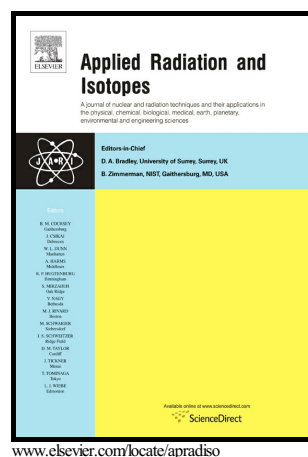


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Investigation of a High-Pressure Pressed Powder Pellet Technique for the Analysis of Coal by Wavelength Dispersive X-ray Fluorescence Spectroscopy

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Abstract

Using the proposed high-pressure pressed powder pellet technique, a coal sample was pressed into an ideal pellet without binders, which provides a solution to the poor self-binding quality of coal for the determination by X-ray fluorescence spectroscopy (XRF). The pellet produced by this method was more compact and smoother, which was particularly meaningful for spectrometer, where the sample is placed over the tube window. Additionally, the high-pressure sample preparation technique effectively eliminated the effect of falling powder and contamination in the Measuring chamber of the spectrometer.

Wavelength Dispersive X-ray Fluorescence Spectroscopy (WDXRF) was applied successfully to the determination of carbon, nitrogen and ash content in coal samples. This could provide an alternative method for the rapid analysis of carbon, nitrogen and ash content in the coal rather than the combustion method or the high-frequency infrared absorption with a slow ashing method. Furthermore, WDXRF could provide simultaneous determination of other major, minor and trace elements by X-ray fluorescence spectroscopy. The XRF results indicated that the sensitivity, precision, and limit of detection for most components were improved when the coal

sample was pressed at 1600 kN compared with preparation at 400 kN.

Keywords

High-pressure pressed pellet, X-ray fluorescence spectroscopy, coal, carbon, nitrogen, ash content

Introduction

Coal is one of the most important industrial energy resources. However, the burning of coal can cause significant environmental pollution. It is important to measure the components in coal samples in order to classify the different types of coal and protect the environment when using coal. Various analytical methods have been used to determine the major, minor and trace inorganic components in coal. These include atomic absorption spectroscopy, inductively coupled plasma atomic emission spectroscopy and inductively coupled plasma mass spectrometry (Booth et al., 1999; Rodushkin et al., 2000; Querol et al., 2001). However, these methods require tedious ashing and acid digestion processes, which are time-consuming and lead to a loss in volatile components.

The X-ray fluorescence spectroscopy offers simultaneous multi-element determination and is non-destructive. There are many previous studies on multi-element determination of coal samples by XRF (Suarez-Fernandez et al., 2001; Gazulla, 2010; Margui et al., 2006; Parus et al., 2000). However, sample preparation for XRF analysis is known to be challenging because of the poor self-binding property of coal. Since coal cannot be directly pressed into a pellet at the pressures used for most sample preparations, a binder is needed to form a stable pellet. The disadvantages of using of a binder will be detailed in the discussion.

Determination of carbon content in coal is generally done by combustion or laser-induced

breakdown spectroscopy (Xiong et al., 2014). Some other important analytes, such as nitrogen and halogens, are generally determined by special methods: Kjeldahl, coulometric titration, chemiluminescence and laser-induced fluorescence methods for nitrogen (Sáez-Plaza et al., 2013; Cao et al., 2005; Jeremy and George, 2009) and ion chromatography or ion-selective electrode for halogens. Additionally, the slow ashing method or laser-induced breakdown spectroscopy (Haider, 2013) are generally used to detect ash. The high-pressure pressed powder pellet technique proposed in our study has been successfully used for the elemental analysis of rocks, soils, sediments, plants. Using this technique, ideal pellets were achieved without binders when using a conventional hydraulic press. This approach improved the sensitivity, precision, limit of detection, and accuracy of XRF determination of various components. In this study, an alternative method for the rapid analysis of carbon, nitrogen and ash content is presented. Advantages of the method include simple sample preparation and rapid analysis in comparison with laborious and time-consuming chemical methods. As far as we know, there are few methods capable of simultaneous determination of major, minor, and trace elements (carbon, nitrogen and halogens included) as well as ash.

Methods and Experiments

An Axios WDXRF (Panalytical, Netherlands) was used at a power of 4.0 kW, maximum voltage of 60 kV and maximum current of 125 mA. An ultra-sharp rhodium target X-ray tube and SuperQ 4.0D software were used. The S-4800 field emission scanning electron microscope (FESEM, Hitachi) magnified the sample 300,000-fold. The maximum resolution was 1 nm. A YAM-3000D computer controlled the electro-hydraulic servo-testing machine (Ji'nan times assay

testing machine Co. Ltd., China) at a maximum pressure of 3000 kN for high-pressure sample preparation. A Rigaku hydraulic press was used for conventional sample preparation, at a pressure of 400 kN.

The coal sample (6 g, ground to 88 μm) was dried at 105°C, weighed and treated with a low pressure polyethylene powder as the backing /mechanical fortification of the pellet. Using the patented high-pressure sample preparation technology (Chinese patent application number: 201310125722.5), the pressure was increased at the speed of 13.3 kN s⁻¹. It took 2 minutes to reach the desired pressure of 1600 KN, and the pressure was held for 40 s. Then, the pressure was quickly dropped to zero, and the pellet was removed from the mold. Coal was pressed into a pellet mold with an inner diameter of 32 mm and an outer diameter of 40 mm. The low-pressure polyethylene was treated as edge or edge and backing to form the pellet. The pellet was numbered and stored in a vacuum desiccator until measured. The calibration was performed with the Chinese national coal reference material, GSC01-GSC16, which represents various types of bituminous coal and anthracite from mines all over China.

