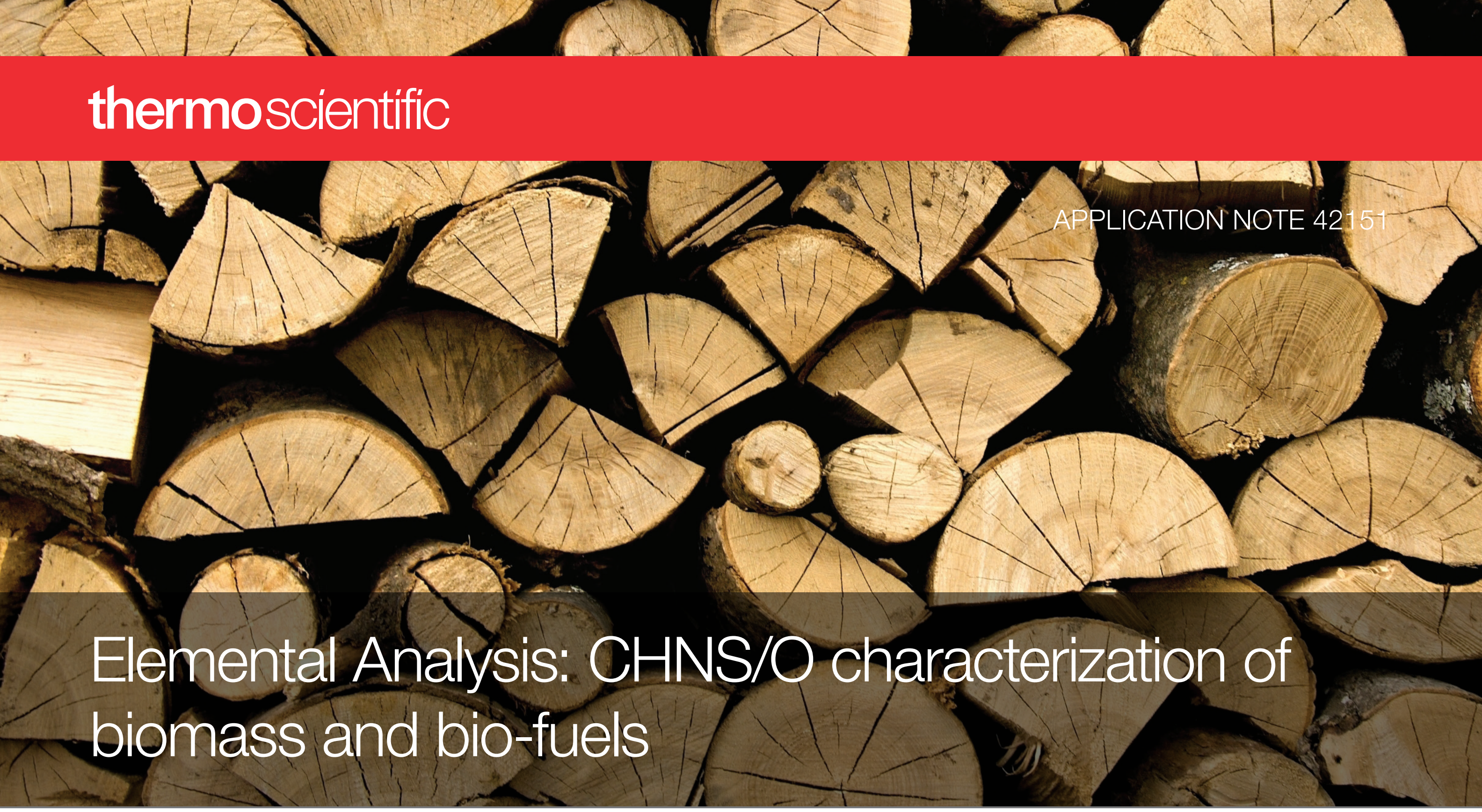

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APPLICATION NOTE 42151

Elemental Analysis: CHNS/O characterization of biomass and bio-fuels

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Goal
This application note reports data on CHNS/O determination of biomass and bio-fuels for quality control purposes, performed with the Flash*Smart* EA.

