Evaluation of minor and trace elements in meteorite "Košice" by calibration-free laser induced breakdown spectroscopy

M. Horňáčková[1], J. Plavčan[1], Z. Grolmusová[1], J. Rakovský[1], M. Kociánová[1], J. Tóth[2], V. Porubčan[2,3], J. Svoreň[3] and P. Veis[1(*)]

[1]*Dept. of Experimental Physics, Comenius Univ., Mlynská dol. F2, 842 48 Bratislava, Slovak Republic*
[2]*Dept. of Astronomy, Physics of the Earth and Meteorology, Comenius Univ., 842 48 Bratislava, Slovak Republic*
[3] *Astronomical Institute of the Slovak Academy of Sciences, Tatranská Lomnica, Slovak Republic*
[(*)]veis@fmph.uniba.sk

Calibration- free laser induced breakdown spectroscopy (CF- LIBS) was used for detection of minor and trace elements and quantitative analysis of meteorite "Košice". As ablating source Q- switched Nd: YAG laser was used. Time resolved spectra (200- 950 nm) of laser induced plasma emission were recorded by echelle type spectrometer equipped with intensified CCD camera (min. gate time 5 ns). By means of LIBS trace elements, like chromium, manganese, potassium, sodium, nickel and phosphorus were identified in examined sample and quantified. LIBS method is suitable as a complementary analysis of meteorites, because provides possibility to detect such elements like chromium, which were not detected by classical geological analysis, ICP- MS and ED XRF.

Introduction. Laser induced breakdown spectroscopy (LIBS) is a versatile method of optical emission spectroscopy for qualitative and quantitative analysis of solid, liquid, gaseous samples and aerosols. The main advantage of this method is that only optical approach to the sample is required. In CF- LIBS determination of electron concentration and temperature is crucial point for precise determination of element concentration. This method was successfully applied to analysis of different types of materials [1-3] and also meteorites [4, 5].

Experimental. Scheme of experimental apparatus is shown in Figure 1.. Q- switched Nd:YAG laser (5 ns pulse duration, 165 mJ maximum energy per pulse, Brilliant EaZy, Quantel) operating at second harmonic frequency 532 nm was used for sample ablation and plasma creation. The laser beam was focused on the sample surface by a 40 mm focal length quartz lens. Fragment of meteorite "Košice" was placed on X- Y- Z stage to be able to change position of laser spot during measurement. Emission from plasma was collected by optical fiber linked with the entrance slit of an Echelle spectrometer (ME 5000, Andor) coupled with intensified CCD camera (iStar, Andor). This spectrometer has a focal length of 195 mm with a numerical aperture of *f* /7, provided average spectral resolution (λ/Δλ) of 5000 and possibility to detect emission spectral lines in wide range 200- 975 nm. Mercury argon calibration lamp (HG- 1, Ocean Optics) was used for wavelength calibration. For data acquisition and analyzing PC was used. All measurements were carried out in air at atmospheric pressure and all measured spectra were corrected to the spectral response of an echelle spectrometer.

Sample. At night of February 28, 2010, superbolide entered the atmosphere over the Eastern Slovakia illuminating the sky and countryside at 22:25 UT. Due to trajectory analysis done by Jiří Borovička, the impact area of possible meteorite was calculated [6]. 78 meteorites were found among them the largest fragment of the weight of 2.17 kg. The total mass recovered is 4.3 kg. Mineralogical analysis implies that the recovered meteorite is classified as an ordinary H5 chondrite [7]. However, this observed meteorite fall is a very rare case of the meteorite with the known heliocentric orbit, which allowed us to place specific meteorite type available for detail study in the Solar system.

Results and discussion. For CF- LIBS analysis, accurate determination of electron concentration and temperature is very important. Stark broadening mechanism of hydrogen H_α line (656 nm) was used for determination of electron concentration using equation [8]

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

where FWHA is full width at half area and n_e is unknown electron concentration. For determination of electron temperature Saha- Boltzmann plot method was used. This method allows placing neutrals and singly ionized species in the same plot. The coordinates for neutrals (2) and for ions (3) in Saha- Boltzmann plot are

$$x = E_k\,,\; y = \left(\frac{I_{ki}\lambda}{g_k A_{ki}}\right) \quad (2) \quad x = E_j + E_{ion}\,,\; y = \ln\left(\frac{I_{ki}\lambda}{A_{ki} g_k}\right) - \ln\left(\frac{2\left(2\pi m_e\right)^{3/2}\left(k_B T\right)^{3/2}}{n_e h^3}\right) \quad (3)$$

where E_k, E_j are energies of levels k and j, E_{ion} is ionization energy of element, I_{ki} is integral line intensity, λ is wavelength, A_{ki} is transition probability, g_k is degeneracy of level k, k_B is Boltzmann constant, T is electron temperature, h is Planck constant. Slope of linear fit in Saha- Boltzmann plot is equal to $-1/k_BT$, and than electron temperature can be easily determined.