Results and Discussion

Only a few certified components are available (S, C, N, P, Cl, As, ash content) in the reference material. In order to increase the number of components determined for the coal samples, the values of 16 trace elements and the value of 10 major elements except P, of the reference material, were verified via ICP-MS and chemical method prior to the calibration experiments

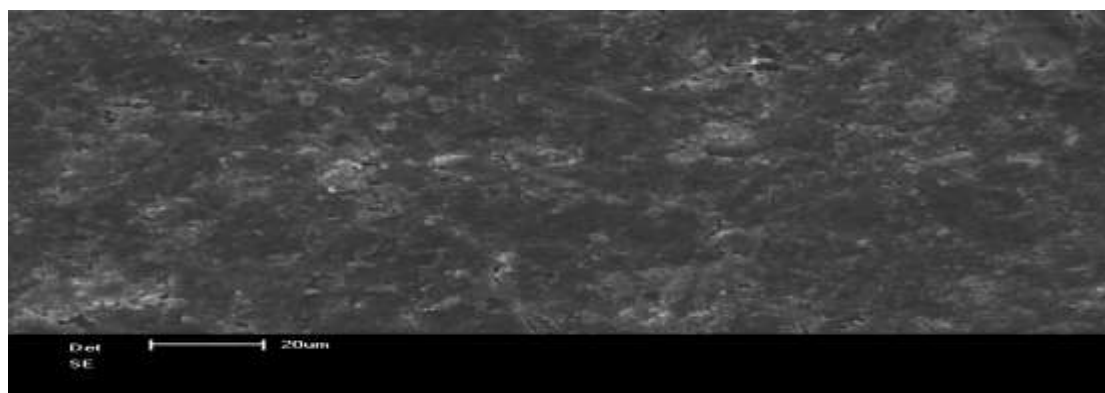
Characterization of the High-Pressure Sample Preparation Technique

The self-bonding property of coal is poor; thus, coal samples are difficult to press into pellet

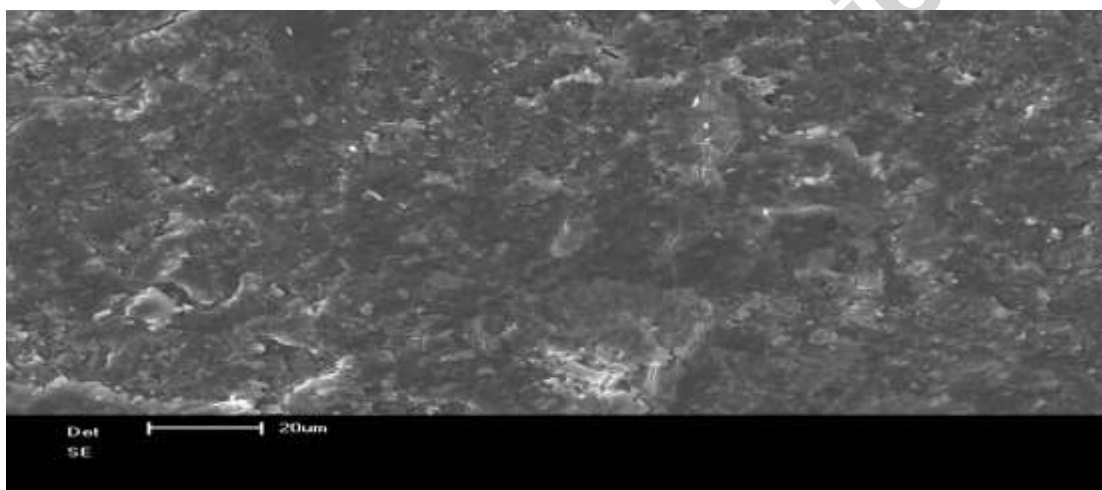
form. In previous studies, the determination of coal and related products by X-ray fluorescence spectroscopy was accomplished by pressing coal powder into a briquette form and adding a liquid (Bettinelli and Taina, 1990) or solid binder (Gazulla, 2010). The ratio of binder to sample ranges from 0.20:9 to 1:1. The addition of a large amount of binder dilutes the sample and reduces the intensity of the analytical line, increases background scattering, and negatively affects the detection limits of low atomic number elements and trace elements.

The addition of binder and the requirement of homogeneity of the sample limit practical applications of the method to the analysis of coal samples. Using the high-pressure pressed powder pellet technique, coal powder can be directly pressed into a pellet, without the need for a binder. The high-pressure pressed pellet technique efficiently eliminates the effect of falling powder. Moreover, the technique prevents contamination of the spectrometer while obtaining pellets with sufficient physical strength and stability without employing polycarbonate films (Margui et al., 2006). It is particularly meaningful for spectrometer, where the sample is placed over the tube window. With increasing pressure, the thickness of the pellet decreased from 4.1 mm (400 kN) to 3.5 mm (1600 kN) because of an increase in the packing density and reduction of the porosity. The surface became compact with mirror-like smoothness, and the background scattering was reduced. Samples prepared at different pressures were imaged using a scanning electron microscope (SEM). The magnified images are shown in Fig 1.

Fig 1. SEM images of coal pellets prepared at 400 kN (a) and 1600 kN (b) (magnified 50 times).



