background emission intensity taken near the tail of the emission line, the BEC was estimated to be about 0.005%. This value may be decreased in the near future.

In the LISPS method, the laser pulse energy and the height of the observation position above the surface of the sample are key factors for realizing high sensitivity analysis. As described in a previous paper, the primary plasma is the source of the shock wave [12]. In order to produce the primary plasma, the laser power density must be higher than about 10^9 W/cm^2. On the other hand, the laser pulse energy closely relates to the total amount of gushed atoms from the sample and determines their total kinetic energy. The kinetic energies of these atoms are mainly consumed in the initial explosion energy for producing the blast wave, the shock wave induced by a point explosion.

Sedov [19] derived, for a blast wave, a theoretical relationship between the propagation time, t, and the distance of the front from the position of the source of explosion, r, as follows:

$$r = (E_o/\alpha\rho)^{1/5} t^{2/5} \qquad (1)$$

where E_o is the initial explosion energy, ρ is the density of the surrounding gas, and α is a constant. From this equation the following equation can easily be derived.

$$v = (2/5)(E_o/\alpha\rho)^{1/2} r^{-3/2} \qquad (2)$$

where v is the velocity of the shock front.

On the other hand, the temperature just behind the shock front, T, can be expressed as follows [20,21].

$$T/T_o = [2\tau M^2/(\tau+1) - (\tau-1)/(\tau+1)][(\tau-1)/(\tau+1) + 2/(\tau+1)M^2] \qquad (3)$$

where T_o is the room temperature, τ is the ratio of the specific heat of the gas and M is the Mach number of the shock wave.

These equations are useful in order to understand qualitatively the characteristics of the plasma. From these equations, it is seen that the temperature just behind the shock front increases with E_o. This was proved in our experiment using Zn as the target. Thus, with increasing the energy of the laser pulse the speed of the luminous front of the plasma increases and plasma temperature also increases. When the plasma temperature is as high as 10,000 K, the background emission intensities become high. Therefore, high power laser pulses do not always bring high sensitivity analysis, although the total amount of gushed atoms become large. For spectrometric analysis, it is essential to enhance the ratio of the analytical emission line to that of the background. For this reason, suitable pulse energy of the laser light should be employed. At this stage, a laser pulse of 300 mJ was used for glass samples to obtain a sufficiently intense analytical emission line. In this case, the amount of sample needed to perform sufficient analyses is about 1 mg. If we employ an improved detection system such as optical multi-channel analysis (OMA) or a polychromator, however, the pulse energy can be decreased and the sensitivity of the analysis will be improved. Also, in such conditions the minimum sample needed will be decreased to ca. 100 ng.

Eqs. 2 and 3 can also explain the experimental fact that the background emission intensity decreases with the distance from the surface of the sample because the intensity of the continuum emission of the plasma decreases with decreasing temperature. Taking the spatial distribution of the emission intensity of the analytical line and that of background spectrum into account, the best position for the observation area must be chosen so that the ratio of the analytical emission line to that of the background emission has the maximum value.

4. Conclusions

It has been proved that a commercial TEA CO_2 laser, which is usually used for laser marking, can be employed as the excitation source for a laser-induced shock wave plasma, with limited application. A good analytical calibration graph was obtained for low-alloy steel standard samples. However, for high-speed steel samples selective vaporization takes place, which makes it impossible to determine tungsten, mainly due to lack of energy density of the focusing laser light. Therefore, the development of a new TEA CO_2 laser is proposed that meets the requirement for LISPS as the exciting source for shock wave plasma. For this purpose a TEA CO_2 laser with a nearly-single mode oscillation and with shorter pulse duration is desirable. If such a TEA CO_2 laser is developed the analytical method presented here will be applicable to any all metal samples.

For glass samples, this LISPS method is quite successful with a promise of high sensitivity analysis. It can be expected that by combining this TEA CO_2 laser-induced plasma with a polychromator, equipment for simultaneous multi-element analysis can be constructed and rapid quantitative analysis of glass samples can be made in the $\mu g\ g^{-1}$ level.

References

[1] E.H. Piepmeier, in E.H. Piepmeier (Ed.), Analytical Application of Lasers, Wiley, New York, 1986, p. 627.

[2] K. Laqua, in N.O. Omenetto (Ed.), Analytical Laser Spectroscopy, Wiley, New York, 1979, p.47.

[3] D.A. Cremers and L.I. Radziemski, in R.W. Solarz and J.A. Poisner (Eds.), Laser Spectroscopy and Its Application, Marcel Dekker, New York, 1987, p.351.

[4] N.G. Basov, O.N. Krokhin and G.V. Skizkov, JETP Lett., 6 (1967) 168.

[5] T.P. Hughes, Plasma and Laser Light, Adam Hilger, Bristol, 1975, p. 435.

[6] K. Kagawa and S. Yokoi, Spectrochim. Acta B, 37 (1982) 789.

[7] K. Kagawa, M. Ohtani, S. Yokoi and S. Nakajima, Spectrochim. Acta B, 39 (1984) 525.

[8] K. Kagawa, S. Yanagihara and S. Yokoi, J. Spectrosc. Soc. Jpn., 34 (1985) 306.

[9] K. Kagawa, Y. Matsuda, S. Yokoi and S. Nakajima, J. Anal. At. Spectrom., 3 (1988) p.415.

[10] K. Kagawa, Y. Manda, M. Ueda and Z. Li, J. Spectrosc. Soc. Jpn., 40 (1991) 150.

[11] K. Kagawa and H. Kurniawan, in H. Honma (Ed.), Proceedings of the International Work Shop on Strong Shock Waves, Chiba University, Japan, 1992, p. 97.

[12] H. Kurniawan, T. Kobayashi, S. Nakajima and K. Kagawa, Jpn. J. Appl. Phys., 31 (1992) 1213.

[13] H. Kurniawan, T. Kobayashi and K. Kagawa, Appl. Spectrosc., 46 (1992) 581.

[14] M. Tani, H. Kurniawan, H. Ueda, H. Mizukami and K. Kagawa, Jpn. J. Appl. Phys., 32 (1993) 3838.

[15] K. Kagawa, K. Kawai, M. Tani and T. Kobayashi, Appl. Spectrosc., 48 (1994) 198.

[16] A.F. Gibson, T.P. Hughes and L.M. Ireland, Phys. D, 4 (1971) 1527.

[17] K. Kagawa, Y. Deguchi, A. Ogata, H. Kurniawan, N. Ikeda and Y. Takagi, Jpn. J. Appl. Phys., 30 (1991) 1899.

[18] S.D. Rasberry, B.F. Scribner and M. Margoshes, Appl. Opt., 6 (1967) 87.

[19] L.I. Sedov, Similarity and Dimensional Methods in Mechanics, Academic Press, New York, London, 1959, p. 213.

[20] M.J. Zucrow and J.D. Hoffman, Gas Dynamics, Wiley, Chichester, New York, 1976, p. 346.

[21] H. Kurniawan, N. Ikeda, T. Kobayashi and K. Kagawa, J. Spectrosc. Soc. Jpn., 41 (1992) 21.