



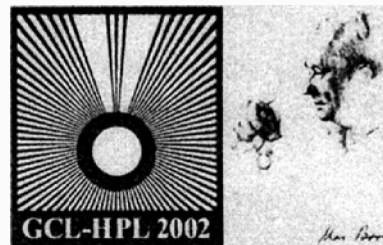
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# In-situ analysis of steel under reduced ambient pressure by laser-induced breakdown spectroscopy

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## ABSTRACT

We report on rapid in-situ analysis of liquid and solid steel samples under reduced ambient pressure by laser-induced breakdown spectroscopy (LIBS) using a transportable system. LIBS denotes a technique where a pulsed laser beam is used to ablate small amounts of the target material. The characteristic optical emission line intensities of the excited species in the laser-generated plasma plume allow a quantitative chemical analysis of the target material. Over a wide range of parameters the expansion of the plume can be described by a generalized shock wave model. LIBS is a fast, non-contact method, which can be carried out under various atmospheric conditions allowing large working distances between the sample under investigation and the detection system. These properties make LIBS applicable to process control especially for vacuum devices used in metallurgy.

Keywords: Laser-induced breakdown spectroscopy, in-situ analysis, steel, reduced ambient pressure

## 1. INTRODUCTION

The standard procedure for metallurgy process control involves several steps including drawing a sample from the melt, transport to the laboratory, sample preparation and finally the analysis of up to 30 elements. Many processes in secondary metallurgy are performed under vacuum typically at a pressure  $p$  of 0.1 to 5 mbar. The purpose is mainly the reduction of gaseous compounds (as  $H_2$ ) from the liquid melt. Here the drawing of samples is especially complicated because it requires either an interruption of the process (opening of the device, drawing of the sample, and renewed evacuation) or the use of an automatic sample drawing system in combination with a vacuum-slucice. A significant reduction of the time necessary to gain information about the composition of the melt can be achieved by analyzing the liquid metal under vacuum direct in the melting pot.

An in-situ analysis of steel in metallurgic vacuum devices requires a fast, non-contact and reliable method with no need of any sample preparation. Laser-induced breakdown spectroscopy (LIBS) meets these demands. A pulsed laser beam is focused onto the sample with laser-light intensities well exceeding the ablation threshold of the material resulting in plasma formation above the target surface. The spectroscopic investigation of the light emitted by the excited species in the plasma plume permits the quantitative determination of the sample's elemental composition by relating characteristic line intensities of the material's constituents. LIBS measurements have been performed on various

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materials<sup>1-6</sup> including solid<sup>7,8</sup> and liquid steel.<sup>10-12</sup> The LIBS results can vary depending on the length of the laser-pulse and the ambient atmospheric conditions during the plasma expansion.<sup>13-15</sup>

In the present paper we report on rapid in-situ analysis of liquid steel and solid steel samples under reduced ambient pressure by LIBS using a transportable system, which was developed in the frame of a co-operation of Voest-Alpine Industrieanlagenbau and the university in Linz. The experimental setup is designed for field application and was tested at a metallurgic vacuum-degassing (VD) device in the steel-mill of Böhler Edelstahl in Kapfenberg.

## 2 EXPERIMENTAL SET-UP

A schematic picture of a typical LIBS setup is shown in Fig. 1. A pulsed laser, which is often a Nd:YAG laser (but also other pulsed laser sources can be used), is focused onto the sample surface by means of mirrors and lenses. The typical laser fluences  $\phi$  at the surface are between 5 and 10 J/cm<sup>2</sup> corresponding to laser-light intensities of several 100 MW/cm<sup>2</sup> for ns-pulses. For solid or liquid metals these intensities are high enough to induce vaporization of the material and subsequent plasma formation above the sample surface typically within some nanoseconds.<sup>16</sup> The laser pulse is absorbed by the plasma, causing an optical breakdown. As a consequence, the hot and radiative plasma expands into the semi-space above the target. After a short delay with respect to the laser pulse the light emitted by the plasma consists mainly of atomic or ionic emission lines and is collected again by lenses and mirrors and focused onto the entrance slit of an optical grating spectrometer. The resulting spectra are then recorded and analyzed in a computer.

