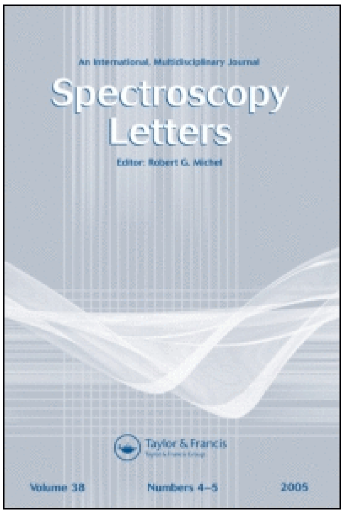

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APPLICATION OF NEAR INFRARED SPECTROSCOPY TO RAPID ANALYSIS OF COALS

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APPLICATION OF NEAR INFRARED SPECTROSCOPY TO RAPID ANALYSIS OF COALS

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ABSTRACT

Comparing near infrared (NIR) spectra with infrared spectra in case of coal samples, we generally notice NIR spectra have less characteristic absorbance bands. However, utilizing merits of NIR spectroscopy (non destructive, high penetration ability, simple sample preparation, rapid analysis) and partial least squares regression (PLS) model, we found that several major properties of coals could be conveniently and rapidly estimated. For examples, multiple correlation coefficient between the measured values vs. the predicted values from obtained spectra, R^2, of moisture, volatile matter, oxygen content, maximum fluidity temperature, solidification temperature were 0.9736, 0.9774, 0.8996, 0.8849 and 0.9282 in respectively although the precision of obtained results were

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not superior to those by methods of American Standard of Testing Materials.

Key Words: Coals; Near infrared (NIR) spectroscopy; Rapid analysis; PLS

INTRODUCTION

NIR spectroscopy is quite useful as a non destructive and a rapid analysis method, which is expanding the application field.[1] Much more, recent trend of compacting the spectrometer and the computer makes it more convenient and appropriate for the analysis at mining fields of resources or the on-line analysis at factories.

The properties of coals are usually estimated by a lot of index, carbon content (C), hydrogen content (H), oxygen content (O), maximum fluidity temperature (MFT) and so on. For example, C, H, O are now measured with an elemental analysis apparatus (using the combustion method) and MFT, SOT are measured under high temperature (about 400–550 degree centigrade) with the gieseler-plastmeter. Still more, testing the moisture content is necessary for more than one hour by the other instrument, the moisture oven. Such measurements of coal properties need plural equipments, much time and energy (heating).

Infrared spectroscopy is widely used for the analysis[2,3,4] of coal and so on because it has a lot of characteristic bands in the wavenumber region (4000–400 cm^{-1}, see Fig. 1). On the contrary, NIR spectra of coals are not so prominent in the region (1100–2500 nm, see Fig. 1). However, NIR

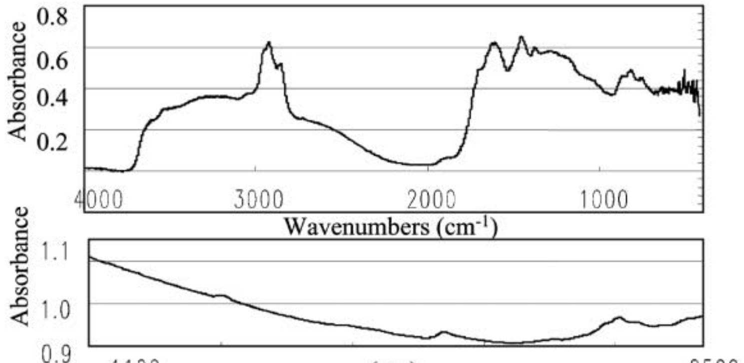

Figure 1. IR and NIR spectra of a representative coal (No.7).

spectroscopy has some characteristic merits. Especially, it can penetrate samples much more than other spectroscopy (infrared, ultra violet, visible) can, which could be suitable for inhomogeneous samples such as coals because it can measure much more samples at once.

