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Presentation of the dissertation thesis

**APPLICATION OF LASER INDUCED BREAKDOWN SPECTROSCOPY (LIBS) FOR
THE ANALYSIS OF GEOLOGICAL MATERIALS AND SYNTHESIZED MATERIALS
WITH SIMILAR MATRIX**

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1 INTRODUCTION

Laser induced breakdown spectroscopy (LIBS), also referred as laser induced plasma spectroscopy (LIPS), is now well-known and established method used for the qualitative and quantitative analysis of different kinds of materials in all physical states. Method is based on the focalization of high-intense laser pulse on the sample surface, and spectral analysis of formed plasma plume emission. During the plasma plume formation and evolution various complex processes take place. Some effects, i.e. matrix effect are still not well-known and need to be studied for complete understanding. In the field of LIBS there are still new challenges, which fascinate scientist over the world. Advances in instrumental equipment (lasers, spectrometers and detectors) have allowed new attractive applications of the LIBS method in different fields (archaeology, geology and mineralogy, chemistry), but still mainly more in the laboratories than in direct use. Applications of LIBS technique are continuously spreading and have reached space as one of the analytical method used on the Curiosity rover mission on Mars.

When dealing with quantitative analysis using the LIBS method, two approaches may be applied. The first one, based on the calibration curves construction, requires measuring of the samples with known composition (reference standard materials) having matrix very similar to the sample under investigation. A calibration-free (CF) approach does not require measuring of reference materials, but on the other hand, plasma parameters have to be determine precisely for accurate quantitative analysis and also some other assumptions (local thermodynamic equilibrium, optically thin plasma, stoichiometric ablation) must be fulfilled when dealing with the CF LIBS approach. The influence of self-absorption effect on the spectral lines needs to be checked in both cases.

Due to the ever increasing in environmental pollution and environmental burden, it is necessary to find and use materials which are available, environmentally friendly, energy saving and reusable or revivable. In the last decades, zeolites have taken place in the different kinds of industry, mainly in chemistry and petrochemistry, where as the catalysts replaced harmful heavy metals. Zeolites as materials which are occurred naturally, are mined across the world in huge amounts, and are also prepared synthetically in laboratories, fulfil conditions as environmentally friendly materials due to the several reasons. There are around 50 types of naturally occurred zeolites and more than 100 have been chemically synthesised in laboratories. Replacement of harmful chemicals (heavy metals, acids, organic compounds) by zeolites has decreased amount of harmful by-products, formed during the catalysed chemical reactions. Since the catalysts increase the rate and efficiency of the chemical reactions, are considered also as energy saving materials. Some of zeolite-based catalysts are reusable after the remediation processes. Zeolites and zeolite-like materials are commonly analysed using wet chemical analyses, which are time consuming, difficult and required use of harmful chemicals as strong acids and bases. Therefore it is necessary to find suitable method for fast, simple and sufficiently precise method for the zeolite analysis.

The most commonly used zeolites in the petrochemical cracking are mordenite, zeolite type Y and ZSM-5. Mordenite and zeolite type Y have its equivalent in the nature, ZSM-5 zeolite is purely synthetic. Therefore these types were selected for the calibration based and calibration free laser induced breakdown spectroscopy analyses. Very important parameter

which determinates zeolites properties and use is silicon to aluminum molar ratio (Si/Al). This key parameter was determined during LIBS and CF LIBS analyses.

The thesis discusses application of two quantitative approaches (calibration based and calibration-free) of the LIBS method for the analysis zeolites and other samples with geological character and is based on the manuscripts accepted and published (*Horňáčková et al. 2012, Horňáčková, Horňáček et al. 2013, Horňáčková, Plavčan et al. 2013, Horňáčková et al. 2014*), or currently in the review process (*Horňáčková, Plavčan et al., submitted- in the review process*), in which thesis author is stated as the first author.

The first chapter of the thesis deals with the theoretical background of the LIBS method. Possibilities of plasma parameters determination, the ways of qualitative and quantitative analyses are presented as well as problems of the self-absorption effect and local thermodynamic equilibrium. Second chapter of the thesis is focused on the description of individual parts of used experimental apparatus and analysed samples. In third chapter, obtained results are presented. Firstly, calibration based analysis of three zeolite types and analysis of five heavy metals (copper, chromium, cadmium, cobalt and lead) loaded in the zeolite matrix. Also limits of detection of mentioned heavy metals are determined. Next part is dedicated to the determination of Si/Al molar ratio by calibration-free approach and description of spectral lines selection process for the increase of CF LIBS accuracy. In general, CF LIBS method is used mainly for the analysis of simple matrices (alloys, oxide materials or glasses) containing low number of elements (less than five). Only some studies are dedicated to the analysis of complex matrices as geological samples, soils or archaeological findings. With increasing number of presented elements, errors in the concentration determination increase and small error in determination of elemental concentration of major elements may lead to higher errors in the concentration of minor elements. As the LIBS method is quasi non-destructive it is suitable for the analysis of rare and precious samples, where sample destruction is absolutely undesirable. And therefore, we have applied calibration-free approach of LIBS method for the analysis of meteorites “Košice” and “Smolenice” fragments. Thanks to the non-destructive character of the LIBS method, comparison of elemental composition of several fragments of the “Košice” meteorite could be done, without significant damage of individual fragments. Other geological samples- acid pitchstone and granite were also analysed by means of CF LIBS and for comparison, electron probe microanalysis (EMPA) measurements were performed. Comparison of both methods is presented and advantages and disadvantages of both methods are presented.

In the last chapter of the thesis, obtained results are summed up and comparison of both approaches is also mentioned. Future plans and perspectives of the LIBS method in our group are presented here.

2 LASER INDUCED BREAKDOWN SPECTROSCOPY (LIBS)

Laser induced breakdown spectroscopy is an analytical method, introduced in the seventies of the 20th century. LIBS method is based on the ablation of sample using high intensive laser pulse focused on the sample surface. In the most of LIBS experiments, pulsed Q-switched Nd:YAG laser are used, providing wavelengths of laser pulses in wide spectral range from UV to NIR (266, 355, 532 or 1064nm). For the laser pulse duration, sample

surface is exposed to the power density of gigawatts per cm^2 . Very short and high intensive laser pulse (duration of a few nanoseconds) causes atomization, ionization and evaporation of small amount of the sample (in order of nanograms or micrograms) and plasma (or spark) creation. Laser induced plasmas have short life time, but on the other hand reach temperatures of 1eV and more. Plasma cools down very quickly and during the cooling process excited atoms and ions fall down in to the ground states, causing emission of light at discrete wavelengths. Plasma emission is then collected and focused to the slit of a spectrometer coupled with a CCD or an iCCD camera. Block scheme of LIBS experimental set-up is depicted in Fig. 1.

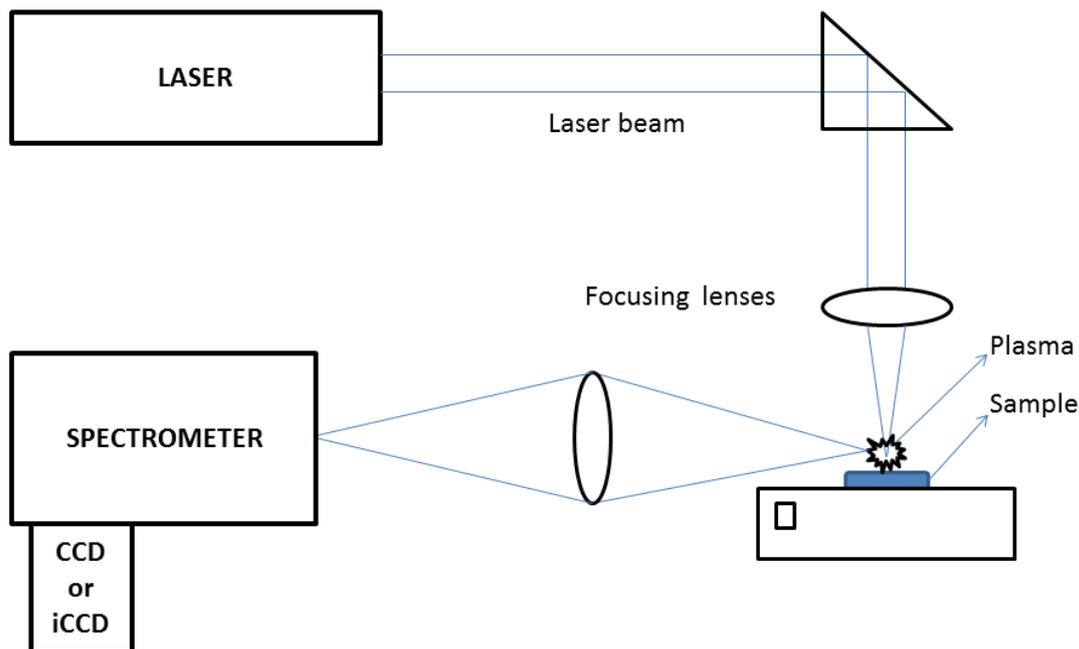


Figure 1 Block scheme of LIBS experimental set-up

LIBS experimental setup is very simple, comparing to other analytical techniques, often containing only laser, spectrometer, charge coupled device, directing and focusing optics and computer for data acquisition and data analysis.

