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Application of near infrared diffuse reflectance spectroscopy for on-line measurement of coal properties

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Abstract−The applicability of the Multi-wavelength Near-infrared sensor to analyze coal properties such as proximate analysis (moisture, ash, volatile matter, fixed carbon), ultimate analysis (carbon, hydrogen, nitrogen, oxygen, sulfur) and heating value is discussed. The most useful wavelengths (1,680, 1,942, 2,100, 2,180, 2,300 nm) for determining coal properties concentration were chosen by analyzing the NIR spectrum according to coal properties. Absorbances at the characteristic wavelength obtained from 128 mixed coal samples, which are using at a conventional thermal power plant, were correlated to the coal properties by using multiple regression analysis. The accuracy of coal analysis was examined by calculating the RMSEC (%), RMSEP (%), comparing the error with ASTM/ISO tolerance and performing paired Student's T-test. The result of on-line coal analysis for all moisture, volatile matter, fixed carbon, carbon, hydrogen and heating value is not different from that of ASTM/ISO traditional methods at 90% confidence level. The technology appears suitable for the determination of several coal prorperties. If calibrated periodically, this on-line analysis of coal properties is helpful to efficiently operate a coal fired power plant.

Key words: NIR, Absorbance, Coal Properties, Real-time Analysis

INTRODUCTION

Rapid or on-line coal analysis is of great interest in the coal industry as it would allow efficient plant operation. Although ISO/ASTM traditional methods have been used to determine coal properties, they are laborious and time-consuming procedures not suitable for a real-time methodology. Nowadays, on-line coal analysis techniques, generally based on nuclear methods, are implemented in the coal industry. But there are health hazards and high requirements to the personnel. Also, they are characterized for reliance on the inorganic constituents to further extrapolate for the calculations of the other coal properties. So recently, in order to find an alternative technique, several research works have studied diffuse reflectance infrared Fourier transform spectroscopy (DRIFT) in the near-Infrared (NIR) range covering the 1,100-2,500 nm region. Near-infrared diffuse reflectance spectroscopy is gaining acceptance as a nondestructive method for rapidly measuring organic minerals like coal. Fuller and Griffiths reported the advantage of DRIFT that is able to characterize scattering samples with very little preparation and a high signal to noise ratio (SNR) in minimal time [1]. The first study of DRIFT applied for coal analysis was a determination of blended coals by relating the composition of the sample to its infrared spectra with factor analysis. It has been successfully applied to characterize coal blends [2,3] and to monitor oxidation of coals and carbon materials [4,5]. Onishchenko et al. used the DRIFT for control of ash and moisture contents of coals on the conveyor belt. Other applications for characterizing of coal macerals have been attempted applying DRIFT with relative success [6].

In the near-infrared range DRIFT is able to characterize coal samples due to advances in data acquisition and chemometrics. Kaihara et al. reported that the modified DRIFT-near IR spectra are able to be correlated with the coal properties such as moisture, volatile matter, oxygen, maximum fluidity temperature, and solidification temperature [7]. Recently, with regard to that, parameters related to acquisition near-infrared coal spectra and their subsequent transformations into analytical values are being investigated. Chemometric techniques such as partial least squares regression (PLS) or genetic algorithm for wavelength selection are developed as well as sample clustering and classification methods in order to obtain more homogeneous clusters with better calibration results [8,9].

The present work is an attempt to analyze coal properties by using not the full NIR spectrum but absorbances from the selected wavelengths for applying easily to a conventional thermal power plant. The objective of this study was focused on the examination of DRIFT-near infrared spectroscopy to analyze not coal powder but lump blended coal on the conveyor belt at the coal feeder in the thermal power plant.