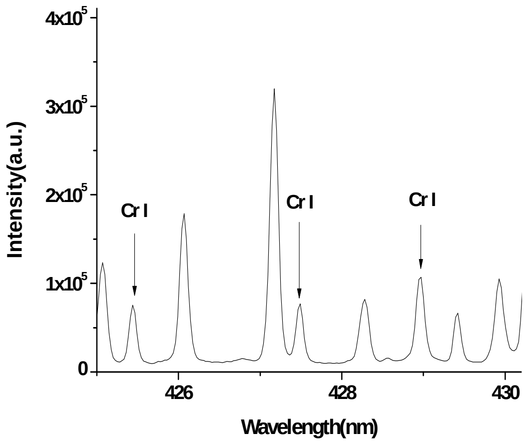

Fig. 1 Three identified lines of neutral chromium

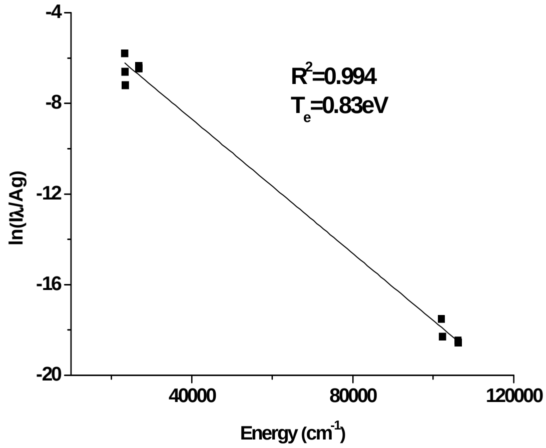

Fig. 2 Saha- Boltzmann plot for Cr I and Cr II

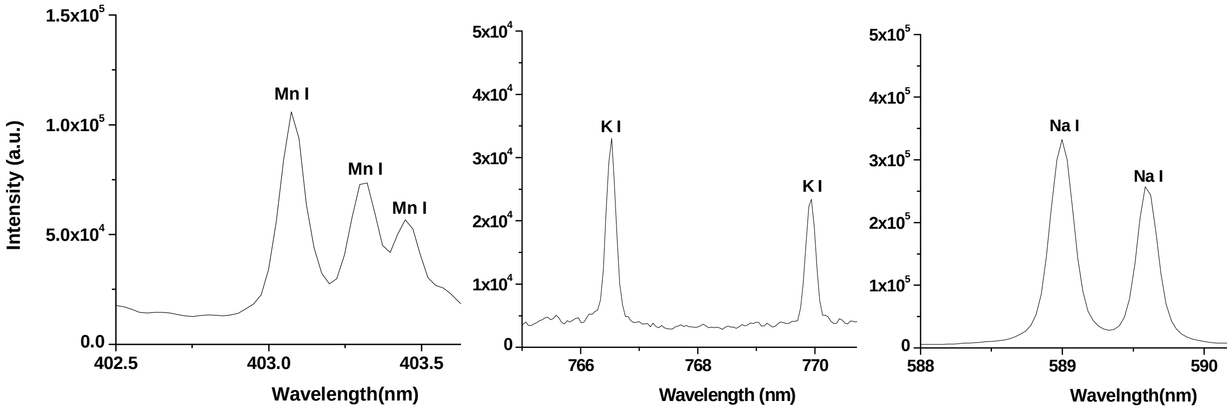

Fig. 3 Spectral lines of manganese sodium and potassium

Spectra were measured 1, 4 and 9 μs after laser pulse and optimal signal to noise ratio was at 1μs. Spectral lines were identified by program, in which NIST atomic lines database [9] was implemented. Temperature determined from Saha- Boltzmann plot for chromium lines (Fig. 2), T_e= 0.83 eV and electron concentration determined using Eq. 1, N_e= 2.5 10^{23} m^{-3} ± 1.1 10^{23} m^{-3}. Major elements occurred in meteorite are Mg, Si and Fe. Ca, Al and Ni are in the range of 1- 2% and trace elements are Cr (Fig. 1), Mn (Fig. 3), P, K (Fig. 3), and Na (Fig.3). Composition of meteorite strongly depends on position, where laser beam was focused. Absolute concentrations of all detected elements will be presented on our poster during the conference.

Acknowledgment. This work was funded from VEGA 1/1157/11, APVV-0685-11 and APVV-0516-10.

References: *[1] B. Praher et al., Spectrochimica Acta Part B 65 (2010) 671–679; [2] J.A. Aguilera et al., Spectrochimica Acta Part B 64 (2009) 685–689; [3] V.S. Burakov, S.N. Raikov, Spectrochimica Acta Part B 62 (2007) 217–223; [4] F. Colao et al., Planetary and Space Science 52 (2004)117–123; [5] M. Dell´ Aglio et al., Geochimica et Cosmochimica Acta 74 (2010) 7329–7339; [6] Borovička J. et al. (2012) Meteoritics & Planet. Sci., to be submitted; [7] Meteoritical Bulletin 100; [8] M. A. Gigosos et al., Spectrochimica Acta Part B 58 (2003) 1489–1504; [9] Ralchenko et al., (2011). NIST Atomic Spectra Database (ver. 4.1.0), [Online]. Available: http://physics.nist.gov/asd [2012, March 2]. National Institute of Standards and Technology, Gaithersburg, MD*