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Preliminary Study on the Determination of Total Carbon, Hydrogen and Nitrogen Content of Calcined Coke

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Abstract: This paper preliminarily studies the current domestic and foreign standards for the determination of total carbon, hydrogen and nitrogen content in calcined coke, and the instruments used. It lays the foundation for the formulation of relevant industry standards in the future, and also provides technical support for the accurate quantification of carbon content in greenhouse gas emissions.

Keywords: Calcined Coke; Total Carbon, Hydrogen and Nitrogen Content; Infrared Absorption Analyzer; Chn Analyzer

1. Introduction

The international community is paying more and more attention to carbon emissions. According to IPCC estimates, the world must achieve carbon neutrality by 2050 in order to achieve the 2°C temperature control target of the Paris Agreement[1]. In recent years, global carbon dioxide emissions have been maintained at around 35 billion tons. Carbon emissions remain high; my country has even formulated the "3060" carbon neutralization goal of peaking carbon[2]. In November 2015, the General Administration of Quality Supervision, Inspection and Quarantine of the People's Republic of China and the National Standards Committee approved and issued the General Rules for Accounting and Reporting of Greenhouse Gas Emissions of Industrial Enterprises, including power generation enterprises, etc.11 items national standards[3]. As far as GHG emission accounting of power generation enterprises is concerned, the "Guidelines for Accounting and Reporting of Greenhouse Gas Emissions for Power Generation Enterprises in China" and "Requirements for Accounting and Reporting of Greenhouse Gas Emissions Part 1: Power Generation Enterprises" both require carbon content. For the production of carbon materials, the carbon content and oxidation rate of its raw materials, products and production processes have a significant impact on future carbon emissions and carbon verification. At present, foreign customers are required to detect carbon content in products such as pre-baked anodes and calcined petroleum coke exported from my country. However, in China, on the one hand, the method standards are not perfect, on the other hand, the testing equipment mainly relies on the United States and Europe. And imported equipment such as Japan, the purchase cost is high, and the penetration rate in traditional carbon production enterprises is not high.

Foreign carbon content determination equipment mainly focuses on the two principles of infrared absorption and thermal conductivity to detect carbon content. In the case of low melting temperature and low results, accurate detection of carbon content can be achieved if a high-temperature (1350℃) resistance furnace is matched. At present, coal and other flammable products are mainly detected by thermal conductivity pool at 1000℃.

2. Sample Preparation and Research Methods

According to the requirements of GB/T 26297.6-2010, prepare representative samples according to the following procedures:

1. Crushing the original sample with jaw crusher to below 3mm;
2. After mixing and shrinking the sample, grind the sample with a sample grinder until it all passes through a 0.15mm test sieve;
3. Put the ground samples into a drying oven, dry at 110℃±5℃ for 2h, and store them in a desiccator for later use.

In order to compare the results, the CHN analyzer[4], elemental analyzer and infrared absorption analyzer were used for the determination of total carbon, hydrogen and nitrogen in calcined coke in this study[5] [6]. Among them, imported equipment is

selected for CHN analyzer to compare with domestic similar equipment, and imported equipment is selected for infrared absorption analyzer and element analyzer. The referenced standards mainly include ISO, ASTM and GB related testing methods for solid mineral fuels, coal and coke.

3. Results and Discussion

3.1 CHN analyzer

In this study, LECO CHN828 carbon, hydrogen and nitrogen analyzer was used to detect three calcined coke samples with different contents. The test conditions are as follows: the sample weight is 200 mg, the multi-point calibration thermal conductivity cell and infrared absorption cell are detected, and the furnace temperature is 1350 ℃, the reaction time is 2.8min. The test results are shown in Table 1

Table 1 Results of CHN analyzer for calcined coke samples

sample	w_{Cd} (%)	w_{Hd} (%)	w_{Nd} (%)
1#	95.92	0.15	0.68
1#	95.78	0.14	0.65
2#	96.80	0.31	0.80
2#	96.97	0.35	0.75
3#	98.64	0.15	1.02
3#	98.96	0.13	1.05

Note: w_{Cd} , w_{Hd} , w_{Nd} respectively expressed as dry basis carbon, hydrogen and nitrogen content, the same below

In this test, the multi-point calibration of standard samples is mainly carried out with reference to ASTM 5373-14 Standard Test Methods for Determination of Carbon, Hydrogen and Nitrogen in Analysis Samples of Coal and Carbon in Analysis Samples of Coal and Coke[7]. and H, For the test of N, the carbon content was tested by method B.The reaction time is concentrated within 80S. It can be seen from the table that the detection results of carbon, hydrogen and nitrogen are reproducible, and the furnace temperature of 1350 ℃ is conducive to the rapid escape of carbon elements in the calcined coke.

