Characterization of Carbon Black Using the Thermo Scientific FLASH 2000 Elemental Analyzer in Compliance with ASTM Method

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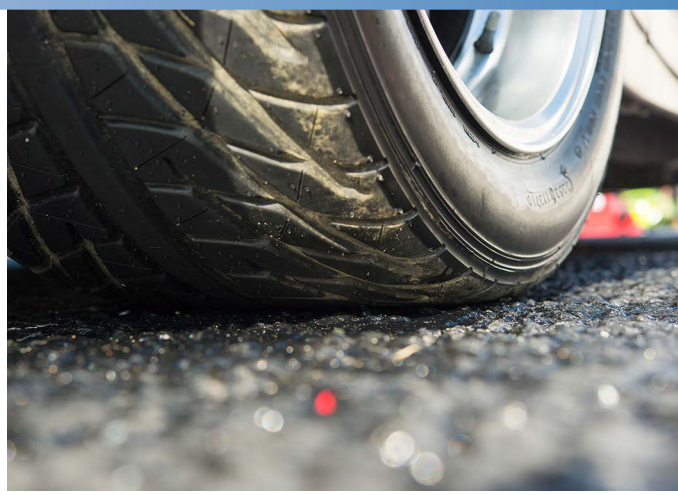
Key Words
ASTM, CHNS/O, Carbon Black, Elemental Analyzer, Heat Values, Repeatability

Goal
Demonstrate the performance of the Thermo Scientific FLASH 2000 Elemental Analyzer in petrochemical applications and the repeatability and reproducibility of data obtained in compliance with ASTM method.



Introduction
Carbon black is a side-material produced by the incomplete combustion of heavy petroleum products such as coal or ethylene cracking tar, and in some cases vegetable oil. Carbon black is widely used as a model compound for diesel soot for diesel oxidation experiments. Other uses are as a reinforcing filler in tyres and other rubber products, while in plastics, paints, and inks carbon black is used as a color pigment.

In a typical production process of carbon black, the elemental content is periodically monitored and tested for quality control, in particular, carbon quantification. The amount of the total carbon content is a requirement for the calculation of carbon dioxide emissions and it can also be used in calculations to estimate yield of the process. The official method for carbon, nitrogen and hydrogen determination is described in the ASTM D5373 Method.

As the demand for improved sample throughput, reduction of operational costs, and minimization of human errors increases, a simple and automated technique, allowing fast analysis with an excellent reproducibility, is the key for efficient elemental analysis.

The Thermo Scientific™ FLASH™ 2000 Organic Elemental Analyzer (Figure 1) enables fast quantitative determination of the elements in large concentrations with no need for sample digestion and provides important advantages in terms of time and automation. The Elemental Analyzer, which operates with dynamic combustion of the sample (Dumas method), provides automated 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 Xperience Data Handling Software calculates automatically 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.

Figure 1. FLASH 2000 CHNS/O Analyzer.

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Methods

For CHNS determination the instrument 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 200R Autosampler together with oxygen. After combustion, the resultant gases are carried by a helium flow to a layer filled with copper, then swept through a GC column that provides the separation of the combustion gases, before detection by a thermal conductivity detector (TCD). Total run time is less than 10 minutes. (Figure 2).

For oxygen determination, the system operates in pyrolysis mode. Samples are weighed in silver capsules and introduced into the pyrolysis chamber via the MAS 200R Autosampler. The reactor contains nickel coated carbon at 1060°C. The oxygen in the sample, combined with the carbon, forms carbon monoxide which is then chromatographically separated from other products and detected by the TCD (Figure 2).

A complete report is automatically generated by the Eager Xperience Data Handling Software and displayed at the end of the analysis.

Results

Different types of carbon black samples were analyzed on the basis of the different elemental contents to demonstrate the performance of the system and to show the repeatability obtained without any matrix effect.

To verify the complete combustion of high containing carbon samples, carbon determination was evaluated in a carbon mesoporous reference material (99.95 C%, Aldrich No. 699624). The instrument was calibrated with 2–3 mg of BBOT* standard using K factor as calibration method while the sample was weighted at about 2 mg. Table 1 shows the data obtained with good repeatability and the average is comparable with the expected value, indicating complete oxidation of the sample. Three samples were then analyzed to verify the repeatability of carbon determination.

*BBOT: 2,5-*Bis* (5-tert-butyl-benzoxazol-2-yl) thiophene

Table 1. Carbon determination.

