



Application of diffuse reflectance spectroscopy for quick laboratory assessment of Estonian oil shale quality

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Abstract. Diffuse reflectance spectroscopy in near infrared region was used as a fast laboratory method for quantitative assessment of the calorific value and the moisture content of Estonian oil shale. Samples of different calorificity were collected from Narva open-cast mine and from beneficiation plant of Estonia underground mine, Estonia. The set of crushed oil shale samples, which moisture content was varied were tested by the help of a commercial multipurpose analyser, where Fourier-transform spectrometer recorded spectra in near infrared region and the software used partial least squares regression method. Results were related to the values of calorificity and moisture content, obtained by the bomb calorimeter and weighing methods, respectively. Bands characterizing organic and inorganic parts of the samples as well as the presence of the free water were ascertained by the infrared spectroscopy. Using the software provided by the analyser, the calorific value and the moisture content of samples were predicted. The prediction error of the lower calorificity was 1 MJkg^{-1} and prediction error of the weight percent of the moisture content was 1.35%. The comparison between achieved results and the values obtained from earlier laser-induced breakdown spectroscopy (LIBS) measurements shows that in laboratory conditions more precise prediction can be made by diffuse reflectance measurements. Further improvement of the prediction accuracy could be achieved by modified software which considers observed nonlinear effects in spectra.

Key words: crushed oil shale, diffuse reflectance spectroscopy in near infrared region, assessment of calorific value and moisture content.

1. INTRODUCTION

In Estonian energy production, renewable sources have an increasing importance but at least during the following decade, oil shale will be the dominating raw material for combustion at power plants and for production of shale oil [1]. The optimization of the working regimes of both processes need online control of the oil shale quality which varies from place to place, depending on the oil shale deposit.

The quality of oil shale is often characterized by its calorific value. Currently, a precise determination of the oil shale calorific value is made in laboratory conditions by the bomb calorimetric method [2]. This procedure has typically several time-consuming steps (sampling, transportation, averaging the initial sample to analytical sample, grinding, measuring moisture content and finally, determining the calorific value in bomb). The total duration determining the calorific value could take several hours. Accordingly, this routine method is not suitable for fast quality control of non-stop processes.

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Among methods applied for quality control of raw material on running conveyer belt, the optical method based on the laser-induced breakdown spectroscopy (LIBS) has the advantage of being rapid, non-destructive and relatively safe [3–5]. In case of this method, a focused laser beam evaporates the material and emission spectra of chemical elements is recorded [6]. For oil shale analysis, our previous study demonstrated that the concentrations of main ingredients of pellets pressed from oil shale powders can be found on the basis of LIBS spectra by using methods of multivariate analysis [7]. LIBS was further applied for the determination of the calorific value and the moisture content of crushed oil shale samples on the mock-up of the conveyer belt [8]. Results of the two last studies showed that LIBS method could be implemented for obtaining online information of the oil shale quality.

Another optical method used for the assessment of the quality of the raw material is the diffuse reflectance spectroscopy (DRS), which records spectra in infrared or near infrared (NIR) regions [9,10]. As spectra arising in these regions are caused by vibrations of chemical compounds, they are more directly related to the properties of material (e.g. calorific value and moisture) than that of atomic spectra of LIBS. The method is widely used in food and beverage industry, agricultural tests and petrochemical industry [11,12], and it has potential for online measurements over moving conveyor belt [13,14]. The method of NIR DR spectroscopy was successfully used in studies of various quality parameters of coal and biomass/coal samples, applying different data processing methods [15–18]. For oil shale powder samples, it was possible to

predict the yield of shale oil by the NIR DR spectroscopy [19–21]. Nevertheless, there are no studies where NIR DR spectroscopy had been used to predict the calorific value and moisture content of the oil shale.

The aim of the present study was to evaluate the suitability of NIR DR spectroscopy for determining the calorific values and moisture content of crushed oil shale. An extra task of the study was the comparison of results of DR spectrometry with those obtained by LIBS, and thus, the present study uses the same set of samples of crushed oil shale which were used for LIBS studies [8]. NIR spectra were recorded at different values of moisture content. For quantitative analysis, multivariate calibration models were applied.

