TECHNICAL NOTE

High Automation of Thermo Scientific Flash*Smart* CHNS/O Analyzer using the MultiValve Control (MVC) Module

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Key Words

Accuracy, Automation, CHNS, Flash Combustion, Organic Chemistry, Oxygen, Pyrolysis, Unattended Analysis

Goal

To demonstrate the performance of the MultiValve Control (MVC) Module on the Flash*Smart* Elemental Analyzer.

Figure 1. Thermo Scientific Flash*Smart* Analyzer.

Introduction

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

The Thermo Scientific™ Flash*Smart*™ Elemental Analyzer (Figure 1) is equipped with two totally independent furnaces allowing the installation of two analytical circuits that can be used sequentially and are completely automated through the Thermo Scientific™ MultiValve Control (MVC) Module (Figure 2).

Each analytical circuit accepts 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.

The 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.

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Figure 2. Thermo Scientific MultiValve Control Module.

For oxygen determination, the system operates in pyrolysis mode. Samples are weighed in silver containers and introduced into the pyrolysis reactor (right furnace) from 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 complete report is automatically generated by the Thermo Scientific™ Eager*Smart*™ Data Handling Software and displayed at the end of the analysis.

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) from the Thermo Scientific™ MAS Plus Autosampler with oxygen. After combustion the resulted gases are conveyed by a helium flow to a layer filled with copper, then swept through a GC column that provides the separation of the combustion gases, and finally, detected by a Thermal Conductivity Detector (TCD). The total run time is less than 10 minutes. (Figure 3).

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	250 ml/min for CHNS
Oxygen Injection Time	5 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
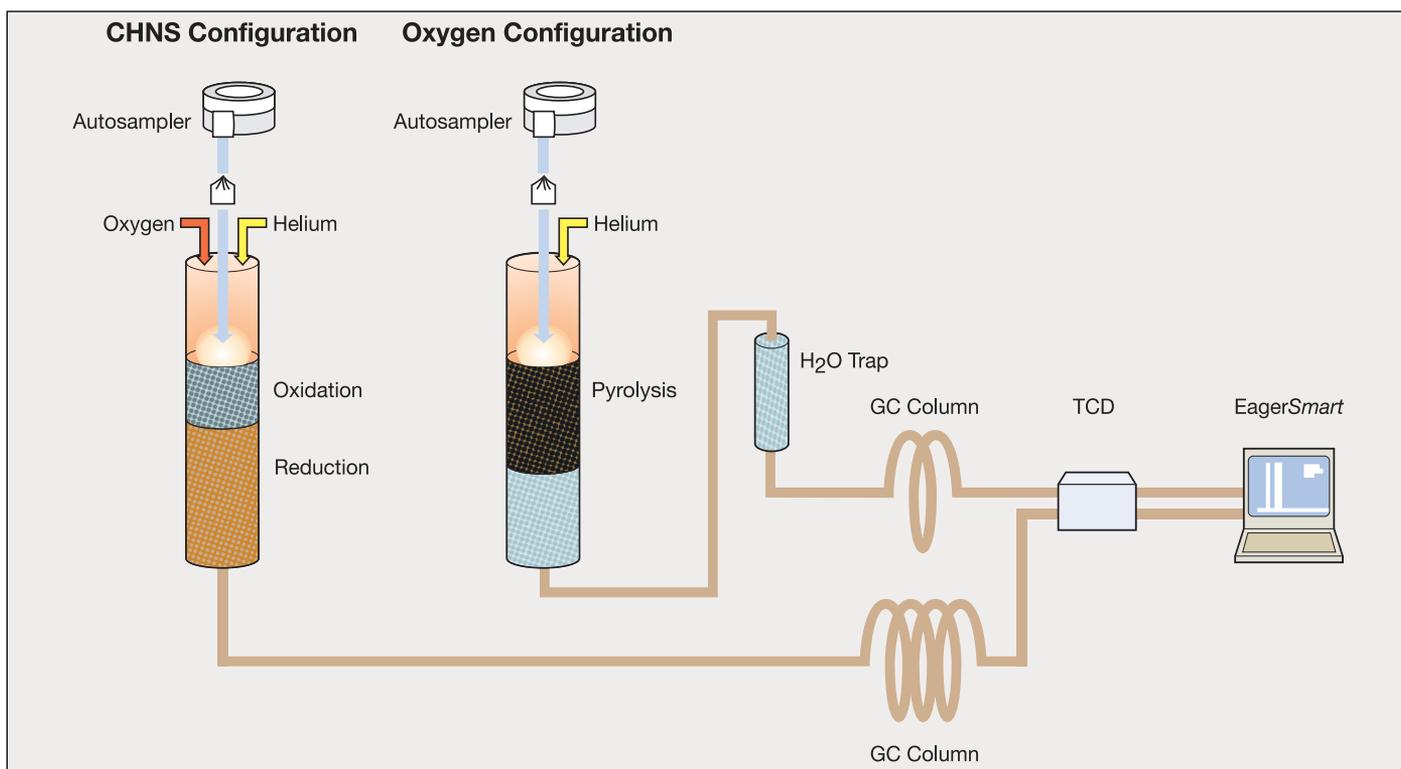
Figure 3. Flash*Smart* CHNS/O configuration.