(a)



(b)

Sensitivity of the 18 analytes of different pressure pressed pellets

Sensitivity is defined as being the net intensity obtained per unit of concentration. To calculate the sensitivity, the measured intensities must not be corrected for matrix effects and one must assume a linear relation between intensity and concentration (Rousseu R.M., 2001). The sensitivity for each analyte, i , is calculated from the slope, m_i , of the calibration line as follows.

$$m_i = \frac{I_p - I_b}{C_i} \quad (1)$$

m_i is the slope of the calibration line for analyte i

I_p is the the peak intensity of an analyte i

I_b is the the background intensity of an analyte i

C_i is the concentration of an analyte i

The sensitivity of the 18 components was improved for pellets pressed at 1600 kN in comparison to pellets pressed at 400 kN. We attributed this enhanced sensitivity to the increase in the packing density and a reduction of the porosity, which corresponds to an increase of the number of atoms in the unit area of the pellet. A quantitative assessment of the sensitivity is specified in Table 1. Root mean square (RMS) is a measure of the average deviation of a theoretical value from an observed value. The RMS value was calculated using the following equation:

$$RMS = \sqrt{\frac{\sum (C^T - C^C)^2}{(n - k)}} \quad (2)$$

C^T is the concentration calculated by regression analysis

C^C is the concentration in the reference materials

n is the number of reference materials

k is the number of parameters calculated from the regression (slope, ordinate at the origin and inter-element coefficients)

Most of the RMS values for calibration curves of components except Al_2O_3 in pellets pressed at 1600 kN were also much improved compared with those of pellets pressed at 400 kN. The high-pressure pressed pellets reducing the error introduced by sample preparation, which is the

main source of error (see Table 1).

Table 1 Sensitivity for each analyte of different pressure pressed pellets

component	400KN Sensitivity	400KN RMS	1600KN Sensitivity	1600KN RMS	sensitivity1600KN/ sensitivity400KN
C	169.72	1.87996	170	1.86583	1.00
N	1558.8	0.09187	1574.2	0.06417	1.01
S	29.14	0.17904	31.7	0.16831	1.09
Cl	17.92	0.00307	18.41	0.00232	1.03
Sr	50.87	0.00361	56.33	0.00176	1.11
Zr	127.68	0.00835	147.27	0.00449	1.15
Pb	559.7	0.00029	565.93	0.00029	1.01
As	264.71	0.00005	268.2	0.00003	1.01
SiO ₂	85.44	1.06735	91.29	0.88955	1.07
Al ₂ O ₃	32.71	0.24543	33.18	0.29324	1.01
Fe ₂ O ₃	1832.54	0.35435	2063.49	0.15866	1.13
MgO	44.6	0.05134	44.89	0.03322	1.01
CaO	51.54	0.171	54.46	0.11619	1.06
Na ₂ O	86.29	0.03505	87.19	0.01337	1.01
K ₂ O	60.56	0.07897	63.24	0.02772	1.04
P ₂ O ₅	35.9	0.01425	37.3	0.00768	1.04
MnO	9.32	0.00151	10.6	0.00107	1.14
TiO ₂	83.11	0.05215	89.56	0.02179	1.08

The unit of sensitivity is cps/10⁻², and the Sr,Zr,Pb,As is cps/10⁻⁶

Precision of the method of different pressure pressed pellets

The precision of the method is estimated in terms of the relative standard deviation (RSD=SD/mi×100%), where SD is the standard deviation and mi is the mean intensity of the ith element in each of the samples. Ten pellets of GSC01, GSC03, GSC05, and GSC07 were all pressed at 400, 800, and 1600 kN. Intensity variation did not change much as a function of pressure. The relative standard deviations for each analyte pressed at 800 kN and 1600 kN pressures were improved compared with that of the 400 kN pressure (see Table 2). The precision of the analytical

concentrations determined for MnO, Na₂O and P₂O₅ were not improved with an increase in pressure, because of their trace level concentrations. Therefore, a pressure of 1600 kN was determined to be optimal for sample preparation.