EXPERIMENTAL

1. Coal Samples

For checking the possibility of multi-wavelength near-infrared sensor to analyze the coal properties, four representative coals were used corresponding to the three sizes of coal (under 2 mm, 2-5 mm, over 5 mm) and the speed of the conveyor belt (1.2, 1.6, 2.0 m/s). In the field test, one hundred and twenty-eight coal samples which are binary blended coal were obtained from a coal feeder sampling port in a conventional thermal power plant. The size of coal samples was generally 10%, <1 mm; 30%, <10 mm; 50%, <100 mm; 10%, >100 mm. They were analyzed for all moisture, humidity, heating value, proximate analysis (initial moisture, ash, volatile matter, fixed carbon) and ultimate analysis (carbon, hydrogen, nitrogen, oxygen, sulfur by ISO/ASTM standard methods. The composition of coal

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Table 1. Composition of coal samples at the coal feeder

Property		No. of samples for		Min-Max*
		Calibration	Prediction	
All moisture (%)		39	89	10.65-22.43
Heating value (kcal/kg) (air dry basis)		39	56	5790-6838
Proximate analysis (%)	Initial moisture	39	77	3.8-9.52
	Volatile matter	39	77	28.33-37.05
	Ash content	39	77	7.83-18.99
	Fixed carbon	39	77	40.97-53.48
Ultimate analysis (%)	Carbon	39	70	64.37-75.10
	Hydrogen	39	70	4.07-5.09
	Nitrogen	39	70	0.87-1.94
	Sulfur	39	70	0.30-1.30
	Oxygen	39	70	6.61-12.90

*The values of maximum and minimum on each coal property

samples used for the field test appears in Table 1.

2. Data Analysis and Analytical Method

Reflectance data were measured by KJT-500 (KETT, Japan) and analyzed with a multiple linear regression program. This sensor has one reference wavelength (1,680 nm) which is used for making the constant baseline of the NIR spectrum by AGC (automatic gain control) and four characteristic wavelengths (1,940, 2,100, 2,180, 2,300 nm). When coal samples are moving on the conveyor belt, NIR light of this equipment installed above the conveyor belt is directed at 90º on the coal samples. And this sensor detects the absorbances at the characteristic wavelengths. 39 coal samples were used for calibration of coal properties at the coal feeder in the thermal power plant and about 80 coal samples were predicted by equations which were made from the previous calibration.

RESULTS AND DISCUSSIONS

1. Test in the Simulated Coal Feeder

Near infrared reflectance spectra of coal samples for confirming the selected wavelengths appropriate are shown at Fig. 1. It was found that near infrared reflectance spectra of representative coal samples have characteristic wavelengths such as 1,940 nm (O-H str. First overtone) [POH], 2,100 nm & 2,180 nm [C-H str.+C-H def.] [CH2] and 2,300 nm ([2amide I+amideIII] [CONHR] [10,11].

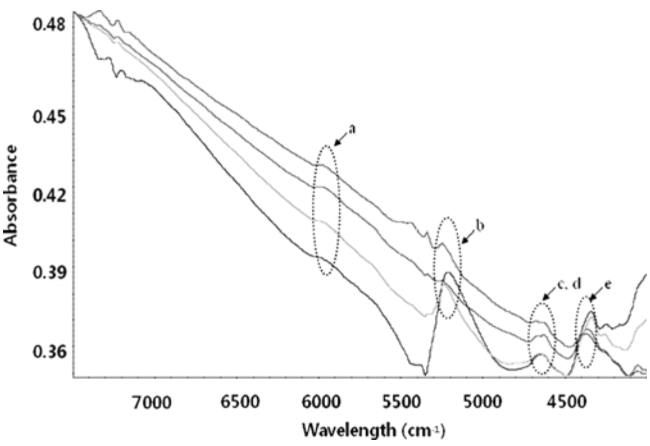

Fig. 1. Near infrared reflectance spectra for the four representative coal samples (a: 1,680 nm, b: 1,940 nm, c: 2,100 nm, d: 2,180 nm, e: 2,300 nm).

