Application Note: 42169

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

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Key Words

- Catalyst
- Coal
- Coke
- Diesel
- Heat value
- Oil

Introduction

Elemental analysis is fundamental in petroleum chemistry. Using an automatic analyzer, rapid and accurate percentage of Carbon, Nitrogen, Hydrogen, Sulfur, and Oxygen (CHNS/O) 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 that are harmful and hazardous to the environment. Specifications and legislative limitations on hazardous and toxic pollutants from vehicle emissions were introduced due to the increasing atmospheric pollution recently. For example, the trend in developed countries is towards reducing the oxygen and sulfur contents in gasoline fuels. Sulfur oxides formed during combustion may get converted into acids that promote corrosion of engine parts and exhaust systems. Sulfur oxides formed in the exhaust are undesirable atmospheric pollutants. Sulfur also reduces the effectiveness of exhaust gas catalytic converters. The presence of sulfur in diesel causes wear in diesel engines as a result of the corrosive nature of its combustion by-products and increases the amount of deposits in the combustion chamber and pistons. Active sulfur in fuel tends to attack and corrode injection system components.

To meet these new regulations it is necessary to develop appropriate sensitive techniques and test procedures. One of these regarding the determination of sulfur in which content must reach ppm levels has been recently introduced. The Thermo Scientific FLASH 2000 CHNS/O Analyzer permits the fast quantitative determination of CHNS/O in petrochemical materials. To perform total sulfur determination at trace levels in many materials, such as gasoline, diesel, lubricants, graphite, etc. the FLASH 2000 Elemental Analyzer has been coupled with the flame photometric detector (FPD). This method combines the advantages of the elemental analyzer with the sensitivity, selectivity and robustness of the FPD.

Methods

For CHNS determination the elemental analyzer operates according to the dynamic flash combustion of the sample. Samples can be weighed in a tin capsule and introduced into the combustion reactor via the Thermo Scientific MAS 200R Autosampler. They can be also directly injected, by means of a syringe, via the Thermo Scientific AS 3000 II Liquid Autosampler. In both cases a proper amount of oxygen was used. 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, and finally, detected by a thermal conductivity detector (TCD). Total run time is 10 min. (see 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 and finally the sulfur is measured by the flame photometric detector (FPD). Total run time 5 min. (see Figure 3). For oxygen determination, the system operates in pyrolysis mode. Samples can be weighed in silver capsules and introduced into the pyrolysis chamber via the MAS 200R Autosampler or directly injected via the Thermo Scientific AI/AS 3000 II Liquid Autosampler or AS 3000 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 (See Figure 2). A complete report is automatically generated by the Thermo Scientific Eager Xperience data handling software and displayed at the end of the analysis.