2. SAMPLES

The samples investigated during present study were similar as in our previous study with LIBS and are listed in Table 1 [8]. Most of the samples (11) were collected from Narva (Estonia) open-cast mine, from the 7th trench's west side exposure (outcrop), from different layers of oil shale and limestone interlayers A-F2 [22]. Additional 4 samples labelled with EST were taken from the stopped conveyor belt of the beneficiation plant of Estonia underground mine.

All samples were crushed by jaw crusher to the fraction of 0–25 mm. One part of each sample was used for the determination of calorific value by the bomb calorimeter method (ISO 1928). Calorific values Q^d of dry samples are presented in Table 1.

Table 1. Calorific value and moisture content of samples

No.	Index of layer	Q^d (MJ/kg)	Moisture content W (w%)						
			W1	W2	W3	W4	W5	W6	W7
1	B	21.123	0.5	3.7	7.6	11.3	14.9	18.6	21.6
2	C	15.581	0.5	3.6	7.2	10.8	14.5	18.1	21.7
3	A+A'	13.605	0.5	3.7	7.4	10.8	14.4	18	22.3
4	ESTQ11.4	12.758	0.5	3.7	7.5	11.2	14.9		
5	E	12.616	0.5	3.6	7.2	10.7	14.4		
6	ESTQ8.0	10.064	0.5	3.6	7.3	11	14.7	18.3	
7	F1	9.493	0.5	3.7	7.4	11.1	14.7		
8	ESTQ7.0	9.1	0.5	3.7	7.3	11	14.6	18.3	
9	D	6.813	0.5	3.6	7.3	10.8	14.3		
10	F2	4.502	0.5	3.7	7.5	11.2	14.9		
11	ESTQ1.5	3.055	0.5	3.7	7.4	11.1	14.6		
12	B/C	2.32	0.5	3.9	7.6	11.4	15	17.9	
13	D/E	1.811	0.5	3.8	7.6	11.3	14.9		
14	C/D	0.721	0.5	3.7	7.4	11	14.4		
15	B/A'	0.503	0.5	3.8	7.5	11.3	15		

Another part of samples was kept in hermetically closed jars between measurements of spectra. The moisture content of samples was determined by oven-drying method. Differently from the previous study [8], the moisture content of samples was increased from low to high moisture level (up to 20%) by pipetting 4% of the sample weight into the jar, followed by subsequent “homogenization” in closed jars, which lasted about 10 hours at room temperature.

Before the measurements with increasing moisture content, samples were dried in the evacuated oven at the temperature of 105 °C for about 24 hours. These dry samples were characterized by 0.5 weight percent of moisture content.

Overall, seven remarkably different values of moisture content were set (Table 1). For a number of samples, the highest moisture contents (see columns W6 and W7, Table 1) could not be set as they were not able to absorb such amount of water.

3. DEVICE AND PROCEDURE OF MEASUREMENTS

The NIR spectra from crushed oil shale samples were measured and the data were processed by multi-purpose analyser MPA-FT-NIR (Bruker Optik GmbH), where IR spectrum in 12500–3600 cm^{-1} (800–2780 nm) interval was recorded by Fourier transform spectrometer. The device worked in diffuse reflectance mode. Figure 1 passes the idea of collection of light reflected from a sample [23]. Lumps of oil shale with different size and random orientation filled tightly a rotating Petri dish of 90 cm diameter. The centre of the incident light beam of $\approx 3 \text{ cm}^2$ cross-section area was at 2.5 cm distance from the rotation axis. Light, partly reflected from oil shale lumps at very different angles, is collected by the integrating sphere. The inner surface of the sphere has a

very diffuse coating with high reflection and evenly dispersed light is formed due to the multiple reflections inside the sphere, which is detected by detector. The relative remittance R' is determined as the ratio of intensity of the signal from the sample of the reference non-absorbing surface.

