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APPLICATION NOTE 42218

Elemental Analysis: CHNS/O determination in coals

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Keywords

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Goal

This application note reports nitrogen, carbon, hydrogen, sulfur and oxygen data in coal samples, the relative Heat Values and CO_2 Emission Trade Evaluation according to ASTM D5373-02 Method.

Introduction

Coal is the largest source of energy worldwide but it is also considered as a source of pollution since various toxic chemicals are released in the environment as by-products during the coking process. Environmental pollutants such as sulfur dioxide, sulfuric acid and hydrogen sulfide are related to sulfur concentration on coal. The composition of coal varies depending on the place where it formed and which kind of soil or rock determined its formation. This means that its composition and properties affect its final use and its impact on the environment.

Given environmental concerns and regulations, the elemental analysis of coal is important for its quality control. In particular sulfur quantification helps identify pollutants. The method for CHN determination is described in ASTM D5373-02 Method. The method covers the analytical determination of nitrogen, carbon and hydrogen in coal and coke samples.

As the demand for improved sample throughput and reduction of operational costs increases, an automated technique, providing analysis with excellent reproducibility is needed. The Thermo Scientific™ Flash*Smart*™ Elemental Analyzer (Figure 1) enables the fast quantitative determination of the elements in large concentrations with no need for sample digestion. The system, which operates with dynamic flash combustion of the sample, provides automated

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and simultaneous CHNS determination in a single analysis run and it provides oxygen determination by pyrolysis in a consequent run. From the CHNS/O data obtained, the dedicated Thermo Scientific™ Eager*Smart*™ Data Handling Software calculates the heat value GHV and NHV (Gross Heat Value and Net Heat Value, both expressed in kcal/kg) and the CO_2 Emission Trade data.

Methods

For CHNS determination, the Flash*Smar*t EA Analyzer operates with the dynamic flash combustion of the sample. Samples are weighed in tin containers and introduced into the combustion reactor via the Thermo Scientific™ MAS Plus Autosampler with oxygen. After the combustion the analyte gases are carried in a helium flow to a layer containing copper, then swept through a GC column which provides the separation of the combustion gases. Finally they are detected by a Thermal Conductivity Detector (TCD). Total run time is less than 10 minutes (Figure 2).

For the determination of oxygen, the system operates in pyrolysis mode. Samples are weighed in silver containers and introduced into the pyrolysis chamber via the MAS Plus Autosampler. The reactor contains nickel coated carbon at 1060 °C. When the oxygen in the sample is combined with carbon, it forms carbon monoxide which is then chromatographically separated from other products and detected by the TCD Detector (Figure 2). A report is generated by the Eager*Smart* Data Handling Software.

Figure 1. Thermo Scientific Flash*Smart* Elemental Analyzer.

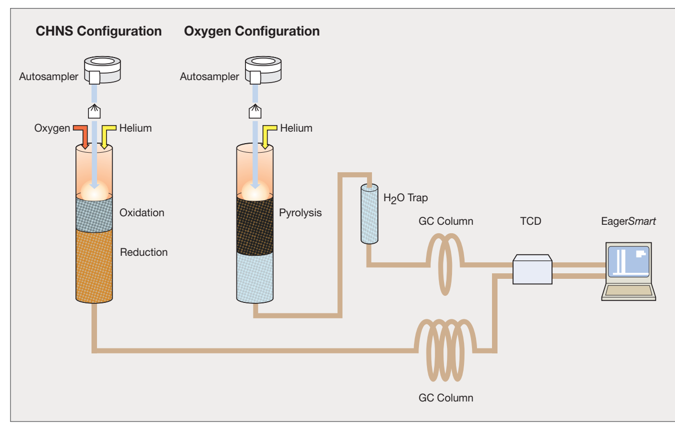

Figure 2. CHNS/O configuration.

