Fully automated analysis for CHNS and trace sulfur through an Elemental Analyzer

Liliana Krotz, Francesco Leone, Walter Galotta and Guido Giazzi, Thermo Fisher Scientific, Strada Rivoltana, 20090 Rodano (MI), Italy

ABSTRACT

Elemental analysis is used as the analytical basis for quality control of industrial products and R&D purposes. This poster presents CHNS and trace sulfur data of pure organic standards, reference materials and several matrices to evaluate the accuracy and precision of the data using different configurations and detectors through the Thermo Scientific™ Flash*Smart*™ Elemental Analyzer.

INTRODUCTION

The determination of carbon, nitrogen, hydrogen, and sulfur by combustion analysis is commonly used for the characterization of raw and final products in many application fields for quality control and R&D purposes. In order to perform analysis with high throughput and reduced cost per sample, laboratories need an automated analytical technique, allowing fast analysis with excellent reproducibility and accuracy for any concentration range.

The Thermo Scientific™ Flash*Smart*™ Elemental Analyzer (Figure 1), operating with the dynamic flash combustion of the sample (modified Dumas method) with the Thermal Conductivity Detector (TCD), meets modern laboratory requirements, in terms of accuracy, reproducibility, and high sample throughput. The Elemental Analyzer is equipped with two totally independent furnaces. The furnaces are installed with two analytical circuits, which are used alternatively and are controlled by the Thermo Scientific™ MultiValve Control™ (MVC) Module (Figure 2). Each analytical circuit can receive its own autosampler.

The Flash*Smart* EA enables to perform trace sulfur determinations, when coupled to the Flame Photometric Detector (FPD) (Figure 5). This configuration combines the advantages of the elemental analyzer with the sensitivity and robustness of the FPD Detector. The Elemental Analyzer can be configured for CHNS determination on the left channel with the TCD Detector and for trace sulfur analysis on the right channel with the FPD Detector. By switching from helium to nitrogen or argon (as carrier gas), the proprietary MVC Module enables to manage and reduce helium carrier gas consumption and consequently operational costs, when the instrument is in Stand-By Mode.

Figure 1. Thermo Scientific Flash*Smart* EA.

Figure 2. MVC Module.

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 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, the gases are detected by a Thermal Conductivity Detector (TCD) (Figure 3).

For trace sulfur determination, samples are weighed in tin containers and introduced into the combustion reactor (right furnace) via the MAS Plus Autosampler with oxygen. After combustion the resulted gases are carried by a helium flow to a layer filled with copper, then swept to a water trap, and a GC column. Finally, they are detected by a Flame Photometric Detector (FPD) (Figure 3).

A complete report is automatically generated by the dedicated Thermo Scientific™ Eager*Smart*™ Data Handling Software.

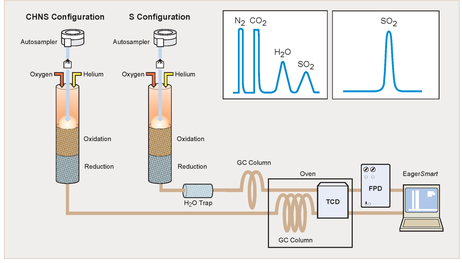

Figure 3. CHNS configuration (left reactor) and Trace S (right reactor) configuration.

The pneumatic circuits for CHNS by TCD Detector and trace sulfur determination by FPD Detector are pre-set in the system. The MultiValve Control Module allows the switch from one circuit to the other. The Eager*Smart* Data Handling Software controls the MVC Module and avoid the need for manual intervention on the configuration.

The Eager*Smart* Data Handling Software window (Figure 4) shows how to change from the Left to the Right furnace. It allows the switching from CHNS determination performed by TCD Detector to trace sulfur analysis configuration performed by FPD Detector. It also enables the switch from helium carrier gas to nitrogen or argon gas when the instrument is in Stand-By Mode.

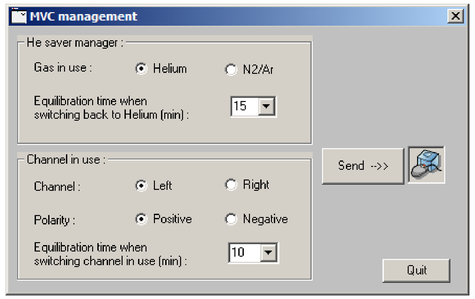

Figure 4. Eager*Smart* Data Handling Software MVC Module Management window.