Table 2. Precision of the method of different pressure pressed pellets

Co m.	GSC01						GSC05						GSC07					
	A(k	RSD	B(k	RSD	C(k	RSD	A(k	RSD	B(k	RSD	C(k	RSD	A(k	RSD	B(k	RSD	C(k	RSD
	cps	(%)	cps	(%)	cps	(%)	cps	(%)	cps	(%)	cps	(%)	cps	(%)	cps	(%)	cps	(%)
)	A)	B)	C)	A)	B)	C)	A)	B)	C
C	98.	1.9	99.	1.3	99.	0.7	95.	4.7	96.	2.1	105	1.3	92.	2.5	93.	2.5	94.	1.6
	95	6	12	8	57	4	48	7	83	9	.11	1	78	8	03	3	97	7
N	1.6	2.1	1.6	0.7	1.6	0.5	1.6	1.5	1.7	1.3	1.8	1.1	1.6	1.8	1.6	1.3	1.6	1.1
	7	7	1	9	1	7	3	2		2	1	3	7	5	8	8	0	
S	96.	0.5	96.	0.5	97.	0.5	445	0.8	443	0.2	447	0.2	166	0.5	166	0.4	166	0.3
	01	6	91	3	51	1	.6	4	.58	8	.23	8	.44	5	.34	6	.7	4
Cl	5.5	0.5	5.5	0.5	5.6	0.4	9.2	0.7	9.2	0.4	9.2	0.3	5.0	0.9	5.0	0.9	5.1	0.4
	4	2	6	1	6	6	1	7	5	1	9	7	1	3	3	0	9	3
Sr	261	0.6	262	0.3	264	0.3	94.	1.3	94.	0.5	95.	0.3	45.	0.5	45.	0.3	46.	0.3
	.59		.33	9	.35	7	12	3	61	6	94	3	13	7	43	8	53	1
Zr	118	0.5	120	0.4	123	0.4	84.	1.6	85.	0.6	85.	0.5	73.	0.3	74.	0.4	76.	0.2
	.01	9	.83	2	.33	0	97	8	12	4	88	3	59	1	14	3	11	9
A	9.6	0.4	9.6	0.4	9.7	0.4	12.	0.8	11.	0.3	11.	0.3	9.1	0.5	9.1	0.2	9.2	0.2
s	8	3	9	3	5	0	13	4	74	7	99	6	4	7	7	7	2	8
P	9.9	0.4	9.9	0.4	10.	0.4	12.	0.8	12.	0.4	12.	0.4	8.9	0.7	9.1	0.3	9.2	0.3
b	3	8	2	4	06	3	27	3	26	8	87	2	8	0	3	9	3	6
Si	241	0.4	242	0.3	243	0.3	153	1.0	153	0.4	154	0.3	260	0.6	261	0.3	262	0.2
O	.77	8	.08	8	.45	1	.47	7	.85	1	.56	5	.32	5	.59	0	.35	7
2																		
Al							137	1.2	138	0.6	138	0.4	227	0.6	229	0.2	231	
2	252	0.4	253	0.4	255	0.4	.63		.54		.82	3	.21	1	.56	9	.74	0.2
O	.84	8	.74	4	.63	1												9
3																		
Fe							74.	0.7	74.	0.5	75.	0.3	229	0.4	231	0.4	233	
2	155	0.3	156	0.3	157	0.3	89	8	95	4	45	8	.63	9	.65	0	.52	0.2
O	.75	9	.46	7	.29	5												
3																		
M	7.5	0.5	7.5			0.4	1.6	1.3	1.6	0.5	1.7	0.5	4.5	0.9	4.6	0.4	4.7	0.4
g	3	2	8	0.7	7.7	3	3	9	8	9	4	6	7	7	9	2	2	3
O																		
C	14.	0.5	14.	0.5	14.	0.3	12.	0.6	12.	0.8	12.	0.5	13.	0.5	13.	0.3	14.	0.3
a	22	7	76	4	89	7	03	9	15		57		89	0	95	8	2	8

O																			
K	3.4	0.5	3.4	0.5	3.5	0.4	0.7	1.2	0.7	0.7	0.7	0.5	4.7	0.4	4.8	0.3	5.1	0.3	
₂	7		8	7	5	0	1	2	3	5	6	8	8	0	9	4	6	4	
O																			
N	0.7	1.2	0.7	0.5	0.7	0.5	0.5	2.5	0.5	1.4	0.6	1.4	1.2	0.7	1.2	0.6	1.3	0.8	
_{a2}	5	1	4	2	5	3	6	5	7	4	7	7	8	7	9	2	1	7	
O																			
M	1.9		1.9	0.3	1.9	0.4	1.2	0.6	1.2	0.4	1.2	0.4	2.1	0.8	2.1	0.5	2.2	0.3	
_n	5	0.7	5	8	7	1	3	5	6	4	4	7	5	7	8	2	7	8	
O																			
Ti	13.		13.	0.3	13.	0.3	5.6	0.8	5.5	0.5	5.6	0.3	10.	0.6	10.	0.3	10.	0.3	
_O	52	0.4	72	7	76	3	6	9	7	3	8	9	29	7	33	8	43	6	
₂																			
P ₂	13.	0.5	13.	0.5	13.	0.4	3.5	1.0	3.5	0.5	3.6	0.4	2.1	0.9	2.2	0.8	2.2	0.8	
_O	01	8	06	4	17	6	7	9	8	6	7	5	8	5	4	6	8	8	
₅																			

Com. is component.A is the average count rate of the consecutive measurement of 10 pellets pressed under 400KN 40s of the same sample, the unit is kcps

B is the average count rate of the consecutive measurement of 10 pellets pressed under 800KN 40s of the same sample, the unit is kcps.

C is the average count rate of the consecutive measurement of 10 pellets pressed under 1600KN 40s of the same samples, the unit is kcps.

Limit of detection of different pressure pressed pellets

The limit of detection (LOD) is an important performance parameter for characterizing XRF instruments. After the optimized measurement conditions are determined and the instrument was calibrated, the LOD was calculated as three times the square-root of the background noise of each element, from measurement of different coal reference materials. That is, LOD can be defined by the function below:

$$LOD = \frac{3}{S_i} \sqrt{r_b}$$

Where S_i is the sensitivity (counts per second divided by concentration), r_b is the background counts per second, and t_b is the measurement time. The LOD can also be estimated as 3 times the standard deviation of multiple measurements (consecutive measurements of 10 different pellets)

from the analysis of the same samples. 10 pellets of GSC02, GSC04, GSC08, and GSC12 were pressed at 1600 kN and 400 kN. The LOD are listed in Table 3.

The LOD is related to the matrix of the sample. The scattering of the background intensity and the sensitivity of the analyses can change due to differences in the components and concentrations of the samples, and the detection limit is also different. The proposed methodology to evaluate LODs, on the basis of the standard deviation of repeated sample measurements, has the advantage of including most of the sources of measurement errors, which gives a more robust estimate.

