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TECHNICAL NOTE 42286

Elemental Analysis: Fully automated double channel analysis for CHNS determination by TCD Detector and trace sulfur by FPD Detector

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CHNS, Combustion, Elemental Analysis, MVC Module, Trace Sulfur

Goal

To demonstrate the performance of the all-in-one Thermo Scientific Flash*Smart* Elemental Analyzer for CHNS determination by TCD Detector and trace sulfur by FPD Detector.

Introduction

Carbon, nitrogen, hydrogen, sulfur analysis by combustion is commonly used for the characterization of raw and final products of any 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: for example accuracy, reproducibility, and high sample throughput. The Flash*Smart* 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 accept its own autosampler.

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

Figure 2. Thermo Scientific MultiValve Control (MVC) Module.

The Flash*Smart* EA performs also trace sulfur determinations, when it is coupled with the Flame Photometric Detector (FPD). This configuration combines the advantages of the elemental analyzer with the sensitivity and robustness of the FPD Detector. The Flash*Smart* Elemental Analyzer can be configured for CHNS determination (performed on the furnace on the left) with the TCD Detector and for trace sulfur analysis (performed on the furnace on the right) with the FPD Detector.

By switching from helium to nitrogen or argon, the proprietary MVC Module allows to manage and reduce helium carrier gas consumption and consequently operational costs, when the instrument is in Stand-By Mode.

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 samples are detected by the TCD Detector. Total run time is less than 10 minutes (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 FPD Detector. Total run time is less than 5 minutes (Figure 3).

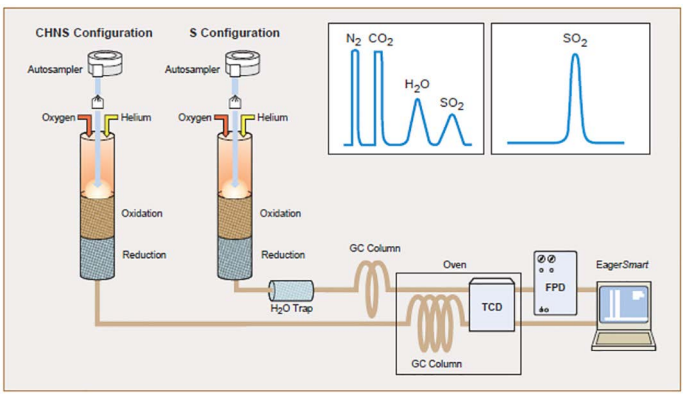

Figure 3. CHNS and trace sulfur configuration.

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

Both pneumatic circuits for CHNS by TCD Detector and trace sulfur determination by FPD Detector are preset in the system. The MVC Module allows the switch from one circuit to the other. The dedicated Eager*Smart* Data Handling Software controls the MVC Module and does not require manual intervention on the configuration.

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

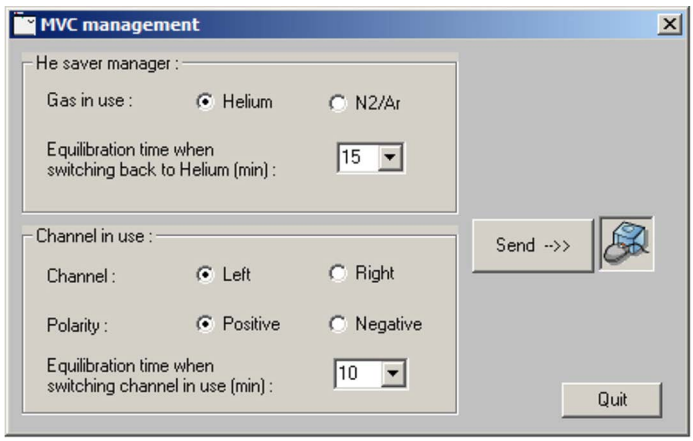

Figure 4. Eager*Smart* Data Handling Software MVC Module Management window.

Results

Typical analytical tests were performed for CHNS and trace sulfur configuration during one day. The repeatability, accuracy and the stability of the system were evaluated, when the configuration is switched from CHNS to trace sulfur and vice versa. The results obtained were compared with the theoretical values and the acceptable range, according to the technical specification of the system. At the end of the day, the Flash*Smart* EA was set in Stand-By Mode to reduce the consumption of helium. The Auto-Ready function is also activated via the Eager*Smart* Data Handling Software, in order to start 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 0.5–2.0 mg Thermo Scientific Pasta Reference Material using Quadratic Fit as the calibration method. Sulfanilamide for CHNS and Pasta for sulfur analysis were analyzed as unknown without recalibration of the instrument, in four series and in triplicate each series.

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

Table 1 shows CHNS analysis 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% (0.2). For Pasta Reference Material the value is 0.136 S% (±0.004).

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

To evaluate the performance of the Analyzer using both detectors, several samples in a large range of concentration were analyzed. The standard used for calibration depends on the matrix analyzed. Samples were analyzed in both configurations for the comparison of the results. The liquid reference solutions (mix of lubricant in iso-octane) were weighed in hard tin containers. Table 2 shows the expected data and the acceptable range (±) of the reference materials analyzed.

Table 3 shows the type and weight of standard used and the samples analyzed. Table 4 shows the CHNS and sulfur data of the same matrices analyzed in both configurations. Table 5 shows the CHNS of different matrices analyzed by TCD Detector while Table 6 shows the sulfur data of different matrices analyzed by FPD Detector.

Table 2. Expected data of Reference Materials.