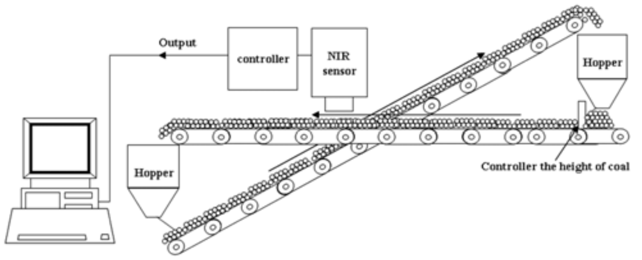

Fig. 2. Simulated coal feeder for testing the multi-wavelength NIR sensor.

NIR spectra of mixtures are additive; therefore, absorption should be proportional to concentration in accordance with the Beer-Lambert law. So the analysis consists of making reflectance measurements at selected wavelengths and solving the equation of the form. The measurement of complex and heterogeneous material such as coal by using log 1/R data usually results in multi-term equations in an attempt to compensate for the overlap of characteristic wavelength bands.

$$\text{predicted, \% or kcal/kg}=A_0+A_1X_1+A_2X_2+A_3X_3+A_4X_4 \quad (1)$$

Where X_1, X_2, X_3 and X_4 are reflectance measurement (log 1/R) or derivatives of these, at wavelengths λ_1 (1,940 nm), λ_2 (2,100 nm), λ_3 (2,180 nm) and λ_4 (2,300 nm). A_0 is the regression constant and A_1, A_2, A_3 and A_4 partial regression coefficients.

The possibility of analyzing the coal properties by this method was tested at the simulated coal feeder in the laboratory which is shown at Fig. 2, using four representative coal samples.

The test was performed according to the size of coal and the speed of the conveyor belt. Scatter diagrams of the calibration about three important coal properties are presented in Fig. 3. Due to the AGC making the constant baseline of the NIR spectrum, there are no effects on the NIR spectrum of the same coal at various conditions. These diagrams and Table 2 indicate that a linear relationship exists between log 1/R and constituent concentration of coal except carbon, nitrogen and sulfur over the entire constituent range tested. Especially, Fig. 3 shows the result of calibration on the three representative coal properties (all moisture, volatile matter and heating value).

Table 3 shows the partial regression coefficients of Eq. (1) at the simulated coal feeder. As shown in Table 3, reflectance measurements (log 1/R) at the selected wavelengths are counterbalanced with each other, if there is no relation between the coal properties and reflectance measurement (log 1/R) at the selected wavelength.

2. Test at the Coal Feeder in the Commercial Thermal Power Plant

On the basis of the lab-test results, this technology was applied at a commercial thermal power plant. But as the measurement environment was different from laboratory conditions such as the species of coal, the temperature, the amount of dust in the air, vibration etc., the accuracy was poor for prediction of coal properties.

