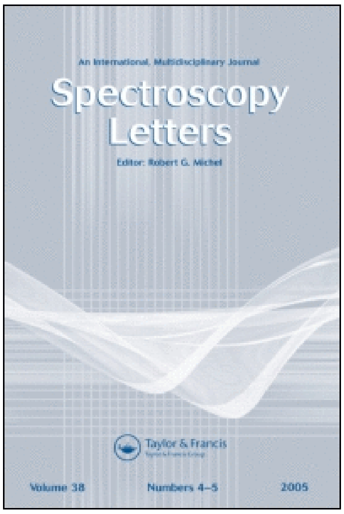

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Quantitative Elemental Analysis of Solid Samples by Arf-Excimer Laser-Ablated atomic Emission Spectrometry

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QUANTITATIVE ELEMENTAL ANALYSIS OF SOLID SAMPLES BY ArF-EXCIMER LASER-ABLATED ATOMIC EMISSION SPECTROMETRY

Key Words: Atomic emission spectrometry; ArF excimer laser; laser-ablated plasma

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Abstract

Quantitative analysis of chromium in standard low alloy steel samples by excimer laser ablated plasma atomic emission spectrometry was obtained. A calibration curve was developed which related the chromium concentration in a solid steel matrix to the intensity ratio of Cr(I) 520.84 nm to Fe(I) 516.75 nm. The chromium concentration determined ranged from 0.062 to 1.31 %. A detection limit of 20 μg/g (approximately 0.002 %) was estimated.

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INTRODUCTION

In recent years there has been considerable interest both from the fundamental and pragmatic point of view in laser ablated plasma production for use in direct elemental analysis of solid samples. A comprehensive review paper of lasers in atomic spectroscopy was published by Thiem et al.[1] Laser-ablated atomic emission spectrometry (LA-AES) is a potentially powerful tool for the study of elemental concentrations on solid surfaces. There are several advantages to LA-AES compared to conventional analysis methods, including the high spatial resolution provided by the focused laser pulse, the small (ng-µg) sampling size, the ability of the laser-ablated plasma to vaporize and excite the solids in one step without extensive sample preparation, and the ability to analyze through a window or at a certain distance from the sample. LA-AES has been primarily achieved by the use of solid state lasers such as Nd: YAG, Nd: glass and Ruby.

The recent development of powerful UV-excimer lasers has opened new possibilities in analytical atomic spectroscopy by providing efficient atomization and excitation processes. A series of recent publications[2-4] from this laboratory has shown that the shape, size and emission spectra of an ArF-excimer laser-ablated plasma are largely dependent on the atmospheric surroundings, gas composition and the pressure.

Spatial discrimination may be desirable to increase the line-to-background (L/B) ratio in atomic emission spectrometry.

In this paper, the preliminary results for the quantitative analysis of chromium in standard low-alloy steel samples by ArF-excimer LA-AES through space-resolved techniques and studies are described. This is the first report of quantitative analysis by ArF-excimer laser ablated-AES.

EXPERIMENTAL

The experimental instrumentation, setup and procedures used in this study have been detailed previously[3,4] and briefly described here. An ArF-excimer laser (Questek 2420, Billerica, MA, λ = 193 nm) beam with 120 mJ/pulse (about 77 mJ/pulse on the metal surface due to the lens reflection), pulse duration of 10 ns and repetition rate of 1 Hz was used for laser ablation. The laser beam was focused to a spot size of 0.65 mm^2 which results in a power density of 1.2×10^9 W cm^{-2} by two silica spherical lenses.

The solid samples were placed in a stainless steel chamber which could be evacuated by a roughing pump and filled with a helium gas (99.997 %). A series of National Institute of Standards & Technology (NIST) (Gaithersburg, MD) steel standards were used at an atmospheric pressure of helium. Table 1 shows the elemental composition of the standard low-alloy steel samples.

Table 1. The elemental compositions (%, by weight) of NIST standard steel samples used in this work.

Sample	Fe	Cr	Ni	Mn
1261a	95.6	0.69	2.00	0.67
1262a	95.3	0.30	0.60	1.05
1263a	94.4	1.31	0.32	1.50
1264a	96.7	0.06	0.14	0.25

The monochromator and focusing lens were mounted onto a stainless steel multi-axis stage which allowed simultaneous movement by micrometer positioners for space-resolved emission spectrometry. Prior to each measurement, the photodiode detector was calibrated with the use of the lines of a mercury emission lamp. The atomic emission of the laser-ablated plasma was detected by a photodiode array system (Model 77115, Oriel Co.) which consists of 512 detector elements ($\Delta\lambda$ = 0.33 nm/element) with 2.5 mm height by 50 μm width and processed by an IBM/AT compatible computer. The emission was integrated within 2s (two laser shot) of exposure time and averaged 16 spectra taken for each sample.

