PHYSICAL CHEMISTRY 2014

12th International Conference
on Fundamental and Applied Aspects of
Physical Chemistry

The Conference is dedicated to the
25. Anniversary of the Society of Physical Chemists of Serbia

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September 22-26, 2014
Belgrade, Serbia

ISBN 978-86-82475-30-9

Title: PHYSICAL CHEMISTRY 2014 (Proceedings)
Editors: Ž. Čupić and S. Anić
Published by: Society of Physical Chemists of Serbia, Studenski trg 12-16, 11158, Belgrade, Serbia
Publisher: Society of Physical Chemists of Serbia
For Publisher: S. Anić, President of Society of Physical Chemists of Serbia
Printed by: "Jovan" Priting and Publishing Company; 200 Copies;
Number of pages: 6+ 441; **Format**: B5; Printing finished in September 2014.

Text an Layout: "Jovan"

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12th International Conference on
Fundamental and Applied Aspects of
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Organized by
The Society of Physical Chemists of
Serbia

in co-operation
with

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Boreskov Institute of Catalysis of Siberian Branch of the Russian Academy of Sciences

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ANALYTICAL CAPABILITY OF PLASMA INDUCED BY IR TEA CO_2 LASER PULSES ON COPPER TARGET

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ABSTRACT

Spatially-resolved time-integrated optical emission spectroscopy was applied for investigation of copper plasma produced by a nanosecond Infrared (IR) Transversely Excited Atmospheric (TEA) CO_2 laser, operating at 10.6 μm. The maximum intensity of emission, with sharp and well resolved spectral lines, and negligibly low background emission, was obtained from a plasma zone 8 mm from the target surface. The favorable signal to background ratio obtained in this plasma region, indicate possible analytical application of TEA CO_2 produced copper plasma. Detection limits of trace elements present in the Cu sample were in the order of 10 ppm.

INTRODUCTION

The plasma in LISPS (Laser-Induced Shock-Wave Plasma Spectroscopy) is generated by focusing of the laser beam onto the sample but at reduced gas pressures [1]. The created plasma, usually spherical in shape, emits from most of the volume intense and sharp spectral lines (mostly of the elements present in a target) with low background emission intensity. Good signal to background ratio, along with a linear relationship between spectral line intensity and elemental concentration in the sample, makes LISPS a suitable method for spectrochemical analysis [2,3].

Generation of copper target plasma, with low intensities of TEA CO_2 laser pulses was not reported in the literature until recently [4]. The aim of this investigation was to test the applicability of TEA CO_2 laser induced copper plasma under reduced air pressure for trace element spectrochemical analysis.

EXPERIMENTAL

Plasma was initiated by irradiation of a copper target with IR TEA CO_2 laser pulses. Typical output pulse energy was 150 mJ, and repetition rate during experiments was 1.5 Hz. The laser/optical pulse had a gain switched spike followed by a slowly decaying tail. Full width at half maximum of the spike was about 100 ns while the tail duration was ~2 μs. The energy sustained in the initial spike was about 35% of the total irradiated laser energy.

Copper sample was placed in a glass vacuum chamber closed with NaCl and CaF_2 windows. Minimum air pressure during the experiments was ~0.1 mbar. Preparation of a target surface before irradiation was an essential process, because of high reflectivity of copper for CO_2 laser emission line(s). The enhancement of surface absorption was achieved by increasing the target surface roughness. The target surface was mechanically treated with 320-grit SiC abrasive paper. Such procedure created clearly visible scratches (1 to 6 μm wide) on freshly prepared copper surface.

The optical emission from the plasma was viewed in the direction parallel to the target surface. By changing the position of plasma along the direction of a laser beam, while keeping the constant distance between focusing lens and a target, different parts of plasma were observed, i.e., a spatial plasma resolution was achieved. The horizontal part of the plume was projected by an lens on the entrance slit of a monochromator (Carl-Zeiss PGS2 dispersion 0.7 nm/mm). For the time-integrated spatially resolved measurements Apogee Alta F1007 CCD camera was used.

In this work we have used time-integrated space-resolved laser induced plasma spectroscopy (TISR-LIPS). TISR-LIPS was successfully applied for studying various laser induced plasma systems [5], and may be considered as similar to time-resolved spatially integrated emission spectroscopy. The method relies on the fact that intense plasma background spectral continuum emission is mostly emitted from a region close to the sample surface, while in further-out regions of the plasma the continuum emission is largely reduced. Thus, instead of time-gated detection the position-selective spectra were recorded. The time-integrated measurements provide average values in the different plasma spatial zones.