The limit of detection of most components in pellets pressed at 1600 kN was improved in comparison to pellets pressed at 400 kN (see Table 3). We attributed this to the reduction in analytical error in sample preparation achieved by the high-pressure pressed pellet technique and the standard deviation of consecutive measurement of 10 pellets of the same sample is minimized. The limits of detection of S were not improved with an increase in pressure, because the lower total counts originated from the lower detection efficiency of lower energy ranges. For MnO, Na₂O and P₂O₅ a high LOD value may be due to the trace level concentrations present in the samples, which are inherently difficult to analyze.

Table 3. Comparison of limit of detection of a method of different pressure pressed pellets

Com.	LDM (GSC02)			LDM (GSC04)			LDM (GSC08)			LDM (GSC12)		
	A	400KN	1600KN	A	400KN	1600KN	A	400KN	1600KN	A	400KN	1600KN
C	35.37	16400	5436	81.22	7638	3951	66.84	583	506	72.61	3678	3193
N	0.89	1105	270	1.13	534	480	1.13	362	260	1.15	353	336
S	0.56	211	198	1.06	273	222	2.43	322	405	2.59	416	296
Cl	0.007	14	10	0.023	10	8	0.016	8	8	0.041	8	8
Sr	158	3.5	2.6	52	1.2	1	108	1.4	1.2	93	1	0.9
Zr	748	26	19	92	3.2	2.4	343	6.4	5.4	349	3.4	1.1
As	2.3	0.9	0.3	2	0.6	0.5	3.6	0.7	0.6	4.7	0.4	0.3
Pb	22	1.6	1.2	5.7	1	0.9	16	1.4	0.8	8.9	1	0.6
SiO ₂	29.62	10632	4241	3.24	790	712	11.66	5238	3870	7.35	2010	1480
Al ₂ O ₃	15.41	4608	2276	1.21	261	212	6.66	2520	2013	5.15	1407	922
Fe ₂ O ₃	2.07	482	347	1.17	331	193	1.33	294	245	2.15	217	187
MgO	0.47	124	83	0.074	18	15	0.23	63	56	0.22	24	20
CaO	0.99	157	63	0.43	38	22	0.83	132	98	1.08	132	42
K ₂ O	0.46	100	81	0.026	12	19	0.35	63	46	0.18	26	18
Na ₂ O	0.29	86	50	0.047	30	36	0.26	120	100	0.075	16	10
MnO	0.022	7	8	0.006	2	4	0.013	3	6	0.007	2	2
TiO ₂	1	341	166	0.16	24	20	0.39	105	95	0.32	32	28
P ₂ O ₅	0.16	42	40	0.039	8	16	0.045	15	18	0.052	4	6

Column A is the average content of the component. The unit of As, Pb, Sr, Zr is $\mu\text{g g}^{-1}$, the rest is %m/m.

The Determination of Carbon and Nitrogen Concentrations in Coal Samples

Carbon content is one of the important indexes of coal quality. In general, Chinese coal is high in carbon with contents ranging from 54% m/m to 77.46% m/m. Determination of carbon and nitrogen by XRF was difficult because the fluorescence yield is low for low atomic number elements such as C and N (see Table 4). High-pressure sample preparation, without the addition of a binder (except HBO₃, the other binder containing carbon), facilitated the direct measurement of carbon in coal samples. The sensitivity of C content determination was improved. The introduction of synthetic multi-layer crystals allowed the measurement of C by XRF. The carbon was analyzed using a WDXRF (Panalytical, Netherland), PX4 synthetic multi-layer crystal, 4000 μm coarse collimator, and a 75 μm Be window, at 30 kV and 120 mA. The 2θ of the C K α line was 44.355° , and significant line overlap was imposed by the 2OK α (47.2790°), CaL α (35.7851°), 2FeL α 1(34.6078°), 2TiL β 3(47.6614°), and 2MnL α 1(38.4395°) lines. Inter-element interference was corrected by empirical coefficients, and the correlation coefficient of the C calibration was 0.9235. In part, deviations between the experimental results and certified values were attributed to the presence of carbon in three different chemical forms (organic carbon, carbonate, and elemental carbon). The presence of these forms caused a small, but significant, wavelength shift in the position of the carbon line. Furthermore, the penetration depth of C in coal samples was only 2 μm . It was still a great challenge to grind the sample to the 2 μm particle size required for modern techniques. The carbon measurements were negatively affected by particle size effects and surface roughness. However, the accuracy, precision, and linear calibration of C

were substantially improved by using ultrafine sample preparation (Parus et al., 2000). The absolute error of the carbon content decreased to 0.40–1.50% m/m. The intensity of the carbon line decreased with each subsequent irradiation, which is probably due to the radiolysis (Alexander Pleßow, 2013). Thus, newly prepared samples and those stored in vacuum desiccators prior to analysis were preferred.

The content of nitrogen is also important for the evaluation of the quality of coal. When coal burns, about 25% m/m of nitrogen is converted to nitrogen oxide, polluting the environment. No previous reports of the determination of N in coal by XRF were found in the literature. In this study, nitrogen was analyzed by XRF using a PX5 synthetic multi-layer crystal. The 2θ of the N $K\alpha$ line was 32.923° , and significant line overlap was imposed by the $CaL\beta_1$ (36.6648°), $2FeL\alpha_1$ (34.6078°), TiL_1 (31.8780°), $TiLn$ (31.3568°), and $2MnL\alpha_1$ (38.4395°) lines. The content of nitrogen in coal was low, ranging from 0.64–1.33% m/m. The N $K\alpha$ line was strongly absorbed by C, H, and O in coal. The empirical coefficient method was applied to correct for matrix effects, and the correlation coefficient of the N calibration was 0.9143. The penetration depth of N for coal samples was only 0.71 μm . Ultrafine sample preparation was also preferred. The correlation curves of corrected concentration versus certified concentration of C and N are shown in Figure 2 and Figure 3. Comparison of C and N content between XRF analysed values and certified values is shown in Table 4.