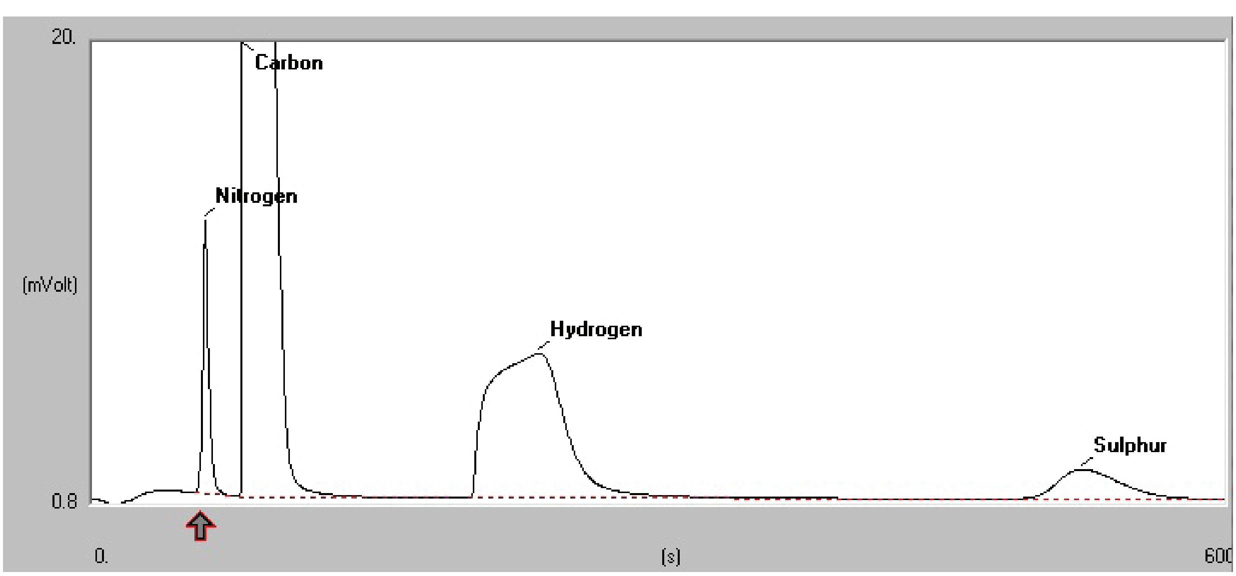

Figure 3. Typical CHNS chromatogram.

Results

Different coal samples were analyzed to demonstrate the reproducibility in the Flash*Smart* EA. Samples were homogenized by a ball mill.

Table 1 shows the CHNS data of six coal samples, which were analyzed ten times consequently. The calibration was performed with 2–3 mg of BBOT (2,5-Bis (5-ter-butyl-benzoxazol-2-yl) thiophene) OEA Standard. No matrix effect was observed when changing the sample. Figure 3 shows a typical CHNS chromatogram.

Table 1. CHNS Repeatability of 10 determinations of coal samples.

Sample	A				B			
Element	N%	C%	H%	S%	N%	C%	H%	S%
	1.93	88.48	3.76	4.16	1.15	81.54	4.18	0.41
	1.95	88.51	3.76	4.19	1.15	82.45	4.17	0.41
	1.94	88.34	3.76	4.21	1.14	82.53	4.17	0.41
	1.93	88.21	3.75	4.20	1.14	82.36	4.17	0.40
	1.93	87.95	3.74	4.21	1.13	81.99	4.17	0.41
	1.95	88.49	3.75	4.20	1.14	82.14	4.16	0.40
	1.93	88.21	3.74	4.20	1.13	81.86	4.16	0.40
	1.94	88.45	3.75	4.21	1.14	82.60	4.18	0.40
	1.94	88.46	3.76	4.21	1.13	81.59	4.14	0.41
	1.94	88.04	3.73	4.18	1.14	82.02	4.16	0.41
Mean %	1.94	88.31	3.75	4.20	1.14	82.11	4.17	0.41
RSD %	0.41	0.23	0.28	0.39	0.65	0.46	0.28	1.27

Sample	C				D			
Element	N%	C%	H%	S%	N%	C%	H%	S%
	1.00	79.31	4.34	0.31	1.75	77.77	4.27	0.54
	1.00	79.85	4.37	0.32	1.76	78.14	4.25	0.53
	1.01	80.31	4.40	0.32	1.75	78.24	4.26	0.54
	1.00	79.98	4.38	0.31	1.75	77.95	4.23	0.52
	1.00	79.41	4.34	0.31	1.75	77.94	4.23	0.52
	1.01	80.07	4.38	0.30	1.75	77.91	4.24	0.54
	1.01	79.88	4.38	0.32	1.75	77.76	4.23	0.52
	1.01	79.56	4.37	0.31	1.75	77.90	4.24	0.54
	1.01	79.82	4.36	0.31	1.76	78.23	4.24	0.53
	1.02	80.16	4.40	0.30	1.77	78.64	4.26	0.53
Mean %	1.01	79.83	4.37	0.31	1.75	78.05	4.24	0.53
RSD %	0.67	0.40	0.48	2.37	0.40	0.34	0.34	1.65

