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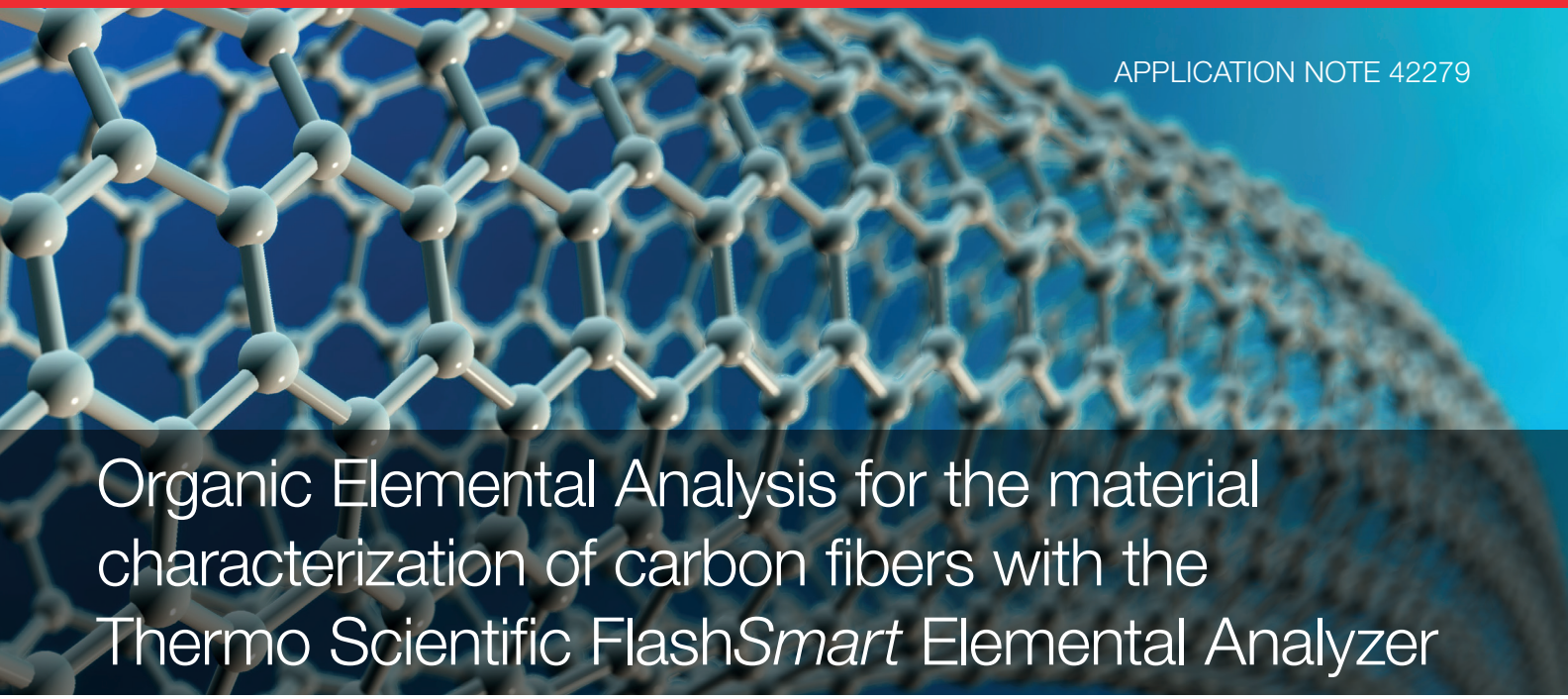
APPLICATION NOTE 42279



Organic Elemental Analysis for the material characterization of carbon fibers with the Thermo Scientific Flash*Smart* Elemental Analyzer

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Keywords

CHNS, Combustion, Elemental Analysis, Carbon Fibers, Material Characterization, Oxygen, Quality Control, Trace Sulfur

Goal

To show how organic elemental analysis with the Thermo Scientific Flash*Smart* Elemental Analyzer enables to perform material characterization on carbon fibers for quality analysis purposes.

Introduction

Carbon fibers are fibers, mostly composed by carbon, whose properties make them a versatile material to be used for a variety of applications (from aerospace, civil and military engineering, to motorsports, and other competition sports). Carbon fibers are highly stiff, tensile strong. They have superior chemical resistance, and are temperature tolerant.

When combined with other materials, they form a composite. For example with a plastic resin, it forms carbon-fiber-reinforced polymer (often referred to as carbon fiber) which has a very high strength-to-weight ratio, and is extremely rigid although somewhat brittle. However, carbon fibers are also composited with other materials, such as with graphite to form carbon-carbon composites, which have a very high heat tolerance.