RESULTS AND DISCUSSION

Direct observation of the laser-ablated plasma using atomic emission spectroscopy is the simplest method and

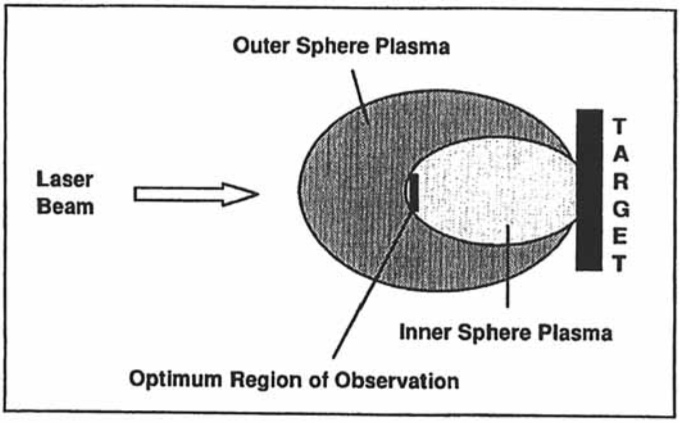

Fig. 1. Schematic diagram of the ArF excimer laser-ablated plasma.

offers the potential of simultaneous multielement analysis. Since metals and their alloys are the most widely used materials in industry, it is very important to know their composition with rapid and precise methods of on-line analysis.

Our previous work[3,4] showed that high L/B ratio could be obtained under an atmospheric pressure of helium gas because of the relatively high thermal conductivity [360.36 (10^{-6} cal s^{-1} deg^{-1} cm^{-1}) at 298 K][5] and through space-resolved spectrometry.

A schematic diagram of the plasma produced by the interaction of the excimer laser beam with metal target is shown in Fig. 1. The plasma consists of two distinct regions,

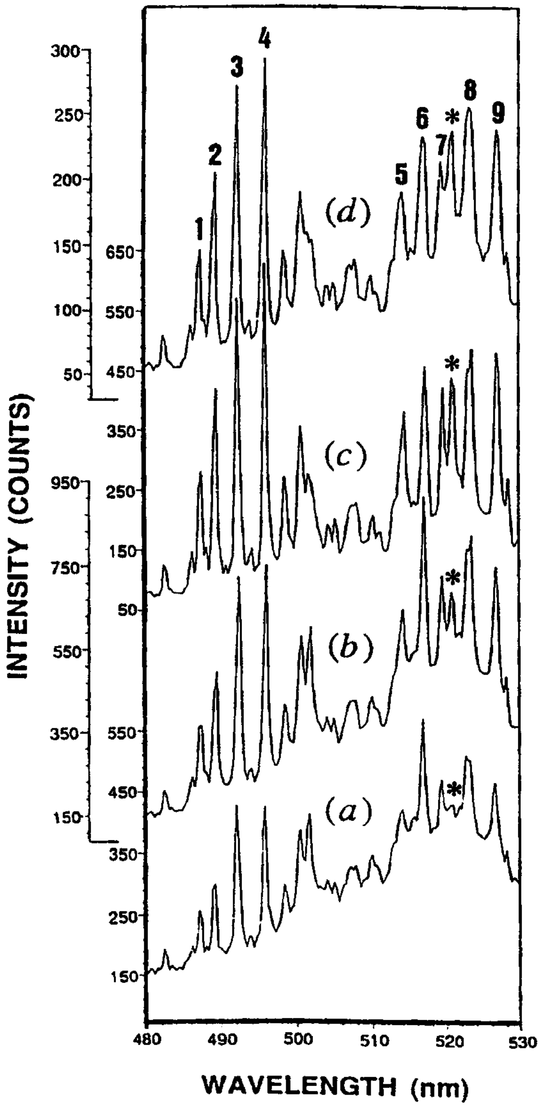

Fig. 2. Space-resolved spectra of the ArF excimer laser-ablated plasma with standard steel sample (NIST 1263a) in an atmospheric pressure of helium at (a) 0.6 mm, (b) 1.0 mm, (c) 1.6 mm, and (d) 2.0 mm, from the surface.

Table 2. The assignments of the observed emission lines in the laser-ablated plasma.

Element	Wavelength (nm)		Label in
	Exp.	Ref.[6]	Fig. 2 & 3
Fe(I)	487.33	487,13	1
	489.22	489.15	2
	492.04	492.05	3
	495.80	495.76	4
	513.79	513.95	5
	516.56	516.75	6
	519.01	519.49	7
Cr(I)	520.55	520.84	*
Fe(I)	522.99	522.72	8
	526.65	526.95	9

called the "inner sphere plasma" and "outer sphere plasma", under an atmospheric pressure of helium.

The spectra emitted by the laser-ablated plasma vary depending significantly on the location of the plasma after the irradiation of the laser pulse. This is illustrated in Fig. 2 showing a part of the spectra (480 nm-530 nm) at different positions. High background continuum was observed near the metal surface.