Sample	E				F			
Element	N%	C%	H%	S%	N%	C%	H%	S%
	0.81	65.85	4.43	0.18	1.14	79.71	4.30	0.28
	0.81	65.85	4.48	0.17	1.14	78.98	4.22	0.27
	0.82	65.65	4.40	0.18	1.14	79.48	4.25	0.28
	0.81	65.80	4.41	0.18	1.14	79.83	4.26	0.28
	0.82	65.96	4.46	0.16	1.14	79.54	4.24	0.27
	0.83	66.18	4.40	0.17	1.15	79.53	4.24	0.27
	0.82	65.81	4.47	0.17	1.15	79.63	4.24	0.28
	0.82	65.45	4.41	0.18	1.14	79.40	4.23	0.28
	0.81	65.53	4.39	0.16	1.15	80.07	4.27	0.27
	0.81	65.01	4.40	0.16	1.15	79.64	4.26	0.28
Mean %	0.82	65.71	4.42	0.17	1.14	79.58	4.25	0.28
RSD %	0.86	0.49	0.75	5.12	0.45	0.36	0.54	1.87

Table 2 shows the oxygen data from the coal samples. The calibration was performed with 1–2 mg of BBOT (2,5-Bis (5-tert-butyl-benzoxazol-2-yl) thiophene). Table 3 reports the heat value GHV and NHV (Gross Heat Value and Net Heat Value expressed in kcal/kg) and the CO_2 Emission Trade, which are automatically calculated by the Eager*Smart* Data Handling Software. Figure 4 shows a typical chromatogram of oxygen determination.

Table 2. Oxygen determination of coal samples in triplicate.

Sample	A	B	C	D	E	F
Oxygen %	1.10 1.11 1.09	3.42 3.44 3.43	5.36 5.36 5.34	3.83 3.77 3.80	14.84 14.85 14.94	4.28 4.28 4.26
Av. Oxygen %	1.10	3.43	5.35	3.80	14.88	4.27
RSD %	0.91	0.29	0.22	0.79	0.37	0.27

Table 3. Heat Values and CO_2 Emission Trade calculation of coal samples.

Sample	A	B	C	D	E	F
GHV (kcal/kg)	8589	8030	7827	7709	6273	7810
NHV (kcal/kg)	8397	7816	7602	7491	6047	7592
CO_2 E.T.	92.07	91.97	91.93	91.22	95.14	91.76