3.2 Elemental analyzer

In the test, the Thermo CHNS/O elemental analyzer of was used to test the above samples. The test conditions were as follows: the sample weight was 1 mg, the multi-point calibration thermal conductivity cell was detected, the furnace temperature was 950 ℃, and the reaction time was 12 min. The test results are shown in Table 2

Table 2 Determination results of calcined coke samples by elemental analyzer

sample	w_{Cd} (%)	w_{Hd} (%)	w_{Nd} (%)
BBOT	72.72	6.07	6.45
Niacin Thiophene	78.49	10.00	2.61
1#	92.37	0.12	0.67
1#	88.90	0.16	0.66
2#	95.75	0.30	0.79
2#	95.67	0.38	0.70
3#	97.06	0.15	1.03
3#	96.95	0.16	1.06

In this determination, mainly referring to ISO 29541-2010 Solid mineral fuels — Determination of total carbon, hydrogen and nitrogen content — Instrumental method standard[8], BBOT and Niacin

Thiophene were used as standard samples for multi-point calibration. The standard values of standard samples are shown in Table 3. The overall Comparing the results with the CHN analyzer, it can be seen that the content of hydrogen and nitrogen is consistent, and the carbon content is systematically low. The reason may be that the furnace temperature of 1000 ° C is not enough to volatilize all the carbon elements. The general firing condition of calcined coke products is 1300 Incubate at ℃ temperature for 5h. In addition, due to the small sample size of 1 mg, individual samples may be uneven to a certain extent, resulting in unstable results.

Table 3 Standard sample values of BBOT and Niacin Thiophene

standard sample	C		H		N	
	%	Range (±)	%	Range (±)	%	Range (±)
BBOT	72.53	0.30	6.09	0.10	6.51	0.10
Niacin Thiophene	78.46	0.30	9.97	0.10	2.61	0.30

In order to compare the performance of the domestic CHN analyzer and the above equipment, this paper uses the SDCHN 536 hydrocarbon and nitrogen element analyzer of SANDY Instrument Company to test the above three samples. The furnace temperature is below 1000°C, and the reaction time is 2min. The test results are shown in Table 4

Table 4 Determination results of SDCHN elemental analyzer

sample	w_{Cd} (%)	w_{Hd} (%)	w_{Nd} (%)
1#	94.75	0.22	0.68
1#	95.11	0.22	0.67
2#	96.15	0.18	0.78
2#	95.38	0.24	0.78
3#	97.41	0.22	1.15
3#	97.82	0.22	1.12

This test is carried out in accordance with GB/T 30733-2014 Instrumental method for the determination of carbon, hydrogen and nitrogen content in coal[9], which is modified by ISO 29541-2010 Solid mineral fuels — Determination of total carbon, hydrogen and nitrogen content — Instrumental method, using CHN content The coal standard samples with high, medium and low requirements were calibrated at multiple points. Comparing the results with the above, it can be seen that the carbon content is closer to the LECO measurement result than the Thermo result, and the nitrogen content is also within the allowable range, but the hydrogen content deviates more from the above equipment. , the possible reason is that the chemical stability of the coal standard sample is poor, and the hydrogen content varies greatly with temperature and time. In the ASTM standard, it is not recommended to include the coal standard sample as the standard sample, but only as an internal control quality control.

3.3 Infrared absorption analyzer combined with ONH analyzer

According to the above test results and the current situation of the existing instruments, this paper adopts the method of infrared absorption analyzer combined with ONH analyzer to detect the total carbon, hydrogen and nitrogen content in the calcined coke, and uses the infrared carbon and sulfur analyzer to detect the total carbon content. The conditions are: 1350 ℃ furnace temperature, weighing 200 mg, reaction time less than 1 min, the calibration substances used are shown in Table 5; use ONH or conventional CHN analyzer to detect H and N content, the test conditions are: sample weighing 100 mg, Multi-

point calibration thermal conductivity cell detection, furnace temperature 950 ℃ to 1050 ℃, reaction time 3min. The test results are shown in Table 6

Table 5 Commonly used calibration substances and their total carbon, hydrogen and nitrogen contents

Name	Formula	C(%)	H(%)	N(%)
EDTA	$C_{10}H_{16}N_2O_8$	41.1	5.5	9.6
Phenylalanine	$C_9H_{11}NO_2$	65.4	6.7	8.5
Acetanilide	C_8H_9NO	71.1	6.7	10.4
BBOT	$C_{26}H_{26}N_2O_2S$	72.5	6.1	6.5
Graphite	C	100.0		

