APPLICATION NOTE

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Thermo Scientific Flash*Smart* Elemental Analyzer: Fully Automated Double Channel Analysis for Petrochemical Applications

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Key Words
Accuracy, Automation, CHNS, CO_2 Emission Trade Factor, Flash Combustion, Heat Values, Oxygen, Petrochemistry, Pyrolysis, Unattended Analysis

Goal

To demonstrate the performance of the Thermo Scientific Flash*Smart* Elemental Analyzer in petrochemical applications.

Introduction

Elemental analysis is an important technique in petroleum chemistry. Using an automated analyzer, rapid and accurate weight percentage carbon, nitrogen, hydrogen, sulfur, and oxygen (CHNS/O) data can be obtained together with the relative heat value calculation to ascertain the quality needed for better engine performance and to help with the identification of vehicle exhaust constituents, harmful and hazardous to the environment. Specifications and legislative limitations on hazardous and toxic pollutants from vehicle emissions have been introduced due to increasing atmospheric pollution.

Figure 1. Thermo Scientific Flash*Smart* Analyzer.

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

Each analytical circuit can accept its own autosampler and be configured and automatically switch between the independent analytical setups to increase sample throughput and maximize system up-time. In this way, the system copes effortlessly with the wide array of laboratory requirements such as accuracy, day to day reproducibility, and high sample throughput. The MVC Module also ensures lower helium consumption (used as carrier gas) by switching from helium to nitrogen or argon gas, when the instrument is in Stand-By Mode. Therefore, the cost of analysis is significantly lower.

Figure 2. Thermo Scientific MultiValve Control 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) 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).

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).

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 s for CHNS
Sample Delay	12 s for CHNS 0 s for Oxygen
Total Run Time	Less than 600 s for CHNS Less than 300 s for Oxygen

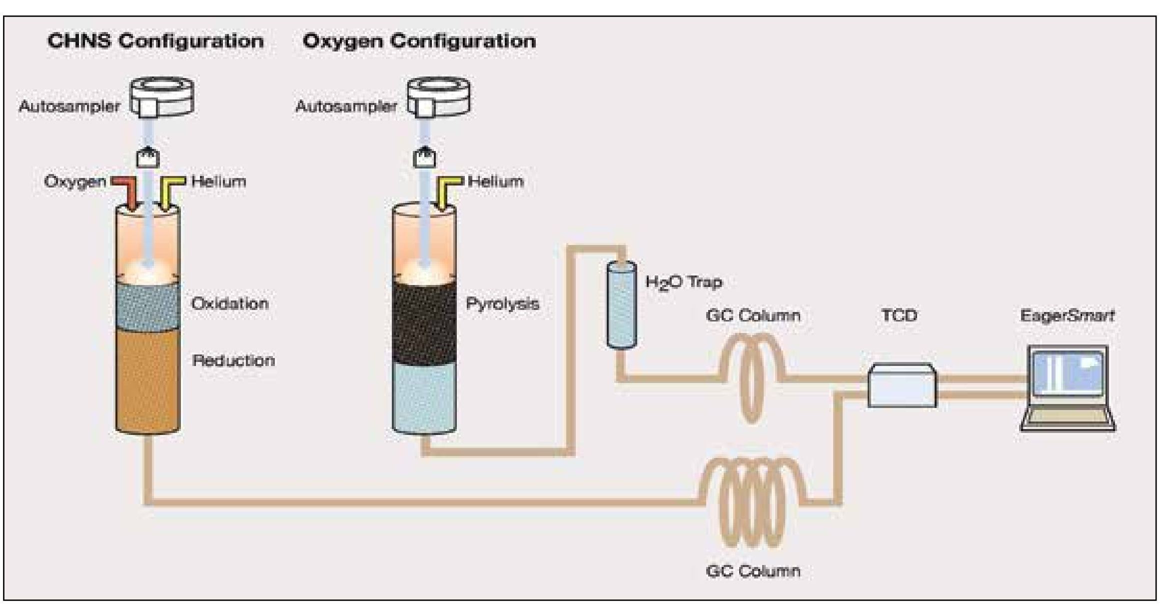

Figure 3. CHNS/O configuration of the Flash*Smart* EA.

A complete report is automatically generated by the Thermo Scientific™ Eager*Smart*™ Data Handling Software and displayed at the end of the analysis. The Eager*Smart* Data Handling Software allows the automatic calculation of both GHV and NHV heat values (Gross Heat Value and Net Heat Value, both expressed in kcal/kg), and the CO_2 Emission Trade data.