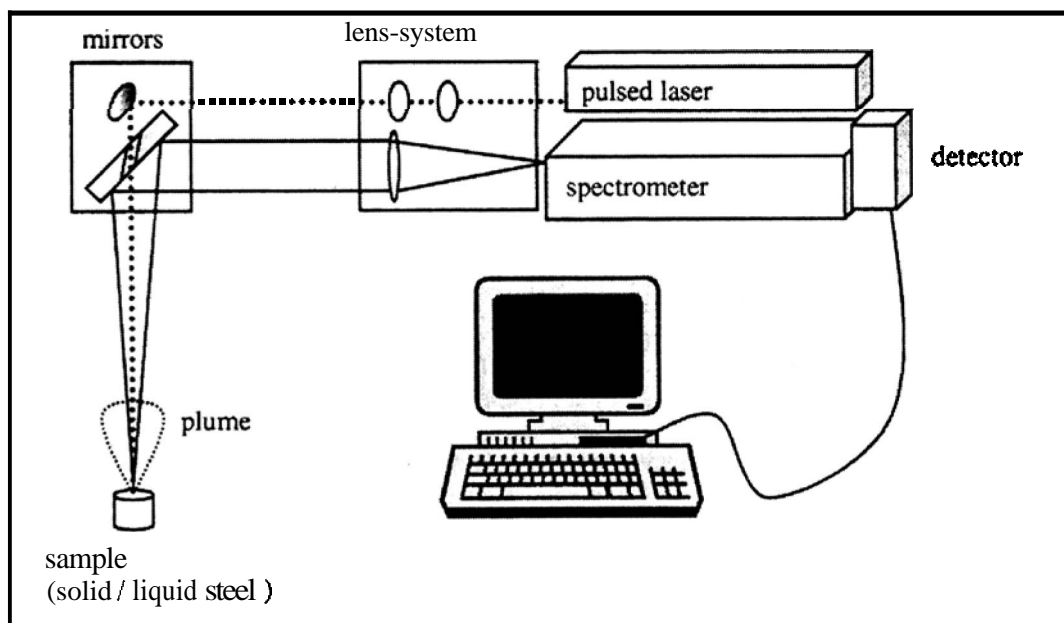


Figure 1: Typical LIBS setup

### 3, PLUME EXPANSION

In a small vacuum chamber the propagation of the plasma plume **from** a solid stainless steel target **was** visualized perpendicular to the laser beam by means of an **ICCD-camera (Photometrics)** equipped **with** a standard Nikon 5011.8 objective. This system includes a **gateable** micro-channel plate image-intensifier. The gate had a variable delay with respect to the laser pulse. Pictures of the visible plasma plume were recorded for various delay times,  $t$ , laser-pulse energies,  $E$ , and Ar background pressures,  $p(\text{Ar})$ . The laser **used** here **was** KrF excimer-laser emitting at a wave-length of  $\lambda = 248 \text{ nm}$  with a pulse-length  $\tau_l = 30 \text{ ns}$  and was focused to a spot of  $0.72 \text{ mm}^2$ . The visible plume, which can be detected immediately after the laser pulse, originates from excited ions, atoms and small molecules. The **maximum** intensity,  $I$  of the emitted light decreases with increasing delay time. The plume can be recorded for several  $\mu\text{s}$ , depending on  $E$  and  $p(\text{Ar})$ . Figure 2 shows time-resolved photographs of **the** plasma plume. To quantify the expansion of the plume the boundary was defined at 10% of  $I_{\text{max}}$ .