On the other hand, finding of the suitable experimental conditions for the LIBS measurements (laser pulse energy, time delay, gate width, laser wavelength, ambient gas, reduced or low pressure) may be sometimes time-consuming and optimal conditions varying from sample to sample. But when the optimal conditions are found, LIBS analysis is become very fast.

As it is clearly seen form Fig. 2 in the first stage of plasma formation, immediately after the laser pulse, strong continuum emission dominates. In this time also emission of ions starts, subsequently neutral atoms and as the last, emission of molecules occurs. Therefore it is very important to choose the suitable delay, when the acquisition starts, duration of acquisition (delay time and gate width) for the observation of particular species and also the condition of local thermodynamic equilibrium must be fulfilled in the observation time. In LIBS, detection of neutral and ionic spectral lines is necessary for the qualitative and quantitative analysis, so delay times are usually set to $\sim 1\mu\text{s}$ and gate widths of several

microseconds are usually used. For the molecular spectroscopy, for example in LAMIS (Laser Ablation Molecular Isotopic Spectrometry), later times are chosen for signal acquisition, several microsecond of delay time and up to tens of microseconds of gate width (*Russo et al. 2011, Sarkar et al. 2013, Mao et al. 2011*).

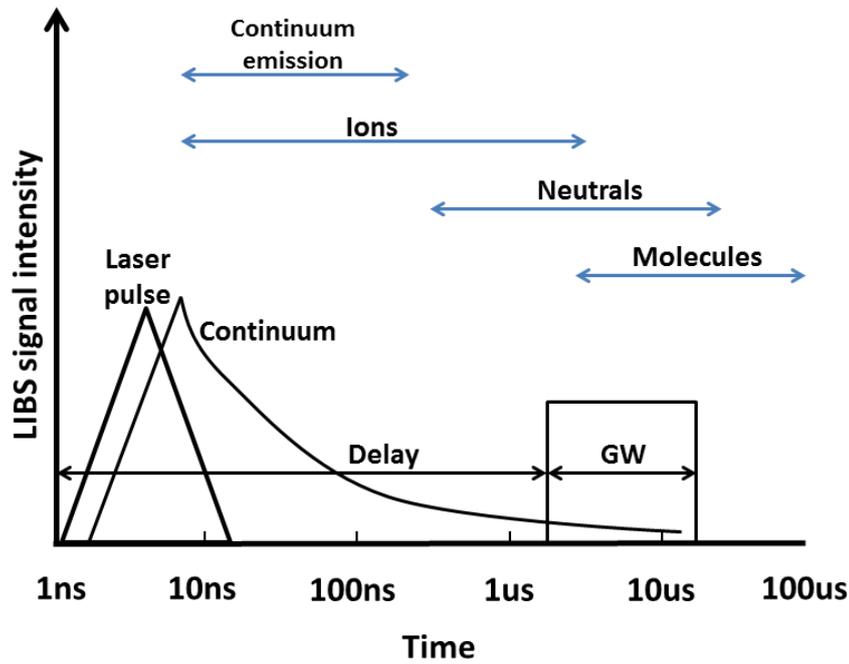


Figure 2 Important time intervals of LIBS (*Miziolek et al. 2006*)

3 DIAGNOSTICS OF LASER INDUCED PLASMA

3.1 DETERMINATION OF ELECTRON DENSITY

Based on the work of *Gigosos et al. (2003)* electron density can be calculated from the broadening of hydrogen H_α line (656.28nm) using equation

$$FWHA = 0.549nm \left(\frac{N_e}{10^{23}m^{-3}} \right)^{0.67965} \quad (1)$$

where FWHA is full width at half area of hydrogen alpha line. FWHA (Fig. 3) parameter is much less sensitive to ion dynamics effects than the full width at half maximum (FWHM) parameter (*Gigosos et al. 2003*), therefore is the use of FWHA more advantageous than FWHM parameter.

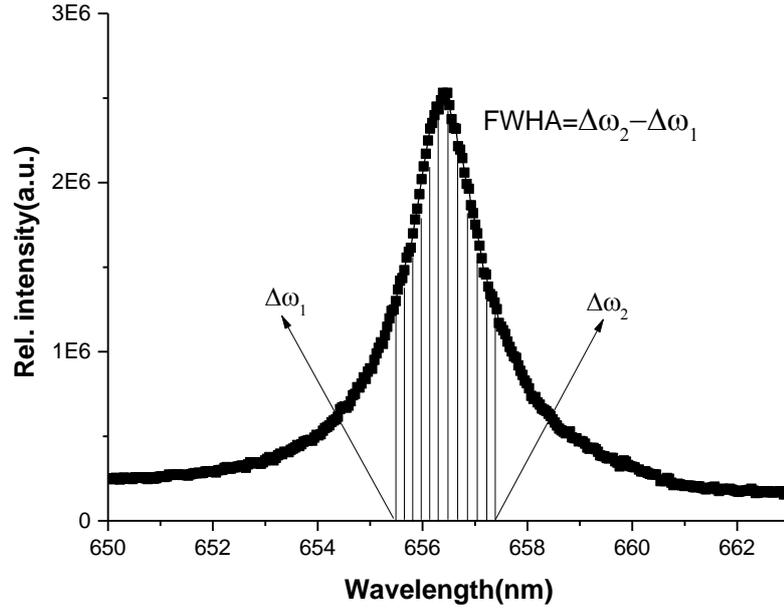


Figure 3 FWHA parameter for hydrogen H_α spectral line (*Gigosos et al. 2003*)

3.2 DETERMINATION OF ELECTRON TEMPERATURE

According to the fact, that in the LIBS spectra, both neutral and ionic spectral lines are usually occurred, there is a possibility to evaluate separately electron temperature from neutral and separately from ionic lines. In LTE both evaluated values of electron temperature should be the same. In order to evaluate more precisely the electron temperature (using the spectral lines with the highest difference of upper energy levels values possible) a combination of Boltzmann excitation distribution (in each ionisation degree) with Saha ionization distribution is used. Ionization distribution can be calculated according to the Saha equation:

$$\frac{N_e N^{II}}{N^I} = \frac{2U^{II}(T)}{U^I(T)} \frac{(2\pi m_e k_B T)^{3/2}}{h^3} e^{-\frac{E_{ion}}{k_B T}} \quad (2)$$

where N and $U(T)$ is the number density and the partition function for neutral atoms I and singly ionized atoms II , E_{ion} is the ionization energy and h is the Planck constant. Coordinates of data points in the Saha-Boltzmann plot are then obtained using following expressions (*Tognoni et al. 2007*)

$$x = \begin{cases} E_k & \text{for neutral lines} \\ E_j + E_{ion} & \text{for ionic lines} \end{cases} \quad (3a, 3b)$$

$$y = \begin{cases} \ln\left(\frac{I_{ki}}{A_{ki}g_k}\right) & \text{for neutral lines} \\ \ln\left(\frac{I_{jh}}{A_{jh}g_j}\right) - \ln\left(\frac{2(2\pi m_e k_B T)^{3/2}}{N_e h^3}\right) & \text{for ionic lines} \end{cases} \quad (4a, 4b)$$

As in the Boltzmann plot method, the slope of linear regression through the data points is equal to $-1/k_B T$, where electron temperature can be determined. The advantage of the Saha-Boltzmann plot method is higher precision of temperature determination due to higher

differences in the upper energy levels of used neutral and ionic spectral lines (*Aguilera and Aragón 2007*).