The pneumatic circuits for CHNS and oxygen determination are setup 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.

The Eager*Smart* Data Handling Software page, which controls the MVC Module (Figure 4), shows in the lower panel 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.

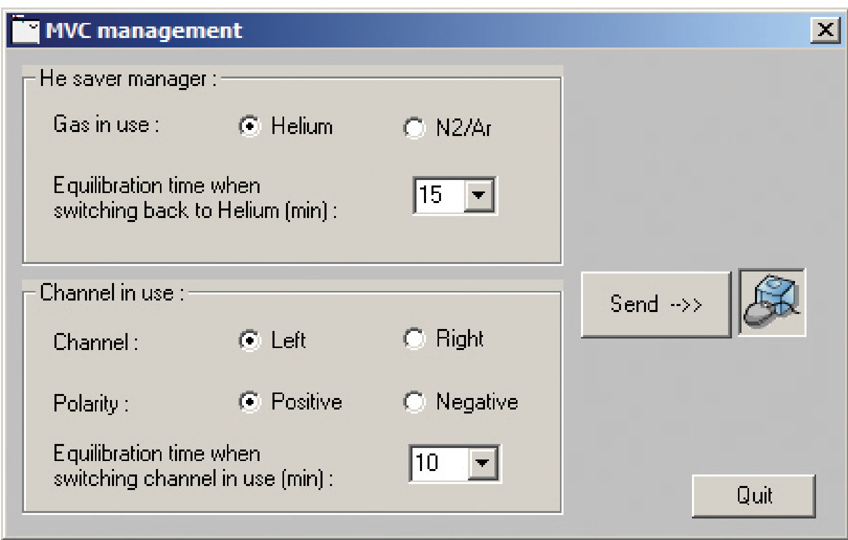

Figure 4. Eager*Smart* Data Handling Software: the MVC management page.

Results

Several petrochemical samples with different concentrations were chosen to evaluate the repeatability and accuracy of the instrument when the configuration is switched automatically from CHNS to oxygen and vice versa through the MVC Module. After each series of CHNS, the instrument is switched to oxygen determination to perform analysis and after completion, the system returns to CHNS determination. The switching from one configuration to the other was performed to evaluate the data and the stability of the system. The system was stable and ready for analysis in only ten minutes after the MVC Module switched between CHNS and O reactors. All data are accurate and precise and demonstrate that there is no effect caused by the change of configuration from combustion to pyrolysis, or vice versa. This highlights the modularity, automation, and stability of the Flash*Smart* Analyzer. At the end of every day, the instrument is set to Stand-By Mode to reduce helium consumption.

The Auto-Ready Function is also activated through the Eager*Smart* Data Handling Software for the automated wake-up of the system to ready condition for the following morning.

Table 1 shows the CHNS/O results obtained on coal samples, which were analyzed in duplicate, alongside the GHV and NHV heat values (Gross Heat Value and Net Heat Value, both expressed in kcal/kg), and the CO_2 Emission Trade data. Solid samples were homogenized by a ball mill.

For CHNS, the system was calibrated with 2–3 mg of BBOT* standard using K factor as the calibration method while the sample weight was 2–3 mg. For oxygen determination, 1–2 mg of BBOT was analyzed as standard using K factor as the calibration method while the sample weight was 1–2 mg.

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

Table 1. Coal samples: CHNS/O, Heat Values and CO_2 Emission Trade Data.