Sample	C%	Average C%	RSD%
Carbon Mesoporous Reference Material	99.91 99.58 99.86 99.71 99.68 99.69 99.82 99.72 99.69 99.41	99.71	0.143
HPG AR - 2029	99.79 99.85 99.68 99.66 99.70	99.75	0.081
Thermal Black	99.26 99.16 99.16 99.16 99.26	99.26	0.055
Soft Black (carcass)	97.63 97.33 97.53 97.50 97.59	97.61	0.119

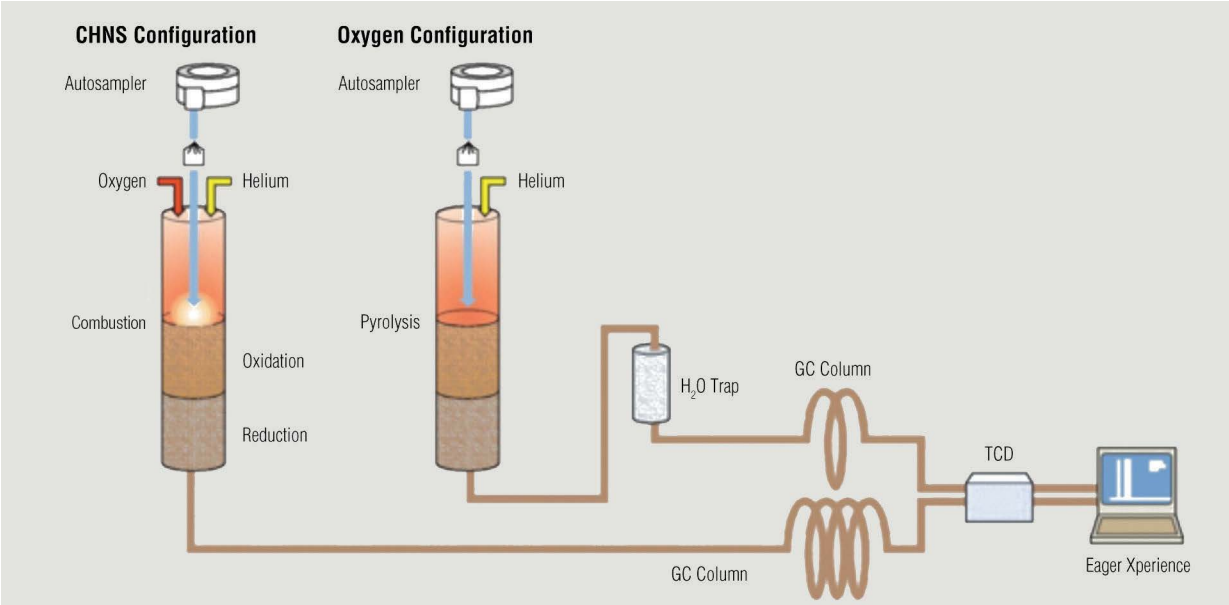

Figure 2. CHNS/O configuration.

Table 2 shows the repeatability of CHNS determination of carbon black samples. The Elemental Analyzer was calibrated with 2–3 mg of BBOT standard using K factor as calibration method while the sample was weighted at 2–2.5 mg.

Table 3 shows the repeatability of CHNS determination of other carbon black samples. Table 4 shows the oxygen data and the heat values GHV and NHV (Gross Heat Value and Net Heat Value, both expressed in kcal/kg), and the CO_2 Emission Trade data calculated automatically by the Eager Xperience Data Handling Software.

Table 2. CHNS data of carbon black samples.

Sample	N%	RSD%	C%	RSD%	H%	RSD%	S%	RSD%
1	0.131 0.137 0.133	2.493	95.609 95.542 95.773	0.124	0.384 0.361 0.359	3.861	1.433 1.452 1.443	0.649
2	0.136 0.134 0.140	2.156	96.329 96.242 96.301	0.046	0.420 0.412 0.408	1.496	0.711 0.704 0.709	0.505
3	0.172 0.171 0.172	0.331	94.592 94.512 94.642	0.458	0.520 0.520 0.524	0.458	1.741 1.728 1.757	0.841
4	0.089 0.084 0.088	3.179	99.365 99.498 99.506	0.080	0.322 0.319 0.321	0.452	–	–
5	0.189 0.186 0.186 0.181 0.180	1.968	95.693 95.629 95.825 95.835 96.082	0.182	0.321 0.324 0.322 0.319 0.317	0.811	0.296 0.289 0.292 0.280 0.290	2.075

Table 3. CHNS data of carbon black samples.

