

Analysis of trace metals in comparison of laser-induced breakdown spectroscopy with LA-ICP-MS

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Abstract

Laser-induced breakdown spectroscopy (LIBS) and LA-ICP-MS (laser ablation inductively coupled plasma mass-spectrometry) were used for the detection of trace metals in a solid matrix consisting of KBr and two oxides. The results of both methods were compared to investigate the strengths and weaknesses of both methods. Most difficulties for quantification of LIBS data are related to matrix effects and self-absorption. The influence of the sample preparation on detection and quantification for LIBS data is not significant, with typical deviations in the range of <10%. In the case of LA-ICP-MS the detection limits are in principle lower and the quantification is also more precise, but the preparation method strongly influences these data. The oxidation state of the elements as well as the absorption coefficient of the trace metals influence the detection limits of LIBS. The plasma temperatures and the electron densities were determined from the emission spectra, and are typically in the range of 6000–10 000 K and between 6.2×10^{17} – 6.8×10^{17} cm⁻³.

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1. Introduction

The pollution of the environment increased rapidly during the last years, especially the contamination of soil and groundwater. There is an increasing need to determine concentration of contamination rapidly and precisely, in particular those of toxic heavy metals. Most available methods utilize expensive equipment or consist of time-consuming laboratory analyses, resulting in the need for fast and in-situ methods [1].

LA-ICP-MS is one of the most established analytical methods for the quantification of trace elements. This technique has been applied in laboratories for many years for the precise analysis of trace elements with concentrations of less than 1 ppm. LIBS is an elemental analysis method that requires in principle only optical access to the sample surface and can therefore be used as a real in-situ method. Several trace elements can be measured simultaneously at limits of detection in the parts per million range [2].

For both methods, a laser pulse is applied to ablate the sample. Vaporization and ionization of the material, resulting in a hot plasma, is used to analyze that material directly by LIBS. In LA-ICP-MS, the ablated material is transported using a carried gas to the ICP, where the particles are vaporized and ionized. The analysis of LIBS utilizes the emission from the de-excitation of atoms and ions, which is analyzed in a spectrometer. The elements are identified by their unique spectral signatures. The analysis in LA-ICP-MS is based on the production of ions within the ICP source, which are then recorded accordingly to their m/z ration. Quantification is based on external reference materials and internal standardization.

Some advantages of LIBS are the speed of analysis, the ease or absence of sample preparation, its relatively low cost, and the possibility to build portable instruments that allow real field analysis [1]. The problems of LIBS are due to the large number of factors, which influence the observed spectral intensities, and the large deviations in quantitative analysis [3].

Our studies show that LIBS can be used as a complementary method or an alternative technique to LA-ICP-MS. Several parameters, such as laser energy, irradiation

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wavelengths, and some matrix effects that may influence the detection and quantification of the trace elements are studied in detail.

2. Experimental setup

2.1. Experimental technique for LIBS

An ArF excimer laser (Lambda Physik LPX 300) emitting at 193 nm and a XeCl excimer laser emitting at 308 nm were used as irradiation sources. The laser was focused on the sample surface by a lens with 100-mm nominal focal length. An optical attenuator is used to vary the energy of the laser pulses. The fluence at the sample surface was normally between 0.5 and 3 J/cm². The plasma emission is collected with a fiber optic in the distance of 5 cm to the target, which is coupled to the input slit (25 μm) of a spectrometer (Princeton Instruments, 1200 lines/mm), and is detected by a gated intensified CCD camera (Princeton Instruments). The time delay between the laser pulse and the start of the measurement was chosen in order to maximize the signal to ground signal (Bremsstrahlung) ratio. Typical experiments applied time delays between 900 and 1200 ns and an acquisition time of 200 ns. The spectra of 50 laser pulses were accumulated to obtain satisfactory signal intensity. The samples were mounted on a computerized *x*, *y*, *z* table to change the positions between the measurement in order to avoid too deep ablation craters.