The pneumatic circuits for CHNS and oxygen determination are set up simultaneously in the same system which allows the MVC Module to automatically switch between the reactors through the Eager*Smart* Software without any operational action by the user.

Figure 4 shows the internal parts of the Flash*Smart* Analyzer.

Furnaces

Adsorber Filter and Oven

GC Column and TCD Detector

Figure 4. Flash*Smart* CHNS and oxygen internal circuits.

The Eager*Smart* Data Handling Software MVC Module management page (Figure 5), shows in the lower part how to switch from left to right furnace to pass from CHNS determination by combustion to oxygen analysis by pyrolysis. The upper panel of the page indicates how to switch from helium carrier gas to nitrogen or argon gas when the instrument is not in use for analysis.
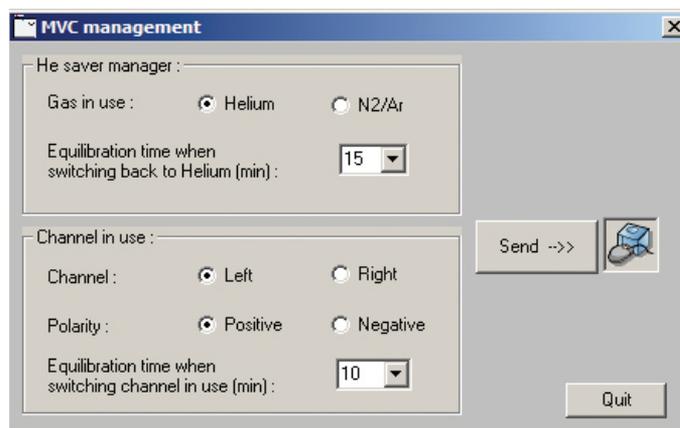
Figure 5. The MVC Module Management page on the Eager*Smart* Data Handling Software.

Results

Typical analytical tests were performed for CHNS and oxygen configuration during several non-consecutive days to evaluate the repeatability, accuracy and the stability of the system when the configuration is switched from CHNS to oxygen, and vice versa. The experimental data obtained were compared with the theoretical values and the acceptable range according to the technical specification of the system.

At the end of each day, the instrument was set to Stand-By Mode to reduce the consumption of helium gas. The Auto-Ready function was activated through the Eager*Smart* Data Handling Software to wake-up the system before analysis began the next day.

During day 1, the instrument was calibrated for CHNS with methionine standard and for oxygen with BBOT standard (2, 5-Bis (5-ter-butyl-benzoxazol-2-yl) thiophene), using K factor as the calibration method. Then, three runs of sulfanilamide and BBOT were analyzed as unknown to verify the calibration.

Table 1 shows the sequence of analysis for CHNS while Table 2 shows the sequence for oxygen determination.

The theoretical values and the acceptable range according to the technical specification of the system of sulfanilamide are 16.27 N% (±0.16), 41.84 C% (±0.30), 4.68 H% (±0.07) and 18.62 S% (±0.2). While for BBOT the value is 7.43 O% (±0.1).

Table 1 . CHNS sequence of analysis for day 1.