At 8 cm^{-1} spectral resolution, the average of 64 spectra was saved. During the recording of these spectra Petri dish made 2.7 revolutions. At a fixed moisture content each sample was characterized by at least three averaged spectra, the time interval between the recordings of spectra was ≈ 1 min. Overall, 355 spectra were recorded.

4. SPECTRA

Figure 2a presents the dependence of absorbance A on the wave number ν . Here, the term “absorbance” is just the apparent absorbance, introduced as an analogous to that in transmission spectroscopy and defined as $A = \log(\frac{I}{I_0})$, its value is directly related to the concentration of absorbing species [10].

Here, like in further figures, the absorbance is presented as a function of wavelength.

At a fixed calorificity the bias component of absorption spectra gradually increased with the growth of the moisture content, whereby in case of samples with higher calorificity the bias was more intensive. At $\nu > 7500 \text{ cm}^{-1}$ ($\lambda < 1300 \text{ nm}$) the absorption bands were missing and at $\nu < 3800 \text{ cm}^{-1}$ ($\lambda > 2600 \text{ nm}$) the absorption was very large. For further analysis of spectra, only the narrower spectral range with the characteristic absorbing bands was selected.

Closer examination of presented spectra in the 1200–2600 nm range showed a good signal-to-noise ratio, which allowed to characterize samples by the first derivative of the spectrum. Figure 2b demonstrates that this data

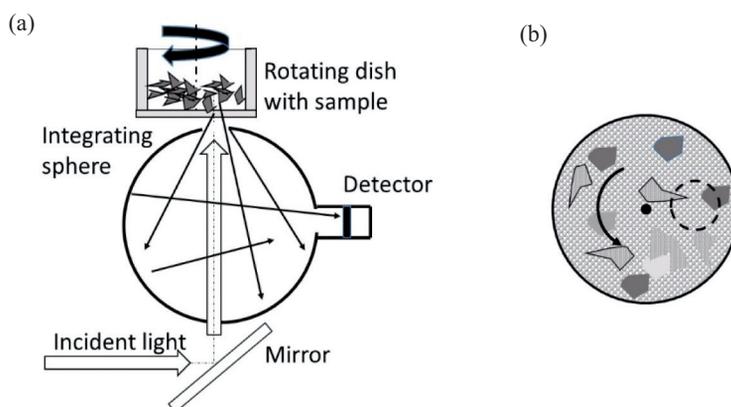


Fig. 1. (a) sample illumination and collection of reflected light; (b) top view of Petri dish; dashed line indicates the area of incident light beam.

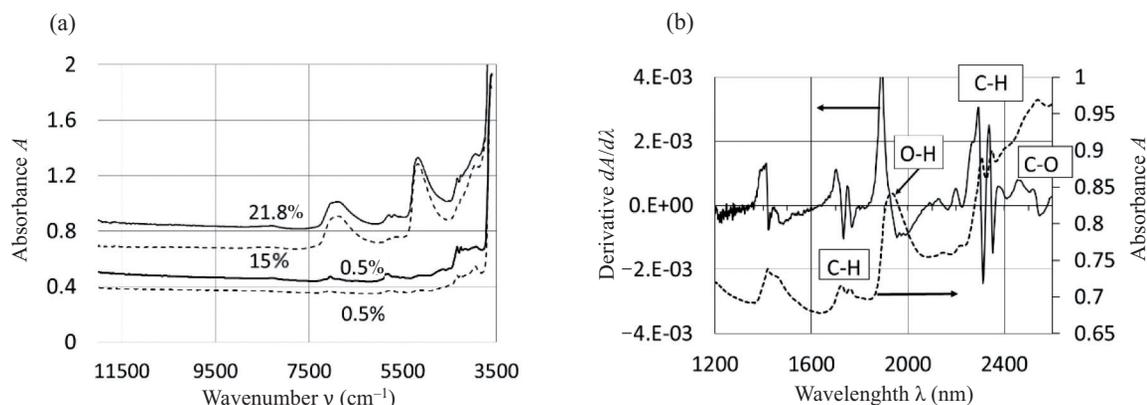


Fig. 2. (a) absorbance spectra of samples with drastically different values of calorificity and percentage of moisture content (indicated in figure); sample B ($Q^d = 21.123 \text{ MJkg}^{-1}$, solid lines); sample BC ($Q^d = 2.32 \text{ MJkg}^{-1}$, dashed lines). (b) absorbance and its derivative as a function of wavelength with the indication of characteristic absorbing bands; sample F1 ($Q^d = 9.4 \text{ MJkg}^{-1}$, $W_w = 7.5\%$).

