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

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Goal

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

Introduction

Graphene is a single layer of graphite. It is a single atom-thick layer of carbon atoms that are arranged in a flat, hexagonal lattice structure. Graphene has been used for centuries in pencil leads. It has important properties as it is thin and light weight, while being 200 times stronger than the strongest steel, Finally, it has high thermal and electrical conductivity. These properties allow the use of graphene in semiconductor, electronics, battery energy and composites industries, and as touch screens component in devices, water filtration systems, medial sensors and much more.

Elemental analysis is key for the characterization of graphene to evaluate its quality. Carbon, nitrogen, hydrogen, sulfur by combustion analysis, 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 essential.

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The Thermo Scientific™ Flash*Smart*™ Elemental Analyzer for CHN/O determinations, based on the dynamic combustion of the sample, provides automatic and simultaneous CHN 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 CHN 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 CHN 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 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, they are detected by a TCD Detector. The total run time is less than 7 minutes (Figure 3).

For trace sulfur analysis, after combustion the resulted gases are carried by a helium flow to a catalyst, a layer filled with copper and a water trap. The gases are carried by a helium flow through a short GC column and finally they are detected by the FPD Detector (Figure 4).

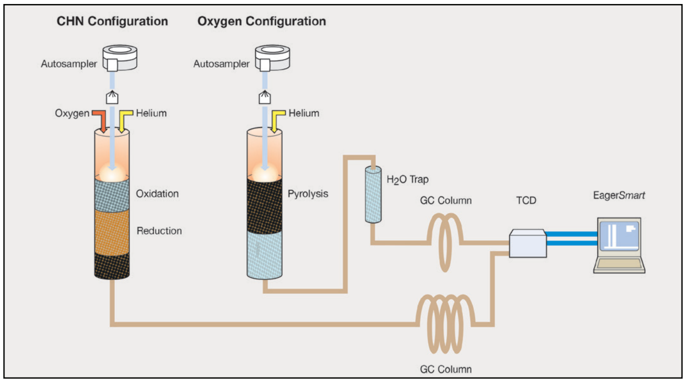

Figure 3. Flash*Smart* CHN/O Configuration.

Analytical Conditions	
CHN Reactor Temperature	950 °C
Oxygen Reactor Temperature	1060 °C
GC Oven Temperature	75 °C
Helium Carrier Flow	140 ml/min for CHN 100 ml/min for Oxygen
Helium Reference Flow	100 ml/min
Oxygen Flow	300 ml/min for CHN
Oxygen Injection Time	15 sec for CHN
Sample Delay	12 sec for CHN 0 sec for Oxygen
Total Run Time	less than 420 sec for CHN less than 300 sec for Oxygen

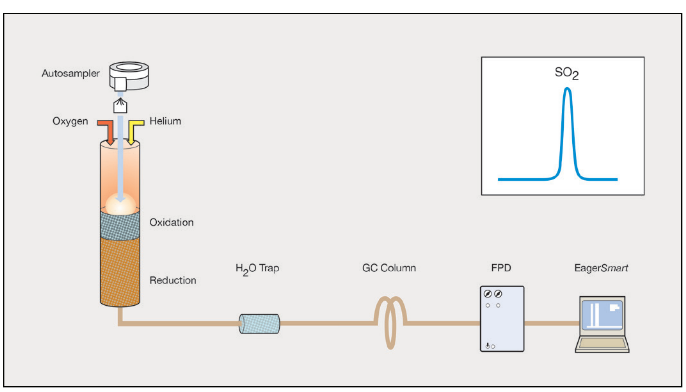

Figure 4. Sulfur Configuration by FPD.

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 gas chromatographically separated from other products and detected by the TCD Detector (Figure 3).

A complete 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 CHN 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 CHN 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.

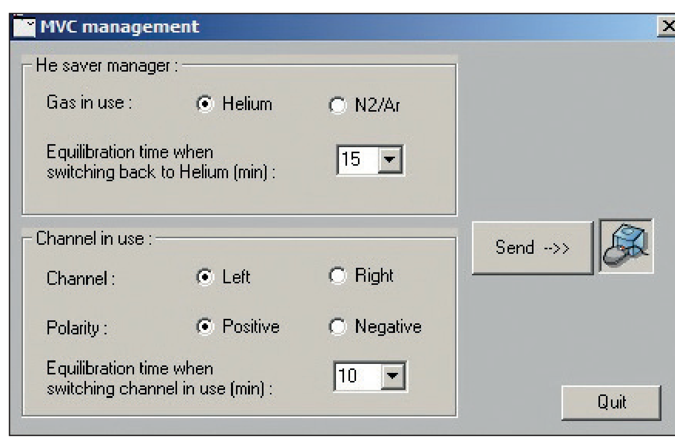

Figure 5. The MVC Module management window on the Eager*Smart* Data Handling Software.

Results

For CHN determination, the instrument was calibrated with acetanilide standard while for oxygen analysis BBOT standard (2, 5-Bis (5-ter-butyl-benzoxazol-2-yl) thiophene) was used. In both cases K factor was used as the calibration method. Figure 6 shows the calibration curve for carbon, the main element of graphene. Figure 7 shows a typical CHN chromatogram and Figure 8 shows a typical oxygen chromatogram.

