



# Discrimination of moist oil shale and limestone using laser induced breakdown spectroscopy



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## ABSTRACT

Laser-induced plasma emission spectra of Estonian oil shale and associated limestone with varying moisture content were studied. Time gated spectra excited by 1064 nm laser radiation were recorded. Spectral lines for determination of plasma parameters were selected. Moisture causes the reduction of the intensity of the total emission, and increases the intensity of the  $H_{\alpha}$  line. It was found that the effect of the moisture content on the plasma temperature and electron concentration was inconsiderable. Using the ratio of intensities of  $H_{\alpha}$  and Mg spectral lines, it was possible to distinguish reliably between limestone and oil shale independently of their moisture content.

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## 1. Introduction

Laser induced breakdown spectroscopy (LIBS) has been successfully applied for qualitative and also quantitative analysis of geological highly heterogeneous materials like soils, sediments, mineral rocks and meteorites [1–3]. Several industrial LIBS applications for the mineral percentage evaluation and material sorting on the moving conveyor belt have been reported [4–7]. More extensive overviews of the different application area of LIBS are given in the recent reviews [8,9]. In the present paper results of LIBS application for the characterization of Estonian oil shale are described.

Estonian oil shale is a sedimental carbonaceous fuel with complicated composition of organic and mineral matter, which has been the main energy resource in Estonia as well as an important raw material in chemical industry [10]. Most of Estonian  $CO_2$  emission is coming from the oil shale sector. Minimization of the environmental impact, the more efficient usage of oil shale and optimization of industrial processes are important tasks for Estonian society.

Estonian oil shale is characterized by the high hydrogen to carbon ratio about 1.5, which is distinct from coal and is more comparable to that of crude oil [10]. Carbonates in form of calcite and dolomite dominate in the mineral part of oil shale. The mineralogical composition of the carbonate part (limestone) is given in Table 1 [10].

The kerogenic limestone that contains additionally to the carbonates a small amount of other minerals and organics is associated with oil shale.

The mineral and elemental composition of dry Estonian oil shale according to [10,11] is presented in Table 2.

The chemical structure of the organic part of oil shale, kerogen, is evaluated in [12] by the model of geo-macromolecule, which has an empirical chemical formula  $C_{421}H_{638}O_{44}S_4NCl$ .

The basic quality parameter of the oil shale as mined is its heating value, which has a strong correlation with the content of organic matter, kerogen [13]. The excavated so called mountain massive contains in addition to the oil shale a certain amount of limestone-rich interlayers and water up to 14% [11]. The mineral and elemental composition of this kerogenic limestone is approximately the same as for oil shale, except that the percentage of organics is low, close to zero. The investigation [10] has been established that the average composition of the main components of oil shale is quite constant throughout the Estonian oil shale basin. Hence, the composition of an oil shale sample is determined by the relative amounts of organic and mineral parts in the sample.

According to Table 2, the content of organic matter in dry oil shale is uniquely related to its hydrogen content. Thus, the estimation of the organic percentage in oil shale by the intensity of H line in LIBS spectra seems to be a promising method. However, in real conditions the mined oil shale contains water, which is another source of hydrogen. The presence of water complicates the usage of H line for the estimation of the kerogen percentage.

The moisture effects to LIBS spectra of geological materials are reported only in few papers. In [4,5] it was found that moisture causes strong alteration in LIBS spectra of different materials. In [14] Martian analog wet and dry rocks were studied with the aim to distinguish the LIBS signal variations caused by the sample heterogeneity from the effects caused by water under Martian environment conditions. The effects of different water content to LIBS signal of soil samples was under the study in [15], where the changes in intensities were attributed to the plasma quenching by water vapor. In the earlier LIBS study of moist soil and sand samples [16] was reached to similar conclusions. In

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**Table 1**  
Mineralogical composition of limestone.

Mineral	Formula	Content, %
Calcite	CaCO <sub>3</sub>	69.1
Dolomite	CaMg(CO <sub>3</sub> ) <sub>2</sub>	30.6
Siderite	FeCO <sub>3</sub>	0.3

[4,5,15,16] the conclusion was made that for getting reliable results and for the compensation of weakening of the LIBS signal, the energy densities for damp samples should be considerably higher than for dry samples. The potentials of LIBS for in situ monitoring moisture content of fresh food, particularly cheese, were demonstrated in [17].

The aim of our present study was to find out the moisture effect on the LIBS spectra of the high grade oil shale as well as of kerogenic limestone samples. With this aim a set of analytical spectral lines was found and the electron concentration and the excitation temperature of laser induced plasma as a function of time, laser fluence and samples' water content, were investigated.

Another objective was to ascertain characteristics of LIBS spectra less affected by moisture and thus enabling better distinguishing between oil shale and limestone.