preprocessing emphasizes steep edges of peaks, thus making the interpretation of spectra easier. Five distinguishable groups of bands exist in the selected spectral range. The most intensive band around 1950 nm (5130 cm^{-1}) belongs to O-H and is related to the presence of free water [24], while a peak near 2500 nm (4000 cm^{-1}) characterizes carbonates [25,26]. Both bands near 1700 and 2300 nm belong to C-H vibrations [27]. Near 1400 nm (7100 cm^{-1}) O-H and C-H bands are overlapped and this part is not used for analysis.

In Fig. 3a spectra of dry samples with very different calorific values can be seen. Differences in spectra correspond to the oil shale chemical composition, whose organic part is described by empirical formula $\text{C}_{421}\text{H}_{638}\text{O}_{44}\text{S}_4\text{NCl}$ [28], and the main components of the mineral part are CaCO_3 and $\text{CaMg}(\text{CO}_3)_2$ [26]: samples of higher calorificity have more intensive absorption at C-H bands, while samples of lower calorificity have larger absorption of C-O band. Additionally, because of a low moisture content, the absorbance near 1950 nm is practically missing.

Absorption of O-H band with the peak at 1950 nm has a strong dependence on the moisture content (Fig. 3b). Besides, the moisture content affects the absorbance of bands belonging both to organic (1700 and 2300 nm) and mineral (near 2500 nm) components of the samples.

Figure 4a shows the absorbance of C-H peaks at 2305 nm as a function of calorificity at a fixed moisture content: absorbance is a sublinear function of calorificity, which indicates to the saturation of the absorbance at higher calorific values. Similar non-linear trends were observed in case of all used moisture values.

In case of a certain sample, the absorbance was a linear function of the moisture content (Fig. 4b) but slopes of dependences differ remarkably.

5. DATA PROCESSING AND RESULTS

Above presented analysis gives proper physical background of NIR spectra but it does not guarantee the accuracy needed for the assessment of the calorific value

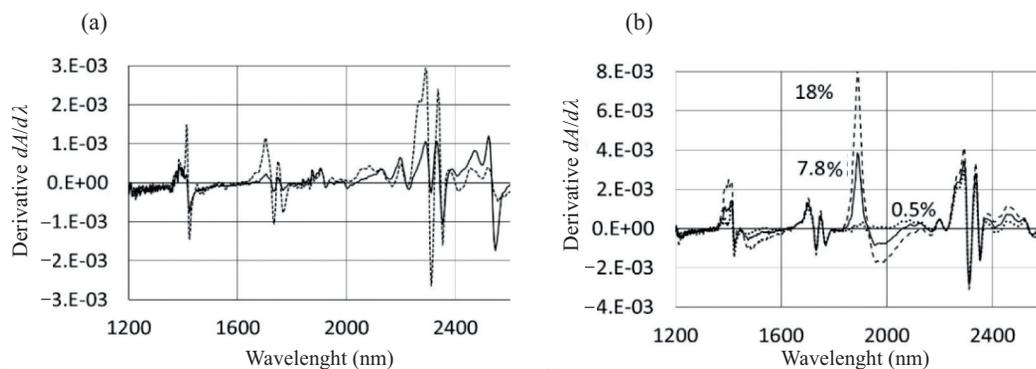


Fig. 3. (a) spectra of dry samples, $W_w = 0.5\%$; dashed line – sample A+A' ($Q^d = 13.6 \text{ MJ/kg}$); solid line – sample B/A' ($Q^d = 0.5 \text{ MJ/kg}$). (b) spectra of sample A+A' at three different values of $W_w = 0.5, 7.8$ and 18% .