Near the edge of inner sphere plasma shows the ideal emission spectra (highest L/B ratio) for spectrochemical analysis [Fig. 2 (c)]. The analysis of emission spectra reveals

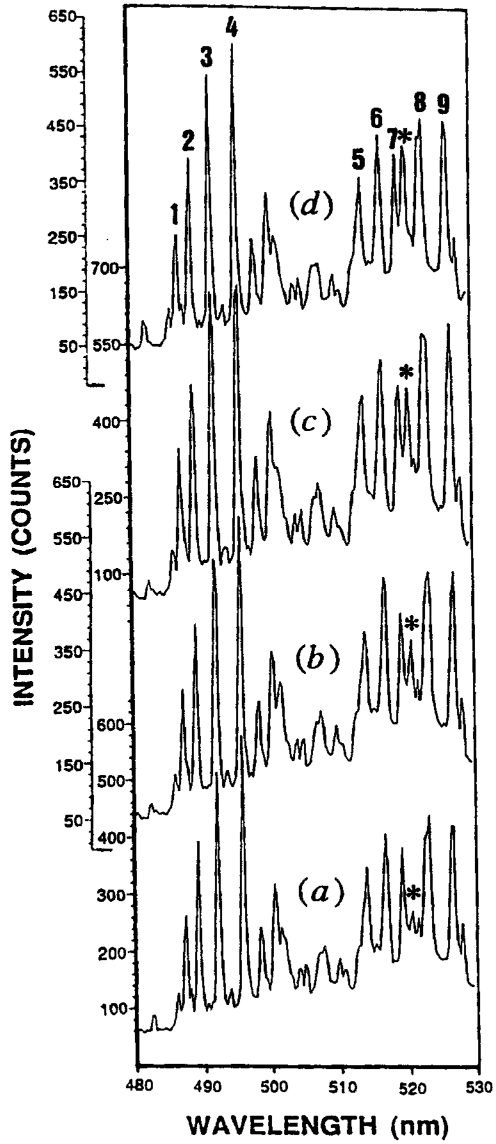

Fig. 3. ArF excimer laser-ablated emission spectra of NIST standard steel samples; (a) 1264a, (b) 1262a, (c) 1261a and (d)1263a, at the optimum region of observation in the plasma under an atmospheric pressure of helium.

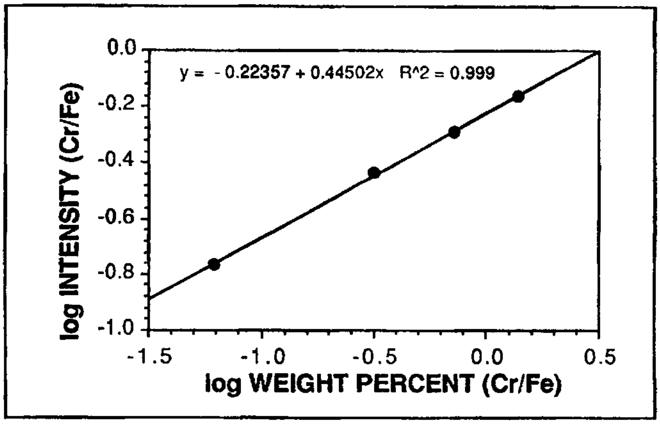

Fig. 4. Calibration curve for chromium; Intensity ratio of the Cr(I) 520.84 nm to the Fe(I) 516.75 nm line versus the concentration ratio of Cr/Fe.

that the majority of the lines are in fact assigned to Fe(I), as detailed in Table 2.

Chromium neutral atom line [Cr(I)] was observed at 520.55 nm (ref. 520.84 nm). Fig. 3 shows the emission spectra of different samples at the optimum region of observation in the plasma. The role of space-resolved observation is emphasized for an optimum line-to-background (L/B) of emission in the plasma. For internal standardization, the line pair of Cr(I)/Fe(I) (520.84 nm/516.75 nm) was selected.

Four NIST samples were used to establish a calibration curve for Cr(I) at 520.84 nm. These are shown in Fig. 4. The concentration ratio in weight percent of Cr/Fe were 0.062, 0.315, 0.720, and 1.377. Each data point was obtained by subtracting the average background from the line intensity. The intensity was measured by integrating the emission of the plasma over two laser shots. The logarithmic calibration curve for Cr concentration was linear up to a concentration of 1.31 %. The slope of the line fit to the four concentration points is 0.44502 with a correlation coefficient, r = 0.999.

CONCLUSION

The major advantage of the ArF excimer LA-AES is the ability to perform direct detection of solid samples in real time. A direct spectrochemical analytical method of solid samples with good linearity has been developed by ArF-excimer laser-ablated atomic emission spectrometry (LA-AES). The detection of emission signals can be performed in an optimum location of the ablated plasma without time delay.

The sensitivity of the signal depends on the chemical matrix of the sample, with an estimated detection limit (based on the spectrum) of 20 µg/g (aproximately 0.002 %) in low-alloy steel samples. A more detailed analytical performance characteristic study of the ArF excimer LA-AES is in progress, including accuracy, precision and other metals and will be reported in due course.

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