4 QUANTITATIVE ANALYSIS BY MEANS OF LIBS

4.1 CALIBRATION BASED LIBS

For the LIBS quantitative analysis relation between intensity I_{ik} of spectral line and number density N of species s is used

$$I_{ik} = F_C N_s A_{ik} g_k \frac{e^{-E_i/k_B T_e}}{U_s(T_e)} \quad (5)$$

where F_C is the factor taking into account efficiency of detection system, A_{ik} is transition probability (Einstein's coefficient) g_k is degeneracy of the k level, E_i is energy of upper level, k_B is Boltzmann constant, T_e is electron temperature and U_s denotes partition function at given temperature.

Method of the internal standard is a calibration based approach, when intensity of analyte spectral line is normalized with the intensity of spectral line of matrix. Internal standard line selection requires some assumes: (i) both spectral lines should be in the same ionization degree, (ii) elements should have similar ionization energies and (iii) energies of upper levels should be very similar. This method compensates the dependence of calibration curves on the plasma parameters (electron density and temperature) (*Elhassan et al.*) and also reduces influence of the LIBS signal fluctuations and effects of the matrix interferences (*Lasheras et al. 2013*).

4.2 CALIBRATION FREE LIBS

Calibration free approach of laser induced breakdown spectroscopy is a quantitative approach, which allows determination of an elemental concentration of the examined samples without using of the reference standard materials, so it is not necessary to obtain the calibration curves. Another advantage of this approach is, the matrix effect need not be taking into account. On the other hand some assumptions must be fulfilled when using the calibration free approach, i.e. i) stoichiometric ablation, which means, the composition of created plasma is the same as the material composition, ii) plasma is in the state of local thermodynamic equilibrium (LTE) and iii) plasma emission is optically thin (*Ciucci et al. 1999*). Also very important and crucial step in the CF process is accurate determination of electron density N_e and temperature T_e .

If plasma is in the state of local thermodynamic equilibrium (LTE), the integral intensity of an optically thin emission spectral line can be described by the following equation

$$I_{\lambda}^{ki} = A_{ki} N_k^s = A_{ki} n^s g_k \frac{e^{-E_k/k_B T}}{U^s(T)} \quad (6)$$

where A_{ki} is the transition probability between levels i and k , N_k^s is the population density of level k , g_k is the degeneracy of level k , n^s is the number density of species s , $U^s(T)$ is the

partition function of species s at the temperature T and E_k is the energy of level k (Tognoni et al. 2007).

The measured intensity depends on the efficiency of collection and detection system, and then the integral intensity should be corrected as

$$\bar{I}_\lambda^{ki} = F_C n^s A_{ki} g_k \frac{e^{-E_k/k_B T}}{U^s(T)} = F_C n^p C^s A_{ki} g_k \frac{e^{-E_k/k_B T}}{U^s(T)} \quad (7)$$

where \bar{I}_λ^{ki} denotes the integral line intensity corrected to the relative spectral efficiency of the used detection and the collection system F_C , n^p and C^s are total particle density in plasma and the relative concentration of species s in the plasma (Tognoni et al. 2007).

Taking the logarithm of Eq. 59, we obtain

$$\ln \frac{\bar{I}_\lambda^{ki}}{A_{ki} g_k} = \frac{-E_k}{k_B T} + \ln \frac{F_C n^p C^s}{U^s(T)} \quad (8)$$

and then, Eq. 60 can be rewritten in a linear form

$$y = ax + b \quad (9)$$

where

$$a = -\frac{1}{k_B T} \quad x = E_k \quad y = \ln \frac{\bar{I}_\lambda^{ki}}{A_{ki} g_k} \quad b = \ln \frac{F_C n^p C^s}{U^s(T)} \quad (10 \text{ a, b, c, d})$$

As it is clearly seen from Eq. 62a and Eq. 62d, the slope of a linear line a is equal to the temperature of plasma and the intercept b is related to the concentration of species s , C^s (Tognoni et al. 2007). Then concentration of species s can be calculated from the consequent equation

$$C^s = \frac{1}{F_C n^p} U^s(T) e^b \quad (11)$$

If all the spectral lines of all the elements present in the examined sample are measured, the normalization relation can be used

$$\sum_{s'} C^{s'} = \frac{1}{F_C n^p} \sum_{s'} U^{s'}(T) e^{b'} = 1 \quad (12)$$

where the s' index represents all the elements in all the ionization stages, which are not negligible (Tognoni et al. 2007). From the previous equation, the F factor can be determined

$$F_C n^p = \sum_{s'} U^{s'}(T) e^{b'} \quad (13)$$

and then concentration of species s can be calculated using the equation

$$C^s = \frac{U^s(T) e^b}{\sum_{s'} U^{s'}(T) e^{b'}} \quad (14)$$

This CF LIBS model proposed by Ciucci et al. (1999) is based on the assumption of the ideal plasma, which is optically thin. But laser induced plasma formed during the LIBS experiments is very often thick for some wavelengths. The profiles of spectral lines, especially of resonant lines of major elements, are affected by the self-absorption effect. Intensity of observed spectral lines are lower, what leads in the under estimation of an elemental concentration. Therefore it is necessary to discriminate between non-saturated and saturated spectral lines, which are used for the elemental concentration determination during the CF LIBS analyses, and when it is possible, to correct spectral lines affected by the self-absorption effect.

4.3 DETERMINATION OF THE DETECTION LIMITS

Limit of detection (LOD) represents the elemental concentration at which we can declare that given element is presented in the analysed sample or not (or when we can distinguish between the signal and the background). The lowest elemental concentration which can be measured by given apparatus with acceptable precision and reproducibility is referred to as limit of quantification (LOQ) (Thomsen *et al.* 2003). According to the IUPAC, limit of detection (LOD) is given as

$$LOD = \frac{K\sigma_B}{S} \quad (15)$$

where σ_B is standard deviation of the background signal and S is the slope of the linear calibration curve and K is the numerical factor expressing the required confidence level (Long *et al.* 1983). In LIBS, usually $K=3$, what represents confidence level of 99.86%, is used.

5 RESULTS

5.1 CALIBRATION BASED ANALYSES OF DIFFERENT TYPES OF ZEOLITES

Based on this relation calibration graph, which represent dependency between elemental concentration and intensity of LIBS signal, based on the measurements of known samples is constructed and consequently, elemental concentration of unknown sample can be determined from the calibration curve.

Due to the different physico-chemical properties and structure of investigated zeolite types, we have decided to construct the calibration curve for each zeolite type. Silicon to aluminum molar ratio (Si/Al molar ratio) was selected as a dependency parameter (X-axis), because this parameter is very important and determines the properties and use of zeolite.

For the calibration curves construction spectral lines of silicon Si II (634.71nm) and aluminum Al I (394.40nm) were selected and fitted using Lorentz profile to create calibration curves. Both amplitude of spectral line and area under the spectral line were determined and calibration curves for both parameters and for all three zeolite types were constructed. Calibration curves of mordenite, zeolite type Y and ZSM-5 are depicted in Fig. 4 and 5.

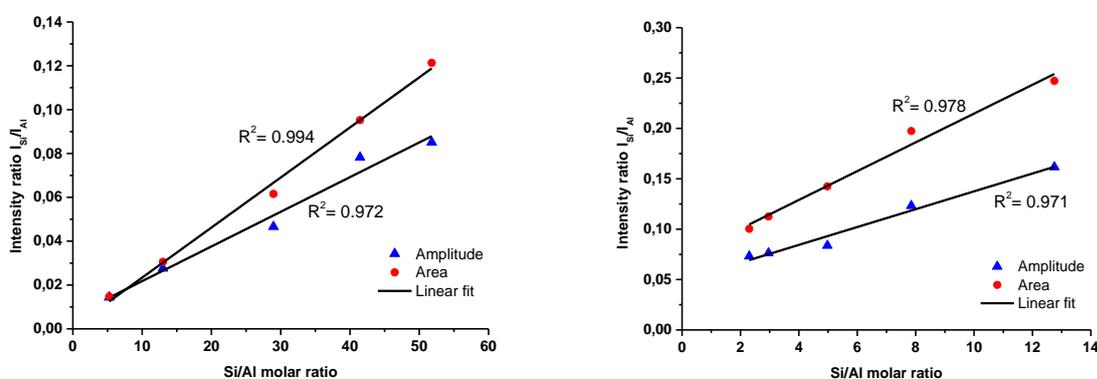


Figure 4 Calibration curve for mordenite (left) and zeolite type Y (right) obtained both for peak area and amplitude

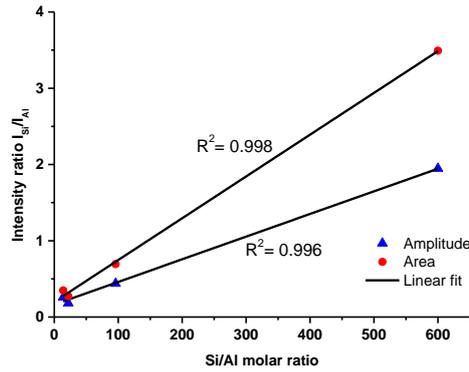


Figure 5 Calibration curve for zeolite ZSM-5 obtained both for peak area and amplitude

5.2 CALIBRATION BASED ANALYSES OF ZEOLITES CONTAINING HEAVY METALS

For this purpose, twenty-five samples were prepared with different concentration of each heavy metal (copper, cobalt, cadmium, chromium and lead) in the concentration range approximately of 0.05-0.5wt.% loaded into zeolite type Y (Si/Al=2.49).