Run	Sample name	Day/Month	Injection Time	Type	Weight (mg)	N%	C%	H%	S%
1	Tin containers	11/01	09:05	Blank					
2	Methionine	11/01	09:17	By-Pass					
						Theoretical value			
3	Methionine	11/01	09:30	STD	2.655	9.39	40.25	7.43	21.49
4	Methionine	11/01	09:42	STD	2.730	9.39	40.25	7.43	21.49
5	Methionine	11/01	09:54	STD	2.986	9.39	40.25	7.43	21.49
						Experimental data			
6	Sulfanilamide	11/01	10:06	UNK	3.428	16.39	41.57	4.64	18.75
7	Sulfanilamide	11/01	10:18	UNK	3.078	16.36	41.68	4.68	18.78
8	Sulfanilamide	11/01	10:30	UNK	2.985	16.26	4.66	5.05	18.81
						Theoretical values			
	Sufanilamide					16.27	41.84	4.68	18.62
						Accepted Range (±)			
	Sufanilamide					0.16	0.30	0.07	0.20

Table 2. Oxygen sequence of analysis for day 1.

Run	Sample name	Day/Month	Injection Time	Type	Weight (mg)	O%
1	Silver containers	11/01	10:52	Blank		
2	BBOT	11/01	11:01	By-Pass		
						Theoretical value
3	BBOT	11/01	11:09	STD	1.902	7.43
4	BBOT	11/01	11:18	STD	2.083	7.43
5	BBOT	11/01	11:26	STD	2.086	7.43
						Experimental data
6	BBOT	11/01	11:34	UNK	1.981	7.44
7	BBOT	11/01	11:43	UNK	2.005	7.43
8	BBOT	11/01	11:51	UNK	2.124	7.41

Then methionine and sulfanilamide for CHNS, and BBOT for oxygen analysis were analyzed as unknown without recalibration of the instrument, in four series each day with each series run in duplicate, across a period of 35 days. After each series of CHNS measurements, the instrument was switched to oxygen determination to perform analysis and, after completion, the instrument switched back to CHNS. The switching between CHNS and O configurations was performed to evaluate the data and the stability of the system. The Analyzer was stable and ready for analysis in only ten minutes after the switching.

Table 3 shows the CHNS average data obtained during the period of switching, while Table 4 shows the oxygen average data.

All results are acceptable and according to the specification of the instrument, indicating no effect due to configuration switching by the MVC Module from combustion to pyrolysis, or vice versa confirming the stability of the Flash*Smart* Analyzer.

Table 3. CHNS average data.

Day / Month	Standard	No. Runs	N%	RSD%	C%	RSD%	H%	RSD%	S%	RSD%
11/01	Methionine	8	9.38	0.56	40.29	0.09	7.43	0.24	21.58	0.39
	Sulphanilamide	8	16.37	0.31	41.62	0.10	4.67	0.39	18.68	0.56
12/01	Methionine	8	9.45	0.47	40.27	0.12	7.42	0.14	21.60	0.22
	Sulphanilamide	8	16.38	0.32	41.67	0.14	4.67	0.22	18.69	0.21
13/01	Methionine	8	9.34	0.53	40.32	0.39	7.39	0.92	21.58	0.26
	Sulphanilamide	8	16.33	0.32	41.75	0.21	4.65	0.32	18.68	0.19
14/01	Methionine	8	9.40	0.83	40.23	0.39	7.38	1.02	21.53	0.25
	Sulphanilamide	8	16.29	0.38	41.81	0.20	4.65	0.20	18.70	0.29
15/01	Methionine	8	9.43	0.47	40.33	0.47	7.41	0.46	21.56	0.39
	Sulphanilamide	8	16.32	0.42	41.74	0.13	4.64	0.22	18.66	0.22
19/01	Methionine	4	9.45	0.56	40.42	0.11	7.41	0.31	21.6	0.16
	Sulphanilamide	4	16.43	0.45	41.76	0.22	4.64	0.31	18.68	0.16
25/01	Methionine	4	9.4	0.3	40.49	0.49	7.42	0.46	21.37	0.61
	Sulphanilamide	4	16.29	0.8	41.78	0.24	4.63	0.35	18.51	0.84
26/01	Methionine	2	9.33	0.43	40.41	0.27	7.39	0.78	21.49	0.63
	Sulphanilamide	2	16.22	0.15	41.75	0.09	4.63	0.36	18.52	0.29
27/01	Methionine	6	9.34	0.31	40.41	0.18	7.43	0.31	21.39	1.06
	Sulphanilamide	6	16.23	0.42	41.77	0.12	4.63	0.19	18.44	1.31
28/01	Methionine	6	9.32	0.37	40.41	0.20	7.43	0.15	21.45	0.61
	Sulphanilamide	6	16.28	0.27	41.76	0.05	4.65	0.12	18.67	0.09
29/01	Methionine	8	9.33	0.28	40.31	0.15	7.40	0.56	21.44	0.29
	Sulphanilamide	8	16.23	0.51	41.68	0.19	4.64	0.36	18.60	0.42
01/02	Methionine	6	9.36	0.63	40.31	0.17	7.37	0.50	21.46	0.31
	Sulphanilamide	6	16.28	0.32	41.62	0.14	4.62	0.07	18.53	0.41
02/02	Methionine	8	9.34	0.40	40.34	0.19	7.39	0.88	21.39	1.3
	Sulphanilamide	8	16.36	0.39	41.72	0.10	4.64	0.22	18.60	0.48
04/02	Methionine	4	9.41	0.47	40.29	0.37	7.37	0.75	21.59	1.82
	Sulphanilamide	4	16.36	0.70	41.73	0.17	4.64	0.29	18.74	0.27
09/02	Methionine	6	9.44	0.52	40.26	0.40	7.38	0.66	21.58	0.47
	Sulphanilamide	6	16.27	0.77	41.69	0.15	4.63	0.32	18.65	0.31
10/02	Methionine	8	9.38	1.10	40.43	0.14	7.40	0.93	21.43	0.85
	Sulphanilamide	8	16.24	0.40	41.77	0.12	4.64	0.19	18.60	0.38
11/02	Methionine	8	9.39	1.21	40.34	0.30	7.38	0.66	21.43	0.69
	Sulphanilamide	8	16.26	0.44	41.69	0.27	4.62	0.32	18.62	0.55
12/02	Methionine	16	9.40	0.73	40.31	0.15	7.38	0.51	21.45	1.55
	Sulphanilamide	16	16.24	0.62	41.69	0.16	4.62	0.33	18.68	0.75