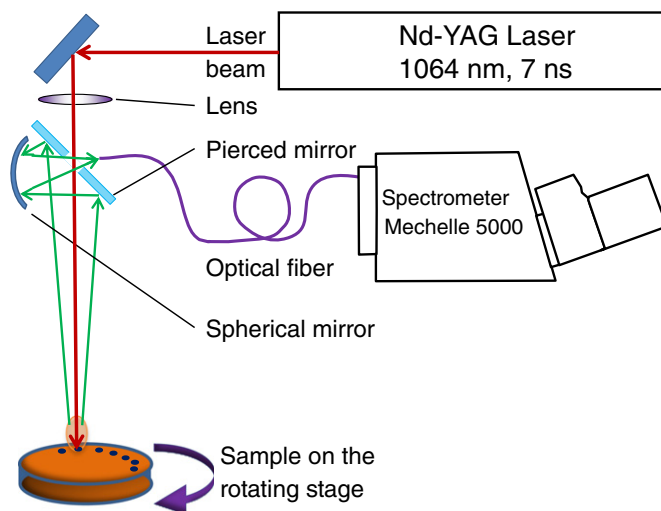
## 2. Experimental

Measurements of LIBS spectra were performed with the collinear recording scheme presented in Fig. 1. The Nd:YAG laser ( $\lambda = 1064$  nm, 7 ns pulse width) created plasma plume. The repetition rate of 0.6 pulses per second was used in experiments.

The laser beam was focused onto the target by a fused silica lens of 60 cm focal length. To avoid air breakdown, the position of the focal point was always below the sample surface. The laser spot size was about 0.45 mm in diameter. The laser fluence on the samples' surface was varied in the range of 15–50 J/cm<sup>2</sup>. To avoid the effects caused by the samples' surface modification due to the laser radiation and ensure that a fresh surface was available for each laser shot, a stepper motor rotated the sample to the new position after each laser shot. Radiation emitted by laser induced plasma was collected collinearly with a pierced mirror, a spherical mirror of 5 cm focal length and an optical fiber of 50  $\mu$ m core diameter connected to the spectrometer. The Mechelle-5000 spectrometer coupled with a time-gated CCD camera allowed to record spectra in 230–850 nm range. The instrumental function (full width at half maximum (FWHM)) was measured using the low pressure Hg lines and was found to range from 0.045 nm at 230 nm to 0.155 nm at 750 nm. Acquisition parameters like the delay time,  $t_d$ , between the laser pulse and the beginning of the time gate, the width of time gate (exposure time),  $t_g$ , and the number of accumulations were set using the Andor Solis software. The wavelength

**Table 2**  
Mineral and elemental composition of dry Estonian oil shale.

Component	wt.%	Element	at.%
ORGANICS	29.2	Al	0.75
SiO <sub>2</sub>	12.1	C	28.39
CaCO <sub>3</sub>	43.58	Ca	5.13
MgCO <sub>3</sub>	6.98	Fe	0.25
FeS <sub>2</sub>	2.28	H	33.93
Al <sub>2</sub> O <sub>3</sub>	3.26	K	0.32
CaO	0.07	Li	0.42
MgO	0.08	Mg	0.99
CaSO <sub>4</sub>	0.17	N	0.07
Fe <sub>2</sub> O <sub>3</sub>	0.17	Na	0.06
TiO <sub>2</sub>	0.14	O	26.69
Na <sub>2</sub> O	0.16	S	0.64
K <sub>2</sub> O	1.28	Si	2.36
Li <sub>2</sub> O	0.53	Ti	0.02



**Fig. 1.** The principal scheme of LIBS measurements.

calibration of the spectrometer was done with the help of a low pressure mercury lamp, and the relative sensitivity with the help of the deuterium–halogen calibration source (Ocean Optics DH-2000).

Samples were cut out from high grade oil shale and kerogenic limestone rocks coming from the Estonia Mine (North East Estonia). 4 samples of high grade oil shale and 4 samples of kerogenic limestone were analyzed. The samples had diameter of 40 mm, thickness of 10 mm and weight about 20 g. The moisture content in samples was varied and its amount was evaluated by weighting procedure (balances Kern EG 220-3NM of 1 mg resolution).

The next procedure of the evaluation of the moisture content has been used. Firstly room-dry samples were dried in the oven at the temperature of 95–105 °C for 5 h. Weighting showed that already after 3 h drying the samples' weight did not decrease anymore and we assumed that after 5 h drying they were completely dry.

Samples were always weighted directly before and immediately after the acquisition of spectra. We moisturized samples by soaking them in distilled water for 2 h. Before the following weighting and spectra recording samples were slightly wiped with a filter paper. To get intermediate moisture contents, we let samples to dry in lab air or in the oven, after that we held them in hermetically sealed small containers at least for 2 h to ensure more even distribution of moisture. During the acquisition time of spectra (about 100 s) the mass losses of moist samples were attributed mainly to water evaporation. The relative uncertainty of the evaluation of the moisture percentage was better than 2%. It must be pointed out that the weighting procedure gives only the average volume moisture content, whereas for LIBS analyses the surface moisture is much more important.

## 3. Results and discussion

All elements listed in Table 1, except sulfur, were detected in recorded LIBS spectra for both, oil shale and limestone. We identified more than 140 spectral lines using the National Institute of Standard and Technology (NIST) electronic database [18]. As the content of nitrogen in oil shale is very low, recorded strong lines of atomic nitrogen in case of both, oil shale and limestone most likely originated from the ambient air.

Fig. 2 presents two characteristic regions of recorded spectra. In Fig. 2a UV part of the spectra with the carbon C I 247.86 nm line is presented. Other identified lines in this spectral interval belong to Si I and Fe II, among which the most prominent lines are Si I 250.69 nm, Si I 251.61 nm and Fe II 251.90 nm.

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