For calibration curves construction we have decided to normalize the intensity of heavy metals spectral lines to the intensity of matrix spectral lines, what means to use spectral lines of matrix as the internal standards. For this purpose spectral lines of silicon, aluminum, calcium and magnesium were used.

Calibration curves were constructed for all heavy metals (copper, chromium, cadmium, cobalt and lead) using five samples for each calibration curve and constitute dependency between elemental concentration and intensity of spectral line of given element. Points in the calibration curves representing average value of five measurements obtained from 250 spectra. Some of obtained calibration curves are presented in Fig. 6-10.

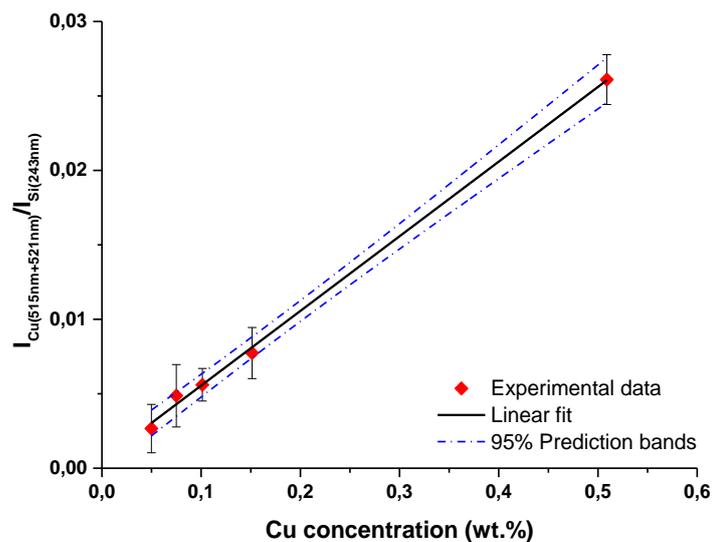


Figure 6 Calibration curve for copper obtained using two Cu I spectral lines (515.32nm and 521.82nm) and silicon Si I line (243.52nm) as an internal standard

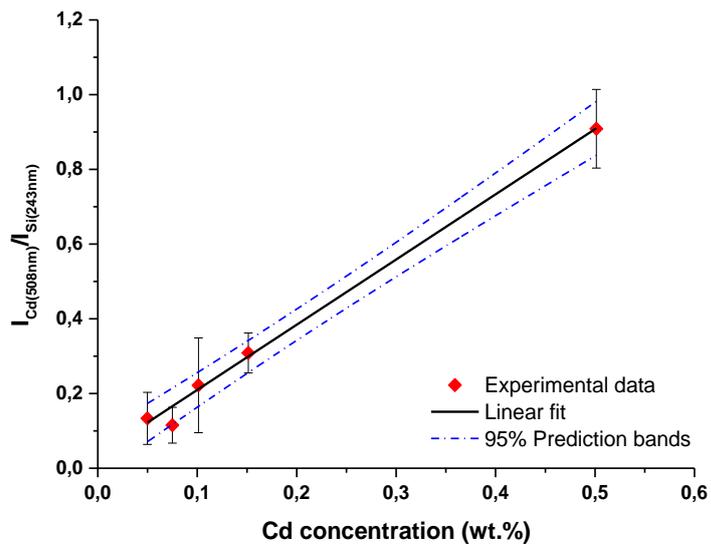


Figure 7 Calibration curve for cadmium obtained using Cd I spectral line (508.58nm) and silicon Si I line (243.52nm) as an internal standard

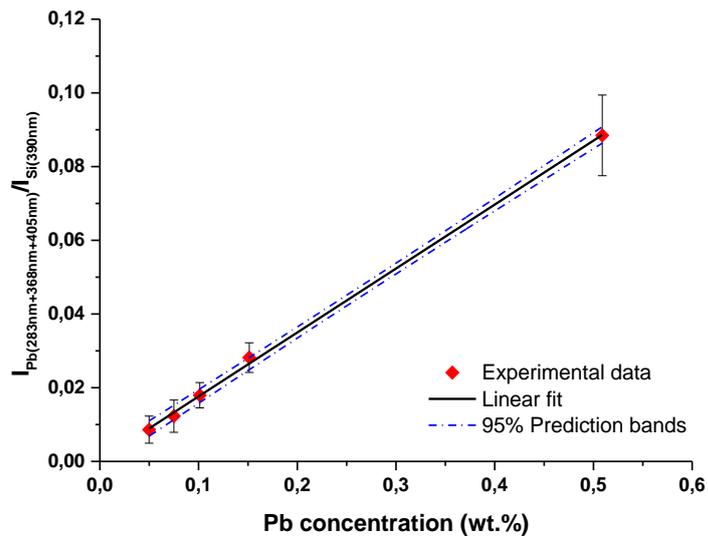


Figure 8 Calibration curve for lead obtained using three Pb I spectral lines (283.31nm, 368.34nm and 405.78nm) and silicon Si I line (390.55nm) as an internal standard

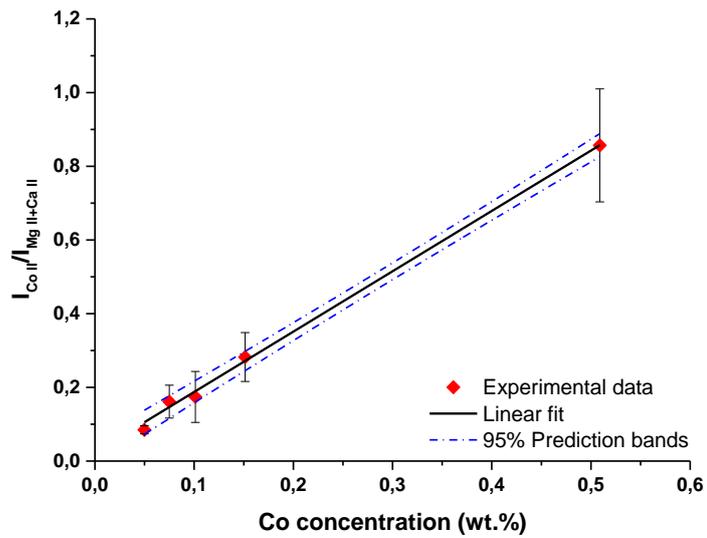


Figure 9 Calibration curve for cobalt obtained using ionic spectral lines Co II (236.38nm, 239.74nm, 258.22nm and 258.72nm) and ionic spectral lines Ca II (393.37nm) and Mg II (280.27nm)

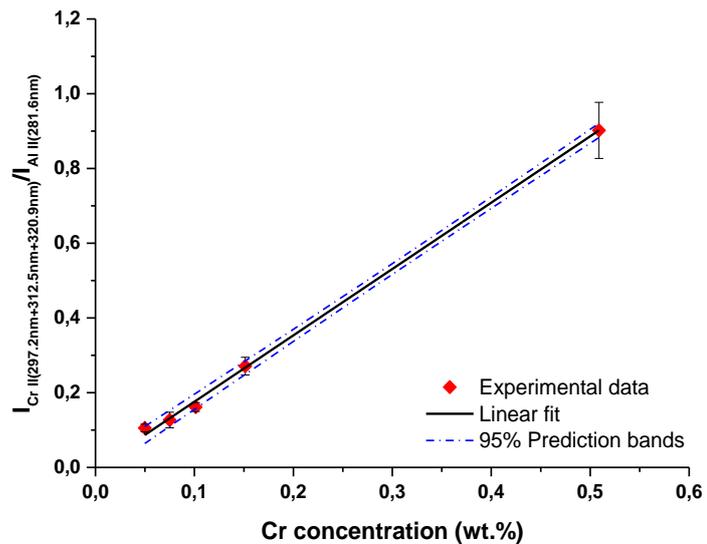


Figure 10 Calibration curves for chromium obtained using ionic spectral lines Cr II(297.17nm, 312.50nm and 320.92nm) and aluminum ionic spectral line Al II (281.62nm)

For the determination of the detection limits, generally, resonant spectral lines are used. In our study spectral line of copper Cu I 324.75nm, singly ionized spectral line of cadmium Cd II 226.50nm, lead neutral spectral line Pb I at 405.78nm, neutral chromium spectral line Cr I at 425.43nm and neutral cobalt line Co I at 348.94nm were used. Obtained detection limits are listed in Tab. 1.