2.2. Experimental technique for LA-ICP-MS

The experimental setup for LA-ICP-MS is described in details some elsewhere [4]. Briefly a pulsed (Lambda Physik) ArF excimer laser ($\lambda = 193$ nm) and a quadrupled Nd: YAG (Q-switched Quantel Brilliant B, emitting at 266 nm) were used to ablate the sample. The ablated material is transported by an argon flow to the inductively coupled plasma source, i.e. the ICP torch, where the particles are vaporized, atomized and ionized. The ions are passed into the vacuum via the sample and skimmer cone interface, where a lens stack focuses the ion beam into a quadrupole mass spectrometer (PERKIN-ELMER ELAN 6000, Norwalk, USA). The ions are separated by mass per charge ratios and detected using a scanning electron multiplier.

3. Results and discussion

3.1. Sample preparation

NIST 610, 612 and 614, glass samples were used as standard references to calibrate the LA-ICP-MS data. The sample measurements were carried out with pressed pellets, consisting of a matrix (5% Al₂O₃, 15% CaCO₃,

80% KBr) and variable concentrations of transition metal salts (PbCl₂, CuCl₂, CrCl₃, CrCl₃·6H₂O, CrCl₂, Cr₂O₃, CrO₃, CrP, CrPO₄, Cr(NO₃)₃ and Cr). The influence of the sample preparation methods was analyzed by preparing three different samples types, i.e. finely ball-milled, roughly ball-milled and unground pellets. The grain size in the different pellets varies significantly, resulting in variation of the ablation diameter under same experimental conditions. In the case of the unground samples, very rough crater bottom surfaces were detected with a crater diameter of 600 μm, i.e. 100 μm larger than for the finely ball-milled samples.

The highest reproducibility was obtained by LA-ICP-MS on NIST 610 standard reference samples with a relative standard deviation (R.S.D.) of 1–2%. In the case of the finely ball-milled sample pellets, the R.S.D. for LA-ICP-MS was between 4 and 10% for the matrix elements, and 12–25% for the trace elements. The unground samples revealed a R.S.D. of 40–50% for matrix elements and up to 150% for the metals. These data indicate that the distribution of the added elements depend significantly on the sample preparation procedure. For LIBS a similar R.S.D. is detected for the matrix elements as well as for the trace metals. In the case of unground samples, the deviation is 12–25%, and for the finely ball-milled pellets between 4 and 9%. The standard deviation of the LIBS results is improving with an increasing number of accumulations.

3.2. Calibration curves/detection limits

In the case of LA-ICP-MS, the concentration of the trace elements were measured using non-matrix matched calibration standards using internal standardization. The LIBS-calibration curve must be determined for each experimental setup and any changes can affect the calibration. One important feature of emission spectroscopy is the possibility of self-absorption, which results in a non-linear relation of emission intensity and concentration as shown in Fig. 1. Self-absorption in spectroscopy occurs, when the number of gas phase species is large enough to absorb part of the emitted light. Self-absorption in our experiments occurs for Cu(I) approximately 250 ppm and for Cr(I) depending on the chromium salt, in the range of 250–500 ppm.

Both methods allow measurements in the lower parts per million range. The detection limit for Cu is for LA-ICP-MS 2–5 ppm, and <10 ppm for LIBS. The Chromium detection limits for LA-ICP-MS are also < 10 ppm, and for LIBS, dependent on the oxidation stage between 5 and 25 ppm.

3.3. The matrix effects in LIBS

In the spectral range from 270 to 700 nm only four emissions lines of Chromium(I) and two emissions line

of Cu(I) could be used for the quantitative analysis. It was impossible to define an isolated line of Pb(I, II), due to the low intensity of some Pb lines, and the interference, i.e. overlapping, with strong Ca(I) and K(I) lines.