In this report, we tried estimation of such properties of coals by the NIR spectra although we generally took less characteristic absorbance bands than those obtained by infrared spectra. As a result, we found that we could predict some important properties of coals by just measuring the NIR spectra and using the PLS regression model toward obtained NIR spectra.

Apparatus and Sample Preparation

We got 15 coals[5] (powders under 100 mesh from different mines) from Pennsylvania State University coal bank via Dr. Gary Mitchell. The major properties of the coals are listed in Table 1.

NIR 6500 (NIRSystems Co.) was used for obtaining the NIR spectra of coals with the diffuse reflection cup. Coal powders (from 2.99 g to 3.01) were placed into the cup (35 mm in diameter by 10 mm deep) and covered with a quartz plate.

Table 1. Major Properties of Sample Coals

	Proximate Analysis				Ultimate Analysis			Thermo Plastic Properties		
No.	Mo	Ash	VM	FC	C	H	O	IS	MF	So
1	10.43	14.47	34.16	40.93	58.66	4.08	7.31	385	411	432
2	2.64	19.76	30.74	46.86	64.60	4.38	6.83	406	440	473
3	6.81	11.42	38.38	43.40	64.66	4.74	7.27	376	421	456
4	5.97	11.30	40.49	42.24	65.36	4.80	7.93	379	423	454
5	5.20	13.17	39.23	42.40	66.15	4.80	9.02	396	420	438
6	2.00	9.25	38.63	50.12	72.72	5.00	5.91	373	428	470
7	4.73	5.56	42.40	47.31	72.91	5.60	9.42	400	419	438
8	2.40	10.00	35.16	52.44	72.99	4.99	7.33	387	440	477
9	3.74	6.32	45.00	44.93	73.40	5.58	9.29	387	420	442
10	2.32	10.64	32.52	54.52	74.55	4.74	5.89	404	446	483
11	1.46	10.37	32.11	56.06	75.13	4.82	5.17	376	446	485
12	2.79	5.32	36.48	55.41	77.33	5.37	6.92	403	439	469
13	2.44	6.20	33.46	57.89	79.10	5.05	5.18	397	447	487
14	2.06	3.81	29.51	64.62	82.67	5.04	4.16	383	458	500
15	1.45	4.16	24.62	69.77	83.25	4.67	4.44	404	456	493

NIR spectra were measured at interval of 2 nm (from 1100 nm to 2500 nm and scanned 32 times (about 2 minutes).

Analysis and Discussion

All the procedures of the spectral analysis using the pirouette ver.2.6 are written below.

1. Preprocessing of spectra
   Mean centering all the spectra after multiplicative scattering correction (MSC[6]) in some cases. In case of highly scattering optical samples, a multiplicative effect (differences in measurement path lengths) can occur. Therefore, MSC attempts to account for it. All the spectra are composed of 700 data (every 2 nm from 1100 to 2500 nm).
2. Fabricating first derivation and second derivation spectra after Savitsky-Golay smoothing.
3. Applying PLS regression model[7] to the relation between the preprocessed spectra and measured values of moisture (Mo), volatile matter (VM), oxygen content (O), maximum fluidity temperature (MFT) and solidification temperature (SOT) with a cross validation method (leave one out).
4. A couple of the cross check of the obtained best model and the error of prediction for Mo, VM, MFT, SOT and O were shown in Figs. 2–6, in respectively. Best regression models were determined by the minimum value of standard error of cross validation (SECV). R^2 (multiple correlation coefficient) of SECV of Mo, VM, O, MFT and SOT were 0.9736, 0.9774, 0.8996, 0.8849 and 0.9282 and the SECV of Mo, VM, O, MFT and SOT were 0.45, 0.79, 0.51, 4.55 and 4.76 in respectively.

From these figures (Figs. 2–6), we didn't find special displacements in the predicted errors, i.e., they were random. Therefore, we expect that the precision of this method could be improved much more. However, the precision level by this method is now inferior to those of American Standard of Testing Material (ASTM).

In Table 2, we compared the influence of preprocessing methods. Just in the case of oxygen content, MSC was useful for improving the precision of the regression method. Judging from our results, MSC was not complete.