Sample	Statistic	N %	C %	H %	S %	O %	GHV	NHV	CO_2 E.T.
1	Data	1.81	87.93	3.78	4.15	1.10	8566.25	8372.82	91.97
		1.80	87.98	3.77	4.16	1.11	8565.78	8372.34	91.97
	Std. Dev.	0.007	0.035	0.007	0.007	0.007	0.332	0.340	0.000
	RSD %	0.39	0.04	0.19	0.17	0.64	0.01	0.00	0.00
2	Data	1.07	81.96	4.18	0.36	3.42	8020.87	7806.91	91.95
		1.06	82.04	4.16	0.37	3.41	8021.07	7807.11	91.95
	Std. Dev.	0.007	0.056	0.014	0.007	0.007	0.141	0.141	0.000
	RSD %	0.66	0.07	0.34	1.94	0.21	0.00	0.00	0.00
3	Data	0.99	80.12	4.34	0.32	5.33	7837.23	7615.06	92.10
		1.01	80.10	4.31	0.31	5.31	7837.89	7615.71	92.09
	Std. Dev.	0.014	0.014	0.021	0.007	0.014	0.467	0.460	0.007
	RSD %	1.41	0.02	0.49	2.24	0.27	0.01	0.01	0.01
4	Data	1.72	77.49	4.27	0.54	3.81	7671.76	7453.18	91.05
		1.71	77.56	4.25	0.54	3.78	7673.16	7454.58	91.04
	Std. Dev.	0.007	0.049	0.014	0.000	0.021	0.990	0.990	0.007
	RSD %	0.41	0.06	0.33	0.00	0.56	0.02	0.01	0.01
5	Data	0.77	65.41	4.34	0.16	14.95	6215.57	5992.37	95.46
		0.78	65.26	4.35	0.17	14.96	6215.19	5992.00	95.46
	Std. Dev.	0.007	0.106	0.007	0.007	0.007	0.269	0.262	0.000
	RSD %	0.91	0.16	0.16	4.28	0.05	0.00	0.00	0.00
6	Data	1.10	80.04	4.20	0.26	4.26	7827.76	7612.26	91.99
		1.11	79.93	4.21	0.27	4.25	7827.77	7612.27	91.99
	Std. Dev.	0.007	0.008	0.007	0.007	0.007	0.007	0.007	0.000
	RSD %	0.64	0.10	0.17	2.67	0.17	0.00	0.00	0.00

The performance of the Flash*Smart* Analyzer was evaluated by comparing the repeatability of the CHN data obtained from the coal samples analyzed in Table 1 with the ASTM D 5373 requirements (American Society for Testing Materials Official Method) shown in Table 2.

Table 2. Concentration range and limit of repeatability accepted by ASTM D 5373.

Element	Concentration Range %	Repeatability Limit (r)
Carbon	48.6 to 90.6	0.64
Hydrogen	0.14 to 5.16	0.16
Nitrogen	0.69 to 1.57	0.11

Repeatability Limit (r): The value below which the absolute difference between two test results calculated to a dry basis of separate and consecutive test determinations, carried out on the same sample, in the same laboratory, by the same operator, using the same apparatus.

The precision of the Flash*Smart* EA for CHN determination was demonstrated performing three series of the six coal samples analyzed in duplicate. The calibration of the system was performed with 2–3 mg of acetanilide.

The coal sample was weighted at 2–2.5 mg for sample A, while the other coal samples were weighted at 2.5–3 mg. Table 3 shows the CHN data obtained and the difference (Diff.) calculated between both data. All differences are less than the Repeatability Limit in the Official method, which indicates the complete combustion of the samples and the outstanding performance of the Flash*Smart* EA.

Table 3. CHN data of coal samples.

Series	Elem	Coal Samples											
		A		B		C		D		E		F	
		%	Diff.	%	Diff.	%	Diff.	%	Diff.	%	Diff.	%	Diff.
1	C	88.00 87.90	0.10	82.16 82.00	0.16	80.00 80.13	0.13	77.67 77.49	0.18	65.47 65.20	0.27	79.90 79.77	0.27
	H	3.77 3.73	0.04	4.17 4.15	0.02	4.37 4.38	0.01	4.27 4.23	0.04	4.38 4.35	0.03	4.23 4.24	0.01
	N	1.82 1.78	0.04	1.07 1.10	0.03	0.99 0.96	0.03	1.71 1.69	0.02	0.78 0.78	0.00	1.08 1.09	0.01
2	C	87.79 87.80	0.01	82.22 82.04	0.18	80.19 79.99	0.20	77.55 77.42	0.13	65.54 65.64	0.10	79.88 80.07	0.19
	H	3.75 3.73	0.02	4.16 4.11	0.05	4.39 4.34	0.05	4.29 4.26	0.03	4.33 4.33	0.00	4.20 4.20	0.00
	N	1.80 1.80	0.00	1.05 1.02	0.03	0.99 1.00	0.01	1.71 1.69	0.02	0.76 0.76	0.00	1.09 1.12	0.03
3	C	87.93 88.05	0.12	82.21 82.11	0.11	80.13 80.02	0.11	77.69 77.50	0.19	65.53 65.40	0.13	79.83 80.00	0.17
	H	3.71 3.67	0.04	4.13 4.12	0.01	4.38 4.39	0.01	4.26 4.26	0.00	4.37 4.38	0.01	4.28 4.19	0.09
	N	1.80 1.77	0.03	1.07 1.09	0.02	0.98 0.99	0.01	1.70 1.69	0.01	0.80 0.77	0.03	1.09 1.10	0.01

Table 4 shows the repeatability of CHNS/O determination of carbon black samples analyzed in duplicate, the GHV and NHV heat values (Gross Heat Value and Net Heat Value, both expressed in kcal/kg), and the CO_2 Emission Trade data calculated automatically by the Eager*Smart* Data Handling Software. For CHNS, the system was calibrated with 2–3 mg of BBOT standard using K factor as the calibration method while the sample weight was 2–2.5 mg. For oxygen determination, 1–2 mg of BBOT was analyzed as standard using K factor as the calibration method while the sample weight was 1–2 mg.