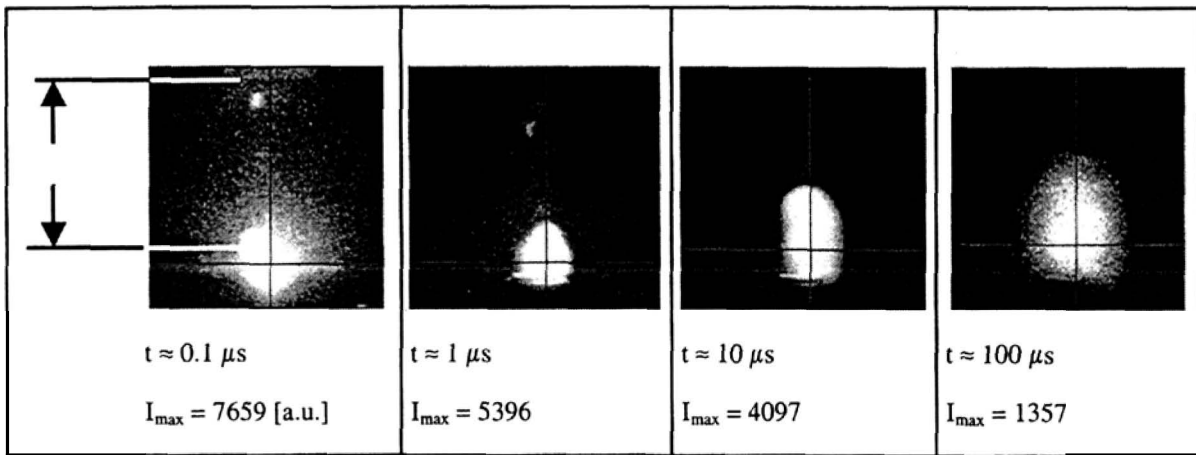


Figure 2: Time resolved photographs of plume expansion **with** delay  $t$  (KrF excimer-laser,  $p(\text{Ar}) = 1 \text{ mbar}$ ,  $E = 36 \text{ mJ}$ ). Positions of  $I_{\text{max}}$  indicated by hair crosses.

Over a wide range of parameters the plume can be described by a generalized shock wave expansion **model**.<sup>16,17</sup> It is based on the laws of mass, momentum and energy conservation. In the course of expansion the energy is redistributed between the **thermal** and kinetic energies of the plume and (internal and external) **shock waves (SW)s**. The expansion is described by the ordinary differential equations for the characteristic radii  $R$  (contact surface, **SWs** positions). The initial stage is similar to the inertial expansion into vacuum, with radius  $R \propto t$ . The internal SW propagates inwards from the contact surface. Later expansion follows the point blast model with  $R \propto t^{2/5}$ . Here, the homogenized plume is decelerated and heated due to the counter-pressure of the ambient gas, which forms an external SW. At a certain distance from the target the plume stops (and slightly contracts), **while** the external SW weakens **and** detaches from the contact surface. The region where the expansion **follows** strong SW **laws** depends on the ratio of initial (vacuum) velocity to ambient sound velocity,  $c_s$ . A unified approach includes all stages.

Figure 3 shows a comparison of the **calculated** contact boundary  $R_c$  and the plume boundaries measured by the gated ICCD camera. The agreement between theory and experiment is good, though virtually no fitting parameters were used. The mass of the plume was taken from the expansion velocity at low pressures. One can clearly see the free expansion - strong SW transition and the stopping point. Their positions (especially for stopping) are in good agreement with theory both in distance and in time. Discrepancies can be due to the non-spherical geometry of real expansion, losses of energy

for sample heating, plasma radiation, recombination processes, etc. Deviations, noticeable for steel at low pressures, may also be due to difficulties in determination of the plume boundary in this region.

Description of expansion dynamics of LIBS experiments performed under higher pressures and/or higher laser fluences requires consideration of hydrodynamic instabilities (as shown in Fig. 4) at the expansion front. As can be seen from Fig. 5 the unstable regime (with instabilities) includes the parameters normally used for LIBS analyses under ambient pressure. In general, the resulting irregular plumes are smaller than expected from the calculated curve in Fig. 3, at least for plumes from a solid steel target produced by means of a KrF-laser.

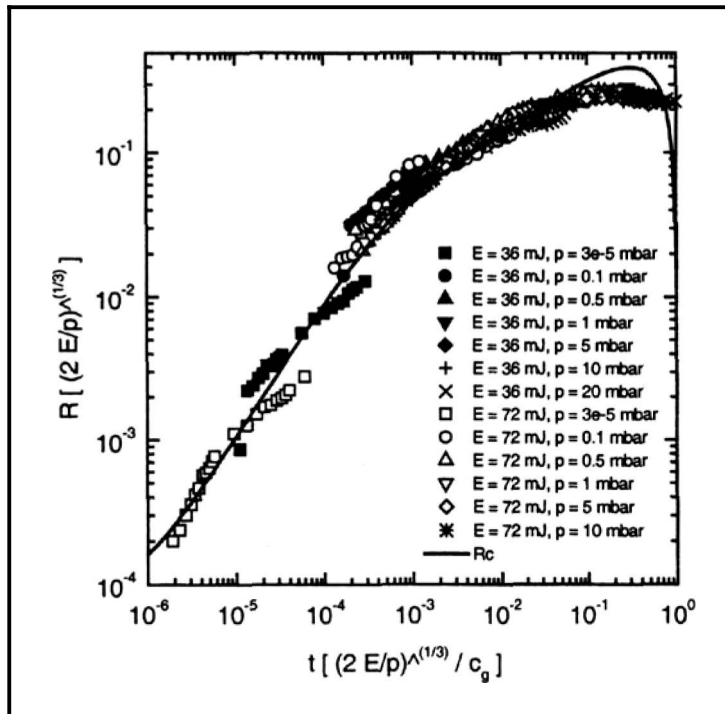


Figure 3: Plume expansion for KrF excimer-laser ablation from solid steel target



Figure 4: Plume expansion from a steel target

(p(Ar) ≈ 10 mbar, φ = 10 J/cm<sup>2</sup>, t = 1.3 ps)