Introduction
Biomass fuels are derived from biological material rather than being the result of geological processes. The biological material takes carbon from the atmosphere and returns it when it is burnt. Biomass derives from burning crops, manure, garbage and most commonly, wood. Burning wood, for the production of energy has been common practice both domestically and industrially for heating and cooking, or to produce steam and electricity for industrial use.

Bio-fuels are an alternative to fossil fuels and are derived mainly from plants and animals, which do not increase the carbon dioxide level in the atmosphere. These alternative fuels are used globally, most commonly for automotive transport. Many manufacturing plants and research laboratories are involved in the characterization of these bio-fuel products to establish their viability for production, carbon dioxide emission levels, impact on water resources, energy balance and efficiency. A common method to characterize these materials is by identifying their energetic value via elemental composition.

As the demand for biomass and bio-fuels testing has grown in the last years, the classical analytical methods showed to be no longer suitable, for their time-consuming sample preparation and for their use of hazardous reagents. For this reason a simple and automated technique is the requirement for modern laboratories dealing with routine analysis.

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The Thermo Scientific™ Flash*Smart*™ Elemental Analysis (Figure 1), based on combustion method, allows the quantitative determination of the elements in a large range of concentration, without the need for sample digestion or toxic chemicals, providing advantages in terms of time and automation.

This method combines the advantages of the elemental analyzer with the sensitivity, selectivity and robustness of Flame Photometric Detector (FPD). The coupling is simple and it allows sulfur determination without any matrix effect.

The Thermo Scientific™ Eager*Smart*™ EA provides dedicated features for the automated calculation of the Heat Values and the CO_2 Emission Trade.

This note presents data on CHNS/O determination in biomass and bio-fuels samples to show the performance of the system and to show the reproducibility of the results obtained.

Figure 1. Flash*Smart* Elemental Analyzer.

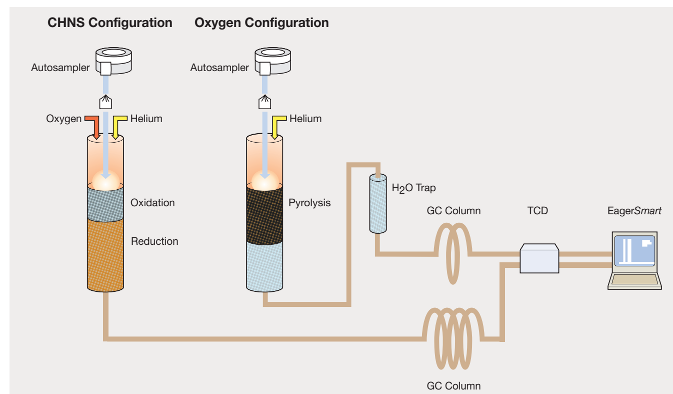

Figure 2. CHNS/O configuration.

Methods

For CHNS determination the Flash*Smart* Elemental Analyzer operates according to the dynamic flash combustion of the sample. Samples are weighed in tin containers and introduced into the combustion reactor 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 which provides the separation of the combustion gases, and finally, detected by a Thermal Conductivity Detector (TCD) (Figure 2). Total run time is less than 10 minutes.

For trace sulfur determination, the gases produced by combustion are carried by a helium flow to a layer filled with copper, then swept through a water trap, a short GC column and finally the sulfur is measured by the Flame Photometric Detector (FPD). Total run time 5 min. (Figure 3).