Table 5 shows the CHNS/O data of gas oil samples analyzed in triplicate, the GHV and NHV heat values (Gross Heat Value and Net Heat Value, both expressed in kcal/kg), and the CO_2 Emission Trade data calculated automatically by the Eager*Smart* Data Handling Software. For CHNS, the system was calibrated with 2–3 mg of BBOT standard using K factor as the calibration method while the sample weight was 2–2.5 mg. For oxygen determination, 1–2 mg of BBOT was analyzed as standard using K factor as the calibration method while the sample weight was 1–2 mg.

Table 4. Carbon black samples: CHNS/O, Heat Values and CO_2 Emission Trade data.

Sample	Statistic	N %	C %	H %	S %	O %	GHV	NHV	CO_2 E.T.
1	Data	0.185 0.186	96.880 96.964	0.291 0.299	0.854 0.866	1.168 1.161	8020.37 8020.67	8005.23 8005.53	105.99 105.99
	Std. Dev. RSD %	0.001 0.381	0.059 0.061	0.006 1.918	0.008 0.987	0.005 0.425	0.209 0.003	0.209 0.003	0.002 0.002
2	Data	0.229 0.230	96.271 95.971	0.344 0.346	1.017 1.020	1.610 1.610	7956.81 7956.82	7939.11 7939.12	105.99 105.99
	Std. Dev. RSD %	0.001 0.308	0.212 0.221	0.001 0.410	0.002 0.208	0.000 0.000	0.005 0.000	0.006 0.000	0.000 0.000
3	Data	0.150 0.149	97.213 97.113	0.281 0.285	1.264 1.253	0.617 0.621	8069.68 8069.49	8055.16 8054.97	105.59 105.60
	Std. Dev. RSD %	0.001 0.473	0.071 0.073	0.003 0.999	0.008 0.618	0.003 0.457	0.135 0.002	0.135 0.002	0.002 0.002

Table 5. Gas-oil samples: CHNS/O, Heat Values and CO_2 Emission Trade data.

Sample	Statistic	N %	C %	H %	S %	O %	GHV	NHV	CO_2 E.T.
1	Data	0.470 0.471 0.471	86.01 85.87 85.86	10.50 10.52 10.49	2.127 2.211 2.214	0.705 0.710 0.699	10222.78 10222.59 10222.99	9661.45 9661.26 9661.66	77.85 77.85 77.84
	Std. Dev. RSD %	0.001 0.12	0.084 0.10	0.015 0.15	0.049 2.26	0.006 0.782	0.200 0.002	0.200 0.002	0.006 0.007
2	Data	0.475 0.476 0.476	85.43 85.31 85.38	10.33 10.30 10.31	2.500 2.534 2.505	0.757 0.759 0.752	10127.79 10127.71 10127.98	9576.62 9576.54 9576.81	78.04 78.04 78.04
	Std. Dev. RSD %	0.001 0.12	0.060 0.07	0.015 0.15	0.018 0.73	0.004 0.477	0.139 0.001	0.138 0.001	0.000 0.000

Table 6 shows the CHNS/O data of biofuel samples analyzed in triplicate. For CHNS, the system was calibrated with 2–3 mg of BBOT standard using K factor as the calibration method while the sample weight was 2–3 mg.

For oxygen determination, 1–2 mg of BBOT was analyzed as standard using K factor as the calibration method while the sample weight was 1–2 mg.

Table 6. CHNS/O data of biofuel samples.