Table 4. Oxygen average data.

Day / Month	Standard	No. Runs	O%	RSD%
11/01	BBOT	16	7.42	0.29
12/01	BBOT	16	7.41	0.44
13/01	BBOT	16	7.38	0.67
14/01	BBOT	16	7.37	0.61
15/01	BBOT	16	7.37	0.79
19/01	BBOT	8	7.37	0.65
25/01	BBOT	4	7.41	0.62
26/01	BBOT	8	7.48	0.27
27/01	BBOT	12	7.41	0.59
28/01	BBOT	12	7.45	0.49
29/01	BBOT	16	7.41	0.29
01/02	BBOT	12	7.42	0.46
02/02	BBOT	12	7.43	0.44
04/02	BBOT	12	7.44	0.56
09/02	BBOT	4	7.47	0.77
10/02	BBOT	12	7.46	0.44
11/02	BBOT	16	7.43	0.36
12/02	BBOT	24	7.45	0.46

To evaluate the linearity of the system, pure organic compounds with a range of CHNS/O amounts were chosen. Instrument calibration was performed with BBOT 6.51 N%, 72.53 C%, 6.09 H%, 7.44 S%, 7.43 O%), Sulfanilamide (16.27 N%, 41.84 C%, 4.68 H%, 18.62 S%, 18.58 O%), L-Cystine (11.66 N%, 29.99 C%, 5.03 H%, 26.69 S%, 26.63 O%), and Acetanilide (10.36 N%. 71.09 C%, 6.71 H%, 11.84 O%) standards (STD) using Linear Fit as the calibration method. For CHNS determination, the standard weight was 2-3 mg for BBOT and Acetanilide, and 3-4 mg for Sulfanilamide and Cystine. For oxygen determination, the weight was 1-2 mg. After the CHNS sequence finished, the instrument automatically switched through the Eager*Smart* Data Handling Software to the oxygen configuration and the oxygen sequence of analyses was automatically performed.

Pure organic standards in a large range of concentration were selected and analyzed as unknown (UNK) to evaluate the calibration, repeatability and accuracy of the data obtained.

Table 5 shows the theoretical percentages of the pure organic standards analyzed as unknown and the accepted range according to the technical specification of the system. Table 6 shows the experimental data obtained. Each standard was analyzed in triplicate.

All data are acceptable and no effect was observed when changing the sample or switching between configurations with the MVC Module.