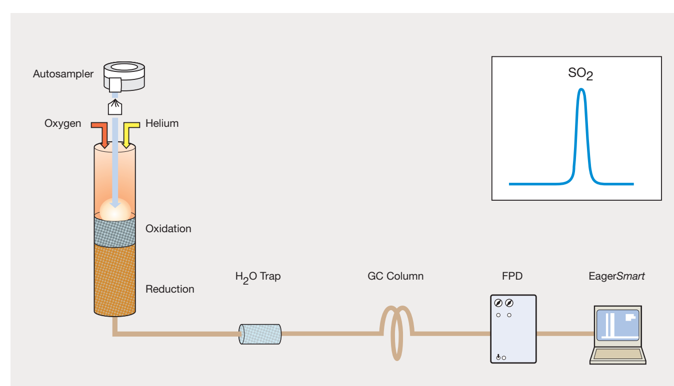

Figure 3. Sulfur configuration by FPD Detector.

For oxygen determination samples are weighed in silver containers and introduced into the pyrolysis chamber via the MAS Plus Autosampler. The reactor contains nickel coated carbon at a temperature of 1060 °C. The oxygen in the sample, combined with the carbon, forms carbon monoxide which is chromatographically separated from other products and detected by the TCD Detector (Figure 2).

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

Results

Different alternative fuels were chosen to show the performance obtained with the system.

The Flash*Smart* EA analyzer was calibrated by BBOT (2,5-Bis(5-ter-butyl-benzoxazol-2-yl)thiophene) standard for CHNS determination and by benzoic acid for oxygen determination. No matrix effect was observed when changing the nature of sample.

The Eager*Smart* Data Handling Software automatically calculates the GHV (Gross Heat Value in kcal/kg) and NHV (Net Heat Value in kcal/kg) using the modified Dulong equations, as well as the CO_2 Emission Trade.

Table 1 shows the CHNS data obtained from different biomass samples. Samples were homogenized by a ball mill.

Table 2 shows the CHNS/O of the vegetals used as biofuels while Table 3 indicates the relative Heat Values and the CO_2 Emission Trade calculated automatically by the software.

Table 1. CHNS determination in biomass samples.

Sample	N%	RSD%	C%	RSD%	H%	RSD%	S%	RSD%
Biomass 1	1.382 1.369 1.396	0.977	40.091 40.090 40.073	0.025	6.421 6.404 6.446	0.326	0.087 0.086 0.089	2.012
Biomass 2	1.187 1.181 1.215	1.499	39.999 40.193 39.764	0.537	5.598 5.574 5.644	0.634	0.112 0.111 0.112	0.259
Stray Pellets	0.5282 0.5160 0.5300	1.452	43.278 43.310 32.245	0.075	5.695 5.759 5.644	1.008	0.149 0.149 0.140	3.631
Sunflower Pellets	0.712 0.719 0.717	0.498	45.531 45.590 45.675	0.158	5.716 5.715 5.612	1.049	0.125 0.124 0.121	1.791

Table 2. CHNS/O determination in vegetals as biofuels.

Sample	N%	RSD%	C%	RSD%	H%	RSD%	S%	RSD%	0%	RSD%
1	5.521 5.790 5.861	3.133	47.119 47.276 47.485	0.388	6.010 5.821 5.959	1.649	0.265 0.277 0.278	2.647	34.311 34.045 34.306	0.444
2	3.534 3.528 3.706	2.816	46.467 46.489 46.600	0.153	5.876 5.946 5.926	0.609	0.182 0.176 0.186	2.776	37.183 37.421 37.199	0.357

Table 3. Heat Values and CO_2 Emission Trade calculation in vegetals as bio-fuels.

Sample	G.H.V.	RSD%	N.H.V.	RSD%	CO_2 e.t.	RSD%
1	4449 4461 4450	0.149	4145 4157 4145	0.167	99.883 88.608 99.877	0.157
2	4255 4245 4255	0.136	3952 3942 3951	0.139	103.056 103.323 103.073	0.145

Table 4 shows CHNS/O determinations of different wood samples while Table 5 includes the GHV (Gross Heat Value in kcal/kg), NHV (Net Heat Value in kcal/kg) and the CO_2 emission trade. The sample data in Table 5 were obtained using the average of the element percentages.

Table 4. CHNS/O analysis of wood samples.