We suppose that the errors are caused by three major factors below.

1. problems on scattering effect

2. prediction error by the PLS regression model
3. errors by the ASTM method

Exact estimation of scattering effect should be needed. Perhaps, this rapid analysis could be potent in case of quality control for relatively homogeneous coals. We are now under investigation of the improvements of this method and the application to other kind of coals.

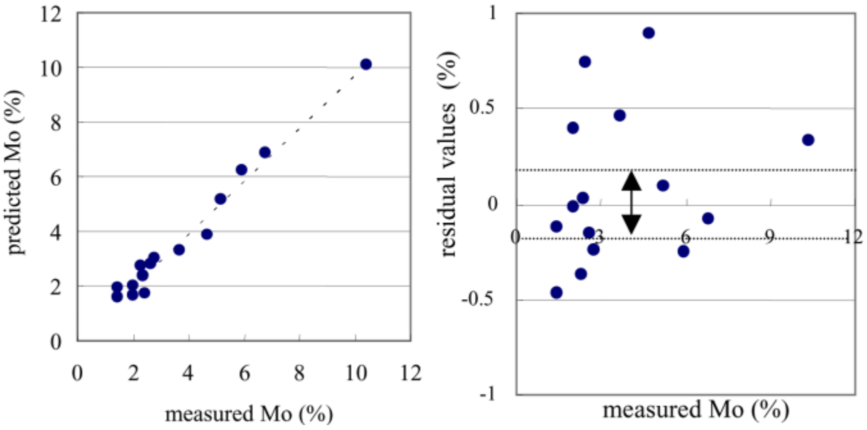

Figure 2. Measured Mo vs. predicted Mo and residual values. The arrowed zone means the allowed error by the method of ASTM, D3173.

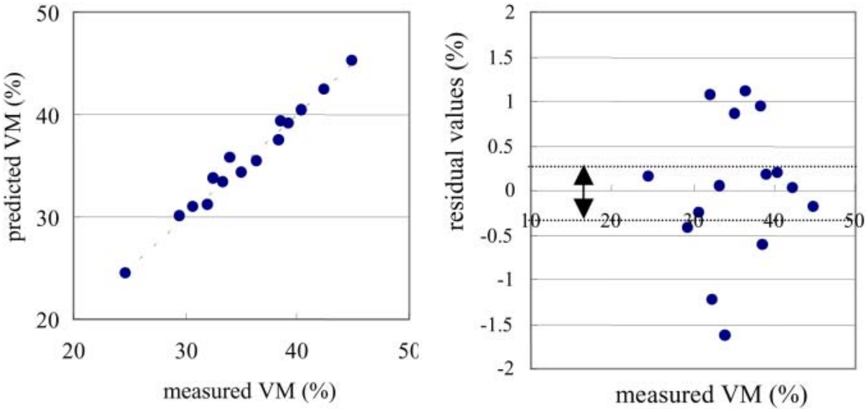

Figure 3. Measured VM vs. predicted VM and residual values. The arrowed zone means the allowed error by the method of ASTM, D3175.

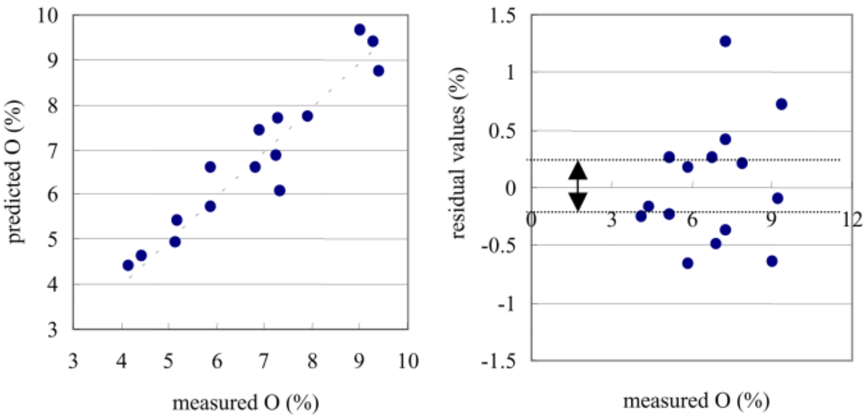

Figure 4. Measured O vs. predicted O and residual values. The arrowed zone means the allowed error by the method of ASTM, D3176.