The intensity of Cr(I) lines in samples containing anhydrous chromium (III) chloride were lower than in samples with chromium(III) chloride·6H₂O. The crystal water in the samples does not affect the LA-ICP-MS measurements. A change of the crystal water content of the matrix using Al(OH)₃ instead of Al₂O₃ did not affect the intensity of the emission lines with LIBS. Much higher laser energies are needed to ablate the sample and to create the plasma when water was added, i.e. by adding water drops onto the surface of the pellets. The resulting ablation volume is much higher and cannot be measured, due to extreme undefined ablation crater.

3.4. Ablation parameters

The LIBS experiments were performed in various backgrounds, i.e. in air, Ar and He. The highest intensities are obtained with the Ar background, followed by He, and air. The increase of the emission intensity in Ar was sometimes too high for the detection with the ICCD camera. No changes of the ratios of ionized vs. neutral species were detected for the different backgrounds, and an increase of intensity of the emission line could also be obtained by applying higher laser fluences. Therefore, the simplest experimental conditions were chosen in the following experiments, i.e. air as background without any chamber.

The irradiation wavelengths have also a pronounced influence on the emissions intensity of LIBS. Fig. 2

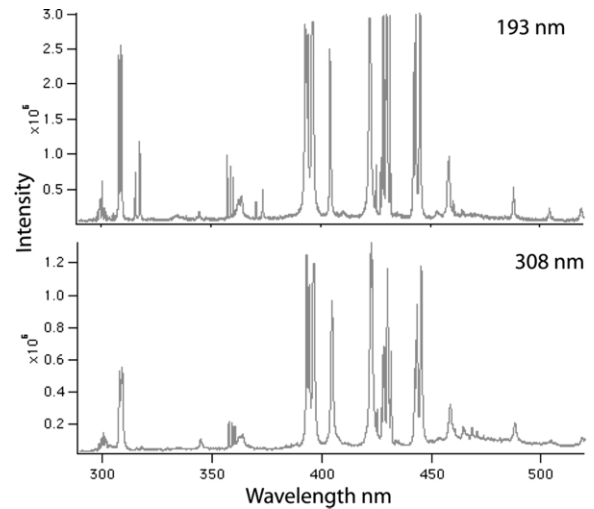


Fig. 2. Emission spectra at different laser wavelengths.

shows the high signal intensity resulting for irradiation with the 193 nm ArF excimer laser. It is possible to detect emission signals for fluences as low as 0.4 J/cm² for 193 nm irradiation while for 308 nm irradiation fluences above 1 J/cm² are necessary. A pronounced influence of the ablation diameter on the emission intensity is detected for 193 nm irradiation. The intensity of the emissions lines increases with increasing ablation diameter, even for constant laser energies (=lower fluence). The variation of the ablation diameter has also an influence on the LA-ICP-MS data as previously shown [5–7]. It is therefore not possible to obtain the concentration directly from the counts comparison with the NIST reference sample, but the ratio of the counts