Sample	N%	C%	H%	S%	0%
1	0.0649 0.0677 0.0666 0.0651 0.0664	45.7746 45.8869 46.1076 45.7568 45.8578	6.1044 6.2031 6.1345 6.1504 6.0941	0.0288 0.0274 0.0285 0.0275 0.0279	47.7422 42.7301 42.4861 42.5882 42.4200
Av	0.0661	45.8767	6.1373	0.0280	42.5933
RSD%	1.7463	0.3055	0.7035	2.1913	0.3370
2	0.0667 0.0662 0.0659 0.0630 0.0660	46.6378 47.0700 46.8560 46.8802 46.9996	5.9850 5.9247 5.9086 5.9816 6.0158	0.0246 0.0249 0.0260 0.0254 0.0259	42.4833 42.4623 42.6421 42.5727 42.3615
Av	0.0656	46.8887	5.9631	0.0254	42.5044
RSD%	2.2329	0.3525	0.7520	2.6259	0.2530
3	0.0882 0.0910 0.0895 0.0902 0.0890	47.1092 47.0881 47.1071 47.0995 47.1042	6.1197 6.1050 6.1088 6.1115 6.1065	0.0312 0.0324 0.0315 0.0331 0.0319	43.2662 43.1915 43.1879 43.3391 43.2539
Av	0.0896	47.1016	6.1103	0.0320	43.2477
RSD%	1.2034	0.0178	0.0949	2.3516	0.1438

Table 5. Heat Values and CO_2 Emission Trade calculation in wood samples.

Sample	G.H.V. (kcal/kg)	N.H.V. (kcal/kg	CO_2 Emission Trade
1	4042	3728	108
2	4069	3763	109
3	4105	3792	109

Table 6 shows the sulfur data of wood samples obtained with the FPD Detector, where the sulfur content is at trace levels. Solid samples were weighed in tin containers with the addition of vanadium pentoxide. Instrument calibration was performed with a soil sample, of which the sulfur value (30 ppm) is the average from an International Round Robin Test (WEPAL, Wageningen Evaluating Programs for Analytical Laboratories, Wageningen University, Netherlands).

Table 6. Trace sulfur determination of wood samples by FPD Detector.

Sample	S ppm	Average S ppm	RSD%
A	36 35 37 37 34	36	3.64
B	44 41 42 42 42	42	2.60
C	52 54 52 55 53	53	2.45

Table 7 shows the CHN/O data of pyrolysis oils. Due to the low concentration of sulfur, determination was performed with the FPD Detector and calibration was performed with a Soil Reference Material (320 ppm). The Sulfur results obtained are shown ined Table 8.

Table 7. CHN/O determination in biomass pyrolysis oils.

Sample	N%	RSD%	C%	RSD%	H%	RSD%	O%	RSD%
1	0.0785 0.0774 0.0784	0.7788	42.1731 41.9498 42.1433	0.2881	7.4361 7.4751 7.4330	0.3150	46.9729 47.5645 47.0198	0.6969
2	0.0856 0.0830 0.0859	1.8799	46.5296 46.2804 46.6817	0.4357	6.9718 6.9984 6.9997	0.2253	43.5343 43.6605 43.4282	0.2671

Conclusions

For the CHNS/O determination in biomass and bio-fuels the Flash*Smart* Elemental Analyzer provides accurate and reproducible results.

Thanks to the dedicated features of the Eager*Smart* Data Handling Software, the Heat Values and the estimated CO_2 Emission Trade value are automatically provided.

The modularity of the Flash*Smart* Elemental Analyzer enables to perform CHNS determination in a single run, oxygen determination in a second run and TOC analysis without any modification of the analytical conditions, allowing high productivity for routine labs.

The Flash*Smart* Elemental Analyzer meets laboratory requirements in terms of automation and high sample throughput.

Table 8. Sulfur determination by FPD Detector in biomass pyrolysis oils.

Sample	S%	RSD%
1	0.0186 0.0189 0.0196	2.6961
2	0.0191 0.0185 0.0187	1.6279

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