Table 1 Obtained limits of detection of five heavy metals in zeolite matrix

Element	Line (nm)	LOD (ppm)
Cu	324.75	14.4
Cr	425.43	16.4
Co	348.94	18.5
Cd	226.50	190.7
Pb	405.78	62.6

Due to the high obtained LOD of cadmium, we performed measurements with high-resolution spectrometer THR 1500 (Jobin Yvon) coupled with an EM CCD camera (Newton, Andor) and without use of an optical fiber. Using of the high-resolution spectrometer and EM CCD camera (Newton, Andor) we obtained almost four times lower LOD for cadmium of 52.6ppm comparing to the one obtained using echelle type spectrometer equipped with an iCCD camera (iStar, Andor).

5.3 CALIBRATION-FREE ANALYSIS OF ZEOLITES BY MEANS OF LASER INDUCED BREAKDOWN SPECTROSCOPY

Using the CF LIBS method, eleven zeolite samples with the molar ratios of Si/Al in the range of 2.3-51.8 were analysed.

To increase accuracy of the CF LIBS method and to predict the influence of self-absorption effect on the spectral lines, strict selection of spectral line was done based on the following parameters:

- Relative population of atoms in absorbing level (lower energy level of transition)
- Value of transition probability (Einstein's coefficient)
- Ratio of atom number densities of singly ionized to sum of all degree of ionisation including neutral atoms for a given element. In our conditions this ratio can be approximated by the ratio of singly ionised to neutral atom number densities (N_{II}/N_I).
- Also supposed elemental concentration as a rough approximation was taken into account

The electron density was calculated using Eq. 1, so from the Stark broadening of hydrogen $H\alpha$ line. FWHM parameter was obtained from the $H\alpha$ (656.28nm) fitting using the Lorentz profile.

Electron temperature was determined from the slope of linear fit of the data points in the Saha-Boltzmann plots. An example of the Saha-Boltzmann plot for silicon and aluminum is depicted on Fig. 11. Temperatures were determined both for silicon and aluminum and for the quantification of silicon to aluminum molar ratios, average of these two temperatures was used. Average electron densities and temperatures for all samples are presented in Fig. 12.

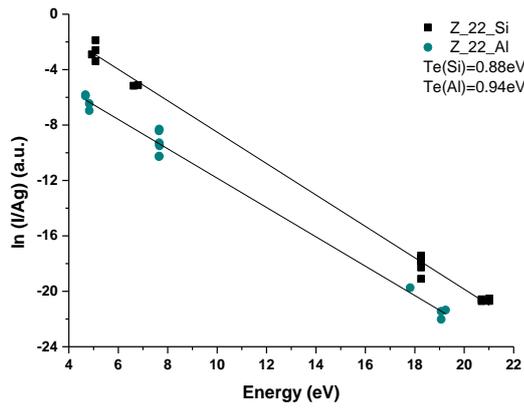


Figure 11 Saha- Boltzmann plot for silicon and aluminum (sample of ZSM-5 with the Si/Al molar ratio of 22)

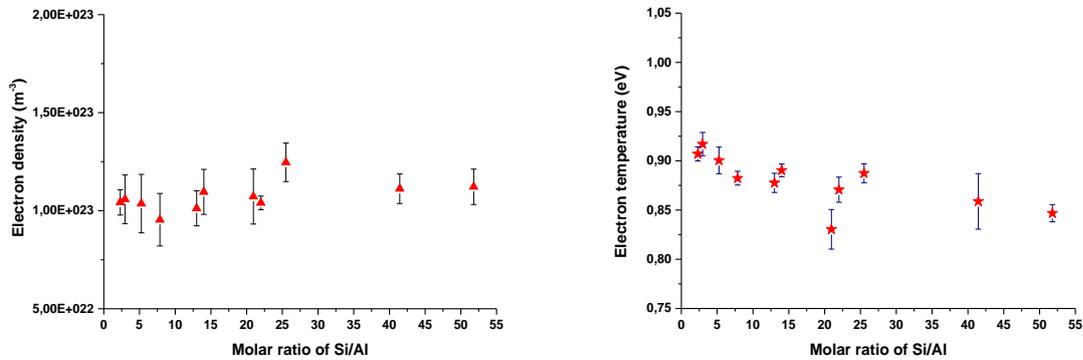


Figure 12 Average electron densities (left) and temperatures (right) for all analysed samples

Saha equation (Eq. 2) was used for the ratio of singly ionized to neutral atom number densities for each element calculation. Percentages of neutral and singly ionized atom number densities for silicon and aluminium are presented in Fig. 13.

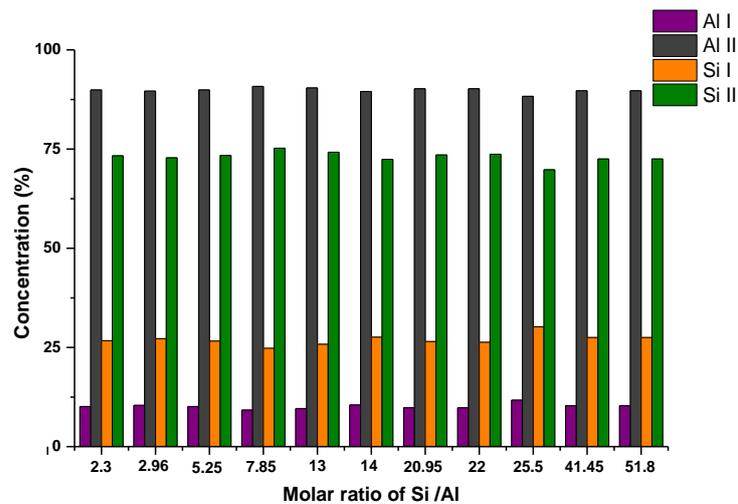


Figure 13 Percentages of atom number densities of neutral and ionic aluminum and silicon for all analysed samples

Comparison of the results obtained by the wet chemical analyses and CF LIBS is presented in Fig. 14. Obtained CF LIBS results are in very good agreement with results achieved by the wet chemical analyses. Relative errors represented by the relative standard deviation (RSD) of CF LIBS measurements were in the range of 1.5-14.4%. Average RSD was of 4.7%.

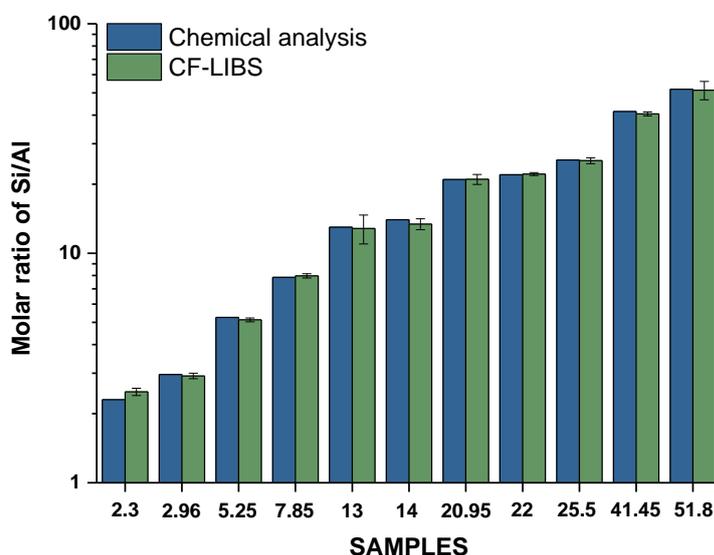


Figure 14 Comparison of results obtained by wet chemical analysis and CF LIBS

5.4 CALIBRATION-FREE LIBS ANALYSES OF COMPLEX MATRICES

It is very important to have a non-destructive technique when dealing with the analysis of precious, valuable or rare samples like archaeological findings, art samples, jewellery, paints and also meteorite fragments. Quasi non-destructive character of the LIBS method has been successfully exploited for the analysis of ceramic and metal artifacts (*Melessanaki et al. 2002*), pottery from Iron age (*Erdem et al. 2008*), archaeological findings from the Southern Italy (*Gaudiuso et al. 2012*), archaeological brooches (*Gaudiuso et al. 2014*), ancient coins (*Pardini et al. 2012*), paint materials (*Kokkinaki et al. 2013*), fossils (*Roberts et al. 2012*) and meteorites (*De Giacomo et al. 2007, Dell'Aglio et al. 2010*).