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Elemental analysis is useful for the material characterization, in order to evaluate the quality. This can be performed with the determination of the high carbon content. The nitrogen, hydrogen and oxygen content give information on the thermal treatment of the fibers. The residual content of hydrogen and oxygen are key for determining the success or failure of the *densification* process.

Carbon, nitrogen, hydrogen, sulfur by combustion and oxygen determination by pyrolysis are commonly used for the characterization of raw and final products in the industry for quality control and R&D purposes. The use of accurate and automated analytical techniques, allowing the fast analysis with an excellent reproducibility, is however essential.

The Thermo Scientific™ Flash*Smart*™ Elemental Analyzer for CHNS/O determinations, based on the dynamic combustion of the sample, provides automatic and simultaneous CHNS determination in a single analysis run and the oxygen determination by pyrolysis in a second run. The Flash*Smart* EA (Figure 1) is equipped with two totally independent furnaces allowing the installation of two analytical circuits, for simultaneous CHNS and oxygen that can be used sequentially and are completely automated through the Thermo Scientific™ MultiValve Control™ (MVC) Module (Figure 2). Each analytical circuit has its own autosampler. In this way the system copes effortlessly with the laboratory requirements such as accuracy, day to day reproducibility and high sample throughput.

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

Figure 2. MVC Module.

The proprietary MVC Module also ensures very low helium consumption by switching from helium to nitrogen or argon gas, when the instrument is in Stand-By Mode. In this way the cost of analysis is significantly reduced.

Low total sulfur contents can be accurately determined by the Thermo Scientific Flash*Smart* Elemental Analyzer coupled with a Flame Photometric Detector (FPD). This method combines the advantages of the Elemental Analyzer with the sensitivity, selectivity and robustness of the FPD Detector. The coupling is simple and it allows the determination of total sulfur at high and low concentrations (up to 5-10 ppm) in the same system without matrix effect.

Methods

For CHNS determination the Flash*Smart* Analyzer operates with the dynamic flash combustion of the sample. Samples are weighed in tin containers and introduced into the combustion reactor (left furnace) via the Thermo Scientific™ MAS Plus Autosampler with the proper amount of oxygen. After combustion the resulted 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. Finally, detected by a Thermal Conductivity Detector (TCD). The total run time is less than 10 minutes. (Figure 3).

For trace sulfur analysis, after the water trap, the gases are carried by a helium flow through a short GC column and finally, detected by the Flame Photometric Detector (FPD), (Figure 4).

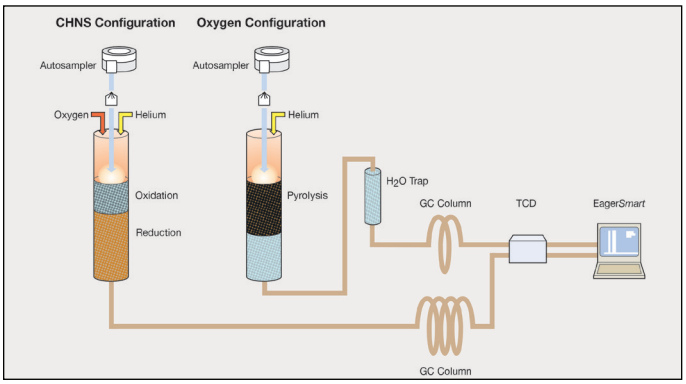

Figure 3. Flash*Smart* CHNS/O Configuration by TCD Detector.

Analytical Conditions	
CHNS Reactor Temperature	950 °C
Oxygen Reactor Temperature	1060 °C
GC Oven Temperature	65 °C
Helium Carrier Flow	140 ml/min for CHNS 100 ml/min for Oxygen
Helium Reference Flow	100 ml/min
Oxygen Flow	280 ml/min for CHNS
Oxygen Injection Time	13 sec for CHNS
Sample Delay	12 sec for CHNS 0 sec for Oxygen
Total Run Time	less than 600 sec for CHNS less than 300 sec for Oxygen

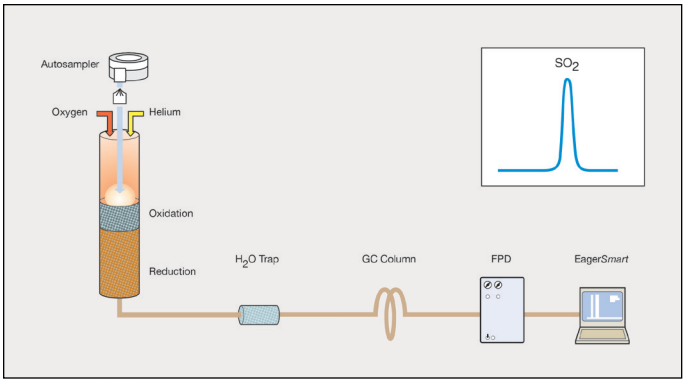

Figure 4. Sulfur Configuration by FPD Detector.