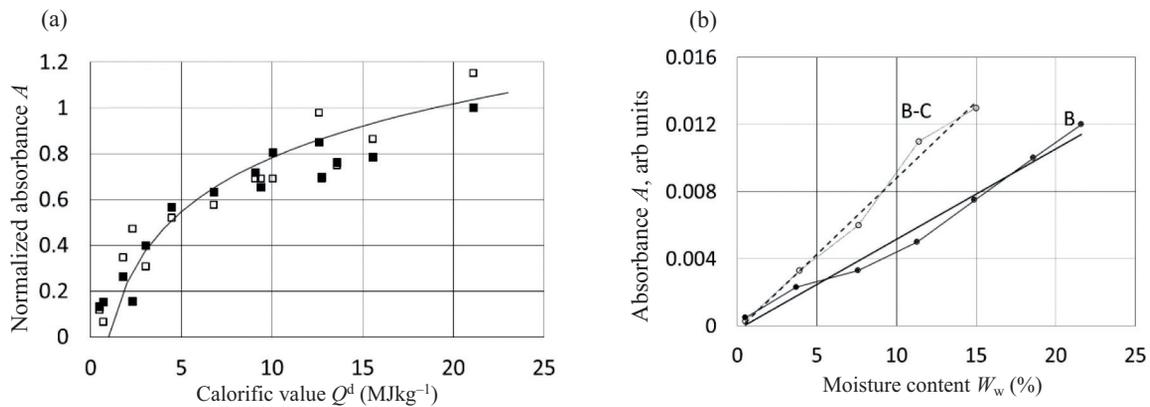


Fig. 4. (a) normalized absorbance as a function of calorificity; $W_w = 14.5\%$; filled symbols – $\lambda = 2305$ nm peak; open symbols – $\lambda = 1725$ nm peak; solid line – logarithmic fit of $\lambda = 2305$ nm data. (b) absorbance as a function of moisture content; open symbols – sample B/C ($Q^d = 2.32$ MJ/kg); filled symbols – sample B ($Q^d = 21.12$ MJ/kg) $\lambda = 1925$ nm peak.

and the moisture content as the measured bands are partly overlapped and therefore, the measured absorbance is the sum of the absorbances of all components (not only the component of interest) in the sample.

The software of MPA-FT-NIR device uses multivariate approach, i.e. instead of the intensity of only one specific band, samples are characterized by the entire selected spectrum. Thus, it is assumed that systematic variations in the spectra are related to the sample composition. For data analysis the device software Quant [23] applies partial least square (PLS) regression [29] method, which expects a linear relationship between the spectral data and property value to be determined.

In order to get out most of the information from recordings, a preprocessing of NIR spectra is usually utilized [30]. The device software proposes a number of different preprocessing methods (e.g. first derivative) as well as suggests spectral intervals for building a model for quantification of results. The combination of preprocessing methods and selected spectral ranges are ordered by software

according to the value of root mean square error of prediction (RMSEP) and the one giving the lowest RMSEP was used.

On the basis of spectra belonging to samples with different calorific values and the moisture content, the software of the device calculated the calibration curve which is then used for analyses of unknown samples. For prediction of properties of samples, the software used two validation types. The “cross validation” (leave one out method [31]) uses the same set of samples for calibration and validation but the “test set validation” uses two independent sets of samples, one for calibration and the other for validating the model. In the present study $\approx 20\%$ of spectra was used for calibration and the remaining $\approx 80\%$ was the test set.

In case of both types of validations, slopes for calibration and prediction dependences differ only a little (Fig. 5a).

Figures 5a and 6a show correlations between the predicted values of calorificity Q^{Pd} and moisture W^P with the calorific value Q^d and moisture W_w , respectively.