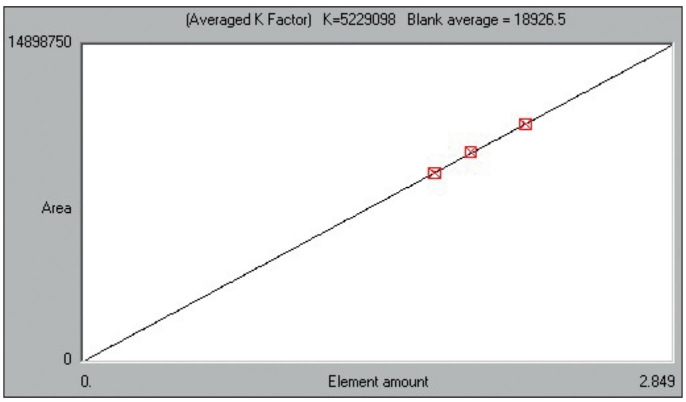

Figure 6. Carbon calibration curves.

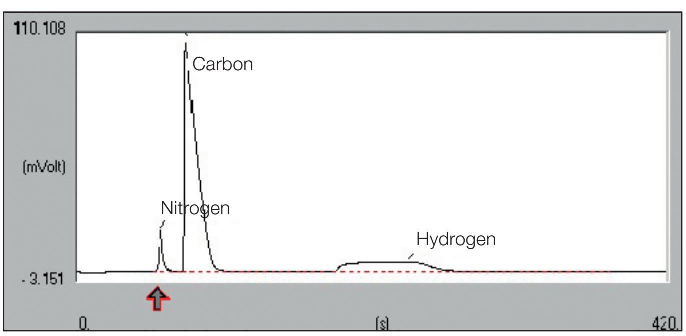

Figure 7. Typical CHN chromatogram.

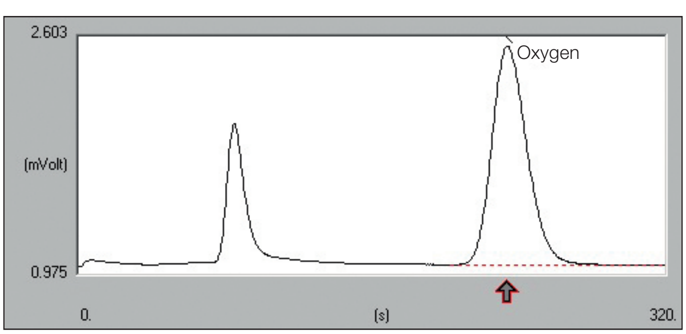

Figure 8. Typical Oxygen chromatogram.

To verify the complete combustion of high containing carbon samples as graphene, carbon determination was evaluated in three organic standards and in Carbon Mesoporous Reference Material (99.95 C%, Aldrich). Table 1 shows the data of the three high carbon containing organic standards while Table 2 shows the data of the Carbon Mesoporous Reference Material. The data were obtained with good repeatability and the average is comparable with the expected value and fall within the technical specification of the Flash*Smart* Analyzer, indicating complete oxidation of the sample.

Table 1. Carbon data of high carbon containing organic standards.

Standard	Theoretical	Acceptable Range	Experimental Carbon	
	C%	(±)	%	RSD%
Polystyrene	91.95	0.30	92.12 92.12 92.11	0.01
Antracene	94.34	0.30	94.22 94.44 94.51	0.16
Fluorene	93.81	0.30	93.87 93.79 93.59	0.15

Table 2. Carbon data of the Carbon Mesoporous Reference Material.

Sample	C%	Average C%	RSD%
Carbon Mesoporous 99.95 C%	99.91 99.58 99.86 99.71 99.68 99.69 99.82 99.72 99.69 99.41	99.71	0.143

Four graphene samples with different element concentrations were analyzed several times to evaluate the repeatability of the data. For samples A and B nitrogen, carbon and oxygen were determined, while for samples C and D nitrogen, carbon, hydrogen and oxygen were determined. Table 3 shows the data of samples A and B and Table 4 shows the data of samples C and D.

Table 3. NC and oxygen determination of Graphene samples A and B.

Graphene Sample	Nitrogen		Carbon		Oxygen	
	%	RSD%	%	RSD%	%	RSD%
A	0.0114 0.0116 0.0116	1.00	99.98 99.91 99.72	0.10	0.0509 0.0507 0.0507	0.23
B	0.0591 0.0600 0.0593	0.79	99.97 99.67 99.96	0.17	0.0203 0.0207 0.0205	0.98

Table 4. CHN and oxygen determination of Graphene samples C and D.

Graphene Sample	Nitrogen		Carbon		Hydrogen		Oxygen	
	%	RSD%	%	RSD%	%	RSD%	%	RSD%
C	0.827 0.819 0.820	0.53	95.35 95.29 95.33	0.03	0.250 0.246 0.245	1.07	1.40 1.40 1.39	0.41
D	0.181 0.190 0.189	0.53	96.64 96.78 96.83	0.09	0.960 0.953 0.959	0.40	1.24 1.25 1.26	0.80

Table 5 shows the sulfur data at trace level obtained with the FPD Detector. The calibration was performed with Soil (33 ppm S) of a WEPAL (Wageningen Evaluating Programs for Analytical Laboratories, Wageningen University, Netherlands) Round Robin Test using Quadratic Fit as the calibration method.

Table 5. Sulfur data obtained with FPD Detector.

Graphene Sample	Sulfur		Graphene Sample	Sulfur	
	ppm	RSD%		Sample	RSD%
A	36 37	1.94	C	42 44	3.29
B	65 62	3.34	D	46 45	1.55

Conclusions

The Flash*Smart* Elemental Analyzer is the optimal solution for the characterization of graphene 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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