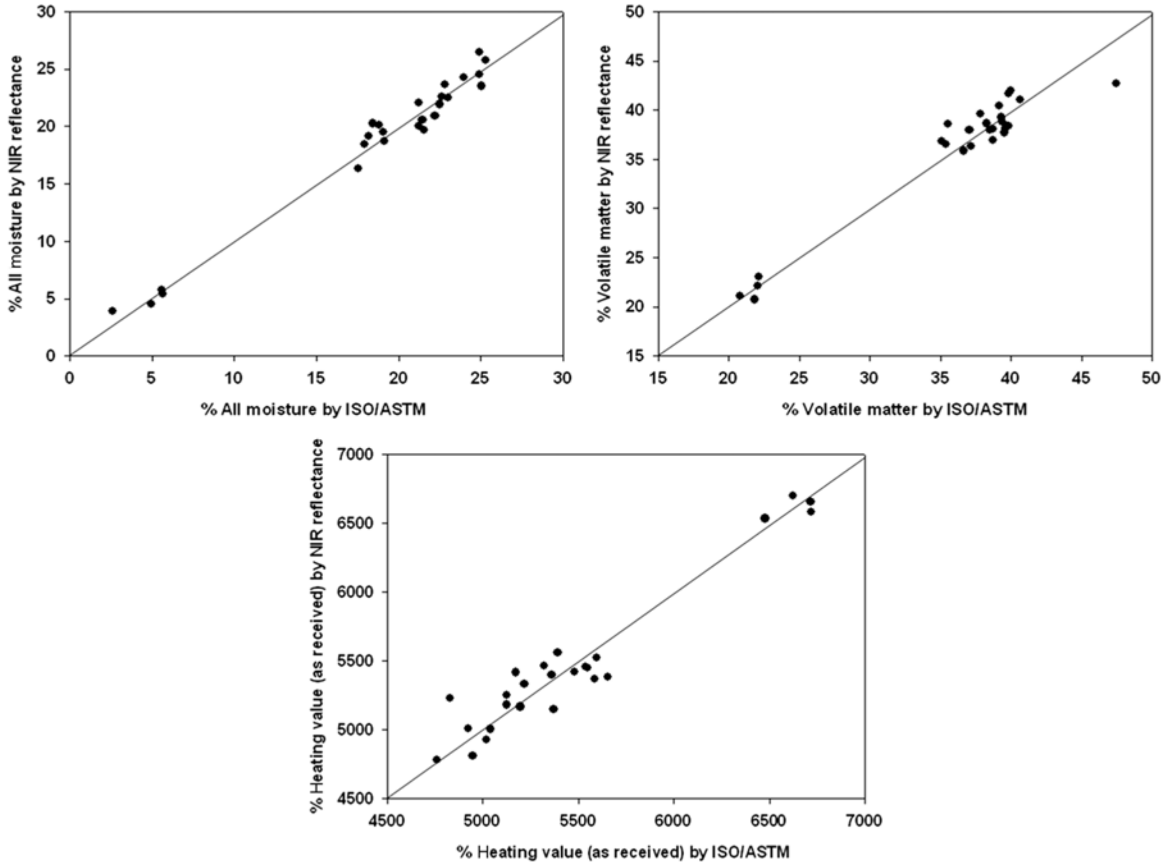

Fig. 3. Scatter diagram showing the calibration data for the analysis of all moisture content, volatile matter and heating value (as received) by NIR.

Table 2. Results for calibration of each property at the simulated coal feeder (No. of samples: 25)

		R	S.D.	Mean	Min-Max*
Moisture (%)	All moisture	**0.99**	1.11	18.82	4.5-23
Proximate analysis (%)	Volatile matter	**0.97**	0.94	36.02	20-47.5
	Ash	**0.97**	0.94	5.62	1.9-17.6
Ultimate analysis (%)	Carbon	0.68	1.82	69.69	66.7-73.2
	Hydrogen	0.96	0.13	5.04	3.9-5.5
	Nitrogen	0.77	0.23	1.05	0.6-1.3
	Sulfur	0.63	0.28	0.32	0.06-1.00
	Oxygen	0.98	0.95	17.33	4.2-23
Heating value (kcal/kg)	As received	**0.96**	168	5470	5120-6720

*Min-Max: Minimum and Maximum of each properties in coal samples

Among these factors, owing to the coal supply in the whole world, it is the biggest reason for the inaccuracy that blend coals are used in the thermal power plant. Each of these factors has an effect on diffuse reflectance and may interfere with compositional determination. Consequently, during three months, NIR reflectance of 39 binary coals was acquisitioned from the multi-wavelengths NIR sensor installed at the coal feeder, and coal samples collected at the same period were analyzed for coal properties by ISO/ASTM method. NIR reflectance was correlated to the coal properties by using multiple regression analysis. After 4 months, about 80 coal samples were predicted by equations which were made from the previous calibration. In view of finding as many properties of coal as possible, humidity and initial moisture among all moisture and heating values of air dry base, dry base and as received base were added to the coal analysis.