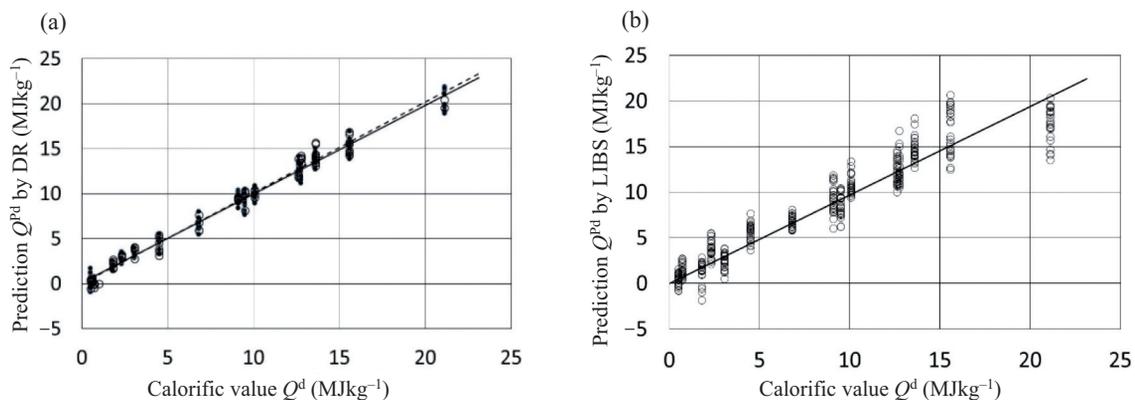


Fig. 5. (a) DR results: test set validation of calorific value Q^{Pd} ; filled symbols – calibration data and dashed line – linear fit for calibration; open symbols – prediction data and solid line – linear fit for prediction. (b) LIBS results: cross validation of calorific value Q^{Pd} ; data taken from [8].

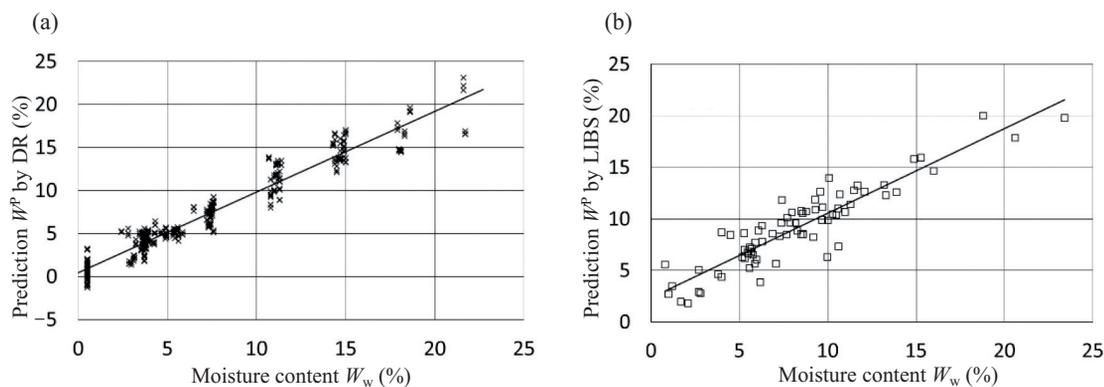


Fig. 6. (a) DR results: cross validation of moisture content W^P . (b) LIBS results: cross validation of moisture content W^P ; data taken from [8].