Table 5. Theoretical values and accepted range of pure organic standards.

Standard	Nitrogen		Carbon		Hydrogen		Sulfur		Oxygen	
	%	Range (±)	%	Range (±)	%	Range (±)	%	Range (±)	%	Range (±)
Acetanilide	10.36	0.10	71.09	0.30	6.71	0.10	N/A	N/A	11.84	0.12
Atropine	4.84	0.07	70.56	0.30	8.01	0.10	N/A	N/A	16.59	0.18
BBOT*	6.51	0.10	72.53	0.30	6.09	0.10	7.44	0.10	7.43	0.10
Benzoic Acid	N/A	N/A	68.85	0.30	4.95	0.08	N/A	N/A	26.20	0.25
CEDFNI**	20.14	0.20	51.79	0.30	5.07	0.08	N/A	N/A	23.00	0.22
Methionine	9.39	0.10	40.25	0.30	7.43	0.10	21.49	0.20	21.45	0.20
L-Cystine	11.66	0.12	29.99	0.28	5.03	0.08	26.69	0.25	26.63	0.25
Nicotinamide	22.94	0.22	59.01	0.30	4.95	0.08	N/A	N/A	13.10	0.14
Sulfanilamide	16.27	0.16	41.84	0.30	4.68	0.07	18.62	0.20	18.58	0.20

*BBOT: 2,5-Bis (5-tert-butyl-benzoxazol-2-yl) thiophene
**CEDFNI: cyclohexanone 2,4-dinitrophenylhydrazone

Table 6. Repeatability and accuracy of pure organic standards.

Standard	Nitrogen		Carbon		Hydrogen		Sulfur		Oxygen	
	%	RSD%	%	RSD%	%	RSD%	%	RSD%	%	RSD%
Acetanilide	10.39 / 10.29 / 10.38	0.53	71.35 / 71.13 / 71.24	0.15	6.71 / 6.73 / 6.75	0.30	N/A	N/A	11.95 / 11.87 / 11.91	0.34
Atropine	4.90 / 4.86 / 4.88	0.41	70.82 / 70.35 / 70.46	0.35	7.97 / 7.93 / 7.93	0.29	N/A	N/A	16.73 / 16.72 / 16.76	0.12
BBOT*	6.50 / 6.51 / 6.52	0.15	72.26 / 72.26 / 72.31	0.04	6.11 / 6.08 / 6.07	0.34	7.47 / 7.52 / 7.51	0.35	7.36 / 7.43 / 7.37	0.51
Benzoic Acid	N/A	N/A	68.80 / 69.13 / 68.94	0.24	4.95 / 4.96 / 4.95	0.12	N/A	N/A	26.00 / 26.15 / 26.03	0.30
CEDFNI**	20.33 / 20.24 / 20.23	0.27	51.83 / 51.85 / 51.76	0.09	5.07 / 5.07 / 5.07	0.00	N/A	N/A	22.84 / 23.12 / 23.09	0.67
Methionine	9.48 / 9.36 / 9.35	0.77	40.30 / 40.42 / 40.53	0.28	7.39 / 7.40 / 7.42	0.21	21.55 / 21.55 / 21.64	0.24	21.36 / 21.34 / 21.50	0.41
L-Cystine	11.63 / 11.74 / 11.73	0.52	30.07 / 30.06 / 30.04	0.05	5.09 / 5.07 / 5.06	0.30	26.77 / 26.83 / 26.79	0.11	26.58 / 26.49 / 26.70	0.40
Nicotinamide	23.16 / 23.12 / 23.15	0.09	59.10 / 58.90 / 58.99	0.17	4.97 / 4.93 / 4.94	0.42	N/A	N/A	13.11 / 13.15 / 13.18	0.27
Sulfanilamide	16.43 / 16.35 / 16.41	0.25	42.05 / 42.06 / 41.95	0.14	4.71 / 4.72 / 4.70	0.21	18.73 / 18.79 / 18.75	0.16	18.72 / 18.57 / 18.66	0.40

Additionally, two tests were performed to show the accuracy and repeatability of organic compounds with high nitrogen and carbon content. For high nitrogen determination, 2-3 mg of Urea standard (46.65 N%, 20 C%, 6.71 H%) was analyzed in triplicate as unknown. The calibration was performed with 2.5 – 3.5 mg of Imidazole standard (41.15 N%, 52.93 C%, 5.92 H%) using K factor as the calibration method.