Fig. 2 Correlation curve of corrected concentrations of carbon vs. certified concentrations.

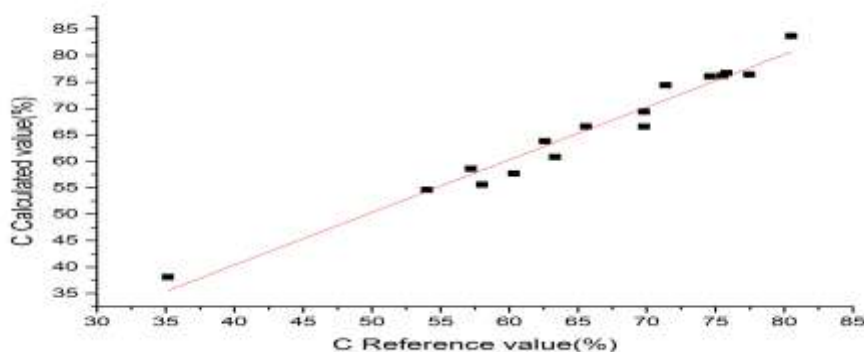


Fig. 3 Correlation curve of corrected concentrations of nitrogen vs. certified concentrations.

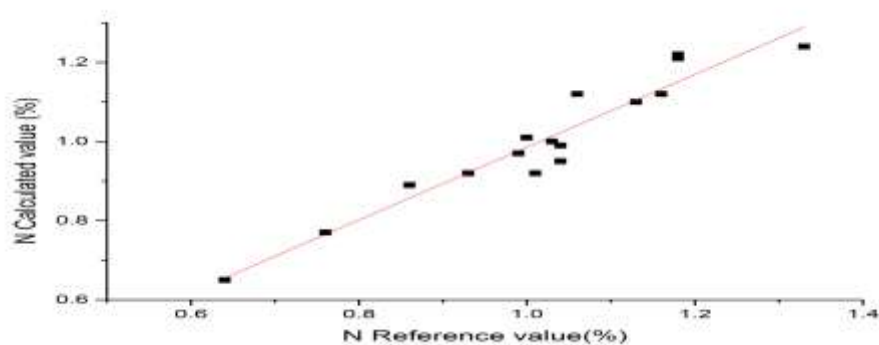


Table 4. Comparison of C and N between XRF analysed values and certified values

	C certified value	C observed value	N certified value	N observed value
GBM1110 5g	78.63±0.38	73.47±0.28	1.16±0.020	1.08±0.020
GBM1110 8m	68.27±0.32	66.19±0.18	1.19±0.030	1.08±0.015
GSC06	75.80±0.51	78.91±0.27	1.18±0.050	1.26±0.031
GSC10	65.58±0.29	65.03±0.26	1.06±0.04	1.10±0.024
GSC11	75.53±0.39	72.55±0.22	1.04±0.03	1.03±0.011
GSC13	54.00±0.56	54.70±0.42	0.99±0.04	1.04±0.018
GSC15	71.37±0.25	71.43±0.34	1.13±0.06	1.08±0.019
GSC16	60.34±0.20	57.40±0.21	1.04±0.04	1.03±0.023

The Determination of 31 Components and Ash Content in Coal Samples

The determination of 31 components in 16 coal reference materials was conducted by WDXRF. The empirical coefficient method was used to correct for matrix effects. Compton scattering radiation was used as an internal standard to compensate for variations in the sample matrix, particle size, packing density, absorption, and operating characteristics of the instrument. The method was evaluated with reference materials not used in the calibration. The average concentration of the 6 consecutive measurements and the standard deviation are given in Table 5. The measurement values of the reference materials agreed well with that of the certified values due to closer particle packing achieved by sample preparation at 1600 kN. The observed differences between the experimental results and expected (reference) concentrations of C and N were attributed to the mineralogical and particle size effects that strongly influence the measurements of low atomic number elements. The effective penetration depths of selected fluorescence X-rays, $CK\alpha$ and $NK\alpha$, were $2\mu\text{m}$ and $0.71\mu\text{m}$, respectively. Ultrafine sample preparation could substantially improve the accuracy of the measurement.

Ash is the residue remaining after complete combustion of coal, and therefore, is an important index in evaluating the quality of coal. Numerous determinations of ash content by the XRF method are reported in the literature. The ash content was broadly proportional to the silicon concentration, and a regression of silicon counts versus nominal ash content was evaluated by Pearce (1990). The ash content in coal was previously measured by XRF using backscattering. The difference between the chemical values and the XRF results was less than 0.5% m/m (Cechak and Thinova, 2001). The ash content of coal was the total of all the oxides in coal minus the sulfur