RESULTS

Typical analytical tests were performed for CHNS and trace sulfur configuration in a single day. The repeatability, accuracy and the stability of the system were evaluated, when the configuration is switched from CHNS by TCD Detector to trace sulfur by FPD Detector and vice versa. The data obtained were compared with the theoretical values and the acceptable range, according to the technical specification of the elemental analyzer. At the end of the day, the Elemental Analyzer was set in Stand-By Mode, in order to reduce helium consumption. The Auto-Ready function can be also activated via the Eager*Smart* Data Handling Software, and it enables the automated wake-up of the system on the following day.

For CHNS determination by TCD Detector, the Elemental Analyzer was calibrated with 2 – 3 mg methionine standard, using K factor as calibration method. For trace sulfur analysis by the FPD Detector, the calibration was performed with 0.5 – 2 mg Thermo Scientific Pasta Reference Material, using Quadratic Fit as the calibration method.

Sulfanilamide was analyzed as unknown in CHNS configuration. Pasta was analyzed as unknown for sulfur analysis. Both were analyzed without recalibrating the Elemental Analyzer, in four series by day and in triplicate each series.

After each series of CHNS, the configuration is switched to sulfur determination and at the end of the series, the Elemental Analyzer is switched to CHNS determination. The data and the stability of the system were evaluated. The system reached stability in ten minutes after the configuration switching.

Table 1 shows CHNS data of sulfanilamide and the sulfur data of Pasta Reference Material. The theoretical values and the acceptable range fall within the technical specification of the system of sulfanilamide: 16.27 N% (±0.16), 41.84 C% (± 0.30), 4.68 H% (±0.07) and 18.62 S% (±0.20). For Pasta Reference Material the value is 0.136 S% (±0.004).

Table 1. CHNS data of sulfanilamide and Sulfur data of Pasta Reference Material.

Series	CHNS by TCD Detector (Left Reactor) Sulfanilamide								S by FPD Detector (Right Reactor) Pasta Ref. Mat.	
	N %	RSD %	C %	RSD %	H %	RSD %	S %	RSD %	S %	RSD %
1	16.39 16.33 16.37	0.18	41.89 41.88 41.81	0.11	4.69 4.69 4.69	0.00	18.61 18.54 18.59	0.19	0.1365 0.1372 0.1370	0.26
2	16.36 16.38 16.34	0.12	41.76 41.86 41.69	0.21	4.67 4.68 4.68	0.13	18.68 18.70 18.67	0.08	0.1385 0.1363 0.1376	0.80
3	16.28 16.29 16.24	0.16	41.72 41.87 41.83	0.19	4.66 4.66 4.67	0.13	18.67 18.64 18.61	0.16	0.1348 0.1345 0.1351	0.80
4	16.21 16.25 16.21	0.14	41.88 41.72 41.81	0.19	4.63 4.67 4.68	0.56	18.73 18.77 18.71	0.16	0.1353 0.1361 0.1357	0.22

To evaluate the performance of the Analyzer using both detectors, several samples in large range of concentrations were chosen. Samples of different application fields were analyzed to show the repeatability of the data in CHNS by TCD Detector and the sulfur by FPD detector when it cannot be determined by TCD Detector.

Table 2 shows the CHNS and sulfur data of the same matrices analyzed in duplicate by both configurations. The sulfur data obtained by TCD and FPD Detectors are comparable.

Table 2. CHNS and sulfur data of the same matrices analyzed in both configurations.

Sample Name	CHNS by TCD Detector (Left Reactor)								S by FPD Detector (Right Reactor)	
	N %	RSD %	C %	RSD %	H %	RSD %	S %	RSD %	S %	RSD %
Pasta	2.14 2.14	0.00	41.17 41.23	0.10	6.49 6.57	0.87	0.134 0.135	0.53	0.1370 0.1360	0.52
Soil 1	0.211 0.212	0.17	2.34 2.34	0.00	0.77 0.76	0.92	0.0236 0.0231	1.51	0.0232 0.0230	0.61
Soil 2	0.123 0.122	0.23	1.55 1.55	0.00	0.34 0.33	2.11	0.0150 0.0149	0.47	0.0142 0.0143	0.50
Catalyst A	-	-	6.76 6.72	0.42	1.26 1.25	0.56	0.0331 0.0329	0.43	0.0327 0.0329	0.43

Table 3 shows the CHN data obtained by TCD Detector and the sulfur data obtained by FPD Detector of matrices containing trace sulfur, analyzed in triplicate. The data obtained show excellent repeatability without matrix effect indicating complete combustion of the samples and proper quantification of the elements.