Reference Material	N%	±	C%	±	H%	±	S%	±
Thermo Scientific Pasta	-	-	-	-	-	-	0.136	0.004
Thermo Scientific Soil	0.210	0.010	2.29	0.07	-	-	0.0230	0.004
Medium Organic Soil	0.133	0.023	1.61	0.09	-	-	0.0140	0.002
Soil Wepal	-	-	-	-	-	-	0.0033	-
Sulfur Powder	-	-	-	-	-	-	99.98	0.30
Ammonium sulfate	21.14	0.20	-	-	6.10	0.10	24.27	0.23
Reference Liquid Solution A	-	-	-	-	-	-	0.0010	0.0002
Reference Liquid Solution B	-	-	-	-	-	-	0.0005	0.0001

Table 3. Standards, reference materials and samples analyzed.

CHNS by TCD Detector (Left Reactor)				S by FPD Detector (Right Reactor)			
Standard for Calibration		Sample Analyzed as Unknown		Standard for Calibration		Sample Analyzed as Unknown	
Name	Weight (mg)	Matrix	Weight (mg)	Name	Weight (mg)	Matrix	Weight (mg)
BBOT*	2–2.5	TS Pasta	3–4	TS Pasta Ref. Mat.	0.5–2.5	TS Pasta Ref. Mat.	1–2
		Ref. Mat.	10–15	Medium Organic Soil Ref. Mat.	0.2–2	TS Soil Ref. Mat	1–2
		TS Soil Ref. Mat.	20–22			Medium Organic Soil Ref. Mat.	1–2
		Catalyst A	9–10			Catalyst A	0.2–0.3
Cystine	2.8–3	Medium Organic Soil Ref. Mat.	0.4–0.5	Soil Wepal***	0.2–1.5	Ref. Liquid Solution A	2–4
Cystine and CEDFNI**	1	Catalyst A	1–1.2			Ref. Liquid Solution B	3–5

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

** CEDFNI: cyclohexanone-2,4-dinitrophenylhydrazone

** WEPAL: Wageningen Evaluating Programs for Analytical Laboratories, Wageningen University, Netherlands

Table 4. CHNS and sulfur analysis 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%
Thermo Scientific Pasta Ref. Mat.	2.14 2.14	0.00	41.17 41.23	0.10	6.49 6.57	0.87	0.134 0.135	0.53	0.137 0.136	0.52
Thermo Scientific Soil Ref. Mat.	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
Medium Organic Soil Ref. Mat.	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 5. CHNS analysis of different matrices analyzed by TCD Detector.

Sample Name	N%	RSD%	C%	RSD%	H%	RSD%	S%	RSD%
Ammonium Sulfate	21.25 21.20 21.25	0.14	-	-	6.09 6.08 6.10	0.16	24.19 24.25 24.27	0.017
Sulfur Powder	-	-	-	-	-	-	99.83 99.98 99.99	0.09

Table 6. Sulfur analysis data of different matrices analyzed by FPD Detector.

Sample Name	S%	RSD%
Reference Liquid Solution A	0.00101 0.00106 0.00103 0.00100 0.00105	2.47
Reference Liquid Solution B	0.00054 0.00051 0.00053 0.00050 0.00051 0.00053 0.00051 0.00056 0.00054 0.00052	3.51

Different matrices were analyzed using CHNS and trace sulfur to show that the configuration can be used for different application fields and that results are repeatable when the sulfur cannot be determined by TCD Detector. Table 7 shows the standard used and the sample matrices analyzed for both configurations with relative weight. Table 8 shows the CHN data obtained by TCD Detector and the sulfur data obtained by FPD Detector. The data obtained show repeatability without matrix effect indicating complete combustion of the samples and proper quantification of the elements.

Table 7. Standards and samples matrices analyzed.

CHNS by TCD Detector (Left Reactor)				S by FPD Detector (Right Reactor)			
Standard for Calibration		Sample Analyzed as Unknown		Standard for Calibration		Sample Analyzed as Unknown	
Name	Weight (mg)	Matrix	Weight (mg)	Name	Weight (mg)	Matrix	Weight (mg)
BBOT	2–2.5	Soil Wepal	15–20	Medium Organic Soil Ref. Mat.	0.2–2	Soil Wepal	3–5
		Catalyst B	9–10			Catalyst B	1–3
BBOT	2.8–3	Graphene	1.5–2			Graphene	1–2
		Carbon fiber	2–2.5			Carbon fiber	0.6–0.7

Table 8. 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 Wepal	0.0227 0.0225	0.62	0.292 0.295	0.72	0.175 0.173	0.81	0.0034 0.0033	2.11
Catalyst B	-	-	3.70 3.70	0.00	0.66 0.65	1.08	0.0041 0.0042	1.70
Graphene	0.0367 0.0363	0.77	99.71 99.62	0.06	-	-	0.0050 0.0049	1.43
Carbon Fiber	0.0667 0.0670	0.32	98.65 98.59	0.04	-	-	0.0031 0.0029	4.71

Conclusion

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 Flash*Smart* Analyzer. The results fall within the expected range.

Data were obtained with an acceptable repeatability and no matrix effect was observed when changing the configuration according to the instrument specifications. The 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.

If maintenance is needed, it can be performed easily, considering that only a reactor is for CHNS and the other is for trace sulfur determination.

No differences in percent was observed switching from CHNS to S determination or changing sample matrix indicating:

- 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 matrix types.

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

- Automated switching from left to right channel, or vice versa.
- Automatically and rapidly switch from one configuration to another.
- Reduced helium (or argon) consumption by switching from helium (or argon) to nitrogen or argon, when the system is in Stand-By Mode.

The same system, hardware, autosamplers, and software can be used for other combinations such as CHN/O, CHN/S, CHNS/CHNS, CHN/CHN, NC/S, N-Protein/S, etc., using consumables upgrade kits.

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