A calibration-free approach of LIBS was applied also on the samples with difficult or complex matrix, containing more than five elements. We had at the disposal three meteorite fragments corresponding to the “Košice” meteorite fall, observed on 28th of February 2010 near the Košice city in eastern Slovakia. According to the higher number of found fragments, some of them were “sacrificed” for the purposes of analysis by destructive techniques. One of found fragments was analysed using inductively coupled plasma mass spectroscopy (ICP MS) (*Ozdín et al. 2014*).

Calibration-free LIBS was selected as a comparative method to ICP MS or EMPA, but with the advantage of quasi non-destructivity, what has allowed comparing three of found fragments and also composition of fusion crust (burned in the atmosphere during meteorite fall) and inner- not burned part of meteorite with minimal damage of each fragment and also minimal material consumption.

Analysis of measured LIBS spectra confirmed presence of three major elements- silicon, magnesium and iron and seven minor elements- aluminum, calcium, chromium, manganese, sodium, nickel and potassium. Trace elements were not detected using LIBS technique.

The results obtained by CF LIBS and ICP MS techniques are compared in Fig. 15. The biggest differences are observed for aluminum and sodium. Determination of elemental concentration of these two elements was influenced by low number of observed spectral lines. The differences, mainly in the minor elements, could also be due to the fact that by the ICP MS another meteorite fragment was analysed. CF LIBS results presented in Fig. 15 are average of all measurements made on all fragments including crusts and inner parts of all meteorite fragments. Error bars in Fig. 15 represents the relative standard deviation of measurements.

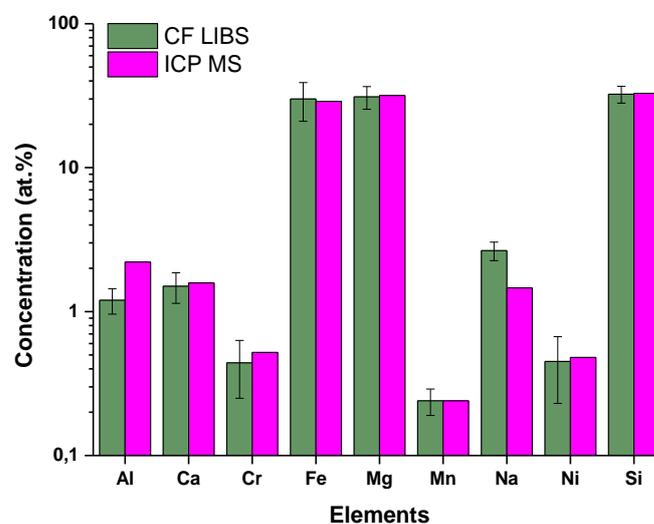


Figure 15 Comparison of ICP MS and CF LIBS results

During the writing of the thesis, we have obtained new iron type meteorite, found in Slovakia near the town of Smolenice, which is not yet classified. Iron type meteorites are composed mainly of iron, nickel and cobalt (with Fe+Ni+Co>95% and 5-25% of Ni). Iron and nickel are presented mainly in the metallic form, what indicates extra-terrestrial origin, because in rocks found on the Earth are these elements presented in the form of oxides as for example FeO, Fe₂O₃, NiO etc. Detailed classification of iron meteorites is done based on the content of nickel and trace elements- gallium, germanium and iridium.

Up to now, only one fragment of meteorite “Smolenice” has been found. According to this fact, it is very important to perform as most non-destructive analyses as possible in order to preserve the sample without significant damage. From this point of view, CF LIBS analysis is very good candidate for this purpose.

By the spectral analysis, iron and nickel was confirmed in the measured LIBS spectra. Due to the very high content of iron, LIBS spectra are overcrowded with neutral and singly ionised spectral lines of iron mainly in the spectral range of 230-430nm.

According to the NIST database, there are more than 13500 neutral and singly ionised spectral lines of iron in the spectral range of 200-900nm. So, it is very high probability of spectral lines interference of iron and minor and trace elements. Therefore it is necessary to select spectral ranges with the lines having high transition probabilities and resonant spectral lines of trace elements and carry out measurements using a high-resolution spectrometer. For this purpose, simulations of the LIBS spectra at given electron density and temperature ($6 \times 10^{23} \text{m}^{-3}$ and 1eV) and supposed elemental composition (95% of Fe, 5% of Ni, 100ppm of Ir and 100ppm of Ge) were performed. First two elements (Fe, Ni) were already evaluated by CF LIBS analysis using Mechelle ME 5000 spectrometer and iridium is supposed that it lay on top edge of already observed densities in the case of iron type meteorites (*Weisberg et al. 2006*). Simulations and calculations have shown spectral regions where spectral lines of trace element (iridium) could be separated from a quantity of iron spectral lines and so where this trace element could be searched for. If we take into account resolution of our high-resolution THR 1500 spectrometer, which is of 0.025nm, in several cases of simulated spectral regions we will be able to detect iridium content up to approximately 20ppm. An example of simulation of the LIBS spectrum for the spectral line of iridium is shown in Fig. 16. Preliminary results of these analyses have determined upper concentration level of iridium of 55ppm. Lower concentration level could be smaller due to the presence of iron spectral lines close to the iridium lines. According to the obtained Ir content, the fragment can be classified in to group II A (Ir content ranging from 0.01-60ppm (*Weisberg et al. 2006*)).

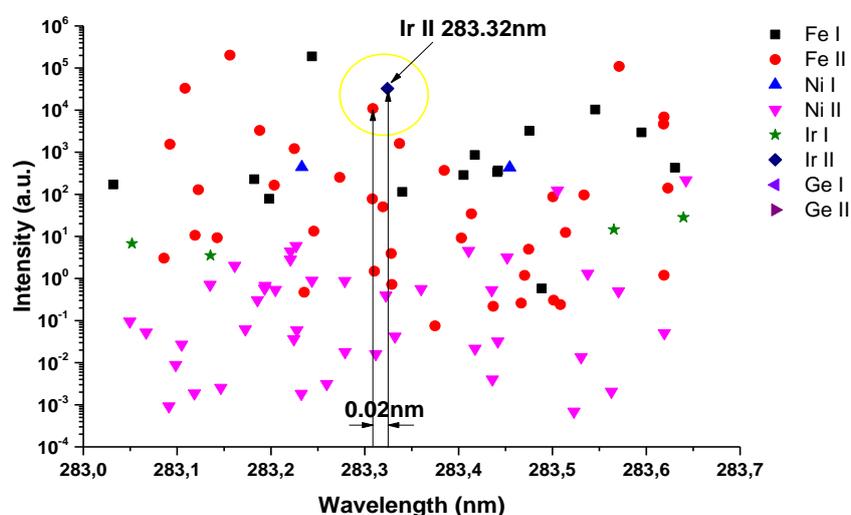


Figure 16 Simulation of LIBS spectra for the detection of Ir spectral lines in the spectral range of 283.0-283.7nm

Further sample representing a complex matrix sample, containing several elements in different elemental ranges (major, minor and trace) analysed by means of calibration-free LIBS was acid pitchstone (rhyodacite). The sample of acid pitchstone was taken from Iceland. In order to compare our CF LIBS results, sample of acid pitchstone was analysed also using the electron micro-probe analysis (EMPA).

Results in at.% were recalculated to the wt.% of oxides for the purpose of comparing with the bulk rock EMPA results. Comparison of both method results are presented in Tab. 2.

Using both of techniques, sodium, silicon, aluminum, magnesium, potassium, calcium, titanium, iron, manganese, barium were quantified. In addition, using electron micro-probe analysis, chlorine, chromium, nickel, zinc and vanadium were quantified. Lithium were detected and estimated only by CF LIBS analysis.