Figure 1: FLASH 2000 Analyzer with MAS 200R and AS 3000 Autosamplers

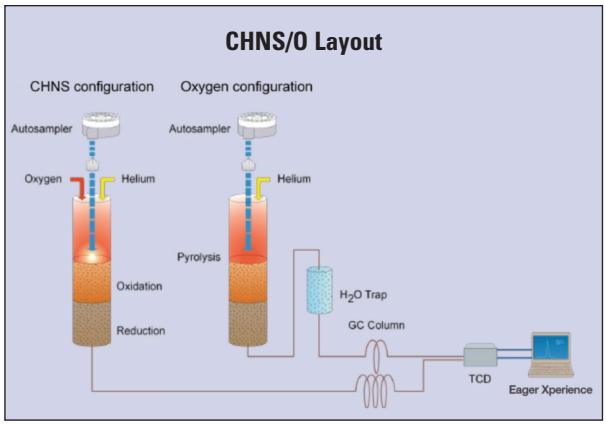

Figure 2: CHNS/O Configurations by TCD detector

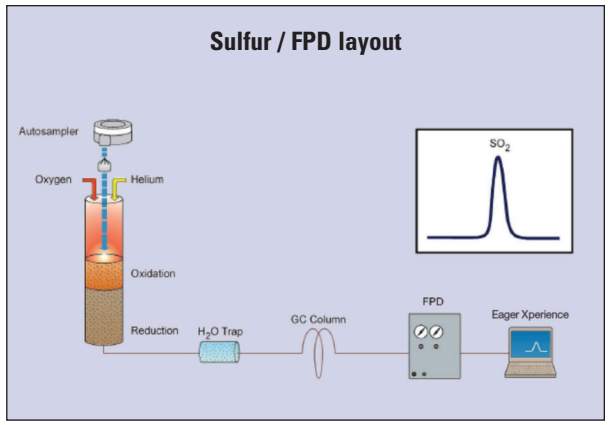

Figure 3: Sulfur Configuration by FPD detector

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.

Tables 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). 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 software.

Sample	N %	C %	H %	S %	O %	GHV	NHV
Coal	1.740	73.006	5.389	0.838	12.733	7316	7040
	1.732	72.950	5.358	0.857	12.731	7316	7040
	1.747	73.238	5.398	0.828	12.813	7313	7037
RSD%	0.431	0.209	0.390	1.752	0.367	0.024	0.025
Hard coal	1.287	80.137	4.621	0.488	4.903	7957	7720
	1.288	80.123	4.513	0.486	5.085	7918	7687
	1.329	80.706	4.617	0.497	5.094	8003	7766
RSD%	1.842	0.414	1.336	1.195	2.144	0.535	0.514
Brown coal	1.988	77.258	3.280	0.386	3.730	7313	7145
	2.006	77.196	3.266	0.386	3.723	7304	7136
	2.028	77.823	3.292	0.397	3.690	7364	7195
RSD%	0.998	0.446	0.397	1.630	0.575	0.442	0.444
Mineralized lignite	0.275	16.512	2.487	0.222	13.036	1651	1524
	0.273	16.480	2.476	0.226	13.046	1651	1524
	0.274	16.553	2.469	0.223			
RSD%	0.290	0.219	0.366	0.962	0.056	0.019	0.020
Lignite 1	0.758	62.281	4.636	0.377	25.202	5589	5357
	0.750	62.357	4.544	0.373	25.540	5574	5343
	0.757	62.24	4.377	0.371			
RSD%	0.559	0.074	2.899	0.724	0.942	0.184	0.192
Diesel 1	0.062	90.543	9.391	0.059	0.300	10211	9709
	0.064	90.202	9.391	0.058	0.271	10212	9710
	0.066	90.152	9.386	0.060	0.286	10212	9710
RSD%	3.104	0.235	0.032	0.994	5.092	0.005	0.006
Diesel 2	0.058	90.058	9.704	0.034	0.226	10289	9770
	0.068	90.064	9.718	0.039	0.256	10288	9769
	0.061	90.023	9.704	0.038	0.243	10288	9769
RSD%	8.297	0.024	0.084	7.684	6.249	0.005	0.006

Table 1: CHNS/O determination and Heat Value calculation of coal, lignite and diesel 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 0 0 0 0	---------	0.422 0.431 0.429 0.434 0.429	1.017
Graphite	0 0 0 0 0	--------	99.889 99.580 99.505 99.725 99.794	0.157	0 0 0 0 0	---------	0 0 0 0 0	--------
Carbon black	0.189 0.186 0.185 0.181 0.180	1.968	95.693 95.629 95.825 95.835 96.082	0.181	0.321 0.323 0.322 0.319 0.317	0.811	0.296 0.288 0.292 0.280 0.290	2.075
Catalyst 1	0.011 0.012 0.011	4.092	1.457 1.457 1.461	0.158	2.990 2.961 2.974	0.488	0 0 0	--------
Catalyst 2	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

Table 2: CHNS determination of petrochemical samples

Table 3 shows the sulfur data obtained with the FPD detector, where the sulfur content is at trace levels. Solid samples were weighed in tin capsules with the addition of vanadium pentoxide, typical "oxygen donor" that allows the total conversion of sulfur. Viscous samples were weighed directly in tin capsules without the additive while liquid samples were weighed in "hard" tin capsules recommended for volatile liquids and closed with a special sealing device.