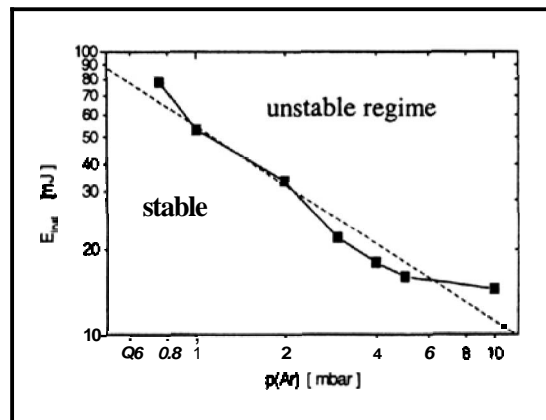


Figure 5: Stable/unstable expansion with a KrF excimer-laser

One should keep in mind that in Fig. 3 normalized coordinates are used. The absolute value of the stopping distance and the stopping time are proportional to  $p^{-1/3}$ . While under atmospheric pressures, the plasma propagation stops after several ten nanoseconds (whereas the light emission continues for some ten microseconds) and the characteristic dimension of the plasma plume is of the order of a few millimeters. With reduced pressure the stopping times and distances can be considerably longer. As a consequence the thermal energy density of the plume, the emitted light intensity and the relative intensity of various atomic or ionic transition lines depend on the ambient pressure. This can be seen, e.g., in the time dependence of the maximum optical emission intensity,  $I_{\max}$  derived from time-resolved photographs (Fig. 6). Similar as reported in ref. [14], we found in our laboratory tests, that at low pressures the detected intensities can be too small to perform a LIBS analysis for a given laser energy. A final proof of principle for liquid steel analysis under reduced pressure therefore had to be performed in a field experiment.

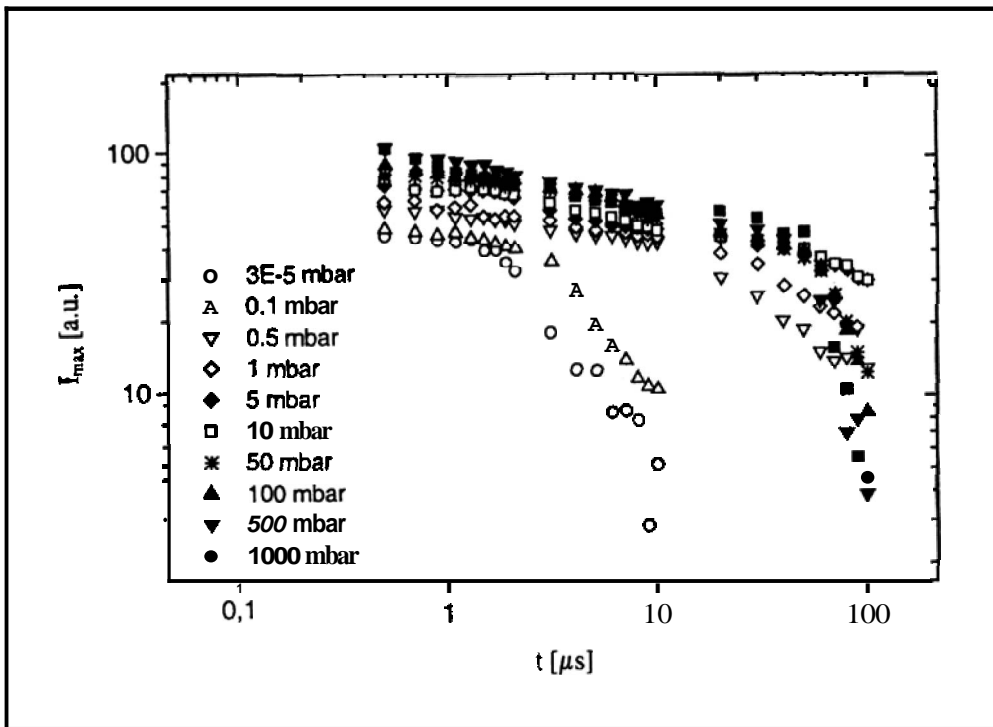


Figure 6: Temporal behavior of the maximum intensity in the plasma plume ( $E = 72 \text{ mJ}$ )