Table 2 Comparison of CF LIBS and EMPA bulk rock analyses (n.d.- not detected)

Oxide	CF LIBS (wt.%)	EMPA bulk rock (wt.%)
Na ₂ O	5.45	4.53
SiO ₂	68.04	71.60
Al ₂ O ₃	16.61	13.41
MgO	0.27	0.20
Cl	n.d.	0.14
K ₂ O	3.41	3.71
CaO	1.80	1.35
TiO ₂	0.45	0.28
FeO	3.65	4.00
MnO	0.08	0.17
Cr ₂ O ₃	n.d.	0.01
NiO	n.d.	0.02
BaO	0.03	<0.01
ZnO	n.d.	<0.01
V ₂ O ₃	n.d.	<0.01
Li ₂ O	0.20	n.d.

Beside the fact that EMPA is very precise method, it requires samples prepared as a thin sections or epoxy plugs with a metallic coating, high vacuum and very light elements are difficult to detect. Two modes of operation can be applied on the analysed samples; *i*) EMPA with focused beam, when analysis of individual mineral phases is possible and *ii*) EMPA with defocused beam, when bulk rock analysis can be performed.

Using LIBS, area with a diameter of 100µm is ablated, so average elemental composition can be obtained, with no or minimal sample preparation and also analyses can be performed in air atmosphere at atmospheric pressure. If the LIBS system is miniaturized to the portable form, it can be successfully used also in field research of geological samples without its total destruction.

6 CONCLUSION

In this thesis laser induced breakdown spectroscopy (LIBS) was applied for the quantitative analysis of synthesized zeolites and natural geological samples using calibration based and calibration free approaches.

Calibration based approach was applied on the analysis of three different zeolite types-mordenite, zeolite type Y and ZSM-5. In this case zeolite samples were prepared as the

pressed pellets with no binding material. Five samples of mordenite with Si/Al molar ratios range of 5.25-51.80, five samples of zeolite type Y with Si/Al molar ratios range of 2.30-12.75 and four samples of ZSM-5 zeolite with Si/Al molar ratios range of 14.00-600.00. Calibration curves were constructed separately for all three zeolite types as the dependency of Si/Al molar and intensity ratio of silicon to aluminum spectral lines using both intensity amplitude and area under the spectral line. Obtained calibration curves were observed to be linear with regression coefficient higher than 0.97. Improvement in linearity was observed for the calibration curves constructed using area under the fitted spectral lines. Non-zero intercepts could result from the use of resonant Al line, but as we wanted to preserve unity of used spectral lines for all analysed samples we have decided to use line which was observed and well-resolved in all measured LIBS spectra. Contribution to the non-zero intercept could be also caused by powdering of samples during the ablation according to the fact that no binding material was used and the compactness of the pellets was not ideal.

Next part of calibration based LIBS was dedicated to the analysis of five heavy metals (copper, chromium, cobalt, cadmium and lead) loaded into the ammonium form of zeolite type Y with the molar ratio of Si/Al of 2.49. Selected elements were loaded into the zeolite by the volume impregnation form the water solution using compounds containing mentioned heavy metals. Five samples for every element were prepared with concentrations in the range of 0.05-0.5wt.%. Calibration curves were constructed using non-resonant spectral lines and spectral lines of matrix (silicon, aluminum, calcium and magnesium) were used as the internal standard lines. Method of internal standard was selected to prevent the influence of plasma parameters on the calibration curve and to reduce the influence of the LIBS signal fluctuations and effects of the matrix interferences. Selection of internal standards spectral lines was based on following assumptions: the same ionization stage of both selected spectral lines, similar values of ionization energies of both elements and similar values of upper energy levels of selected lines. In the case of copper, calibration curves were constructed for the resonant spectral line Cu I (324.75nm) with the use of internal standard line and without the use of internal standard line and for a pair of non-resonant spectral lines (515.32nm and 521.82nm) normalized to the intensity of Si I line. In the case of resonant spectral lines, non-linearity of calibration curves was observed either for case of use of internal standard line or for the case without the use of internal standard line. This non-linearity was probably caused by self-absorption of Cu I 324.75nm line even at small concentration of 0.5wt.%. Calibration curve obtained using non-resonant copper spectral lines was observed to be linear with high regression coefficient. In the case of cadmium, non-resonant spectral line at 508.58nm was selected and normalised to the intensity of silicon Si I spectral line. Obtained calibration curve was observed to be linear with high regression coefficient and intercept very close to zero. Calibration curve for lead was constructed using three Pb I (283.31nm, 368.34nm and 405.78nm) spectral lines normalized to the intensity of Si I spectral line. Using of several lines together with the internal standard line has led to very high regression coefficient and intercept very close to zero. Calibration curves for cobalt and chromium were constructed both for neutral and singly ionized spectral lines. Neutral cobalt lines were normalised to the intensity of silicon Si I line and intensities of singly ionised spectral lines were normalized to the intensities of sum of magnesium Mg II and calcium Ca II spectral lines. Better regression coefficient and lower intercept were observed in the case of calibration curve constructed for

singly ionized cobalt lines normalized to the sum of Ca II and Mg II lines. As in the case of cobalt, also in the case of chromium, calibration curves were constructed both for neutral chromium lines and singly ionised spectral lines. As the internal standards, aluminum spectral lines Al I and Al II were selected. Obtained calibration curves are characterised by high regression coefficients and intercepts very close to zero. On the other hand, for the determination of the detection limits of five heavy metals, the most-intense resonant spectral lines were used. Detection limits of 14.4ppm, 18.5ppm, 16.4ppm, 62.6ppm and 190.7ppm were determined for copper, cobalt, chromium, lead and cadmium, respectively. Detection limits except of the value for cadmium are comparable to the detection limits of these elements found in the literature. In the case of cadmium, the strongest spectral line at 226.50nm was selected. But in this spectral region, sensitivity of the spectrometer is low and moreover decreasing due to the use of an optical fiber and furthermore the noise level is quite high. Therefore we have decided to perform measurements using high-resolution spectrometer and EM CCD camera and three and a half times lower detection limit for cadmium was obtained.

At first, calibration-free approach of the LIBS method was applied for the analysis of simple zeolite matrix (three major elements- silicon, aluminum and oxygen). According to the fact that measurements were carried out in air atmosphere, oxygen was not included in the analyses. Silicon to aluminum molar ratios were determined also by means of calibration-free LIBS and results were compared to results of the wet chemical analysis. Eleven samples with the Si/Al molar ratios ranging from 2.3 to 51.8 were analysed. Plasma parameters were determined from the Stark broadening of hydrogen H_{α} line and Saha-Boltzmann pot method. Selection of spectral lines based on transition probability and energy of lower level of fitted spectral lines and ratio of neutral and singly ionized atom number densities was done, to increase the accuracy. Also elemental concentrations were taken into account. For high elemental concentrations, mainly resonant spectral lines were rejected from the analysis. Average electron temperature used for the evaluations of the intercepts was determined as an average temperature from silicon and aluminum Saha-Boltzmann plots. Results obtained by CF LIBS are in very good agreement with the wet chemical analysis results, with average relative standard deviation of 4.7%.

After successful application of CF LIBS to the analysis of simple matrix, we have tried to analyse also samples with more complicated matrices, like geological materials. During the analyses of fragments of the meteorites “Košice” and “Smolenice” the non-destructive character of the LIBS method was utilized. This allowed us to carry out measurements of several fragment of the “Košice” meteorite and performed comparison of elemental composition between the fragments and crust and inner part of individual fragments. Also in this case, strict selection of spectral lines was applied during the calibration-free analysis. Ten elements were observed in the measured LIBS spectra and nine elements (major and minor) were quantified. Trace elements were not detected. CF LIBS results were compared to the result obtained by ICP MS and an agreement between both of results was observed. During the writing of this thesis, we have received a fragment of the “Smolenice” meteorite. It is an iron type meteorite, but complete classification is not done yet. Iron type meteorites are characterised by the content of $Fe+Ni+Co > 95\%$ and 5-25% of Ni. Classification is performed based on trace elements (iridium, germanium and gallium)

content. Due to the very high iron concentration, measured LIBS spectra are overcrowded by the iron spectral lines and detection of trace elements is very difficult. Therefore, simulation of the LIBS spectra at given conditions (electron density of $6 \times 10^{23} \text{m}^{-3}$ and electron temperature of 1eV) and elemental concentrations (95% of Fe, 5% of Ni, 100ppm of Ir and 100ppm of Ge) were done to determine spectral regions where to search for the trace elements spectral lines using high-resolution spectrometer coupled with an iCCD camera. Iron and nickel contents were determined by the CF LIBS using broadband Mechelle spectrometer coupled with an iCCD camera. Due to the high iron content in the analysed fragment, strict selection of well-resolved spectral lines non-affected by the self-absorption effect was done. According to the simulations, suitable spectral regions for the iridium spectral lines searching were found and preliminary results of this trace element have classified this fragment in to the IIA group with the Ir content between 0.01-60ppm.

