thermo scientific

APPLICATION NOTE 42253

Elemental Analysis: CHN characterization of coals using argon as carrier gas

Authors

Dr. Liliana Krotz, Dr. Francesco Leone and Dr. Guido Giazzi
Thermo Fisher Scientific,
Milan, Italy

Keywords

Argon, ASTM, CHN, Coals, Elemental Analyzer, Helium

Goal

This application note shows the performance of the Thermo Scientific Flash*Smart* Elemental Analyzer for the characterization of coal samples in compliance with ASTM D5373 Method. The analysis were performed using argon as carrier gas.

Introduction

Coal is the largest source of energy worldwide but it is also considered as a major source of pollution since various toxic chemicals are released as by-products during its processing. The composition of coal varies, depending on the place where it was formed and the kind of soil or rocks accompanying its formation. This means that the composition and properties of coal affect its utilization and its environmental impact.

Elemental analysis enables the characterization of coal samples. The method for CHN determination, based on combustion, is described in ASTM D5373. The method covers the instrumental determination of nitrogen, carbon and hydrogen in coal and coke samples.

As the demand for improved sample throughput and reduction of operational costs is steadily increasing, laboratories need an automated technique, which also allows fast analysis with excellent reproducibility.

The Thermo Scientific™ Flash*Smart*™ Elemental Analysis (Figure 1), based on combustion method, allows the quantitative determination of the elements in a large range of concentration, without the need for sample digestion or toxic chemicals, providing advantages in terms of time and automation.

ThermoFisher SCIENTIFIC

Figure 1. Flash*Smart* Elemental Analyzer.

Elemental analyzers with a thermal conductivity detector for nitrogen, carbon and hydrogen determination tipically uses helium as carrier gas. Considering the need for cost efficiencies and the likely increase in helium gas cost, an alternative gas to be used as carrier gas is needed. Argon can be used as alternative to helium in the Flash*Smart* EA.

Methods

The Flash*Smart* EA operates according to 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 combustion the resulted gases are carried by an argon flow to the catalyst, a layer filled with copper and then silver cobaltous-cobaltic oxide. Then, it is then swept through a GC column that provides the separation of the combustion gases, and finally, it is detected by a Thermal Conductivity Detector (TCD). The analytical configuration as well as the TCD Detector are as the same as those used with helium as carrier gas (see Figure 2).

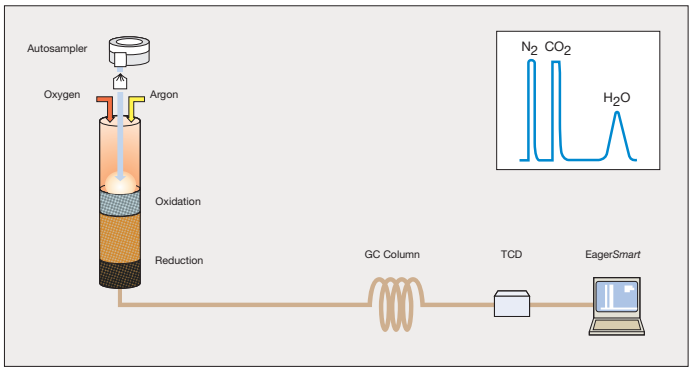

Figure 2. CHN configuration.

A complete report is automatically generated by the Thermo Scientific™ Eager*Smart*™ Data Handling Software. The Eager*Smart* Data Handling Software provides the option “AGO” (Argon Gas Option), which enables to modify the argon carrier flow during the run.

Analytical conditions using argon as carrier gas	
Combustion furnace temp.:	950 °C
Oven temp.:	95 °C (GC column inside the oven)
Argon carrier flow:	70 mL/min
Argon reference flow:	70 mL/min
Oxygen flow:	280 mL/min
Oxygen injection end:	11 sec
Sample delay:	12 sec
Run time:	10–12 min

Results

Several coal samples with different CHN concentrations were analyzed to show the performance of the instrument. Samples were homogenized by a ball mill. To evaluate the repeatability of the system using argon as carrier gases, two Coal Reference Materials were analyzed. Samples were dried at 60 °C for two days. The calibration was performed with 1–4 mg Atropine and 3–4 mg BBOT (2,5-Bis (5-tert-butyl-benzoxazol-2-yl) thiophene) using Linear Fit as calibration method. Table 1 shows the certified CHN values and the uncertainty. Table 2 shows the experimental CHN data obtained with argon as carrier gas.

Six different coal samples were run in two series of analyses, in each series samples were analyzed in duplicate. The statistical data showed in Table 3 is the average of the four determinations.

The performance of the Flash*Smart* Analyzer was evaluated through the comparison of the repeatability of the CHN data obtained against to the ASTM D 5373 requirements showed in (Table 4).

The accuracy of the Flash*Smart* Elemental Analyzer for CHN determination was demonstrated by performing two series of analysis of the 6 coal samples analyzed in duplicate using helium and argon as carrier gas.

Table 1. Coal Reference Materials sample information.