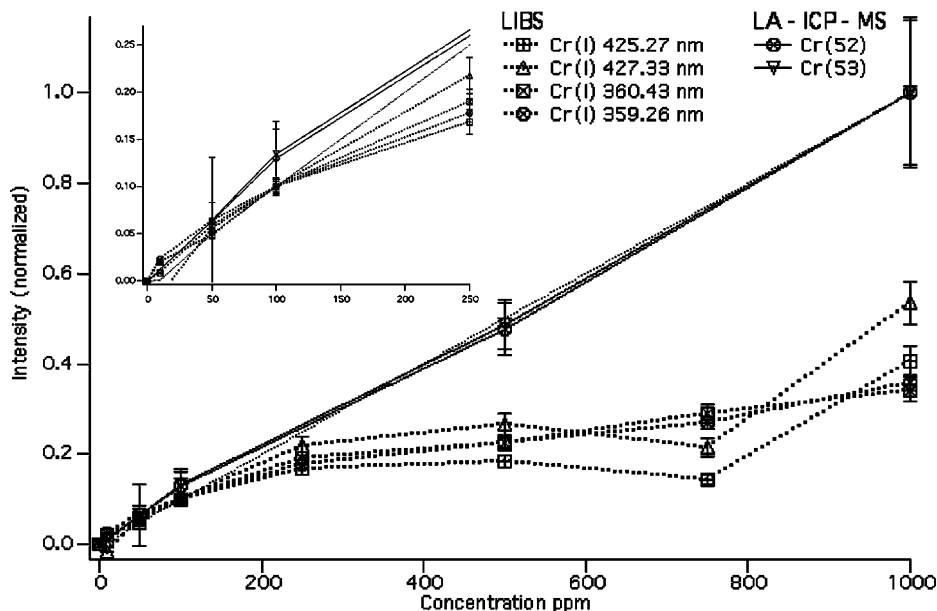


Fig. 1. Calibration curves of the matrix containing CrCl₂ (LIBS and LA-ICP-MS). The intensities are normalized.

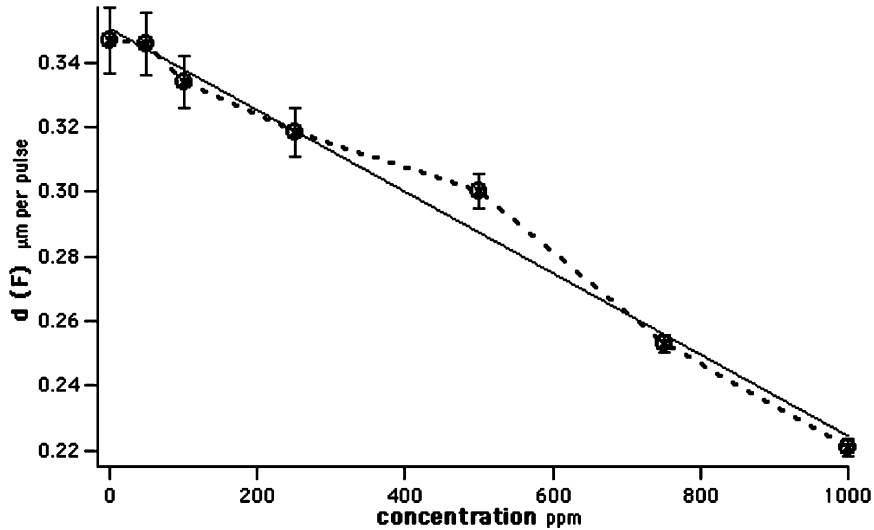


Fig. 3. Ablation depths as a function of the concentration of the matrix containing Cr_2O_3 , CuCl_2 and PbCl_2 for the radiation at 193 nm with 2.1 J/cm^2 .

of trace elements to the counts of matrix elements lead to improved results.

One of the important parameters that influences the analysis for both methods is the ablation rate (ablated depth per laser pulse), which directly influences the ablated volume and the amount of ablated particles, and therefore the plasma density [8]. Laser ablation starts when the fluence exceeds the threshold fluence for the given sample, which depends on the material properties (absorption) and the laser wavelength [9]. The ablation rate is strongly dependent on the irradiation wavelength, e.g. five times larger ablation rates are obtained for 308 nm irradiation compared to 193 nm. The change of the ablation depth as a function of the metal concentration and pulses number is shown for 193 nm irradiation in Fig. 3. The ion signal intensity of matrix elements, which are detected by LA-ICP-MS, is decreasing rapidly in the presence of chromium and copper (shown in Fig. 4), which is due to the decreasing amount of ablated material. The emission intensity of the matrix elements (shown for Cr in Fig. 4a) is constant during measurements with LIBS. This is most probably due to the high concentration of the matrix elements, which results in self-absorption and therefore constant intensities. The intensities/count rate of the trace elements is increasing for both methods with increasing metal concentration even for the decreasing ablation rate. The increase of the metal concentration is larger than the signal decrease due to the smaller ablation rates.

3.5. Plasma temperature determination

A calibration-free (CF-LIBS) method allows a quantitative analysis of elements without the need for calibration curves and overcomes the matrix effect [10]. To apply this method, it is necessary to analyze some

fundamental properties of the plasma. For the calculation of the plasma temperature from the emission spectra, it is assumed that the plasma is in a local thermal equilibrium (LTE) and that the population of the excited atomic levels follows the Boltzmann distribution. The LTE approximation can be validated from the electron densities. The radiation source is considered to be optically thin, because the main ionization process is produced through impact excitation by thermal electrons [10].