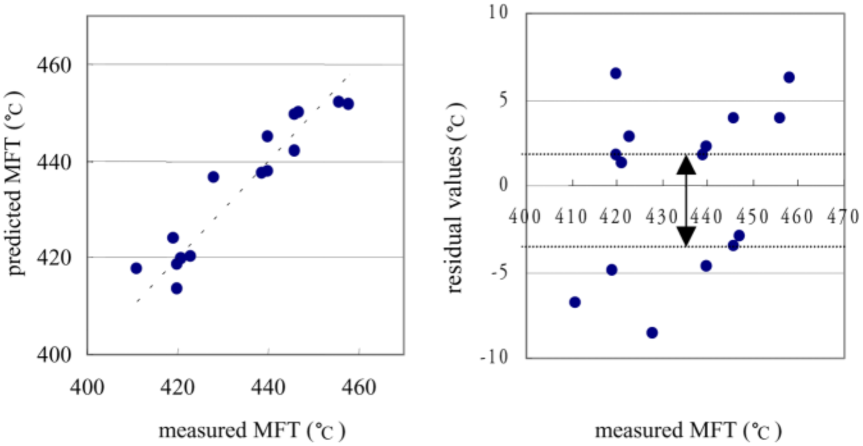

Figure 5. Measured MFT vs. predicted MFT and residual values. The arrowed zone means the allowed error by the method of ASTM, D2639.

CONCLUSION

Using NIR spectroscopy and PLS regression model, we found that some important properties of coals could be estimated with the quite simple sample preparation for getting NIR spectra. Still more, our method doesn't need much time, much energy (heating) and plural instruments. This

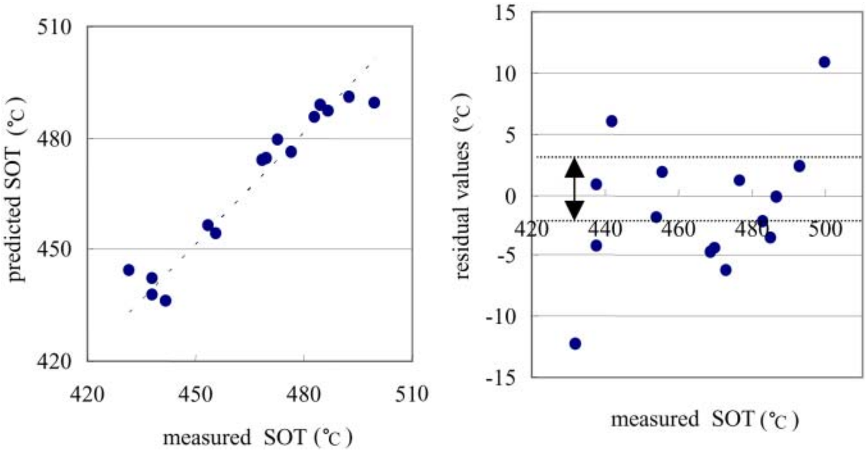

Figure 6. Measured SOT vs. predicted SOT and residual values. The arrowed zone means the allowed error by the method of ASTM, D2639.

Table 2. Comparison of Preprocessing Methods

Properties	Preprocessing	SECV	Numbers of PLS Components
Mo	no use of MSC	0.45	7
Mo	MSC	0.95	4
VM	no use of MSC	0.79	9
VM	MSC	1.29	8
O	no use of MSC	0.67	5
O	MSC	0.51	6
MFT	no use of MSC	4.55	8
MFT	MSC	4.91	2
SOT	no use of MSC	4.76	3
SOT	MSC	7.63	2

method could be a rapid and convenient analysis in factories or mining places although it should be improved on the precision of the prediction.

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