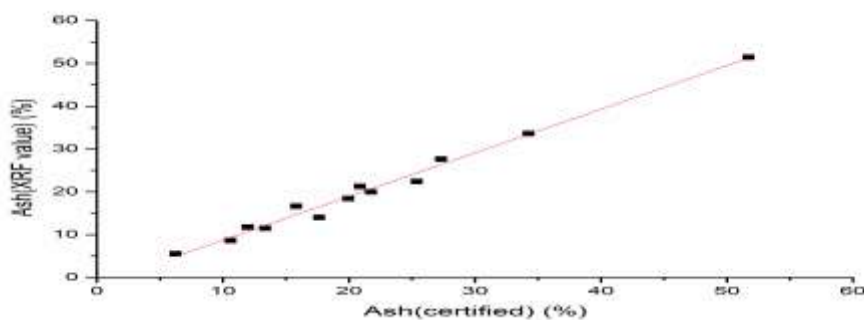
Compo nent	ZBM1211	ZBM1121	ZBM0951	ZBM1081	GBW11113g	GBW11108m						
	chemic al value	XRF valu e	chemic al value	XRF valu e	chemica l value	XRF valu e	chemic al value	XRF valu e	chemic al value	XRF valu e	chemic al value	XRF valu e
S	—	0.65	—	1.31	—	0.36	—	0.65	2.87±0.05	2.22	1.73±0.02	1.61
		±		±		±		±		±		±
		0.01		0.00		0.01		0.01		0.00		0.00
		5		17		1		3		30		17
Cl	—	0.03	—	0.02	—	0.05	—	0.02	—	0.03	—	0.10
		±		1±		7±		9±		8±		±
		0.00		0.00		0.00		0.00		0.00		0.00
		30		20		058		058		32		058
Cr	9.8	23±7	21.1	10±5	14.0	5±1	6.5	14.9±5	16.3	10±4	13.4	
	5±2	±		±		±		±		±		±
		1.1		0.8		0.5		0.8		0.6		1.1
Co		2.5	9±2	6.7	4±1	3.4	11±3	11.1	6.9±2	8.2	2.3±2	2.9
	3±2	±		±		±		±		±		±
		0.8		0.2		0.2		0.2		0.7		0.6
		4.8	16±4	11.3	8±2	6.5	18±3	18.8	11.4±3	12.5	4.1±2	4.4
Ni	5±1	±		±		±		±		±		±
		0.2		0.2		0.2		0.3		0.3		0.2
Cu	8±2	8.8	23±5	23.4	12±3	14.3	17±1	20.0	19.8±4	16.6	9.4±3	7.5
		+		+		+		+		+		+

		0.5		0.4		0.3		0.5		0.3		0.4
		42.2	40±7	34.7	10±3	12.3	36±6	37.5	63±6	64.7	42.5±5	45.3
Zn	38±6	±		±		±		±		±		±
		0.1		0.7		0.5		0.4		1.5		0.8
		2.2	9.2±2	7.7	5.5±1	5.9	10.2±2	12.0	10.5±3	10.1	8.8±2	9.1
Ga	2.7±2	±		±		±		±		±		±
		0.3		0.2		0.2		0.6		0.5		0.4
	—	—	17.7±	15.2	1.8±1	—	5.9±2	3.8	11.6±3	8.5	2.7±1	—
Rb			4	±				±		±		
				0.1				0.2		0.1		
		109.	94.3±1	93.1	295±25	310.	54±9	53.1	89.3±9	93.2	75±8	65.0
Sr	106±15	4±2	2	±2		4±3		±1		±		±2
										1.3		
		4.6	6.0±2	8.0	6.5±2	4.5	18.2±7	18.2	8.2±2	8.8	9.7±2	7.0
Y	6±2	±		±		±		±		±		±
		0.2		0.3		0.2		0.1		0.1		0.1
		44.1	280±23	290	160.8±1	167.	443±26	437.	345±17	340	365±16	352.
Zr	41.6±7	±1		±4	6	7±3		0±		±		2±
								6.7		6.6		5.5
		1.6	5.6±2	5.59	3.8±1	5.3	4.7±2	4.1	5.3±2	5.0	5.4±2	5.1
Nb	1.6±	±		±		±		±		±		±
		0.7		0.6		0.4		0.5		0.4		0.4
		9.3	183±13	162.	65±10	63.9	31±5	27.1	157±	168.	54±	64.1
Ba		±1		5±3		±		±		6±		±
						1.1		4.1		1.3		2.0
		3.8	2.5±1	3.6	1.6±1	2.9	2.5±1	3.3	2.7±1	4.1	2.7±1	3.1
Hf	3.2±1	±		±		±		±		±		±
		0.6		1.0		0.3		0.1		0.6		0.4
		7.5	16.4±3	14.9	16±3	15.0	16±2	20.6	61.3±	60.9	17.6±4	19.8
Pb	6.7±2	±		±		±		±		±		±
		1.1		0.4		0.6		0.9		1.2		0.4
		2.4	8.3±2	8.1	5.6±2	7.6	5.6±2	6.9	2.7±1	3.6	8.2±3	6.4
Th	2.3±2	±		±		±		±		±		±
		0.5		0.5		0.3		0.3		1.3		0.6
		1.3	2.6±1	3.0	3.2±1	3.7	2.8±1	3.2	2.7±1	2.9	1.8±1	2.9
U	0.6	±		±		±		±		±		±
		0.06		0.02		0.03		0.04		0.02		0.03
	—	—	—	5.7	—	—	—	1.4	—	9.0	—	2.9
As				±				±		±		±
				0.2				0.1		0.5		0.1
		0.03	0.023±	0.02	0.15±0.0	0.14	0.030±	0.02	0.087±	0.07	0.029±	0.03
P ₂ O ₅	0.043±	6±	0.002	3±	1	±	0.004	9±	0.002	5±	0.003	0±
	0.009	0.00		0.00		0.00		0.00		0.00		0.00
		10		058		10		058		11		12