Sample	N %	RSD %	C %	RSD %	H %	RSD %	S %	RSD %	O %	RSD %
1	0.503 0.498 0.500	0.425	45.197 45.179 44.952	0.303	5.671 5.638 5.596	0.6631	0.032 0.032 0.033	1.590	37.525 37.458 37.580	0.162
2	1.330 1.337 1.361	1.196	42.985 43.017 42.815	0.252	5.934 5.967 5.938	0.3071	0.142 0.144 0.144	0.928	33.854 33.773 33.815	0.120
3	1.988 1.965 2.010	1.122	42.265 42.055 41.994	0.337	6.041 5.956 5.947	0.8696	0.224 0.217 0.223	1.688	34.123 34.244 34.198	0.179
4	1.974 1.934 1.995	1.507	50.641 50.529 50.651	0.134	5.161 5.111 5.199	0.8623	0.748 0.751 0.737	0.959	32.211 32.263 32.354	0.224

Table 7 shows the CHNS/O data of fuel samples analyzed in triplicate. For CHNS, the system was calibrated with 2–3 mg of BBOT standard using K factor as the calibration method while the sample was weighed at 2–3 mg.

For oxygen determination 1–2 mg of BBOT was analyzed as standard using K factor as the calibration method while sample was weighed at 1–2 mg.

Table 7. CHN/O data of fuel samples.

Sample	N %	RSD %	C %	RSD %	H %	RSD %	O %	RSD %
Fuel 1	0.149 0.151 0.150	0.667	86.610 86.396 86.025	0.370	11.174 11.201 11.143	0.260	2.023 2.013 1.976	1.236
Fuel 2	0.322 0.313 0.322	1.629	82.583 82.208 82.344	0.231	10.336 10.486 10.487	0.833	6.804 6.782 6.913	1.027
Fuel 3	0.307 0.292 0.322	4.886	84.924 85.187 84.959	0.168	11.971 12.067 11.906	0.676	2.642 2.658 2.683	0.777
Fuel 4	0.229 0.220 0.227	2.097	74.289 74.181 74.567	0.268	8.757 8.812 8.701	0.634	16.510 16.624 16.372	0.765
Bio-oil	0.123 0.123 0.123	0.934	38.790 38.677 38.793	0.171	8.036 8.070 7.989	0.506	49.946 50.167 49.971	0.244

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Conclusions

The Thermo Scientific Flash*Smart* Elemental Analyzer is the optimal solution for the analysis of CHNS/O in terms of accuracy, sensitivity, reproducibility, automation, speed of analysis and cost per analysis. All data shown were obtained with an acceptable repeatability and according to the ASTM D5373 method. No matrix effect was observed when changing the sample indicating complete combustion and demonstrating outstanding performance of the Analyzer.

The Flash*Smart* Analyzer allows CHNS determination in a single run. When switching the configuration through the MVC Module, automatic oxygen determination can be performed without any extra modules.

The MultiValve Control (MVC) Module allows the user to:

- Switch automatically from the left channel to the right channel, or vice-versa.
- Significantly reduce helium consumption by switching to nitrogen or argon when the instrument is in Stand-By Mode.
- Insert through the software an external command, for example an actuator for a gas sampling valve.

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 furnace on the left and one reactor on right furnace.
- Fully control by the Eager*Smart* Data Handling Software.

The same system, hardware, autosamplers, and software can be used for other combinations such CHN/O, CHN/S, CHNS/CHNS, CHN/CHN, NC/S, 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.

Through the dedicated Eager*Smart* Data Handling Software, the analyzer can be set up in Stand-By Mode at the end of the analysis, to reduce helium consumption and lower operational costs.

With the Auto-Ready Function, the user can activate the system to ready conditions for the next sequence of analyses in an unattended manner.

In addition to the ASTM D5373 Official Method mentioned in this application, the Flash*Smart* Analyzer also fulfills requirements of other Official Methods. The most relevant are shown in Table 8.

Table 8. Most relevant Official Methods.

Official Organization	Method
ASTM (American Society for Testing Materials)	**Method D 5373.** Standard test methods for Instrumental Determination of Carbon, Hydrogen and Nitrogen in Laboratory Samples of Coal and Coke.
ASTM (American Society for Testing Materials)	**Method D 5291.** Standard Test Methods for Instrumental Determination of Carbon, Hydrogen and Nitrogen in Petroleum Products and Lubricant.
ASTM (American Society for Testing Materials)	**Method D 5622.** Standard Test Methods for the determination of Total Oxygen in Gasoline and Methanol Fuels by Reductive Pyrolysis.
ISO/TS 12902, 2001	Solid mineral fuels – Determination of Total Carbon, Hydrogen and Nitrogen – Instrumental methods.
EN 15104, 2011	Solid biofuels - Determination of Total content of Carbon, Hydrogen and Nitrogen – Instrumental methods.
CEN / TC 343	Solid recovered fuels – Methods for the determination of Carbon, Hydrogen and Nitrogen content.

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