Table 6 Measurement results of infrared absorption tester combined with ONH tester

sample	w_{Cd} (%)	w_{Hd} (%)	w_{Nd} (%)
1#	95.27	0.15	0.65
1#	95.94	0.13	0.67
2#	96.84	0.36	0.78
2#	96.93	0.32	0.80
3#	98.67	0.14	1.04
3#	98.71	0.16	1.05

It can be seen from the above comparison that the results of H and N with CHN element analyzer under the conditions of 950 ℃ to 1050 ℃ are basically reliable, and the results of infrared absorption of total carbon (1350 ℃) can meet the precision requirements. It has important guiding significance for the test of total carbon, hydrogen and nitrogen content in roasted samples such as prebaked anode and coke. The relevant moisture, received basis and dry basis of the sample are calculated in the following formulas (1), (2) and (3)

—for the total carbon content:

$$w_{Cd} = w_{Cad} \times \frac{100}{100 - w_{Mad}} \quad \cdots\cdots(1)$$

—for the hydrogen content:

$$w_{Hd} = \left(w_{Had} - \frac{w_{Mad}}{8.937} \right) \times \frac{100}{100 - w_{Mad}} \quad \cdots\cdots(2)$$

—for the nitrogen content:

$$w_{Nd} = w_{Nad} \times \frac{100}{100 - w_{Mad}} \quad \cdots\cdots(3)$$

w_{Cd} is the content of carbon, dry basis; w_{Cad} is the content of carbon as determined (as analysed);
w_{Hd} is the content of hydrogen; w_{Had} is the content of hydrogen as determined (as analysed);
w_{Nd} is the content of nitrogen; w_{Nad} is the content of nitrogen as determined (as analysed);
w_{Mad} is the moisture content of the sample as analysed.

Conclusion

This paper preliminarily studies the applicability of the current conventional domestic and foreign standards,

instruments and samples for the determination of total carbon, hydrogen and nitrogen content, and thus obtains the general steps and methods for determining the relevant content of calcined coke, and formulates relevant standards for the future. Industry and national standards provide technical routes.

General test strips for total carbon, hydrogen and nitrogen content of calcined coke, prebaked anode and coke products: total carbon test conditions are 1350℃ furnace temperature, sample weight 200mg, reaction time <1min; H, N content The test conditions are as follows: the sample weighing is 100 mg, the multi-point calibration thermal conductivity cell is detected, the furnace temperature is 950℃ to 1050℃, and the reaction time is 3 minutes.

Elemental carbon content detection is a necessary step to ensure accurate accounting of carbon content per unit of calorific value, and is particularly important for greenhouse gas emission accounting of coal-fired power generation enterprises. The research shows that the promotion of elemental carbon detection is conducive to power generation enterprises to reasonably strive for the benefits of carbon emission trading[10], providing detailed content data for enterprises, governments and related research institutions, and also providing necessary technical support for world's Carbon peak carbon neutralization.

References

[1] The 21st United Nations Climate Change Conference. The Paris Agreement [EB/OL]2016, 11, 04.

[2] The 75th United Nations General Assembly. general debate[EB/OL]2020,09,22.

[3] General Administration of Quality Supervision, Inspection and Quarantine, National Bureau of Standards. Announcement on Approving the Release of 11 National Standards including the General Rules for Accounting and Reporting of Greenhouse Gas Emissions from Industrial Enterprises [EB/OL] 2015,11,19.

[4] Hao, L. Study on Determination of Hydrocarbon, Hydrogen and Nitrogen in Coal by LECO CHN628 Elemental Analyzer [J] Energy and Environment, 2019, 2:13-15.

[5] Gong, YL, Hou, DC. Analysis of influencing factors of testing CHN elements with EA3000 element analyzer [J] Analytical Instrumentation, 2021, 2:59-61.

[6] Liu, P, Tang, W, Zhang, BB, Li ZY. Application of High Frequency Induction Combustion-Infrared Absorption Spectrometry to the Determination of Carbon or Sulfur in Inorganic Non-Metal Samples [J] Physical Testing and Chemical Analysis Part B:Chemical Analysis, 2016, 52 :487-496.

[7] ASTM 5373-14 Standard Test Methods for Determination of Carbon, Hydrogen and Nitrogen in Analysis Samples of Coal and Carbon in Analysis Samples of Coal and Coke [S] 2010, 10, 01.

[8] ISO 29541-2010 Solid mineral fuels — Determination of total carbon, hydrogen and nitrogen content — Instrumental method standard [S] 2010, 10, 01.

[9] GB/T 30733-2014 Instrumental method for the determination of carbon, hydrogen and nitrogen content in coal [S]2014, 06, 09.

[10] Zhu DC. Application of Carbon Ultimate Analysis Into Greenhouse Gas Emissions Accounting for Coal-fired Power Plants [J] Power Generation Technology, 2018,8:363-366.