Petrochemical Compounds Characterization with the Thermo Scientific FLASH 2000 CHNS/O Elemental Analyzer

Poster Note 42239

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Overview

Purpose: Characterization of petrochemical compounds by Organic Elemental Analysis.

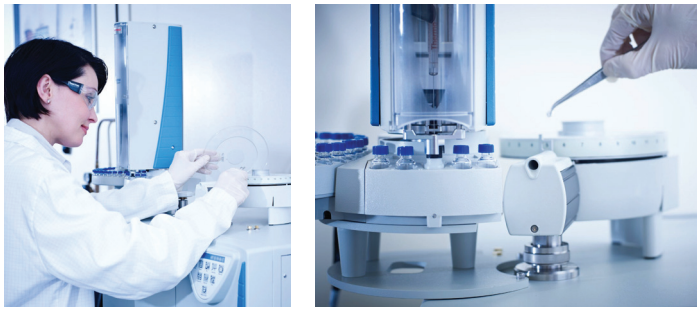
Methods: Samples were analyzed using an elemental analyzer with automated autosamplers.

Results: CHNS/O data are shown to demonstrate the performance of the FLASH 2000 Organic Elemental Analyzer.

Introduction

The Thermo Scientific™ FLASH 2000 Organic Elemental Analyzer (Figure 1), which is based on the dynamic combustion of the samples, provides quantitative and automated simultaneous CHNS determination and the oxygen determination by pyrolysis. Solid, viscous, liquid and gas samples can be analyzed without any matrix effect. From the CHNS/O data, the dedicated Thermo Scientific™ Eager Xperience Data Handling Software calculates automatically the GHV and NHV values (Gross Heat and Net Heat, both expressed in kcal/kg) and the CO_2 Emission Trade data.

FIGURE 1. Thermo Scientific FLASH 2000 with MAS 200R and AS 1310 Autosamplers.



Methods

For CHNS determination the 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 200R Autosampler or injected directly by a syringe through the Thermo Scientific™ AS 1310 Liquid Autosampler with the proper amount of oxygen. After combustion the resulted gases are carried by a helium flow to a layer filled with copper, then swept through a GC column, providing the separation of the combustion gases. Finally, they are detected by a thermal conductivity detector (TCD). Total run time is less than 10 min. (Figure 2).

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. Finally the sulfur is measured by the flame photometric detector (FPD). Total run time 5 min. (Figure 3).

For oxygen determination, the system operates in pyrolysis mode. Samples are weighed in silver containers and introduced into the pyrolysis chamber via the MAS 200R Autosampler or injected directly by a syringe through the AS 1310 Liquid Autosampler. The reactor contains nickel coated carbon at 1060°C. The oxygen present in the sample, combined with the carbon, forms carbon monoxide which is then chromatographically separated to other products and detected by the TCD detector (Figure 2).

A comprehensive report is automatically generated by the Eager Xperience Data Handling Software and displayed at the end of the analysis.

FIGURE 2. CHNS/O configuration

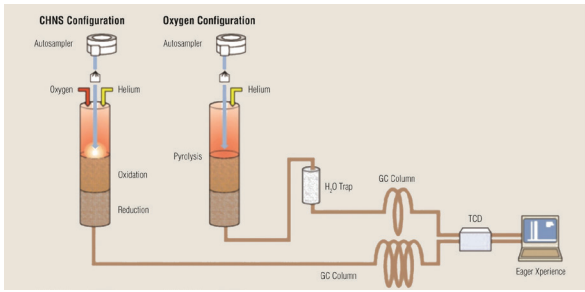
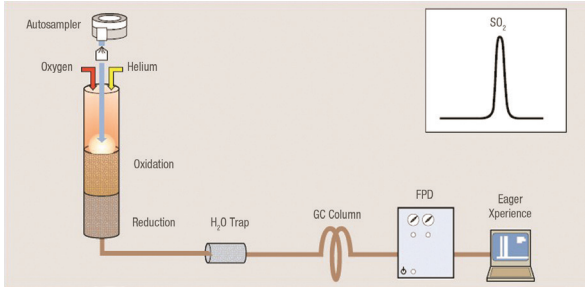


FIGURE 3. Sulfur configuration by FPD detector



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Results

Different solids, viscous and liquid petrochemical samples were chosen to show the reproducibility obtained with the system. Coal, coke, graphite, lignite and catalyst samples were homogenized by a ball mill while viscous and liquid samples were analyzed without pre-treatment.

Table 1 and 2 show CHNS/O and CHNS determination of different matrices. Instrument calibration was performed with 2-3 mg of BBOT (2, 5-Bis (5-ter-butyl-benzoxazol-2-yl) thiophene), while sample weight was 2 – 3 mg. No matrix effect was observed when changing the nature of sample. Table 1 indicates also the heat value GHV (Gross Heat Value in kcal/kg) and NHV (Net Heat Value in kcal/kg) calculated automatically by the Eager Xperience Data Handling Software.