The root mean square error of calibration (RMSEC) and prediction (RMSEP) values obtained by this method have been consid-

Table 3. Partial regression coefficients of Eq. (1) at the simulated coal feeder

	All moisture	Volatile	Ash	Fixed carbon	Carbon	Hydrogen	Nitrogen	Oxygen	Sulfur	HV (as received)
A0	4.8	44.2	4.0	52.8	78.9	5.1	0.9	12.6	−0.5	6786
A1	84.0	−49.3	10.0	−80.1	−57.6	−0.3	1.4	28.0	5.7	−7781
A2	−441.2	180.0	−18.3	484.5	325.7	−5.0	−14.4	−177.2	−32.0	41248
A3	608.9	−282.9	31.6	−598.2	−410.1	1.2	11.3	227.6	45.1	−53474
A4	−197.5	168.6	−47.0	149.92	131.2	5.0	−1.0	−42.7	−17.8	16244

Table 4. Results for calibration and prediction error of each property

		RMSEC	RMSEC (%)	RMSEP	RMSEP (%)	T-value*
Moisture (%)	All moisture	0.98	5.44	1.40	8.66	0.19
	Humidity	0.90	8.02	1.17	11.88	4.15
Proximate analysis (%)	Initial moisture	0.94	13.83	1.02	15.99	3.18
	Volatile matter	0.93	2.67	1.20	3.54	1.22
	Ash	1.35	12.95	1.74	15.12	0.69
	Fixed carbon	0.97	2.02	1.97	4.08	0.58
Ultimate analysis (%)	Carbon	1.24	1.77	1.76	2.49	0.10
	Hydrogen	0.08	1.66	0.13	2.73	0.01
	Nitrogen	0.16	10.24	0.25	16.23	1.17
	Sulfur	0.14	16.31	0.17	20.48	0.22
	Oxygen	0.74	6.52	2.16	21.45	1.16
Heating value (kcal/kg)	Air dry	96.14	1.51	126.30	1.97	0.13
	As received	102.65	1.82	127.16	2.20	1.58
	Dry	111.76	1.64	155.45	2.26	4.02

*When the degree of freedom is over 20, The value of student t at 95% confidence level is about 2.086

ered optimistic but adequate for model comparisons. These errors are defined by [12]:

$$\mathrm{RMSEC} = \sqrt{\frac{\sum_{i=1}^{N}(\hat{y}_i - y_i)^2}{(N - A - 1)}} \tag{2}$$

$\hat{y}_i$ are obtained by testing the calibration equation directly on the calibration data and A is the number of components:

$$\mathrm{RMSEP} = \sqrt{\frac{\sum_{i=1}^{N}(\hat{y}_{CV,i} - y_i)^2}{N}} \tag{3}$$

Where $\hat{y}_{CV,i}$ is the estimate for y_i based on the calibration equation with sample i deleted. For comparison purpose all the error values will be expressed in percentage error around the mean:

$$\mathrm{RMSE}(\%) = \frac{\mathrm{RMSE}}{\text{Average property}} \times 100 \tag{4}$$

Also, a T-test was used for confirming the difference between the results of coal properties analyzed by ISO/ASTM method and those analyzed by NIR reflectance method [13].

$$t = \frac{\bar{d}}{S_d}\sqrt{n}, \quad S_d = \sqrt{\frac{\sum(d_i - \bar{d})^2}{n-1}} \tag{5}$$

where d_i is the difference between the results, $\bar{d}$ is obtained by averaging the d_i and n is the number of samples.

The results of calibration and prediction error of every studied property are shown in Table 4.

Table 5 shows the partial regression coefficients of Eq. (1) at the coal feeder in the thermal power plant. As shown in Table 5, reflectance measurements (log 1/R) at the selected wavelengths are counterbalanced with each other, if there is no relation between the coal properties and reflectance measurement (log 1/R) at the selected wavelength.

Considering the possibility of analyzing coal properties from RMSE value and RMSE (%) standpoint, all moisture, volatile matter, fixed carbon, carbon, hydrogen, heating values are able to be correlated with NIR reflectance and analyzed by this technique, considering that both RMSEC (%) and RMSEP (%) are relatively low. With regard to moisture, the impossibility of values the all moisture to humidity and initial moisture was confirmed by comparing the RMSEC (%) and RMSEP (%) of these with those of all moisture. And ash content and sulfur have relatively high RMSEP (%) due to impossibility to absorb inorganic compounds in the NIR region. Also, nitrogen, with very narrow ranges and concentrations below 1% was very difficult to calibrate unless intense signals were distinguished from the matrix spectrum.

