Application note | 000604

Elemental analysis

Carbon dioxide emissions and heat values determination by Flash*Smart* Elemental Analyzer

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Keywords

CHNS, CO_2 emissions, Combustion, Heat Values, Oxygen

Goal

To assess the performance of the elemental analyzer for CHNS/O determination and automated calculation of the CO_2 emission and Heat Values.

Introduction

Greenhouse gases from industry and agriculture are playing a major role in the observed global warning, with carbon dioxide (CO_2) being the principal contributing greenhouse gas. There are both natural and human sources of carbon dioxide emissions. Natural sources include decomposition, ocean release and respiration. Human sources come from activities like cement production, deforestation as well as the burning of fossil fuels like coal, oil and natural gas. As we are globally taking responsibility to lower or limit carbon dioxide emissions, it is important to be able to reliably estimate the CO_2 emission factor in material through the heat calorific values released during the combustion of it which is based on the determination of the percentage of carbon, hydrogen, sulfur, and oxygen.

The Thermo Scientific™ Flash*Smart*™ Elemental Analyzer allows the quantitative determination of carbon, nitrogen, hydrogen and sulfur by combustion, and the oxygen by pyrolysis, while the dedicated Eager*Smart* Data Handling Software permits automatic gross and net heat values calculation and the relative CO_2 emission factor.

Methods

The Flash*Smart* Elemental Analyzer (Fig. 1) is equipped with two totally independent furnaces allowing the installation of two analytical circuits (Fig. 2) that can be used sequentially and are completely automated through the Thermo Scientific™ MultiValve Control™ (MVC) Module. Each analytical circuit has its own autosampler. In this way the system copes effortlessly with the laboratory requirements such as modularity and high sample throughput. In addition, the MVC module allows switching from helium carrier gas to nitrogen or argon gas when the instrument is not in use for reducing the cost of ownership.

Figure 1. Thermo Scientific Flash*Smart* Elemental Analyzer

Results

Different sample matrices were chosen to evaluate the performance obtained with the system for CHNS/O analysis and the automatic calculation of the heat values and CO2 emission factor. The samples were homogenized using a rotor speed mill and/or a ball mill.

Two types of solid samples from petrochemistry with high content of carbon were selected. BBOT 2,5-Bis-(5-tert-butyl-benzoxazol-2-yl)-thiophen was used as standard to calibrate the system and 2-3 mg of samples were analyzed. Table 1 shows the data obtained from carbon black and coal samples.

Three types of liquid and viscous samples from petrochemistry were analyzed. BBOT (2 - 3 mg) was used as standard to calibrate the system for CHNS analysis and BBOT and benzoic acid were used as standards for oxygen determination. Gasoil, bio-oil and diesel samples weight was 2-3 mg, table 2 shows the data obtained.

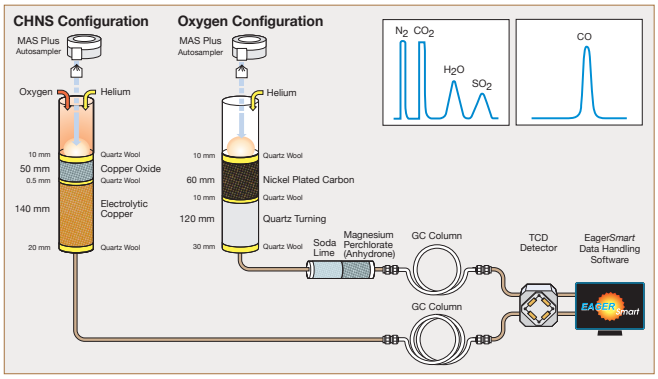

Figure 2. Flash*Smart* CHNS/O configuration

Table 1. CHNS/O, Gross Heat Values (GHV), Net Heat Values (NHV) and CO_2 Emission Trade (E.T.) data of carbon black and coal samples