Table 7 shows the experimental CHN data of Urea in comparison to the theoretical values and the acceptable range. All data are inside the technical specification of the system and show excellent accuracy and precision.

Table 7. CHN data of Urea (46.65 N%, 20 C%, 6.71 H%).

Run	W (mg)	Nitrogen			Carbon			Hydrogen		
		%	RSD%	Acceptable range	%	RSD%	Acceptable range	%	RSD%	Acceptable range
1	2.249	46.58			20.15			6.74		
2	2.185	46.58	0.04	46.36 – 46.96	20.14	0.13	19.80 – 20.20	6.73	0.09	6.61 – 6.81
3	2.157	46.53			20.10			6.74		

For high carbon determination, the calibration was performed with 2 – 3 mg of Acetanilide (10.36 N%, 71.09 C%, 6.71 H%) using K factor as the calibration method. Following, about 2 mg of different high carbon content standards were analyzed in triplicate as unknown.

Table 8 shows the CHN theoretical percentages of the standards analyzed as unknown and the acceptable range. Table 9 shows the experimental data obtained, which are inside the technical specification of the system and demonstrate excellent accuracy and precision of the Analyzer.

Table 8. CHN theoretical data of high carbon content standards.

Standard	Nitrogen		Carbon		Hydrogen	
	%	Acceptable range	%	Acceptable range	%	Acceptable range
Tocopherol Nicotinate	2.61	± 0.07	78.46	± 0.30	9.97	± 0.10
Polyethylene	N/A	N/A	85.70	± 0.30	14.30	± 0.15
Polystyrene	N/A	N/A	92.30	± 0.30	7.70	± 0.10
Antracene	N/A	N/A	94.34	± 0.30	5.66	± 0.09
Fluorene	N/A	N/A	93.81	± 0.30	6.03	± 0.10

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Table 9. CHN experimental data of high Carbon content standards.

Run	Standard	Nitrogen		Carbon		Hydrogen	
		%	RSD%	%	RSD%	%	RSD%
1	Tocopherol Nicotinate	2.63	0.78	78.59	0.04	9.92	0.20
2		2.67		78.54		9.96	
3		2.66		78.53		9.94	
4	Polyethylene	N/A	N/A	92.12	0.01	7.77	0.42
5		N/A		92.12		7.76	
6		N/A		92.11		7.71	
7	Polystyrene	N/A	N/A	85.98	0.19	14.38	0.08
8		N/A		85.67		14.38	
9		N/A		85.73		14.40	
10	Antracene	N/A	N/A	94.22	0.16	5.60	0.21
11		N/A		94.44		5.62	
12		N/A		94.51		5.62	
13	Fluorene	N/A	N/A	93.87	0.15	6.04	0.10
14		N/A		93.79		6.04	
15		N/A		93.59		6.04	

Conclusion

The Thermo Scientific Flash*Smart* Elemental Analyzer is the optimal solution for the analysis of CHNS/O in terms of accuracy, reproducibility, automation, speed of analysis and cost per analysis. All data presented were obtained with an acceptable repeatability and no matrix effect was observed when changing the configuration.

The MultiValve Control (MVC) Module performs the following functions:

- Automated or manual control of two MAS Plus Autosamplers.

- Automated switch from the left channel to the right channel, or vice versa.

- Reduced helium (or argon) consumption by switching from helium (or argon) to nitrogen or argon when the system is in Stand-By Mode.

- Optionally insert through the Eager*Smart* Data Handling Software an external command, for example an actuator for a gas sampling valve.

- Auto-Ready: return automatically to helium carrier gas from Stand-By Mode and prepare for analysis.

The dual analytical configuration capability using the MVC Module allows you to:

- Automatically and rapidly switch from one configuration to another, increasing laboratory productivity.

- Gain continuous operation of the system by using one reactor for CHNS on the left furnace and one reactor on the right furnace.

- Fully control the workflow by the Eager*Smart* Data Handling Software.

The all-in-one Flash*Smart* Analyzer hardware, autosamplers and software can be used for other combinations such CHN/O, CHN/S, CHNS/CHNS, CHN/CHN, NC/S, N-Protein, etc. This can be achieved by only changing the consumables as the hardware and software are complete, illustrating the all-in-one nature of the Analyzer.

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

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