Analytical Conditions	
Reactor Temperature	950 °C
Helium Carrier Flow	150 ml/min
Helium Reference Flow	100 ml/min
Oxygen Flow	250 ml/min
Oxygen Injection Time	5 sec
Sample Delay	3 sec
Total Run Time	300-400 sec

For oxygen determination, the system operates in pyrolysis mode. Samples are weighed in silver containers and introduced into the pyrolysis chamber (right furnace) via the MAS Plus Autosampler. The reactor contains nickel coated carbon maintained at 1060 °C. The oxygen present in the sample, combined with the carbon, forms carbon monoxide which is then chromatographically separated from other products and detected by the TCD Detector (Figure 3).

A comprehensive report is automatically generated by the Thermo Scientific™ Eager*Smart*™ Data Handling Software and displayed at the end of the analysis.

Both pneumatic circuits for CHNS and oxygen determination are preset in the system in order to switch automatically from one circuit to the other, through the MultiValve Control (MVC) Module controlled by the dedicated Eager*Smart* Data Handling Software without the need for manual intervention. The Eager*Smart* Data Handling Software window, which controls the MVC module, Figure 5, shows how to switch from the Left to the Right furnace, to pass from CHNS determination by combustion, to oxygen analysis by pyrolysis. It indicates also how to switch from helium carrier gas to nitrogen or argon gas when the instrument is in stand-by mode.

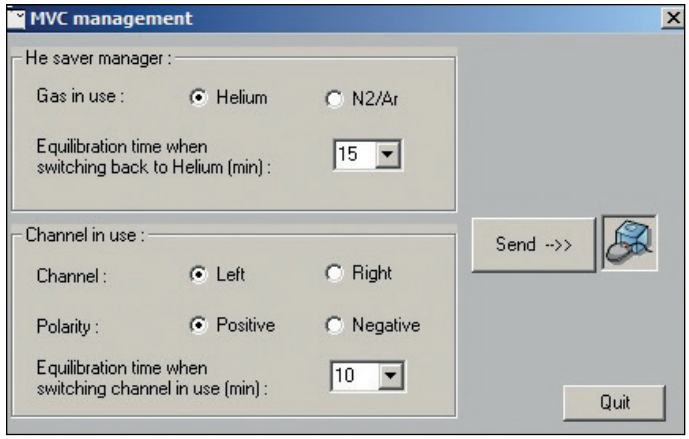

Figure 5. The MVC Module management window on the Eager*Smart* Data Handling Software.

Results

For CHNS analysis and for oxygen determination, the instrument was calibrated with 2-3 mg BBOT (2,5-Bis (5-ter-butyl-benzoxazol-2-yl) thiophene) standard. In both configurations K factor was used as the calibration method. Figure 6 shows the calibration curves for carbon, the main element in carbon fiber samples. Figure 7 shows a typical CHNS chromatogram and Figure 8 shows a typical oxygen chromatogram.

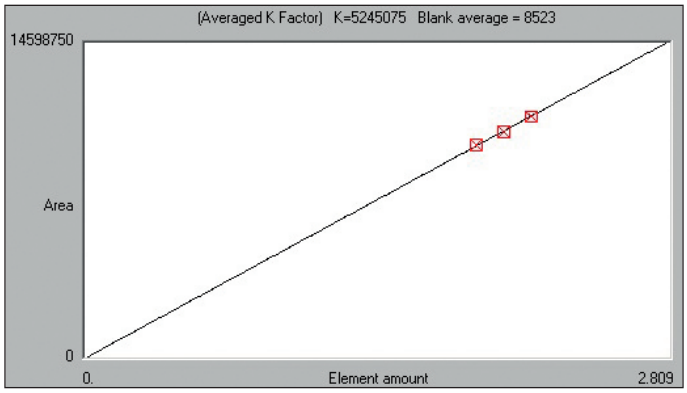

Figure 6. Carbon calibration curve.

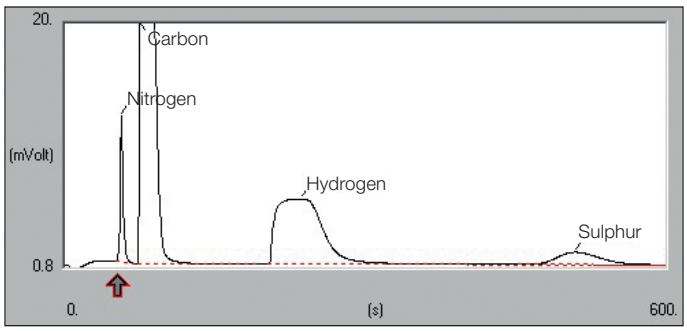

Figure 7. Typical CHNS chromatogram.

