



Elemental Analysis: CHNS/O characterization of rubbers and tires

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Goal

This application note reports data on CHNS/O determination on rubber and tire samples for quality control purposes, performed with the FlashSmart EA.

Introduction

Rubbers and tires are used in a variety of industries and for different final products. Rubber is the main raw material used in manufacturing tires, either natural or synthetic. Crude rubber is primarily hydrocarbon in nature and is thermoplastic. To eliminate undesirable properties such as malodorousness, rubber is treated with sulfur, accelerators, and also antioxidants which extend the life of rubber products by reducing the deterioration caused by atmospheric oxygen (or ozone). The other primary ingredient in tire rubber is carbon black, used to increase stiffness, tensile strength, and resistance to abrasion. Rigorous quality control begins with the suppliers of the raw materials. A tire manufacturer requires the raw materials to be quality tested before they are delivered to the plant.

One of the tests used in the production process is the determination of the elemental composition of rubber. Sulfur content is one of the most important parameters in the quality control of rubber products, as it is the main indicator of the sulfur blooming phenomena, which indicates the loss of quality of the tires.

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

The Thermo Scientific™ FlashSmart™ Elemental Analyzer (Figure 1) allows the quantitative determination of carbon, hydrogen, nitrogen and oxygen in rubbers and tires. The FlashSmart 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.

This note presents data on CHNS/O determination in rubbers and tires to show the performance of the FlashSmart Elemental Analyzer.

Methods

For CHNS determination the FlashSmart EA 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 resultant 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) (Figure 2). Total run time is less than 10 minutes. When using the NCS configuration, a trap filled with anhydrous was installed between the reactor and the GC column.

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™ EagerSmart™ Data Handling Software.

Figure 3 and 4 show the typical CHNS and oxygen chromatograms.

Results

Different rubber and tire samples were chosen to show the performance obtained with the system. The samples were analyzed without any pre-treatment, merely cut into small pieces for the analysis. For CHNS, NCS and sulfur only determination, the addition of Vanadium Pentoxide was used for a complete conversion of the sulfur. The sample was weighed at 2 – 3 mg.



Figure 1. Thermo Scientific FlashSmart Elemental Analyzer.

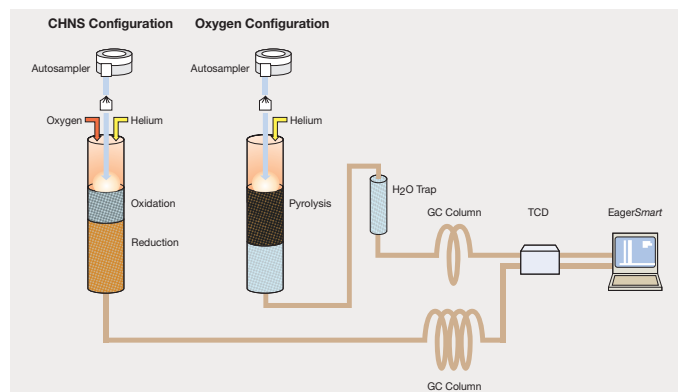


Figure 2. CHNS/O configuration.

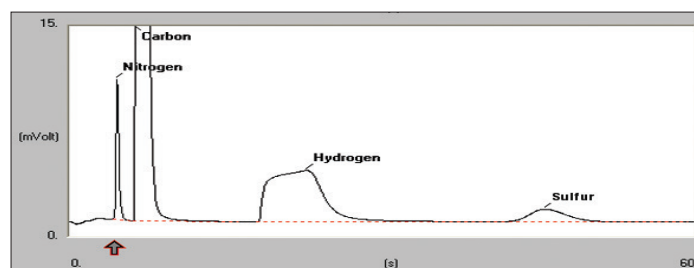


Figure 3. Typical CHNS chromatogram.

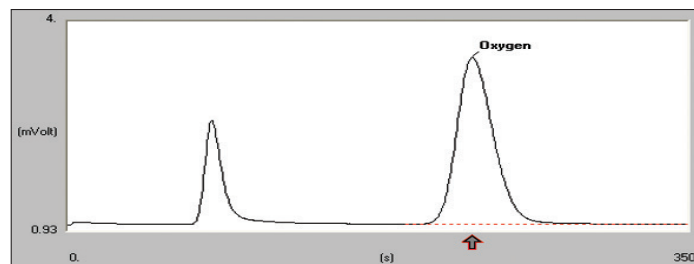


Figure 4. Typical oxygen chromatogram.

For CHNS analysis the instrument was calibrated with BBOT* (6.51 N%, 72.53 C%, 6.09 H%, 7.44 S%) as standard using K factor as the calibration method. For oxygen analysis, Acetanilide (11.84 O%) was used as standard and the K factor as the calibration method.