Reference Material	N%	Uncertainty	C%	Uncertainty	H%	Uncertainty
Coal 1	1.11	0.08	62.99	0.85	3.81	0.43
Coal 2	1.02	0.12	68.67	0.98	4.55	0.34

Table 2. Experimental CHN data of Soils Reference Materials.

Reference Material	Weight (mg)	N%	RSD%	C%	RSD%	H%	RSD%
Coal 1	3.083 3.432 3.243 3.201 3.105	1.09 1.11 1.11 1.09 1.10	0.91	62.75 63.18 62.80 63.18 63.13	0.34	3.89 3.89 3.91 3.85 3.85	0.69
Coal 2	3.378 3.003 3.408 3.183 3.059	1.04 1.04 1.07 1.03 1.04	1.45	68.61 68.60 68.38 68.41 68.25	0.22	4.80 4.73 4.79 4.73 4.75	0.70

Table 3. CHN Repeatability of coal samples.

Coal Sample	Weight (mg)	N%	RSD%	C%	RSD%	H%	RSD%
A	3.167 3.327 3.317 2.914	1.95 1.94 1.92 1.95	0.73	88.18 87.73 87.73 87.90	0.24	3.85 3.84 3.85 3.85	0.13
B	3.393 3.214 3.188 3.334	1.16 1.17 1.17 1.16	0.50	82.35 82.56 82.16 82.48	0.21	4.28 4.25 4.28 4.23	0.58
C	3.350 3.352 3.469 3.471	1.07 1.06 1.07 1.07	0.47	80.01 79.96 80.13 80.11	0.10	4.45 4.45 4.44 4.43	0.22
D	3.390 3.310 3.278 3.379	1.74 1.76 1.76 1.74	0.66	78.28 78.32 78.15 78.02	0.17	4.28 4.24 4.26 4.28	0.45
E	3.296 3.152 3.428 3.219	0.806 0.825 0.811 0.818	1.02	65.50 65.88 65.78 65.86	0.27	4.44 4.44 4.45 4.45	0.13
F	3.342 3.289 3.410 3.339	1.17 1.14 1.15 1.16	1.12	80.08 80.21 80.04 80.10	0.09	4.28 4.23 4.27 4.26	0.51

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

Element	Concentration range (%)	Repeatability Limit (r)
Carbon	48.6 to 90.6	0.64
Hydrogen	0.14 to 5.16	0.16
Nitrogen	0.69 to 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.

For helium, the calibration of the system was performed with 2–3 mg of Acetanilide; coal sample was weighed at 2–2.5 mg, the other coals were weighed at 2.5–3 mg. For argon, the calibration was performed with 1–4 mg Atropine and 3–4 mg BBOT (2,5-Bis (5-tert-butyl-benzoxazol-2-yl) thiophene). For both gases, Linear Fit was used as calibration method.

Table 5 shows the CHN data obtained and the difference (Diff.) calculated between both data using helium as carrier gas.

Table 5. CHN data of coal samples in duplicate using argon as carrier gas.

Serie	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

Table 6. CHN data of coal samples in duplicate using argon as carrier gas.

Serie	Elem	Coal Samples											
		A		B		C		D		E		F	
		%	Diff.	%	Diff.	%	Diff.	%.	Diff.	%	Diff.	%	Diff.
1	C	88.18 87.73	0.45	82.35 82.56	0.21	80.01 79.96	0.05	78.28 78.32	0.04	65.50 65.88	0.38	80.08 80.21	0.13
	H	3.85 3.84	0.01	4.28 4.25	0.03	4.45 4.45	0.00	4.28 4.24	0.04	4.44 4.44	0.00	4.28 4.23	0.05
	N	1.95 1.94	0.01	1.16 1.17	0.01	1.07 1.06	0.01	1.74 1.76	0.02	0.81 0.83	0.02	1.17 1.14	0.03
2	C	87.73 87.90	0.17	82.16 82.48	0.32	80.13 80.11	0.02	78.15 78.02	0.13	65.78 65.86	0.08	80.04 80.10	0.06
	H	3.85 3.85	0.00	4.28 4.23	0.05	4.44 4.43	0.01	4.26 4.24	0.02	4.45 4.45	0.00	4.27 4.26	0.01
	N	1.92 1.95	0.03	1.17 1.16	0.01	1.07 1.07	0.00	1.76 1.74	0.02	0.81 0.82	0.01	1.15 1.16	0.01

Table 6 shows the precision of the CHN data obtained and the difference (Diff.) calculated between both data using argon as carrier gas considering the results showed in Table 3.

All differences fall within or below the Repeatability Limit and they are indicated in the Official method. This shows the good homogeneity and the complete combustion of the samples.

Conclusions

The Thermo Scientific Flash*Smart* Elemental Analyzer enables to perform accurate and reproducible CHN determination in coal samples. Good repeatability was obtained with the Flash*Smart* Analyzer using argon as carrier gas. Data are comparable with those obtained with helium.

The data obtained are according to the ASTM D 5373 method and no matrix effect was observed when changing the sample, indicating complete combustion.

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

ThermoFisher SCIENTIFIC