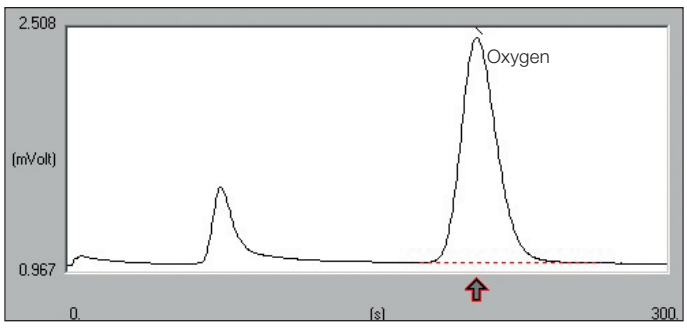

Figure 8. Typical Oxygen chromatogram.

Several carbon fiber samples, with different range of element content, were analyzed in triplicate to evaluate the repeatability of the data. The weight of sample used was 2-3 mg. Table 1 shows the CHNS data of carbon fibers samples while Table 2 reports the relative oxygen data. Table 3 shows the NC/O data of other type of carbon fiber samples with trace sulfur content (under TCD Detector sensitivity).

Table 1. CHNS data of carbon fibers.

Sample	N%	RSD%	C%	RSD%	H%	RSD%	S%	RSD%
1	0.26 0.27 0.27	0.90	89.74 90.45 90.17	0.41	0.81 0.79 0.80	0.70	0.15 0.14 0.14	2.28
2	0.50 0.50 0.51	0.59	90.80 91.34 90.79	0.35	0.29 0.29 0.28	0.85	0.28 0.28 0.27	1.19
3	0.0299 0.0311 0.0295	2.76	98.40 98.97 98.81	0.30	0.0267 0.0279 0.0255	4.49	0.0641 0.0611 0.0626	2.40
4	1.22 1.23 1.22	0.47	93.16 93.20 93.34	0.10	4.07 4.06 4.04	0.38	0.13 0.14 0.12	
5	1.20 1.18 1.20	0.97	91.50 91.49 91.67	0.11	3.93 3.97 3.94	0.53	0.17 0.16 0.16	3.54
6	1.18 1.18 1.17	0.49	89.85 89.86 89.78	0.05	3.60 3.58 3.54	0.86	0.15 0.14 0.15	3.94

Table 2. Oxygen data of carbon fibers.

Sample	O%	RSD%	Sample	O%	RSD%
1	7.36 7.40 7.35	0.35	4	1.30 1.33 1.30	1.32
2	4.58 4.51 4.56	0.83	5	2.80 2.84 2.78	1.09
3	0.26 0.27 0.26	1.04	6	5.38 5.34 5.37	0.39

Table 3. NC/O data of carbon fibers with trace sulfur content.

Sample	N%	RSD%	C%	RSD%	O%	RSD%
A	0.0411 0.0417 0.0413	0.67	97.94 97.72 97.84	0.14	0.0652 0.0672 0.0641	2.40
B	0.0394 0.0395 0.0389	0.82	98.83 98.71 98.67	0.08	0.0402 0.0396 0.0393	1.23
C	0.0424 0.0425 0.0429	0.62	98.76 98.71 98.83	0.06	0.0475 0.0490 0.0490	1.73
D	0.0429 0.0456 0.0441	3.06	99.75 99.86 99.71	0.08	0.0706 0.0708 0.0690	1.39

The trace sulfur content of the samples in Table 3 was determined by FPD Detector. Table 4 shows the sulfur data at trace level. The calibration was performed with the Thermo Scientific Soil Reference Material using Quadratic Fit as calibration method.

Table 4. Sulfur data obtained with FPD Detector of carbon fibers with trace sulfur content.

Sample	S ppm	RSD%	Sample	S ppm	RSD%
A	54 56	2.57	C	43 44	1.62
B	42 44	3.29	D	36 38	3.82

Conclusions

The Flash*Smart* Elemental Analyzer is the optimal solution for the characterization of carbon fibers samples for the quantitative element determination, from trace to high content in terms of accuracy, reproducibility, automation, speed and cost per analysis. All data were obtained with acceptable repeatability and no matrix effect was observed when changing the configuration, indicating the complete combustion of the sample.

In addition, the dual analytical configuration capability using the MVC Module allows performing the following functions:

- Automated control of two MAS Plus Autosamplers.
- Automated switch from left channel to right channel, or vice versa, increasing laboratory productivity.
- Reduction of helium (or argon) consumption by switching from helium to nitrogen or argon when the system is in Stand-By Mode.
- Automated return to helium carrier gas from Stand-By Mode with the Auto-Ready function.
- Full control of the workflow by the Eager*Smart* Data Handling Software.

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