TABLE 1. CHNS/O determination and Heat Value calculation of coal and lignite samples

Sample	N %	C %	H %	S %	O %	GHV	NHV
Coal	1.740 1.732 1.747	73.006 72.950 73.238	5.389 5.358 5.398	0.838 0.857 0.828	12.733 12.731 12.813	7316 7316 7313	7040 7040 7037
RSD%	0.431	0.209	0.390	1.752	0.367	0.024	0.025
Hard Coal	1.287 1.288 1.329	80.137 80.123 80.706	4.621 4.513 4.617	0.488 0.486 0.497	4.903 5.085 5.094	7957 7918 8003	7720 7687 7766
RSD%	1.842	0.414	1.336	1.195	2.144	0.535	0.514
Brown Coal	1.988 2.006 2.028	77.258 77.196 77.823	3.280 3.266 3.292	0.386 0.386 0.397	3.730 3.723 3.690	7313 7304 7364	7145 7136 7195
RSD%	0.998	0.446	0.397	1.630	0.575	0.442	0.444
Mineralized Lignite	0.275 0.273 0.274	16.512 16.480 16.553	2.487 2.476 2.469	0.222 0.226 0.223	13.036 13.046	1651 1651	1524 1524
RSD %	0.290	0.219	0.366	0.962	0.056	0.019	0.020
Lignite 1	0.758 0.750 0.757	62.281 62.357 62.240	4.636 4.544 4.377	0.377 0.373 0.371	25.202 25.540	5589 5574	5357 5343
RSD %	0.559	0.074	2.899	0.724	0.942	0.184	0.192

TABLE 2. CHNS determination of petrochemical samples

Sample	N%	RSD%	C%	RSD%	H%	RSD%	S%	RSD%
Pet coke	1.486 1.534	2.266	96.329 96.756	0.313	0.210 0.235	8.095	0.641 0.643	0.384
Coke 1	1.229 1.228	0.011	86.195 86.665	0.384	4.343 4.322	0.346	0.656 0.616	4.535
Coke 2	0.377 0.370 0.374 0.363 0.369	1.360	98.997 98.917 98.576 98.973 98.836	0.172	-	-	0.422 0.431 0.429 0.434 0.429	1.017
Catalyst	0.007 0.007 0.006	4.478	0.165 0.166 0.171	1.716	1.164 1.154 1.153	0.552	0.408 0.409 0.417	1.253
Crude oil	0.208 0.197 0.206	2.802	84.701 84.563 84.781	0.130	12.368 12.432 12.297	0.545	2.325 2.381 2.393	1.513

The performance of the FLASH 2000 OEA was evaluated by comparing the repeatability of the CHN data with the ASTM D5375 requirements showed in Table 3. The method covers the instrumental determination of nitrogen, carbon and hydrogen in coal and coke samples.

TABLE 3. Concentration Range and Limit of Repeatability accepted by ASTM D5375-02

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 2000 OEA for CHN determination was demonstrated performing two series of samples analyzed in duplicate. The calibration of the system was performed with 2-3 mg of acetanilide. Samples were weighted at 2-3 mg. Table 4 shows the CHN data obtained and the difference (Diff.) calculated between both data. All differences fall within or below the Repeatability Limit indicated in the official method, meaning the good homogeneity and the complete combustion of the samples.

TABLE 4. CHN data of coal and coke samples.

Serie	Elements	Coal 1		Coal 2		Coke	
		%	Diff.	%	%	%	Diff.
1	N	1.28 1.28	0	1.03 1.03	1.03 1.03	1.03 1.03	0
	C	86.12 86.59	0.47	87.47 87.61	87.47 87.61	87.47 87.61	0.09
	H	4.43 4.52	0.09	0.30 0.29	0.30 0.29	0.30 0.29	0.01
2	N	1.31 1.30	0.01	1.04 1.05	1.04 1.05	1.04 1.05	0.01
	C	86.81 86.20	0.61	87.00 87.46	87.00 87.46	87.00 87.46	0.46
	H	4.47 4.43	0.04	0.30 0.29	0.30 0.29	0.30 0.29	0.01

Table 5 shows the repeatability of CHNS/O determination carbon black samples while Table 6 shows the oxygen data and the heat values GHV and NHV (Gross Heat Value and Net Heat Value, both expressed in kcal/kg), and the CO_2 Emission Trade data calculated by the Eager Xperience Data Handling Software. For CHNS, the analyzer was calibrated with 2-3 mg of BBOT* standard using K factor as calibration method while the sample was weighted at 2-2.5 mg. For oxygen determination, 1-2 mg of BBOT was analyzed as standard using K factor while the sample was weighted at 1-2 mg.