From the point of similarity between the predicted values from on-line coal analyzer and the values by ISO/ASTM, as shown in Fig. 4 and the t values from Table 4, those two results about all properties of coal except humidity, initial moisture and heating value (dry base) are not different at the 95% confidence level.

Table 5. Partial regression coefficients of Eq. (1) at the coal feeder in the thermal power plant

	All moisture	Humidity	Initial moisture	Volatile	Ash	Fixed carbon	Carbon	Hydrogen	Nitrogen	Sulfur	Oxygen	HV (air dry)	HV (received)	HV (dry)
A_0	21.8	19.3	1.6	22.8	17.4	58.2	70.9	4.1	3.0	1.7	2.4	6370	5095	6460
A_1	8.2	−11.1	17.1	27.7	20.1	−64.9	−49.9	1.7	−0.3	2.7	22.1	−3925	−2923	−2955
A_2	190.5	279.8	−71.7	3.6	−139	207.5	196.9	−2.3	−13.7	−13.1	−9.5	18022	−561	14091
A_3	−254.6	−297.9	16.5	−120.8	300.9	−196.5	−260	−4.6	0.7	11.6	−71.9	−23819	−3921	−24325
A_4	82.2	64.5	25.7	69.8	−137	41.5	80.2	3.8	12.6	1.3	45.7	7182	2738	9571