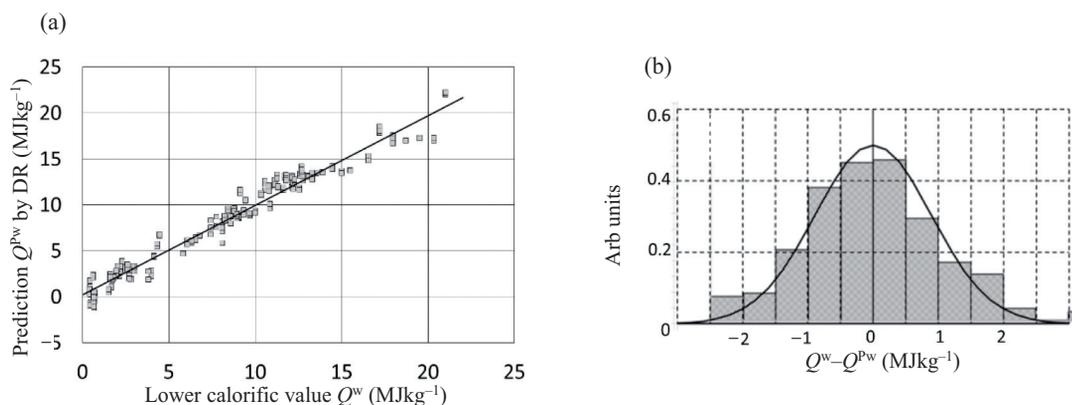


Fig. 7. DR results: (a) cross validation of lower calorific value; (b) histogram corresponding to prediction of lower calorific value; solid line – Gaussian fit characterized by standard deviation 1 MJkg^{-1} .

Compared with LIBS studies of same crushed oil shale samples [8] we see from Figs 5b and 6b that results of DR are better correlated with the results of calorific bomb and weighing methods.

In industry, the basic parameter of oil shale quality is the lower (net) calorific value Q^w [32]. The formulae which allow to calculate the calorificity Q^w on the basis of known values of Q^d and W_w are given by ISO 1928:2009 standard [2]. For prediction of lower calorificity Q^{Pw} , the same procedure was followed but instead of W_w , the prediction values W^P were used. The relationship between Q^w and Q^{Pw} is presented in Fig. 7a; and in Fig. 7b is the histogram of the difference $Q^w - Q^{Pw}$.

6. COMPARISON OF DR AND LIBS RESULTS, FURTHER PROSPECTS

Results of prediction of calorificity Q^d , moisture content W_w , and lower calorificity Q^w are shown in Table 2, LIBS results were taken from [7,8]. In the third and fourth

columns are slopes and correlation coefficients of linear fits between “true” and predicted values of corresponding characteristics, while the root mean square errors of prediction (RMSEP) are in the last column.

The best results are obtained for dry powder samples by LIBS. On the other hand, the time needed for preparation of these samples is comparable with that of the traditional calorific bomb method and in this case the only advantage of LIBS is the possibility to predict the concentrations of oil shale ingredients [7].

One experimental problem, common for both DR and LIBS methods, is the accuracy of the estimation of the moisture content. By weighing the samples, it is possible to calculate the moisture content in the body of lumps while DR and LIBS give the moisture at the lumps’ surface. The balance between the moisture at the surface and inside the samples depends on the surrounding environment and the balance could change in time, which leads to the increase of the prediction error. It is the likely reason of higher prediction error in the case of LIBS measurements where the experiments were carried out in an airflow, which

Table 2. Results of prediction of oil shale main characteristics

Technique	Samples	Characteristic	Processing	Slope	R^2	RMSEP
DR	Crushed oil shale, variable moisture content	Q^d	Cross validation	1.00	0.98	0.85 MJ/kg
			Test set validation	1.00	0.97	0.84 MJ/kg
		W_w	Cross validation	0.94	0.93	1.35%
			Test set validation	0.97	0.94	1.33%
LIBS	Crushed oil shale, variable moisture content	Q^w	Cross validation	0.974	0.96	1 MJ/kg
		Q^d	Cross validation	0.91	0.91	1.76 MJ/kg
			W_w	Cross validation	0.83	0.82
LIBS	Powder, dry	Q^d	Cross validation	1	0.98	0.24 MJ/kg

causes faster changes in the moisture content at the lumps' surface. Furthermore, the moisture affects not only these parts of spectra which are directly related to the moisture content, like O-H band near 1950 nm, but due to the matrix effect, it causes also changes in other parts of spectra (Figure 3b). As a result, the uncertainty of determination of moisture content influences also the accuracy of the determination of the calorificity.

Due to the use of integrating sphere, the role of fluctuations in DR spectra, caused by a random orientation of faces of oil shale lumps, was almost negligible. Contrary, in case of LIBS, even the average intensity of a spectral line found from 100 LIBS spectra needs extra normalization [8]. For this purpose, the average intensity of a line was normalized by the average of the total intensity in 220–850 nm range [8]. This procedure gave a better signal-to-background ratio but it did not allow to exclude “blank” spectra caused by laser beam impacting between lumps of tested samples [3]. This circumstance seems to be the main reason why the prediction error of Q^d in case of LIBS is two times larger than in case of DR. Carrying out the normalization of intensity of a spectral line belonging to a single spectrum by the corresponding total intensity allows the discrimination of outliers.