Sample	Statistic	N%	C%	H%	S%	O%	GHV (kcal/kg)	NHV (kcal/kg)	CO_2 E.T.
Carbon black	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
	RSD%	**0.473**	**0.073**	**0.999**	**0.618**	**0.457**	**0.002**	**0.002**	**0.002**
Coal 1	Data	1.81 1.80	87.93 87.98	3.78 3.77	4.15 4.16	1.10 1.11	8566.25 8565.78	8372.82 8372.34	91.97 91.97
	RSD%	**0.39**	**0.04**	**0.19**	**0.17**	**0.64**	**0.01**	**0.00**	**0.00**
Coal 2	Data	1.07 1.06	81.96 82.04	4.18 4.16	0.36 0.37	3.42 3.41	8020.87 8021.07	7806.91 7807.11	91.95 91.95
	RSD%	**0.66**	**0.07**	**0.34**	**1.94**	**0.21**	**0.00**	**0.00**	**0.00**

Finally, other matrices such as biomass, wood, saw dust, compost and waste materials were chosen with different element content. BBOT (2 - 3 mg) was used as standard to calibrate the system for CHNS analysis and benzoic acid or aspartic acid were used as standards for oxygen determination.

Table 3 shows the data obtained for vegetal used as biomass, wood and saw dust; samples weight was 2 – 4 mg for CHNS and about 1 mg for oxygen determination.

Table 4 shows the data of compost samples; the sample weight was 3 – 4 mg for CHNS analysis and for oxygen determination about 0.5 – 1 mg.

Table 2. CHNS/O, Gross Heat Values (GHV), Net Heat Values (NHV) and CO_2 Emission Trade (E.T.) data of gasoil, bio-oil and diesel samples

Sample	Statistic	N%	C%	H%	S%	O%	GHV (kcal/kg)	NHV (kcal/kg)	CO_2 E.T.
Gasoil	Data	0.475	85.43	10.33	2.500	0.757	10127.79	9576.62	78.04
		0.476	85.31	10.30	2.534	0.759	10127.71	9576.54	78.04
		0.476	85.38	10.31	2.505	0.752	10127.98	9576.81	78.04
	RSD%	**0.12**	**0.07**	**0.15**	**0.73**	**0.477**	**0.001**	**0.001**	**0.001**
Bio-oil	Data	0.0665	64.28	6.79	1.37	24.94	6402.69	6040.77	93.19
		0.0672	64.22	6.75	1.39	25.06	6398.34	6036.42	93.25
		0.0659	64.39	6.78	1.37	24.97	6401.65	6039.72	93.20
	RSD%	**0.98**	**0.13**	**0.31**	**0.84**	**0.25**	**0.05**	**0.04**	**0.03**
Diesel	Data	0.105	85.51	12.84		0.421	10845.17	10159.28	73.69
		0.104	85.58	12.82	-	0.426	10844.98	10159.08	73.69
		0.103	85.44	12.82		0.424	10845.06	10159.17	73.69
	RSD%	**0.59**	**0.08**	**0.09**	**-**	**0.59**	**0.00**	**0.00**	**0.00**

Table 3. CHNS/O, Gross Heat Values (GHV), Net Heat Values (NHV) and CO_2 Emission Trade (E.T.) data of vegetal as biomass, wood and saw dust samples

Sample	Statistic	N%	C%	H%	S%	O%	GHV (kcal/kg)	NHV (kcal/kg)	CO_2 E.T.
Biomass	Data	3.53	46.47	5.88	0.182	37.18	4255	3952	103.06
		3.53	46.49	5.95	0.176	37.42	4245	3942	103.32
		3.71	46.60	5.93	0.186	37.20	4255	3951	103.07
	RSD%	**2.82**	**0.15**	**0.61**	**2.78**	**0.36**	**0.14**	**0.14**	**0.14**
Wood	Data	0.0882	47.11	6.12	0.0312	43.27	4108.47	3794.45	109.09
		0.0910	47.09	6.10	0.0324	43.19	4103.42	3790.43	108.96
		0.0895	47.11	6.11	0.0315	43.19	4108.48	3794.97	109.09
		0.0902	47.10	6.11	0.0331	43.34	4101.25	3787.74	108.90
		0.0890	47.10	6.11	0.0319	43.25	4105.09	3791.58	109.00
	RSD%	**1.20**	**0.02**	**0.09**	**2.35**	**0.14**	**0.08**	**0.08**	**0.08**
Saw dust	Data	0.0734	48.02	6.14		44.39	4134.47	3819.43	109.88
		0.0725	47.89	6.16	-	44.54	4128.01	3812.96	110.07
		0.0722	47.92	6.13		44.45	4131.97	3816.92	109.96
	RSD%	**0.86**	**0.14**	**0.25**	**-**	**0.17**	**0.08**	**0.09**	**0.09**