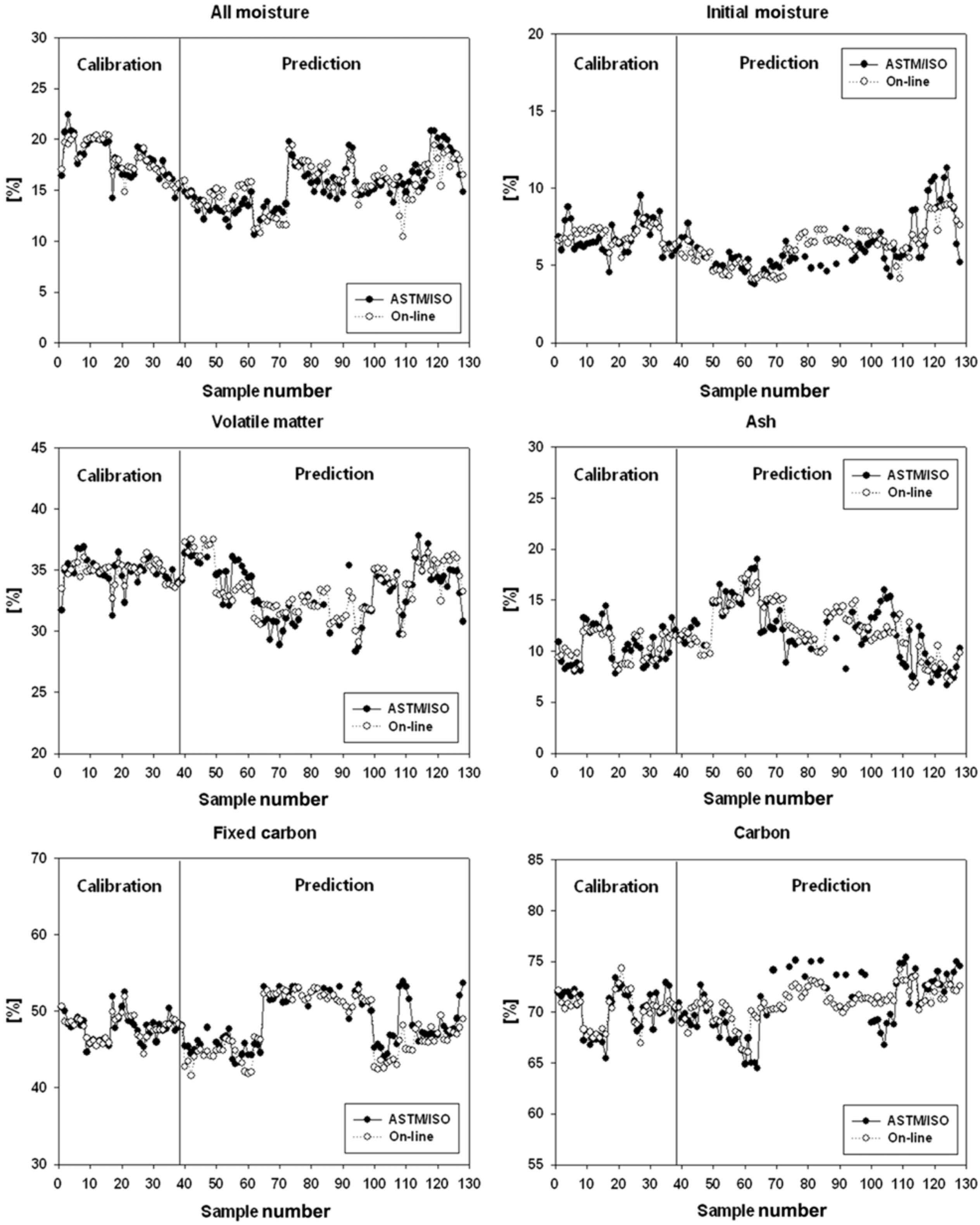

Fig. 4. Comparison the predicted value from on-line coal analyzer with the value by ISO/ASTM.

The reproducibility levels allowed by ASTM/ISO reference method are considered in Table 6. As expected, all moisture, volatile matter, carbon and hydrogen present good precision level, with many samples in the precision range defined by the norm. Although heating value error is higher than the reproducibility tolerances of the ISO/ASTM reference methods, the result is considerably good as the applicability of the method could be focused on a semi-quantitative approximation.