CF LIBS approach was also used for the analysis of acid pitchstone and granite samples. Electron micro-probe analysis was used as a comparative method to the CF LIBS. In the case of more homogeneous sample of the acid pitchstone, mineral phases were not distinguishable using LIBS method due to the laser spot size to be much larger than dimensions of individual minerals. Therefore average elemental composition was determined using several measurements and these results were compared to the EMPA whole rock analysis. Results were in a good agreement, but using EMPA more elements were quantified. On the other hand, very light elements like lithium were detected only by LIBS. In the case of granite sample, LIBS can be used for the analysis of individual mineral phases due to the larger dimensions of minerals (plagioclase, K-feldspar, quartz and biotite).

Thanks to the non-destructive character of the LIBS method and any or minimal requirements on the sample pre-treatment it is suitable for the qualitative and quantitative analysis of rare and precious samples. Comparing to the other analytical methods, i.e. EMPA, ICP MS, where samples have to be prepared as the thin sections or the epoxy plugs coated by a metal layer or samples are milled to the dust and totally destroyed. Another advantage of the LIBS method is possibility of very light elements detection. On the other hand, accuracy of the calibration based and calibration-free LIBS is still poorer and detection limits are higher comparing to the ICP MS technique.

Therefore, an effort in this way should be made and our future plans consist in that, to improve detection limits using high-resolution spectrometer and EM CCD camera and by decreasing of noise level, which influences the detection limits in the negative way. We would like to focus on the detailed study of spectral lines profiles to evaluate self-absorption effect already at low concentrations using high-resolution spectrometer and iCCD camera to increase accuracy of the CF LIBS method. And finally, our attention will be focused on the quantitative analysis of trace elements in the meteorite fragments using spectra recorded in VUV range by the high-resolution spectrometer and broadband spectra recorded by Mechelle spectrometer, but without using of the optical fiber what will allow us to have the spectra from 200nm to 975nm.

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AFC06 Hulík, Jakub 16% - Kociánová, Mária 12% - Grolmusová, Zuzana 12% - Horňáčková, Michaela 12% - Plavčan, Jozef 12% - Rakovský, Jozef 12% - Veis, Pavel 12% - Kopáni, Martin 12%: Study of spleen elemental composition using CF-LIBS
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AFC07 Kociánová, Mária 16% - Grolmusová, Zuzana 12% - Plavčan, Jozef 12% - Horňáčková, Michaela 12% - Rakovský, Jozef 12% - Veis, Pavel 12% - Bača, M. 12% - Barta, Peter 12%: Assigning of parts of archaeological bronzeartefacts and their fragments usinglaser-induced breakdown spectroscopy (LIBS)
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AFD08 Plavčan, Jozef 20% - Horňáčková, Michaela 16% - Grolmusová, Zuzana 16% - Kociánová, Mária 16% - Rakovský, Jozef 16% - Veis, Pavel 16%: Sikhote-Alin meteorite, elemental composition analysis using CF LIBS

Recenzované

Lit. 11 zázň., 4 obr.

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AFD01 Grolmusová, Zuzana 50% - Plavčan, Jozef 10% - Horňáčková, Michaela 20% - Kociánová, Mária 10% - Veis, Pavel 10%: Silicon wafer as a support material for LIBS bioapplications

Recenzované

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Recenzované

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AFG01 Grolmusová, Zuzana 70% - Horňáčková, Michaela 10% - Plavčan, Jozef 5% - Veis, Pavel 5% - Kopáni, Martin 5% - Babál, Pavel 5%: LIBS as a diagnostic tool for human soft tissues

Lit. 3 zázň.

In: EMSLIBS 2011 : Euro-Mediterranean Symposium on Laser-Induced Breakdown Spectroscopy. - [Cesme] : [IZTECH], 2011. - S. 164

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AFG02 Grolmusová, Zuzana 20% - Rapčanová, A. 20% - Horňáčková, Michaela 20% - Plavčan, Jozef 20% - Veis, Pavel 20%: Elemental composition of vegetarian fingernail using LIBS analysis

Lit. 2 zázň., 1 obr.

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AFG03 Horňáčková, Michaela 20% - Horňáček, M. 16% - Grolmusová, Zuzana 16% - Plavčan, Jozef 16% - Hudec, P. 16% - Veis, Pavel 16%: Detection of copper, cobalt and chromium in zeolites using laser induced breakdown spectroscopy

Lit. 4 zázň., 1 obr.

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AFG04 Horňáčková, Michaela 23% - Plavčan, Jozef 23% - Grolmusová, Zuzana 23% - Konečný, P. 5% - Holický, Ivan 5% - Veis, Pavel 21%: Analysis of basic mineral phases in granite using calibration free

laser induced breakdown spectroscopy (CF-LIBS)

Lit. 5 zázň.

In: Laser-induced Breakdown Spectroscopy. - Lyon : Université Claude Bernard, 2013. - S. 42

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AFH01 Horňáčková, Michaela 30% - Horňáček, Michal 30% - Hudec, P. 10% - Veis, Pavel 30%: Determination of Si/Al molar ratio in microporous zeolites using calibration free laser induced breakdown spectroscopy (CF-LIBS)

Lit. 5 zázň.

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[ESAS 2012 : European Symposium on Atomic Spectrometry. Tatranská Lomnica, 7.-12.10.2012]

[SCSC 2012 : Slovak-Czech Spectroscopic Conference. 20th, Tatranská Lomnica, 7.-12.10.2012]

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Lit. 6 zázň.

In: Analytika v geológii a v životnom prostredí 2013. - Bratislava : Štátny geologický ústav Dionýza Štúra, 2013. - S. 33. - ISBN 978-80-89343-87-4

[Analytika v geológii a v životnom prostredí 2013. Spišská Nová Ves, 13.-15. 11. 2013]

BDF01 Horňáčková, Michaela 20% - Plavčan, Jozef 16% - Grolmusová, Zuzana 16% - Konečný, P. 16% - Holický, I. 16% - Veis, Pavel 16%: Analýza minerálov v granite metódou LIBS

2 obr., 2 tab.

In: ChemZi. - Roč. 9, č. 1 (2013), s. 10

BEE01 Horňáčková, Michaela 20% - Plavčan, Jozef 16% - Grolmusová, Zuzana 16% - Konečný, P. 16% - Holický, I. 16% - Veis, Pavel 16%: Laser induced breakdown spectroscopy of geological samples with different homogeneity

Popis urobený 27.8.2013

Lit. 13 zázň.

In: 31st International Conference of Phenomena in Ionized Gases [elektronický zdroj]. - Granada : Spanish National Research Council , 2013. - Art. No. PS1-037, s. 1-4 [online]

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URL: http://www.icpig2013.net/papers/188_1.pdf

BEE02 Horňáčková, Michaela 16% - Plavčan, Jozef 14% - Rossi, L. 14% - Maťko, I. 14% - Janikovič, D. 14% - Švec, P. 14% - Veis, Pavel 14%: Analysis of the Fe- Co- B- Si amorphous thin ribbon using laser induced breakdown spectroscopy

Popis urobený 28.8.2013

Lit. 11 zázň.

In: 31st International Conference on Phenomena in Ionized Gases [elektronický zdroj]. - Granada : Spanish National Research Council, 2013. - Art. No. PS3-036, s. 1-4 [online]

[ICPIG 2013 : International Conference of Phenomena in Ionized Gases. 31st, Grananda, 14.-19.7.2013]

URL: http://www.icpig2013.net/papers/188_2.pdf

Štatistika kategórií (Záznamov spolu: 25):

ADC Vedecké práce v zahraničných karentovaných časopisoch (4)

ADN Vedecké práce v domácich časopisoch registrovaných v databázach WOS alebo SCOPUS (1)

AED Vedecké práce v domácich recenzovaných vedeckých zborníkoch, monografiách (1)

AFC Publikované príspevky na zahraničných vedeckých konferenciách (8)

AFD Publikované príspevky na domácich vedeckých konferenciách (2)

AFG Abstrakty príspevkov zo zahraničných vedeckých konferencií (4)

AFH Abstrakty príspevkov z domácich vedeckých konferencií (2)

BDF Odborné práce v ostatných domácich časopisoch (1)

BEE Odborné práce v zahraničných zborníkoch (konferenčných aj nekonferenčných) (2)

Statistics of citations (3):

[o1] Citácie v zahraničných publikáciách registrované v citačných indexoch (2)