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APPLICATION NOTE 42182

Elemental Analysis: CHNS/O determination in carbon

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Goal

This application note reports data on CHNS/O determination on carbon samples needed for quality control purposes, performed with the Flash*Smart* EA.

Introduction

Carbon occurs as a variety of allotropes. There are two crystalline forms, diamond and graphite, and a number of amorphous (non-crystalline) forms, such as charcoal, coke, and carbon black. The most common use of carbon black is as a pigment and reinforcing phase in automobile tires. Coke is the solid carbonaceous material derived from destructive distillation of low-ash, low-sulfur bituminous coal. Coke is also used as a fuel and as a reducing agent in smelting iron ore in a blast furnace.

For quality control purposes, the organic elements in carbon need to be determined. For the determination of carbon, hydrogen, nitrogen, sulfur and oxygen, the combustion method is used.

The Thermo Scientific™ Flash*Smart*™ Elemental Analyzer (Figure 1) allows the quantitative determination of carbon, hydrogen, nitrogen and oxygen in carbon. The Flash*Smart* EA based on the dynamic flash combustion of the sample, provides automated and simultaneous CHNS determination in a single analysis run and oxygen determination by pyrolysis in a second run. To perform total sulfur determination at trace levels, the analyzer has been coupled with the Flame Photometric Detector (FPD).

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Methods

For CHNS determination, the Flash*Smart* EA operates according to the dynamic flash combustion of the sample. Liquid samples are weighed in tin containers and introduced into the combustion reactor via the Thermo Scientific™ MAS Plus Autosampler. Samples can be directly injected, with a syringe via the Thermo Scientific™ AS 1310 Liquid Autosampler. In both cases a regulated amount of oxygen was used. After combustion, the resultant gases are carried by a helium flow to a layer filled with copper, then swept through a GC column that separates the combustion gases. Finally they are detected by a Thermal Conductivity Detector (TCD). Total run time is less than 10 minutes (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 before the sulfur is measured by the Flame Photometric Detector (FPD). Total run time is 5 minutes (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 Plus Autosampler or directly injected via the AI 1310 or AS 1310 Autosamplers. The reactor contains nickel coated carbon at 1060 °C. The oxygen 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 2). A complete report is automatically generated by the Thermo Scientific™ Eager*Smart*™ Data Handling Software.

Results

Different carbon samples were chosen to show the reproducibility obtained with the system. Coal, coke, graphite, lignite and carbon black samples were homogenized by a ball mill.

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 also indicates the Gross Heat Value (GHV in kcal/kg) and Net Heat Value (NHV in kcal/kg) calculated automatically by the dedicated Eager*Smart* Xperience software.

Figure 1. Flash*Smart* Elemental Analyzer coupled with Flame Photometric Detector (FPD).

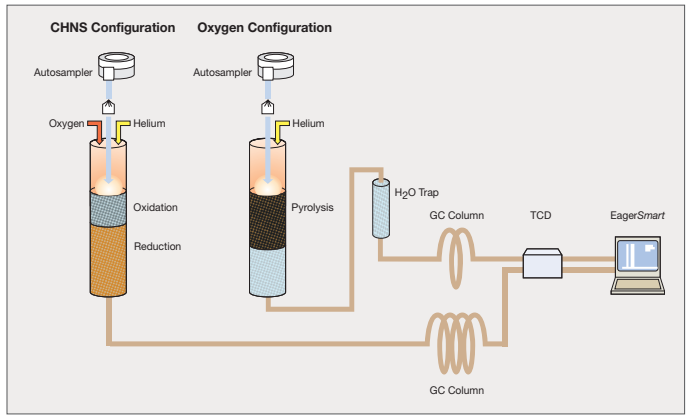

Figure 2. CHNS/O configuration with TCD Detector.

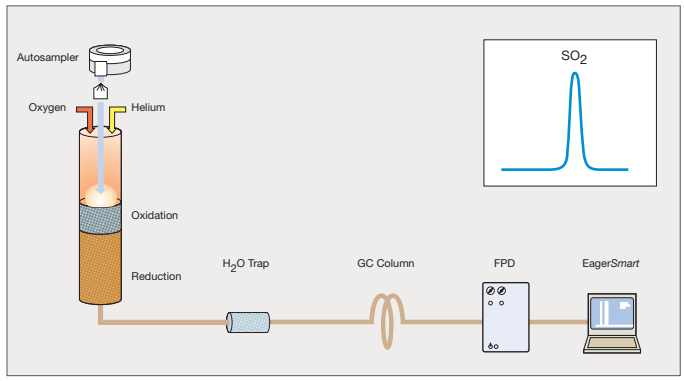

Figure 3. Sulfur configuration with FPD Detector.

Table 1. CHNS/O determination and Heat Value calculation.

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	7131 7304 7364	7145 7136 7195
RSD%	0.998	0.446	0.397	1.630	0.575	0.442	0.444
Lignite 1	0.758 0.750 0.757	62.281 62.357 62.24	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.

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
Calcinated coke	1.086 1.086 1.086 1.089 1.093	0.295	96.934 97.161 97.267 96.965 97.081	0.142	0.0741 0.0703 0.0716 0.0738 0.0754	2.810	1.213 1.219 1.213 1.213 1.211	0.262
Carbon black 1	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
Carbon black 2	0.131 0.137 0.133	2.493	95.609 95.542 95.772	0.124	0.384 0.361 0.359	3.861	1.433 1.452 1.443	0.649
Carbon black 3	0.135 0.134 0.140	2.156	96.329 96.241 96.300	0.0465	0.420 0.412 0.407	1.496	0.711 0.704 0.709	0.505
Carbon black 4	0.172 0.171 0.172	0.331	94.591 94.512 94.642	0.0693	0.520 0.520 0.524	0.458	1.741 1.728 1.757	0.841
Carbon Black 5	0.0896 0.0843 0.0884	3.178	99.365 99.497 99.506	0.079	0.322 0.319 0.321	0.452	––	––
Graphite	––	––	99.889 99.580 99.505 99.725 99.794	0.157	––	––	––	––

Table 3. Trace sulfur determination by FPD Detector.

Sample	Sulfur		Sample	Sulfur	
Nature	ppm S	RSD%	Nature	ppm S	RSD%
Coke	398 404 392	1.507	Graphite	46 46 45	1.264

Table 3 shows trace level sulfur data obtained when using the FPD Detector. Solid samples were weighed in tin containers with the addition of Vanadium Pentoxide, a typical “oxygen donor” that allows the total conversion of sulfur.

Conclusions

For CHNS/O determination for carbon characterization samples, the Flash*Smart* EA performs accurate analysis. Data were obtained with good reproducibility and no matrix effect when changing the sample.

CHNS determination can be performed in a single run with the Flash*Smart* EA. By coupling the Flash*Smart* EA with the FPD Detector, trace levels of sulfur can be analyzed. Oxygen determination can also be performed. Alongside with reproducibility of the data, the Elemental Analyzer offers advantages also in terms of reduced operational costs and analysis efficiency.

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