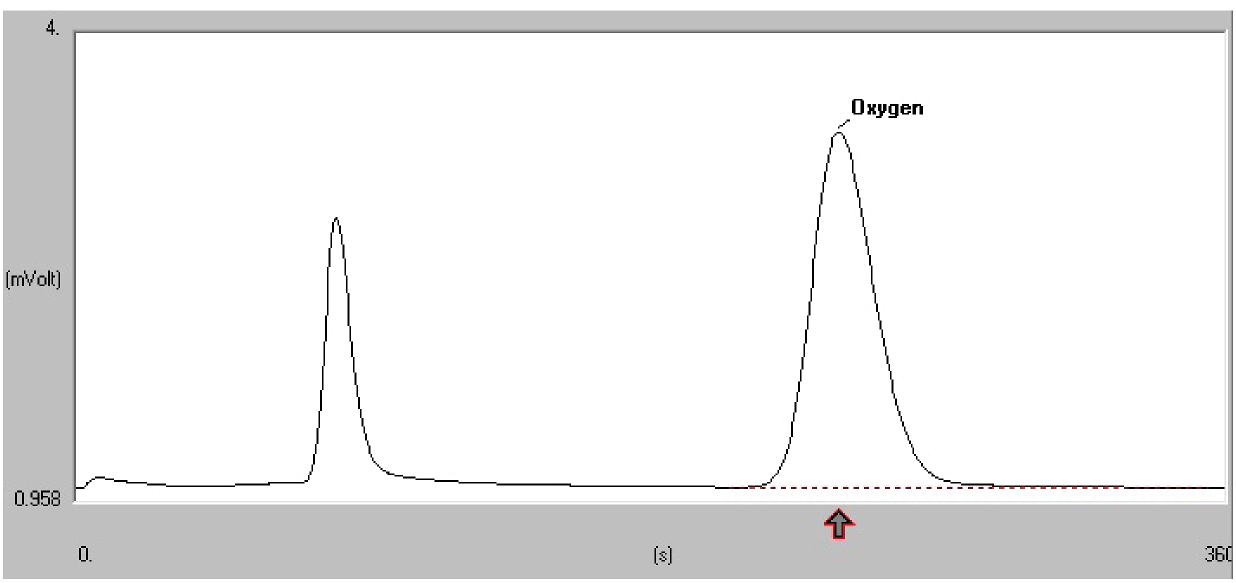

Figure 4. Typical chromatogram of oxygen determination.

Table 4. Concentration Range and Limit of Repeatability* accepted by ASTM D 5373-02.

Element	Concentration Range (%)	Repeatability Limit (r)
Carbon	48.6-90.6	0.64
Hydrogen	0.14-5.16	0.16
Nitrogen	0.69-1.57	0.11

*Repeatability Limit (r): the value below which, the absolute difference between two test results calculated to a dry basis of separate and consecutive test determinations, carried out on the same sample, in the same laboratory, by the same operator, using the same apparatus.

The performance of the Flash*Smart* EA Analyzer was validated by comparing the repeatability of the CHN data with the ASTM D 5373-02 requirements (Table 4).

Table 5. CHN data of coal samples in duplicate using CHN reactor.

Series	Elem.	Coal Samples											
		A		B		C		D		E		F	
		%	Diff.	%	Diff.	%	Diff.	%	Diff.	%	Diff.	%	Diff.
1	C	88.36 88.44	0.08	82.58 82.54	0.04	80.04 79.66	0.38	78.34 78.61	0.27	65.82 65.80	0.02	79.93 79.87	0.06
	H	3.72 3.74	0.02	4.24 4.20	0.04	4.45 4.38	0.07	4.36 4.31	0.05	4.60 4.47	0.13	4.30 4.28	0.02
	N	1.88 1.90	0.02	1.17 1.14	0.03	1.01 0.99	0.02	1.71 1.74	0.03	0.80 0.80	0.00	1.15 1.11	0.04
2	C	88.04 87.95	0.09	82.25 82.06	0.19	79.46 79.73	0.30	77.82 78.38	0.56	66.20 66.03	0.17	80.09 80.18	0.09
	H	3.75 3.73	0.02	4.19 4.18	0.01	4.38 4.38	0.00	4.27 4.30	0.03	4.45 4.41	0.04	4.28 4.30	0.02
	N	1.88 1.88	0.00	1.13 1.11	0.02	0.98 0.99	0.01	1.71 1.74	0.03	0.80 0.80	0.00	1.15 1.15	0.00
3	C	88.28 88.04	0.24	82.35 82.37	0.02	80.06 79.61	0.45	77.96 78.46	0.50	65.94 66.01	0.07	80.10 80.01	0.09
	H	3.74 3.72	0.02	4.20 4.19	0.01	4.44 4.38	0.06	4.27 4.30	0.03	4.49 4.48	0.01	4.29 4.27	0.02
	N	1.83 1.85	0.02	1.14 1.14	0.00	1.00 0.99	0.01	1.71 1.74	0.03	0.80 0.80	0.00	1.18 1.17	0.01

The accuracy of the Flash*Smart* EA for CHN determination was demonstrated by performing three series of analysis of the six coal samples, which were analyzed twice. The calibration of the system was performed with 2–3 mg of acetanilide. Coal sample A was weighed at 2–2.5 mg and coal samples B-F 2.5–3 mg. Table 5 shows the CHN results and the difference (Diff.) calculated between both data. All differences are acceptable and fall within the the Repeatability Limit, which is indicated in the Official method, meaning a good homogeneity and the total combustion of the samples.

Conclusions

For CHNS/O determination in coal samples the Thermo Scientific Flash*Smart* EA Analyzer provides accurate data, which meet the requirements of the ASTM D 5373-02 Method.

No matrix effect was observed when changing the sample, meaning that samples were entirely combusted.

The Thermo Scientific Flash*Smart* EA Analyzer allows CHNS and oxygen determinations with no need for any extra modules, reducing operational cost, while increasing speed of analysis.

Find out more at **www.thermofisher.com/OEA**

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