#### 4. EXPERIMENTS AT A METALLURGIC DEVICE

For the field experiments we used a transportable system, which has been developed from the setup described in ref. [10]. A Q-switched Nd:YAG laser ( $\lambda = 1064 \text{ nm}$ ,  $\tau_1 = 10 \text{ ns}$ ) is focused on the surface of the analyte by a concave spherical mirror. The transportable equipment was mounted on the hydraulic lid of a VD-device in a working stainless steel mill (Fig. 7) connected to the vacuum vessel by a gas-flushed window. The diameter of the vacuum chamber was about 4 m. The distance between the focusing mirror and the surface of the liquid melt in the 50 t pan was also in the order of 4 m and varied depending on the actual filling of the pan. For the treatment the lid is moved hydraulically above the vacuum chamber and the device is pumped down to a pressure of about 1 mbar. From below the pan can be flushed by either Ar or N<sub>2</sub>, which is bubbling through the liquid melt resulting in an open slag free surface, onto which the laser was focused.

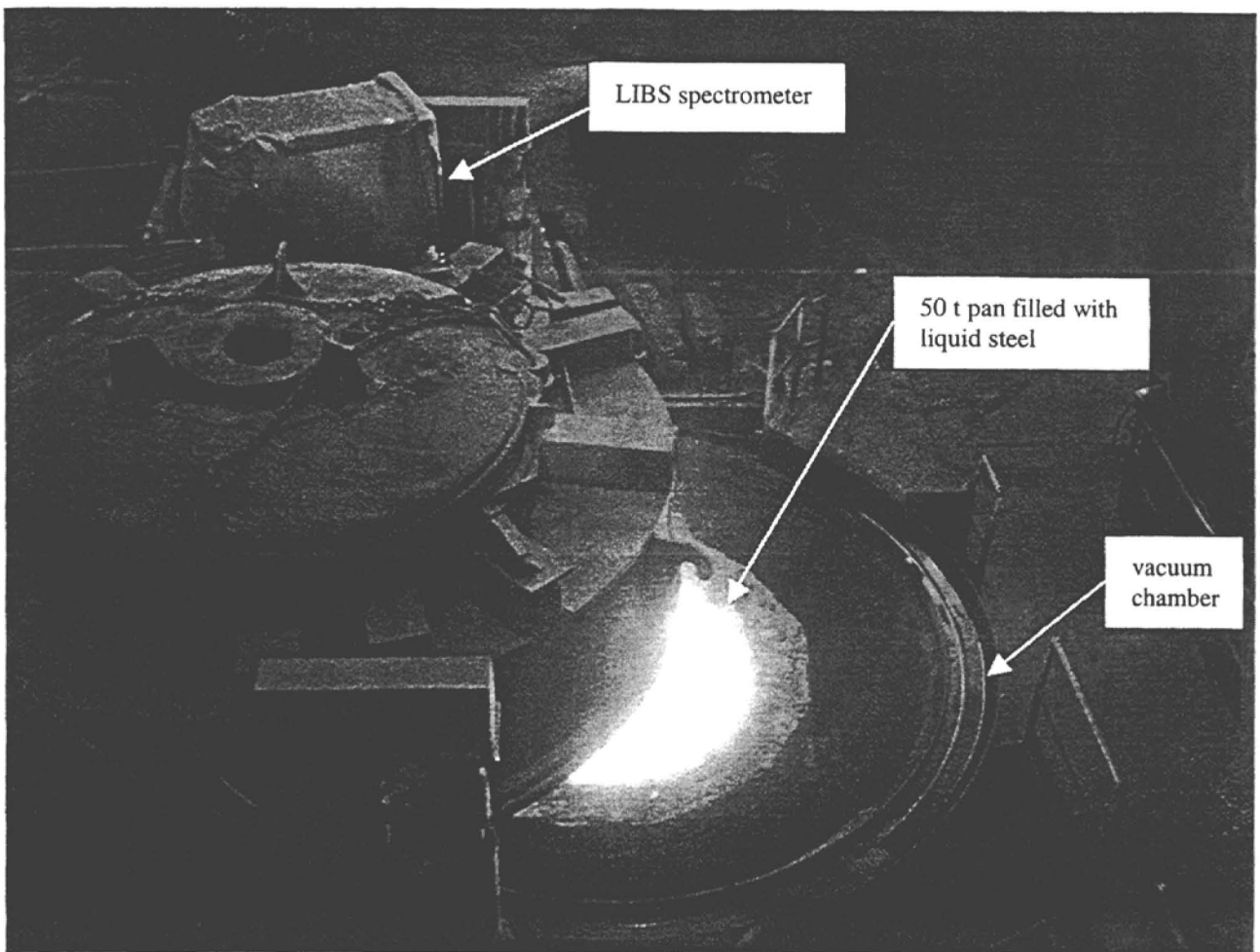


Figure 7: LIBS-spectrometer mounted on lid of a metallurgic vacuum-degassing (VD) device

The experiments are described in detail elsewhere.<sup>18</sup> Facing the harsh environmental conditions, the result of the evaluation of the LIBS spectra was, especially for the determination of the relative content of Cr, Mn and Ni, very satisfactory. Figure 8 shows as example the comparison of the LIBS results to the standard laboratory analysis of the company for 12 different stainless steel heats in the VD-device. The insert shows the spectral region used for Cr. As measure for the relative content we took the intensity ratio of the indicated Cr- and Fe-lines. The error bars show the standard deviation of typically 5 analyses of one heat.

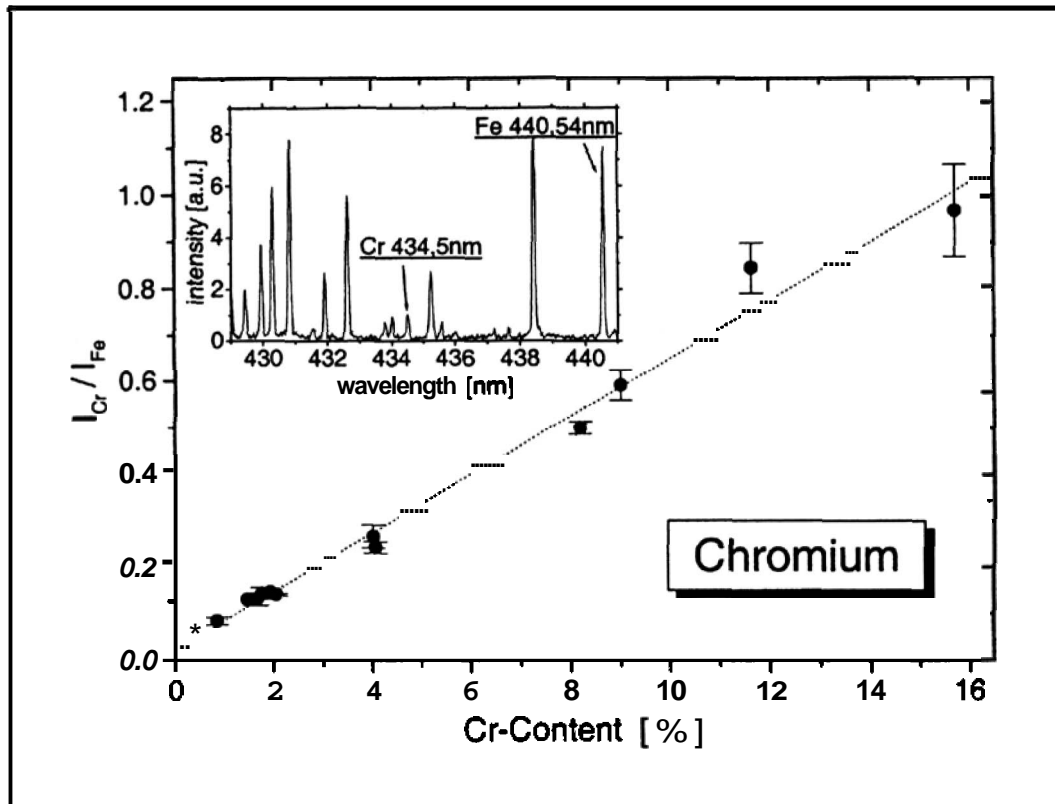


Figure 8: Comparison of in-situ LIBS results with standard laboratory analysis for Cr (Insert: evaluated spectral lines)

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