The final remark concerns the used software. We saw that some bands in NIR spectra (Fig. 3) are directly related to the changes of samples' calorificity and moisture content. However, these dependencies alone did not allow to determine the calorificity/moisture content with sufficient accuracy. The main advantage of used multivariate approach which handles all parts of spectra equally, is diminishing the role of uncontrollable factors. On the other hand, this approach almost neglects the physical background of observed trends in spectra. Additional limitation related to PLS is that it could not satisfactorily reflect the non-linear relationship between absorbance and the calorificity (Fig. 4a). An appropriate data processing

which combines the physical processes with the multivariate regression could improve the accuracy of data analysis. This approach was successfully realized in LIBS studies [33] where different dominant factors as a function of spectral line intensity were combined with PLS correction, and a significant improvement of final results was achieved.

7. CONCLUSIONS

DR spectroscopy was applied for prediction of calorificity and moisture content of crushed 0–25 mm fraction oil shale samples. The study showed that good correlation between calorific value and moisture content determined by traditional methods and those calculated on the bases of NIR DR spectra could be achieved without any additional preparation of samples.

The list of most important findings is given below:

- In the DR spectra, it was possible to separate vibrational bands which characterize organic and inorganic parts of the matter. The most intensive band belongs to O-H which reflects the presence of free water. The moisture has a strong matrix effect and changes of its content cause remarkable changes in other bands of spectra. At a fixed moisture content, the intensity of bands of the organic part of oil shale are non-linear functions of the calorificity.
- For predicting the calorificity and moisture content, the conventional software of the device was used. The accuracy of predictions was governed by a possible difference of the moisture content at lumps' surface from that of inside the lumps.
- Comparison of DR NIR measurements with LIBS results showed that the model of DR NIR predicts the calorificity with higher accuracy. The values of RMSEP are 0.85 MJ/kg and 1.76 MJ/kg, respectively.

- Regularities in spectra indicate that a considerable improvement of final results of both DR and LIBS methods could be achieved by combining the data processing of the multivariate linear regression with the dominant factor model.

Laboratory online control of oil shale quality by NIR-DR spectroscopy is justified in case of selective mining where the oil shale quality changes comparatively slowly.

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Difuusse peegeldusspektroskoopia rakendamine Eesti põlevkivi kvaliteedi kiireks laboratoorseks hindamiseks

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Infrapuna piirkonna peegeldusspektroskoopiat kasutati põlevkivi kütteväärtuse ja niiskusesisalduse kvantitatiivseks määramiseks. Erineva kütteväärtusega tükikivi proovid võeti Narva karjäärist ja Estonia kaevanduse rikastusvabrikust. Katsetes muudeti proovide niiskusesisaldust. Testimisel kasutati tööstuslikku analüsaatorit, kus Fourier' spektromeeter registreeris spektri lähedases infrapuna piirkonnas. Testimise tulemusena saadud kütteväärtusi ja niiskusesisaldust võrreldi tulemustega, mis saadi kalorimeetrilise pommi ning kaalumise meetodeid vastavalt kasutades. Infrapuna spektris tehti kindlaks karakteristikud ribad, mis iseloomustavad nii proovide orgaanilist ja anorgaanilist osa kui ka vaba vee olemasolu. Kütteväärtuse ennustusviga oli 1 MJkg^{-1} ja niiskuse kaaluprotsendi oma 1,35%. Varem kasutatud LIBS-i meetodiga võrreldes olid peegeldusspektroskoopia tulemused täpsemad. Tulemuste arutelu leiti, millise kaevandusmeetodi puhul peaks peegeldusspektroskoopia rakendamine olema kõige efektiivsem ja millised andmetötluse viisid peaksid viima täpsemate tulemusteni.