RESULTS AND DISCUSSION

The plasma was initiated by irradiation of a copper target with a fluence of ~ 8.6 J cm^{-2} in air atmosphere at the pressure of 0.1 mbar. The plasma consisted of two clearly distinguished and spatially separated regions. The first region, close to the target surface (length about 5 mm), was characterized by a whitish color and is known as primary plasma. The

second region, also known as the secondary plasma, was larger in volume, had a hemispherical shape and intense green color, due to emission of the spectral lines of the target. The plasma expanded to a distance of about 15 mm from the surface.

Time-integrated emission spectra of trace elements present in the Cu sample are shown in Fig. 1. The sample was high purity Cu (99.9 %) with traces of Fe (60 ppm), Ca (50 ppm), Ag (50 ppm) and Mg (6 ppm). The spectrum consisted of well-resolved sharp emission lines, and low background emission intensity. Good signal to noise, and signal to background ratios were obtained. The estimated limits of detection (LOD) are presented in Table I. Limits of detection are calculated using the formula LOD = 3 × BEC × RSD_B (BEC - background equivalent concentration, RSD_B - relative standard deviation of the background).

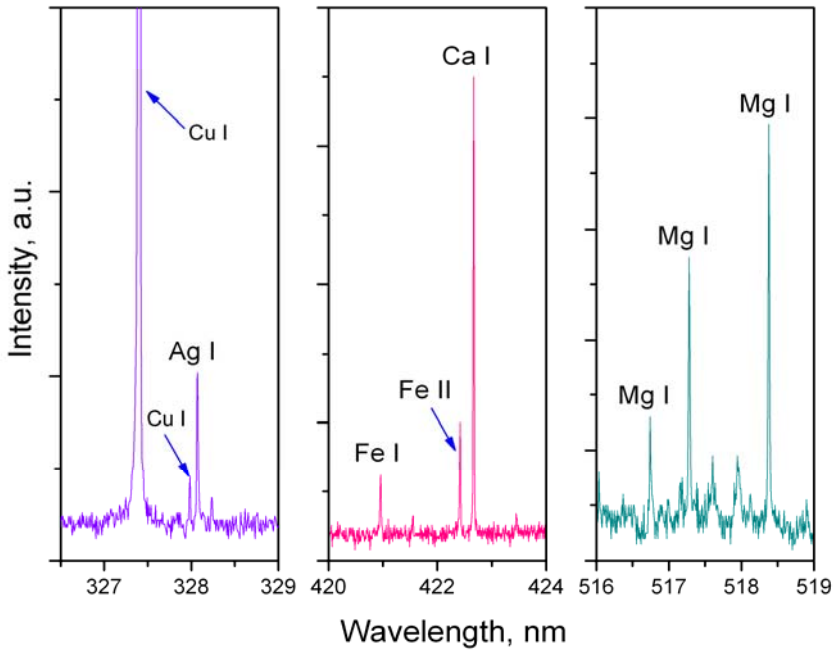

Figure 1. Time-integrated emission spectra of Fe, Ca and Mg obtained at a distance of 8 mm above the Cu surface.

Table 1. Estimated limits of detection.

Element	Wavelength, nm	LOD, mg/kg
Fe	422.42	10
Ca	422.67	4
Ag	328.07	5
Mg	518.36	1

CONCLUSION

The plasma was induced by irradiation of a copper target with 30 MW/cm^2 of TEA CO_2 laser peak intensity, in air at 0.1mbar. Time-integrated optical emission spectroscopy was applied for characterization of spatially-resolved plasma regions. The maximum intensity of Cu emission, and negligibly low background emission, was obtained from a plasma zone 8 mm above the target surface. Time-integrated emission spectra of Fe, Ca, Ag and Mg, which are the elements present in the copper sample as impurities, were used for evaluation of signal to background, and signal to noise ratio, and estimation of limit of detection. Detection limits in the order of 10 ppm imply that TEA CO_2 laser-induced copper plasma under 0.1 mbar air pressure could find analytical application.

ACKNOWLEDGEMENT

This work was supported by the Ministry of Education and Science of the Republic Serbia, project No. 172019.

REFERENCES

[1] A.M. Marpaung, Koo H. Kurniawan, M.O. Tjia and K. Kagawa, J. Phys. D: Appl. Phys., 2001, 34, 758-771.
[2] R. Hedwig, T.J. Lie, M.O. Tjia, K. Kagawa and Koo H. Kurniawan, Spectrochim. Acta B., 2003, 58, 531-542.
[3] Koo H. Kurniawan, T. J. Lie, K. Kagawa and M.O. Tjia, Spectrochim. Acta B., 2000, 55, 839-848.
[4] M. Momcilovic, M. Trtica, J. Ciganovic, J. Savovic, J. Stasic, M. Kuzmanovic, Appl. Surf. Sci., 2013, 270, 486–494.
[5] A. Khumaeni, M. Ramli, Y. Deguchi, Y. Lee, N. Idris, K.H. Kurniawan, T.J.J Lie, K. Kagawa, Appl. Spectrosc., 2008, 62, 1344-1348.