Sample	N%	RSD%	C%	RSD%	H%	RSD%	S%	RSD%
A	0.188 0.185 0.186 0.186	0.676	96.559 96.734 96.817 96.706	0.111	0.300 0.295 0.304 0.308	1.843	0.829 0.848 0.868 0.868	2.193
B	0.273 0.277 0.272 0.273	0.810	96.178 95.899 95.351 96.079	0.159	0.267 0.280 0.272 0.277	12.086	0.823 0.814 0.815 0.817	0.493
C	0.239 0.229 0.239 0.232	2.155	95.768 96.126 95.826 95.700	0.196	0.343 0.350 0.341 0.328	2.697	1.016 1.020 1.019 1.013	0.311
D	0.148 0.146 0.149 0.152	1.681	97.073 97.066 96.966 97.146	0.076	0.282 0.285 0.292 0.286	1.465	1.273 1.267 1.256 1.261	0.583

Table 4. Oxygen data, Heat Values and CO_2 value of carbon black samples.

Sample	O%	RSD%	GHV (kcal/kg)	RSD%	NHV (kcal/kg)	RSD%	CO_2 E.T.	RSD%
A	1.149 1.158 1.152	0.397	8005.53 8005.13 8005.42	0.003	7990.03 7989.63 7989.93	0.003	105.96 105.96 105.96	0.000
B	1.661 1.679 1.661	0.623	7915.43 7915.64 7915.44	0.006	7901.37 7900.58 7901.38	0.006	106.37 106.38 106.37	0.005
C	1.597 1.597 1.602	0.181	7933.81 7933.82 7933.59	0.002	7916.36 7916.37 7916.14	0.002	106.00 106.00 106.01	0.005
D	0.624 0.612 0.616	0.990	8062.31 8062.85 8062.66	0.003	8047.63 8048.17 8047.98	0.003	105.59 105.58 105.58	0.006

For CHNS, carbon black samples were run in two series of analyses. In each series, samples were analyzed in duplicate and the statistical data shown is the average of the four determinations. The system was calibrated with 2–3 mg of BBOT standard using K factor as calibration method while the sample was weighted at 2–2.5 mg. For oxygen determination, 1–2 mg of BBOT was analyzed as standard using K factor while the sample weight was 1–2 mg.

The performance of the FLASH 2000 OEA was evaluated by comparing the repeatability of the CHN data obtained to the ASTM D 5373 requirements shown in Table 5. The repeatability limit (*r*) is 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.

Table 5. Concentration range and limit of repeatability accepted by ASTM D 5373.

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

The precision of the FLASH 2000 OEA for CHN determinations was evaluated from the results shown in Table 3. Table 6 shows the difference calculated between both data of each series of analyses. All differences are acceptable and fall within or below the repeatability limit indicated in the official method, meaning homogeneity and the complete combustion of the samples.

Table 6. CHN data of carbon black samples according to ASTM D 5373 requirements.

Sample	Series	N%	Difference	C%	Difference	H%	Difference
A	1	0.188 0.185	0.003	96.559 96.734	0.175	0.300 0.295	0.005
	2	0.186 0.186	0	96.817 96.706	0.111	0.304 0.308	0.004
B	1	0.273 0.277	0.004	96.178 95.889	0.279	0.267 0.280	0.013
	2	0.272 0.273	0.001	95.851 96.079	0.228	0.272 0.277	0.005
C	1	0.239 0.229	0.010	95.768 96.126	0.358	0.343 0.350	0.007
	2	0.239 0.232	0.003	95.826 95.700	0.125	0.341 0.328	0.013
D	1	0.148 0.146	0.002	97.073 97.066	0.070	0.282 0.285	0.003
	2	0.149 0.152	0.003	96.966 97.146	0.180	0.292 0.286	0.006

Conclusions

The Thermo Scientific FLASH 2000 Organic Elemental Analyzer, based on Dumas method, proved to be a valuable solution for the elemental analysis of carbon black in terms of accuracy, repeatability and sensitivity of results. Its automation, high speed of analysis, and the reduction of long sample preparation processes allow efficient analysis and help reduce overall operational costs.

All data were obtained according to the ASTM D 5373 method. No matrix effect was observed when changing the sample indicating complete combustion.

The advantage of the FLASH 2000 Analyzer lies in the possibility to perform CHNS determination in a single run. Changing configuration, oxygen determination is performed on the same analyzer without the need for any extra modules.

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