Table 4. CHNS/O, Gross Heat Values (GHV), Net Heat Values (NHV) and CO_2 Emission Trade (E.T.) data of compost samples

Sample	Statistic	N%	C%	H%	S%	O%	GHV (kcal/kg)	NHV (kcal/kg)	CO_2 E.T.
Compost	Data	2.14	22.17	2.65	1.47	23.08	1778.3	1641.8	118.3
		2.15	22.24	2.67	1.46	23.12	1776.3	1639.8	118.4
		2.13	22.13	2.66	1.45	23.10	1777.3	1640.8	118.3
	RSD%	**0.47**	**0.38**	**0.38**	**0.68**	**0.09**	**0.06**	**0.06**	**0.06**

Table 5 show the data obtained for waste materials. Multiple repetitions were made to demonstrate that low sample amounts did not have influence on data quality for homogenized samples.

Table 5. CHNS/O, Gross Heat Values (GHV), Net Heat Values (NHV) and CO_2 Emission Trade (E.T.) data of waste materials samples

Sample	Statistic	N%	C%	H%	S%	O%	GHV (kcal/kg)	NHV (kcal/kg)	CO_2 E.T.
Dust from rubber and plastics for power/heat production	Data	0.883	32.00	4.20	0.354	24.17	2998.1	2785.2	99.7
		0.878	31.76	4.12	0.366	23.94	3008.1	2795.2	99.3
		0.897	31.76	4.11	0.374	23.99	3006.2	2793.3	99.4
		0.896	31.84	4.22	0.370	23.91	3009.4	2796.5	99.3
		0.878	31.47	4.10	0.362	23.89	3010.5	2797.6	99.3
		0.890	31.62	4.07	0.340	24.22	2996.0	2783.0	99.8
		0.909	31.68	4.18	0.367	24.12	3000.6	2787.7	99.6
		0.903	31.66	4.13	0.337	23.91	3009.6	2796.7	99.3
		0.877	31.64	4.17	0.353	24.06	3003.2	2790.2	99.5
		0.908	31.79	4.16	0.361	24.19	2997.5	2784.6	99.7
	RSD%	**1.40**	**0.45**	**1.15**	**2.45**	**0.53**	**0.19**	**0.20**	**0.20**
Plastics, paper, dust and wood	Data	0.790	44.28	5.44	0.158	26.71	4370.6	4092.5	95.2
		0.789	44.63	5.46	0.157	27.24	4347.8	4069.7	95.8
		0.777	44.66	5.38	0.158	26.88	4363.4	4085.3	95.4
		0.795	44.61	5.40	0.146	27.08	4354.6	4076.5	95.6
		0.814	44.43	5.42	0.154	26.74	4369.0	4090.9	95.3
	RSD%	**1.70**	**0.36**	**0.58**	**3.29**	**0.84**	**0.22**	**0.24**	**0.24**

Conclusions

The Thermo Scientific Flash*Smart* Elemental Analyzer allows accurate and precise CHNS/O analysis and automated gross and net heat values calculation and the relative CO_2 emission factor calculation by dedicated Eager*Smart* Data Handling Software. All data presented were obtained with an acceptable repeatability and no matrix effect was observed when changing the configuration. The modularity of the Flash*Smart* Elemental Analyzer allows high productivity for routine labs and low cost per analysis through the MultiValve Control (MVC) Module supporting:

- Automated control of two Thermo Scientific™ MAS Plus Autosamplers
- Automated switch 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.
- Auto-Ready: return automatically to helium carrier gas from Stand-By Mode and prepare for analysis.

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