		2.15	12.00±	10.7	3.98±0.1	4.40	5.75±0.	6.11	8.73±0.	8.74	7.42±0.	8.19
SiO ₂	2.16±0.	±	0.15	7±	3	±	13	±	15	±	062	±
	043	0.00		0.01		0.03		0.02		0.00		0.01
		76		3		7		3		47		7
Al ₂ O ₃		1.41	6.56±0.	6.15	3.55±0.1	3.78	4.29±0.	4.40	6.14±0.	5.88	5.34±0.	5.81
	1.57±0.	±	15	±	1	±	094	±	067	±	032	±
	038	0.00		0.00		0.01		0.00		0.00		0.01
Fe ₂ O ₃		30		36		9		96		21		3
		0.66	1.46±0.	1.64	0.50±0.0	0.69	0.34±0.	0.48	3.54±0.	3.66	1.47±0.	1.43
	0.46±0.	±	11	±	3	±	03	±	022	±	0062	±
MgO	04	0.02		0.02		0.01		0.00		0.05		0.01
		1		8		2		65		5		7
		0.10	0.46±0.	0.67	0.13±0.0	0.18	0.083±	0.11	0.30±0.	0.34	0.14±0.	0.13
CaO	0.099±	9±	03	±	1	±	0.01	±	010	±	003	±
	0.01	0.00		0.00		0.00		0.00		0.00		0.00
		15		32		20		56		058		11
K ₂ O		1.13	2.63±0.	2.82	1.03±0.0	1.20	0.39±0.	0.45	0.95±0.	1.08	0.77±0.	1.04
	0.91±0.	±	22	±	8	±	01	±	006	±	005	±
	04	0.00		0.00		0.00		0.00		0.00		0.00
Na ₂ O		78		79		97		26		58		35
		0.01	0.35±0.	0.30	0.031±0.	0.03	0.11±0.	0.17	0.30±0.	0.29	0.084±	0.06
	0.012±	5±	05	±	004	5±	008	±	009	±	0.008	8±
MnO	0.002	0.00		0.00		0.00		0.00		0.00		0.00
		56		11		058		10		15		57
		0.05	0.070±	0.09	0.15±0.0	0.21	0.065±	0.08	0.11±0.	0.09	0.041±	0.03
TiO ₂	0.046±	7±	0.009	±	3	±	0.01	5±	04	8±	0.021	6±
	0.004	0.00		0.00		0.00		0.00		0.00		0.00
		058		055		058		058		10		058
Ash	—	—	0.0024	0.00	0.0039±	0.00	—	—	0.013	0.02	0.008±	0.01
			±	31±	0.001	35±			±	1±	0.001	2±
			0.0004	0.00		0.00			0.0004	0.00		0.00
Ash			05		06				06		07	
		0.07	0.30±0.	0.34	0.16±0.0	0.19	0.15±0.	0.12	0.20±0.	0.24	0.17±0.	0.22
	0.077±	9±	03	±	13	±	01	±	003	±	002	±
Ash	0.005	0.00		0.00		0.00		0.00		0.00		0.00
		29		30		45		45		23		15
		5.56	25.37±	22.4	10.59±0.	8.66	11.95±	11.7	21.72±	20.2	15.78±	16.6
Ash	6.24±0.	±	0.15	2±	09	±	0.11	7±	0.11	3±	0.09	9±
	08	0.04		0.05		0.06		0.05		0.07		0.05
		4		7		8		2		0		3

Note: The unit of S, Cl, C, N, P₂O₅, SiO₂, Al₂O₃, Fe₂O₃, MgO, CaO, K₂O, Na₂O, MnO, TiO₂, Ash is %m/m, the rest is $\mu\text{g g}^{-1}$. Ash is the sum of the concentrations of SiO₂, Al₂O₃, Fe₂O₃, MgO, K₂O, CaO, and TiO₂; — indicates that there is no certified value or the measurement value is below LOD. The sample was pressed at 1600kN.

Fig. 4. The correlation of ash content measured by the combustion method with the calculated XRF results.



Conclusion

To simplify and improve the sample preparation of coal for XRF analysis, a high-pressure pressed powder pellet technique was proposed here. This technique could also be used for other sample types with similar sample preparation challenges as coal, such as those with high silicon contents and biological samples. This study provides a major technological breakthrough for XRF sample preparation. The high-pressure pressed pellet technique eliminated the need for a binder, thus increasing the analytical sensitivity, decreasing the relative standard deviations, and improving limit of detection for XRF analysis of most components.

An alternative quantitative method for determination of carbon and nitrogen content in coal, using a WDXRF, PX4, PX5 synthetic multi-layer crystal and a 4000 μm coarse collimator, was presented. Though the accuracy of the method present here is not comparable with that of the traditional chemical method, it offers a quick assay method of carbon and nitrogen content in coal.

The indirect determination of ash content in coal by XRF was also discussed. The ash content in Chinese coal was approximately equal to the total concentration of SiO_2 , Al_2O_3 , Fe_2O_3 , MgO ,

CaO, and TiO₂.

The techniques described in this paper improve the analysis of coal in terms of analytical sensitivity, precision and LOD. The techniques described are also more time- and cost-effective, as less time and fewer materials are required for preparation and fewer analyses are needed to obtain the relevant data. These techniques are highly important to environmental studies of the effects of coal burning as a major energy source in China.

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Highlights

1. The high-pressure pressed powder pellet technique, without a binder, was used to solve the sample preparation issues related to coal XRF analysis.
2. This was a major technological breakthrough for XRF sample preparation.
3. High-pressure sample preparation technique efficiently eliminates the effect of falling powder and avoids contamination of the spectrometer measuring chamber.
4. Experiments indicated that the sensitivity, precision and limit of detection for most components were improved when the sample was pressed at 1600 kN compared with 400 kN.
5. An alternative method for determination of the carbon and nitrogen content in coal was presented.