Table 3. CHN data by TCD Detector and sulfur data by FPD Detector.

Sample Name	CHNS by TCD Detector (Left Reactor)						S by FPD Detector (Right Reactor)	
	N%	RSD%	C%	RSD%	H%	RSD%	S%	RSD%
Soil	0.0227 0.0225 0.0228	0.67	0.292 0.295 0.293	0.52	0.175 0.173 0.174	0.57	0.0034 0.0033 0.0034	1.72
Catalyst B	-	-	3.58 3.59 3.59	0.16	0.611 0.641 0.618	0.89	0.0062 0.0063 0.0061	1.61
Graphite	0.0500 0.0491 0.0501	1.21	98.26 98.54 98.43	0.14	0.0115 0.0121 0.0121	2.52	0.0036 0.0035 0.0037	2.78
Carbon Fiber	0.0667 0.0670 0.0668	0.23	98.65 98.59 98.52	0.07	-	-	0.0031 0.0029 0.0030	3.32
Graphene A	0.0367 0.0363 0.0362	0.72	99.29 99.36 99.41	0.06	-	-	0.0085 0.0082 0.0086	2.47
Graphene B	-	-	99.74 99.62 99.63	0.07	-	-	0.0058 0.0055 0.0057	2.70
Carbon Standard	-	-	99.81 99.75 99.85	0.05	-	-	0.0056 0.0057 0.0056	1.02

In addition, two sulfur reference materials (sulfur powder and lubricant in iso-octane solution) were analyzed to show the performance of the FlashSmart Elemental Analyzer in two different concentration range: about 100 S% determined by TCD Detector and 5 ppm of sulfur by FPD Detector. Table 4 shows the repeatability of the data obtained..

Table 4. Sulfur data by TCD and FPD Detectors.

Sulfur Powder (99.98 S%, ± 0.30)		Reference Liquid Solution (5 ppm, ± 1 ppm)	
S%	RSD%	ppm S	RSD%
99.83 99.98 99.99 99.81 99.86	0.09	4.8 5.1 4.9 4.7 4.9	4.04

Figure 5. Thermo Scientific FlashSmart EA coupled with FPD Detector.

CONCLUSIONS

CHNS determination (from 100 ppm to 100 %) by TCD Detector and trace sulfur (from 5 ppm to 500 ppm S) by FPD Detector can be performed on the same Flash*Smart* EA. The results fall within the expected range. Data were obtained with acceptable repeatability and no matrix effect was observed when changing the configuration. The Elemental Analyzer can determine 5 ppm and 100 % of sulfur with excellent repeatability.

The double configuration enables to reduce analysis time and to increase the productivity of the laboratory. Both reactors are fully automated through the Eager*Smart* Data Handling Software, which also enables to manage the TCD and FPD Detectors. No differences in percent was observed switching from CHNS to S configurations or when changing sample matrix. This indicates:

- No interference of hydrogen peak on sulfur determination
- No adsorption of sulfur by the water trap
- No adsorption of sulfur in the GC columns
- No influence of the content of nitrogen or carbon present in the sample
- Complete combustion
- Complete conversion of all gases
- Proper quantification of the sulfur in all type of matrix.

The Multi Valve Control (MVC) Module is a device used for performing the following functions:

- Automated switching from the left channel to the right channel or vice-versa.
- Reduced helium consumption by switching from helium to nitrogen or argon, when the system is in Stand-By Mode.
- Automated control of two MAS Plus Autosamplers.
- Auto-Ready: return automatically to helium carrier gas from Stand-By Mode and prepare for analysis.

ACKNOWLEDGEMENTS

We would like to thank Gianfranco Liborio Romero Baeza, IIS Curie-Sraffa student (Milan, Italy) for his collaboration with the analysis during his internship at the Thermo Scientific OEA Application Lab (Milan, Italy).

TRADEMARKS/LICENSING

PO42301 - Presented at the PittCon 2018, Orlando, FL, USA. 26 Feb – 1 March 2018

ThermoFisher SCIENTIFIC