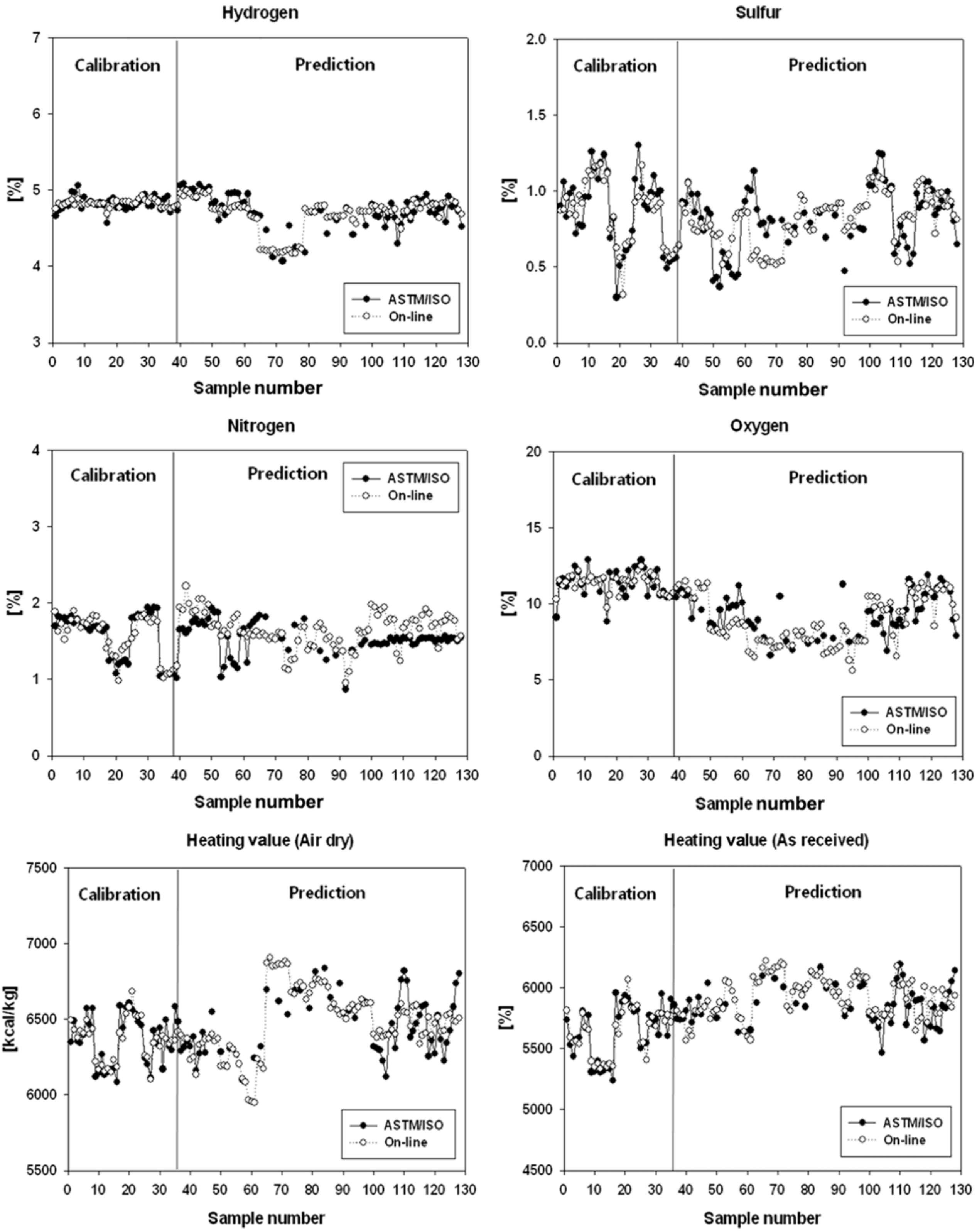

Fig. 4. Continued.

CONCLUSIONS

NIR reflectance based on its near-infrared spectrum can be done with good precision. In some cases, the prediction error is comparable or close to the reproducibility required by the ISO/ASTM norms for coal analyzer and better than those provided by commercial on-line analyzers. Acceptable correlations were found for % all moisture, volatile matter, fixed carbon, carbon, hydrogen and heating

Table 6. Comparison between the error of predicted value by NIR and ASTM/ISO reproducibility tolerance

		S. D (%)	Reproducibility tolerance (%)	No. of samples in reproducibility tolerance/ No. of total samples
Moisture	All moisture	0.98	0.70 (ASTM D3302)	54/89
	Humidity	0.90	-	-
Proximate analysis	Initial moisture	0.94	0.46 (ASTM D5142)	25/77
	Volatile matter	0.93	2.21 (ASTM D5142)	69/77
	Ash	1.35	0.40 (ASTM D5142)	16/77
	Fixed carbon	0.97	-	-
Ultimate analysis	Carbon	1.24	2.51 (ASTM D5373)	57/70
	Hydrogen	0.08	0.30 (ASTM D5373)	66/70
	Nitrogen	0.16	0.17 (ASTM D5373)	26/70
	Sulfur	0.14	-	-
	Oxygen	0.74	-	-
Heating value	Air dry	96.14	90.7 (ASTM D5865)	24/56
	As received	102.65	-	-
	Dry	111.76	-	-

value. The techniqure appears suitable for the determination of several coal prorperties at a coal feeder in a thermal power plant, if the equations of the coal properties of the multi-wave lengths NIR sensor are periodically calibrated for compansating the performance of the NIR source.

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NOMENCLATURE

λ_i : ith wavelength
A : the number of components
A_i : partial regression coefficient
d_i : difference between the predicted value from on-line coal analyzer and the value by ISO/ASTM
$\bar{d}$: average of the d_i
N, n : total number of samples
RMSE : Root Mean Squared Error
RMSEC : Root Mean Squared Error of Calibration
RMSEP : Root Mean Squared Error of Prediction
t : value of student t
x_i : reflectance measurement (1/R)
y_i : value of ith for regression
$\hat{y}_i$: value of predicting y_i
$\hat{y}_{CV,i}$: value of predicting y_i in the calibration set without ith sample

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