Sample	Sulfur		Sample	Sulfur	
Nature	**ppm S**	**RSD %**	**Nature**	**ppm S**	**RSD %**
Catalyst 1	12 14 15	11.177	Crude oil	376 371 397	3.619
Catalyst 2	13 11 11	9.897	Gasoline	66 68 69	2.257
Catalyst 3	73 76 71	3.432	Gas oil	694 675 679	1.467
Coke	398 404 392	1.507	Diesel 1	25 22 21 22	9.03
Graphite	46 46 45	1.264	Diesel 2	58 56 52 57	4.57

Table 3: Trace Sulfur determination by FPD detector

Sample	C%	RSD%	H%	RSD%
iso-octane	84.052	0.142	15.861	0.150
	84.196		15,868	
	84.122		15.854	
	84.133		15.850	
	84.326		15.894	
	84.310		15.889	
	84.182		15.891	
	84.437		15.923	
	84.223		15.894	
	84.352		15.907	
Gasoline	87.053	0.206	12.385	0.336
	87.559		12.316	
	87.712		12.323	
	87.521		12.227	
	87.735		12.315	
	87.861		12.326	
	87.029		12.365	
	87.869		12.339	
	87.881		12.337	
	87.892		12.340	
Diesel	85.34	0.230	14.32	0.200
	85.35		14.31	
	85.64		14.39	
	85.67		14.37	
	85.72		14.38	
	85.73		14.38	
	85.61		14.37	
	85.25		14.34	
	85.26		14.37	
	85.67		14.39	

Table 4: Carbon and Hydrogen reproducibility of iso-octane (84.12 % C, 15.88 % H), gasoline and diesel samples

Table 4 shows the reproducibility of carbon and hydrogen determination in iso-octane, gasoline and diesel samples analyzed by liquid injection through the AS3000 Autosampler. The iso-octane (84.12 C %, 15.88 H %) was used also as standard to calibrate the system and the volume injected for both was 2 µl.

Sample	O %	RSD %
Diesel 1	0.0510	3.076
	0.0500	
	0.0480	
Diesel 2	0.1019	1.165
	0.1043	
	0.1032	
Diesel 3	1.0257	0.920
	1.0374	
	1.0187	
Gasoline 1	4.0144	0.5865
	4.0477	
Gasoline 2	0.8497	1.2868
	0.8653	
Gasoline 3	2.6400	0.1508
	2.6456	

Table 5: Reproducibility of Oxygen determination in diesel and gasoline

Table 5 shows the oxygen data of diesel and gasoline samples analyzed by liquid injection through the AS3000 Autosampler. A solution containing ethanol and iso-octane was used as standard and 2 µl was injected.

Conclusions

All data were obtained with good reproducibility and no matrix effect was observed when changing the sample.

The advantage of the FLASH 2000 Analyzer lies in the possibility to perform CHNS determination in a single run. By introducing small modifications in the configuration, trace sulfur can be analyzed through the FPD detector. Then with a simple change in configuration it is possible to perform oxygen determination.

The official method dedicated to gasoline determination ("Standard Test Methods for the determination of Total Oxygen in Gasoline and Fuels by Reduction Pyrolysis", ASTM D5622-94) confirms the precision levels and the importance of the automatic determination of oxygen in liquid samples.

Through the coupling of a liquid autosampler to our elemental analyzer, key features; such as easy installation, automatic syringe alignment, automatic correction of the volume in weight by the density through the Eager Xperience software, make it is easy to analyze liquid samples with high precision and accuracy.

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