The line integral intensity in a LTE approximation is corresponding to the transition between two levels E_k and E_i of an atomic species s and can be written according to Goddard and Loge as (Eq. (1)):

$$I_{\lambda}^{ki} = N_s A_{ki} \frac{g_k e^{-\frac{E_k}{K_b T}}}{U_s(T)} \quad (1)$$

where N_s is the number density ($\text{particle}/\text{cm}^{-3}$), A_{ki} is the transition probability for a given line, g_k is the degeneracy of the emitting level k , K_b is the Boltzmann constant, and T is the plasma temperature. $U_s(T)$ is the partition function for the emitting species at the plasma temperature.

A Boltzmann plot, where $\ln(I/g_k \cdot A_{ki})$ is plotted vs. E_k , is used to calculate the plasma temperature [10].

One of the main problems in multi elemental, complex matrices is the identification of the lines of a specific element. For the calculation of the plasma temperature, it is also necessary that clearly separated single peaks be used, which are rare in complex matrices. In the range from 270 to 700 nm only a few lines of Chromium(I) could be used for the calculation.

The lines in Fig. 5a present the linear best fit of Chromium(I) data measured in air. In Fig. 5b, the

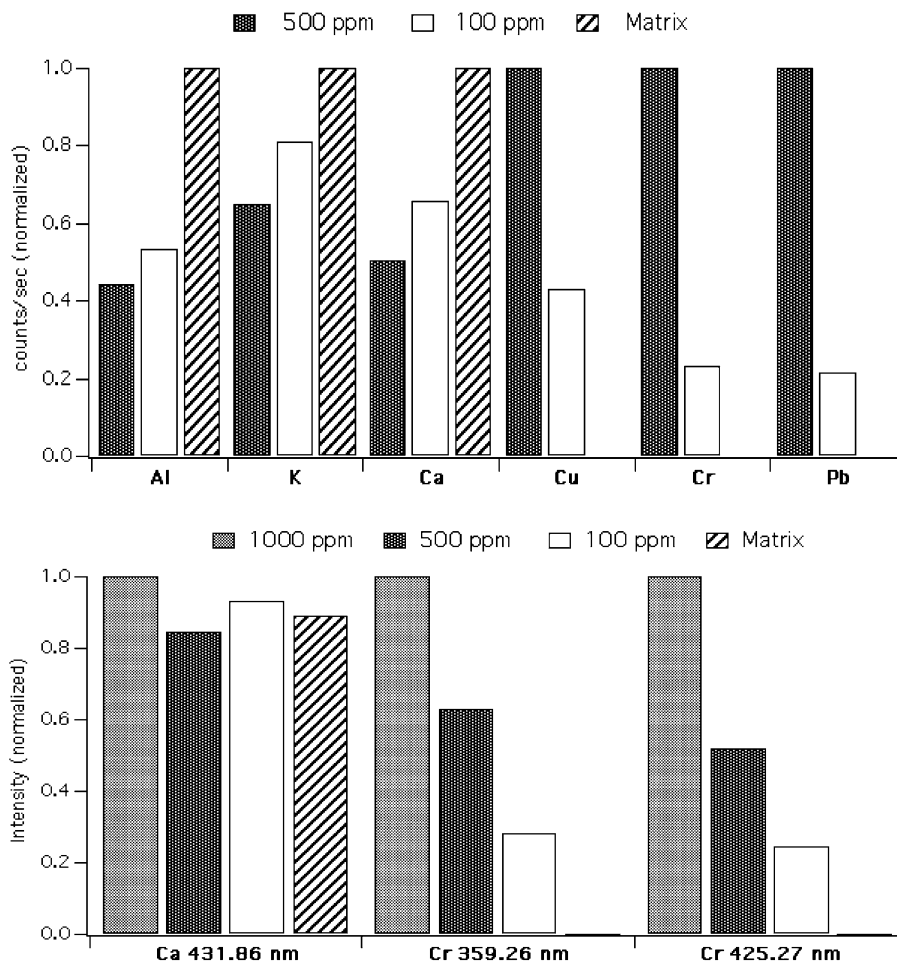


Fig. 4. (a) Counts per second for the LA-ICP-MS experiments, Al, K and Ca are the matrix elements, the counts of each element are normalized to the blank matrix counts ($\text{Al}/\text{Al}_{\text{matrix}}$, $\text{Ca}/\text{Ca}_{\text{matrix}}$, $\text{K}/\text{K}_{\text{matrix}}$, $\text{Cr}/\text{Cr}_{500 \text{ ppm}}$ and $\text{Cu}/\text{Cu}_{500 \text{ ppm}}$). Note, that the matrix counts are decreasing in the presence of the trace metals. (b) Emission intensities of Ca (matrix) and Cr lines. The intensity of the lines is normalized to the intensity of the sample containing 1000 ppm ($\text{Ca}/\text{Ca}_{1000 \text{ ppm}}$ and $\text{Cr}/\text{Cr}_{1000 \text{ ppm}}$). Note, that the intensity of the Ca line is in the same range for all concentrations.