TABLE 5. CHNS data of carbon black samples.

Sample	N %	RSD%	C %	RSD %	H %	RSD %	S %	RSD %
A	0.188 0.185 0.186 0.186	0.676	96.559 96.734 96.817 96.706	0.111	0.300 0.295 0.304 0.308	1.843	0.829 0.848 0.868 0.868	2.193
B	0.273 0.277 0.272 0.273	0.810	96.178 95.899 95.351 96.079	0.159	0.267 0.280 0.272 0.277	2.086	0.823 0.814 0.815 0.817	0.493

TABLE 6. Oxygen data, Heat values and CO_2 value of carbon black samples

Sample	O %	RSD%	GHV (kcal/kg)	RSD %	NHV (kcal/kg)	RSD %	CO_2 E.T.	RSD %
A	1.149 1.158 1.152	0.397	8005.53 8005.13 8005.42	0.003	7990.03 7989.63 7989.93	0.003	105.96 105.96 105.96	0.000
B	1.661 1.679 1.661	0.623	7915.43 7915.64 7915.44	0.006	7901.37 7900.58 7901.38	0.006	106.37 106.38 106.37	0.005

Table 7 shows the reproducibility of CH determination in diesel samples while Table 8 shows the reproducibility of oxygen determination of diesel samples, analyzed by automated liquid injection. The volume injected was 2 ul.

TABLE 7. Reproducibility of CH determination of diesel samples.

Sample	Diesel 1		Diesel 2		Diesel 3	
Element	C %	H %	C %	H %	C %	H %
%	85.34	14.32	84.67	15.37	86.45	13.87
	85.35	14.31	84.72	15.39	86.51	13.92
	85.64	14.39	84.49	15.32	86.26	13.82
	85.67	14.37	84.62	15.34	86.32	13.86
	85.72	14.38	84.53	15.36	86.41	13.90
	85.73	14.38	84.71	15.36	86.59	13.88
	85.61	14.37	84.60	15.36	86.57	13.90
	85.25	14.34	84.55	15.32	86.52	13.93
	85.26	14.37	84.37	15.35	86.67	13.85
	85.67	14.39	84.43	15.33	86.47	13.88
RSD %	0.23	0.20	0.14	0.14	0.02	0.05

TABLE 8. Reproducibility of Oxygen determination of diesel samples.

Sample	O %	RSD %
A	0.0265 0.0224 0.0214 0.0233 0.0233	8.179
B	0.0191 0.0192 0.0181 0.0196 0.0201	3.848

High density diesel samples were weighed in tin capsules for CHNS analysis and in silver capsule for oxygen determination. Table 9 shows the CHNS/O data and the Heat Values of two diesel samples.

TABLE 9. CHNS/O and Heat Value calculation of diesel samples.

Sample	N %	C %	H %	S %	O %	GHV	NHV
1	0.0618	90.54	9.39	0.0587	0.3002	10211	9709
	0.0644	90.20	9.39	0.0585	0.2711	10212	9710
	0.0657	90.15	9.38	0.0596	0.2862	10212	9710
2	0.0579	90.06	9.70	0.0342	0.2259	10289	9770
	0.0681	90.06	9.72	0.0398	0.2560	10288	9769
	0.0614	90.02	9.71	0.0381	0.2431	10288	9769

Table 10 shows the sulfur data of petrochemical samples obtained with the FPD detector (sulfur content is at trace levels). Gasoline and diesel samples were weighed in hard tin capsules closed by a dedicated sealing device. The calibration was performed using reference materials at trace sulfur content.

TABLE 10. Sulfur determination by FPD detector.

Sample	S ppm	RSD %
Catalyst 2	13 11 11	9.897
Coke	398 404 392	1.507
Crude oil	376 371 397	3.619
Gasoline	66 68 69	2.257
Diesel	25 22 21 22	9.03

Conclusion

The Thermo Scientific FLASH 2000 Elemental Analyzer, based on Dumas method, proved to be a valuable solution for the elemental analysis of petrochemical samples in terms of accuracy, repeatability and sensitivity of results. Its automation, high speed of analysis and the reduction of long sample preparation processes allow efficient analysis and help reduce overall operational costs.

All data were obtained with good reproducibility and no matrix effect was observed when changing the sample indicating complete combustion. CHN data of coal and coke were compliant to the ASTM D5375 method.

The advantage of the FLASH 2000 Analyzer lies in the possibility to perform CHNS determination in a single run, then changing the configuration oxygen determinations without any extra modules.

By introducing minor adaptations to the configuration, trace of sulfur can be analyzed through the FPD detector.

Thanks to the coupling of the liquid Autosampler to the elemental analyzer, liquid samples are analyzed with high precision and accuracy. The coupling proved to be easy to install, with automated syringe alignment, the correction of the volume in weight is automated and performed by the Eager Xperience Data Handling Software.

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