* BBOT: 2,5-Bis (5-tert-butyl-benzoxazol-2-yl) thiophene

Table 1. CHNS/O determination of rubber and tire samples.

Sample	N%	RSD%	C%	RSD%	H%	RSD%	S%	RSD%	O%	RSD%
Rubber 1	0.477	0.521	86.118	0.223	7.922	0.165	0.881	2.043	2.023	0.823
	0.481		85.735		7.916		0.899		1.999	
	0.481		85.951		7.941		0.863			
Rubber 2	0.336	2.420	86.560	0.195	7.719	0.303	0.639	1.967	1.932	1.010
	0.321		86.233		7.674		0.634		1.904	
	0.325		86.329		7.707		0.658			
Rubber 3	0.337	2.287	86.250	0.247	7.210	0.706	0.260	3.317	2.218	0.862
	0.324		86.210		7.271		0.254		2.245	
	0.338		86.597		7.312		0.271			
Tire 1	0.792	1.074	73.961	0.153	6.856	0.572	3.151	0.744	4.345	0.254
	0.800		74.140		6.880		3.105		4.325	
	0.783		74.171		6.933		3.122		4.327	
Tire 2	0.529	0.929	75.253	0.110	7.187	0.011	2.972	0.838	3.752	1.953
	0.536		75.370		7.186		2.937		3.695	
									3.609	
Tire 3	0.362	1.546	87.505	0.211	8.958	0.112	0.823	1.226	1.199	0.891
	0.370		87.767		8.973		0.837		1.178	
									1.191	

Table 2. CHNS determination of rubber and tire samples.

Sample	N%	RSD%	C%	RSD%	H%	RSD%	S%	RSD%
Rubber 4	0.628	0.666	82.447	0.208	11.279	0.1045	0.797	0.503
	0.636		82.272		11.300		0.799	
	0.633		82.104		11.298		0.792	
Rubber 5	0.625	0.790	82.210	0.576	11.263	1.123	1.095	3.989
	0.616		82.661		11.114		1.015	
	0.623		83.161		11.366		1.033	
Rubber 6	0.626	0.470	81.962	0.320	11.218	0.243	1.561	0.606
	0.628		81.866		11.249		1.553	
	0.622		82.361		11.272		1.572	
Tire 4	0.454	1.235	79.597	0.0701	6.945	0.0815	1.435	0.930
	0.462		79.676		6.937		1.454	
Tire 5	0.436	1.475	82.672	0.0932	7.137	0.000	1.666	0.0848
	0.427		82.781		7.137		1.668	

Table 1 shows CHNS/O data of different rubber and tire samples while Table 2 shows CHNS only determination of other types of rubber and tire materials. All data were obtained with a good reproducibility and no matrix effect was observed when changing the type of sample.

Table 3 shows the reproducibility of rubber samples analyzed using nitrogen, carbon and sulfur (NCS) configuration.

Table 3. NCS determination of rubber samples.

Sample	N%	RSD%	C%	RSD%	S%	RSD%
Rubber 7	0.277	0.737	85.802	0.247	0.927	0.751
	0.280		85.503		0.936	
Rubber 8	0.290	2.447	85.130	0.068	1.546	1.779
	0.300		85.047		1.585	
Rubber 9	0.293	2.477	84.881	0.108	1.969	1.268
	0.293		84.751		1.934	
Rubber 10	0.283	1.091	83.229	0.001	3.798	1.281
	0.287		83.230		3.730	

Table 4 shows the loss of sulfur value from the tire surface by analyzing its content in a new tire and a six month old tire. This effect is known as a sulfur blooming phenomena.

Table 5 shows the reproducibility of oxygen determination by pyrolysis of rubber samples.

Conclusions

The Thermo Scientific FlashSmart Elemental Analyzer allows the quantitative recovery of the elements from any matrix, with no memory effect when changing the sample.

The CHNS/O determination of tire and rubber samples is performed by the FlashSmart Elemental Analyzer without any pre-treatment of the sample.

The FlashSmart Elemental Analyzer meets laboratory requirements in terms of automation and high sample throughput. The Analyzer is modular and enables laboratories to perform CHNS determination in a single run and, with a configuration change, oxygen determination. Sulfur or nitrogen only analyses can also be performed, with a minor configuration upgrade.

Table 4. Sulfur blooming phenomenon requirements.

Sample	S% (new tires)	S% (six months old tires)
Tire A	2.605	2.484 – 2.499 – 2.487
Tire B	5.894	5.415 – 5.302 – 5.250

Table 5. Oxygen reproducibility of rubber samples.

Sample	O%	RSD%
Rubber A	2.176	0.186
	2.181	
	2.174	
	2.171	
	2.181	
Rubber B	1.825	0.622
	1.819	
	1.837	
	1.810	
	1.810	
Rubber C	2.122	0.303
	2.115	
	2.117	
	2.130	
	2.114	

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