relation of the plasma temperature with the laser energy is shown. The plasma temperatures increase linearly with the fluence for all metal compounds. The difference between the plasma temperature for the $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{Cr}(\text{NO}_3)_3$ could be due to the crystal water which has to be vaporized additionally and possibly also to the different ablation rates, $0.31 \mu\text{m}$ per pulse for $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ and $0.29 \mu\text{m}$ per pulse for $\text{Cr}(\text{NO}_3)_3$, which results in a different energy per volume. The determination of the plasma temperature from the ratio of relative intensities of lines from the same element but from successive ionization stages was not possible due to the low the intensity of the Cr(II) lines [11]. In the case of Cu(II), K(II) and Ca(II), it was even not possible to assign any lines for this type of analysis.

The CF-LIBS method could not be applied in our case due to the high complexity of the matrix.

3.6. Electron density determination

The electron number density can be obtained from the Stark-broadening of the emission lines [12]. The

strong Stark broadening of the *K* emission line at 404.414 nm has been used to determine the electron density, following the procedure suggested by Griem [13]. The Stark broadening parameters, which are necessary for the calculation, are listed in Ref. [13]. For singly ionized non-hydrogenic ions, Stark broadening is caused predominantly by electron impact. The FWHM (full half width maximum) of the lines $\Delta\lambda_{1/2}$ is related to the electron density N_e and $\Delta\lambda_{1/2}$ can be described by Eq. (2).

$$\Delta\lambda_{1/2} = 2W \frac{N_e}{10^{16}} + 3.5A \left(\frac{N_e}{10^{16}} \right)^{1/4} \left(1 - \frac{3}{4} N_D^{-1/3} \right) W \frac{N_e}{10^{16}} \quad (2)$$

where N_e is the electron density in cm^{-3} , N_D is the number of particles in the Debye sphere, W and A are Stark broadening coefficients, which are independent of the density, but related to the electron temperature. The electron density can be used to verify the LTE approxi-

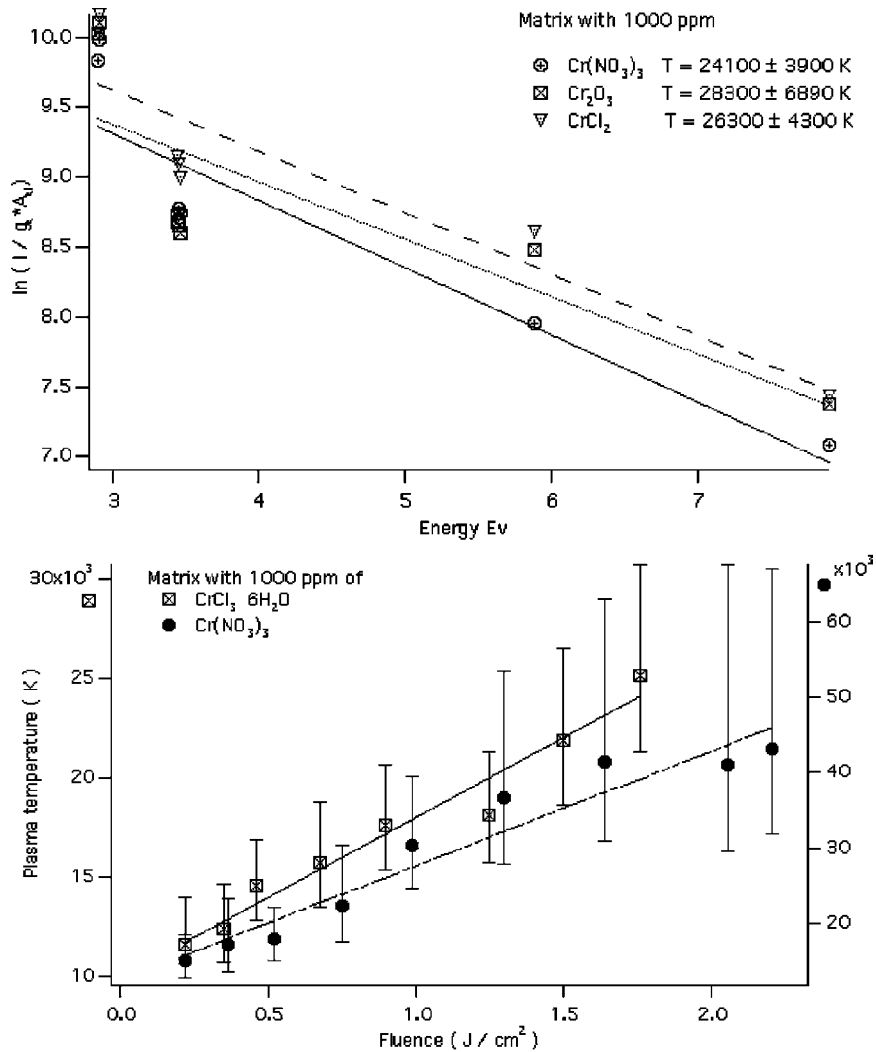


Fig. 5. Determination of plasma temperature, using (a), Cr_2O_3 , or CrCl_2 at the fluence of $0.824 \text{ J}/\text{cm}^2$. (b) Plasma temperature vs. laser fluence for samples with 1000 ppm of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{Cr}(\text{NO}_3)_3$.

mation in the plasma. The criterion has been suggested by Bekefi [11].

$$N_e \geq 1.4 \cdot 10^{14} T^{1/2} (\Delta E)^3 \quad (3)$$

where N_e is the electron density in cm^{-3} , T is the plasma temperature in eV and ΔE is the higher energy difference of the levels whose populations are given by LTE conditions.

The calculated electron densities range from 6.2×10^{17} to $6.8 \times 10^{17} \text{ cm}^{-3}$ and are much higher than the electron density Eq. (3), which varies from 5×10^{16} to $7 \times 10^{16} \text{ cm}^{-3}$, suggesting that the calculation of the plasma temperature based on the LTE condition are valid.

4. Conclusion

The sensitivity of LIBS and LA-ICP-MS were compared for trace elements in a complex matrix. LA-ICP-

MS has the higher sensitivity and lower limit for quantification, especially if finely ball-milled or glass samples are used. LIBS has its advantages with rough ball-milled or unground samples. This suggests, that LIBS could be for certain conditions a complementary technique to the more precise and sensitive LA-ICP-MS.

The intensity of the emission lines of LIBS is influenced by the background conditions, by the irradiation wavelength and by the ablation rate. The ablation rate is dependent on the trace metal concentration and effects the ablation process, which of course is than influencing the detection capabilities of both techniques.

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