

Elemental Analysis: CHNS/O characterization of polymers and plastics

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Keywords

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Goal

This application note shows CHNS/O determination for polymers and plastics with the FlashSmart EA, needed for material quality control.

Introduction

The chemical composition of polymers and plastics is connected with their chemical, physical, mechanical properties. The development and production of polymers and plastics requires quality control of raw materials, additives, stabilizers, intermediate and finished products. The analysis of the behavior of polymers and plastics during molding and the evaluation of their lifetime contribute to define their quality. For the material characterization and the quality control testings of polymers and plastics, nitrogen, carbon, hydrogen, sulfur and oxygen are determined. Nitrogen determination is crucial, and the importance of sulfur determination has increased also. Nitrogen containing compounds are used in the production process of polymers and plastics to trigger a polymerization reaction. They can also be used as additives for the addition of specific properties to polymers and plastics.

As additives, nitrogen containing compounds provide the final product with specific properties, and they act as: stabilizing emulsion polymers, chain transfer agents and other polymerization modifiers to control molecular weight, plasticizers to increase flexibility, stabilizers to prevent polymer degradation, crosslinkers used to modify polymer networks.

As the demand for material characterization testing has grown in recent years and elements are present at trace levels, the classical analytical methods showed to be no longer suitable, for their time-consuming sample preparation and for their use of hazardous reagents. For this reason an automated technique providing accurate data at trace levels is the requirement for modern laboratories dealing with routine analysis.

The Thermo Scientific™ FlashSmart™ Elemental Analyzer (Figure 1), meets laboratory requirements such as accuracy, day to day reproducibility and high sample throughput. It improves the productivity of the laboratory over traditional methods, as it is automated and modular. CHNS determinations can be performed in a single analysis run and oxygen determination by pyrolysis in a second run. The FlashSmart EA can be configured to perform a single nitrogen determination or trace sulfur analysis when coupled to the Flame Photometric Detector (FPD).

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

Methods

For CHNS or CHN determination the FlashSmart Elemental Analyzer operates with 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 produced gases are carried by a helium flow to a layer containing copper, then swept through a GC column, which provides the separation of the combustion and finally, detected by a Thermal Conductivity Detector (TCD).

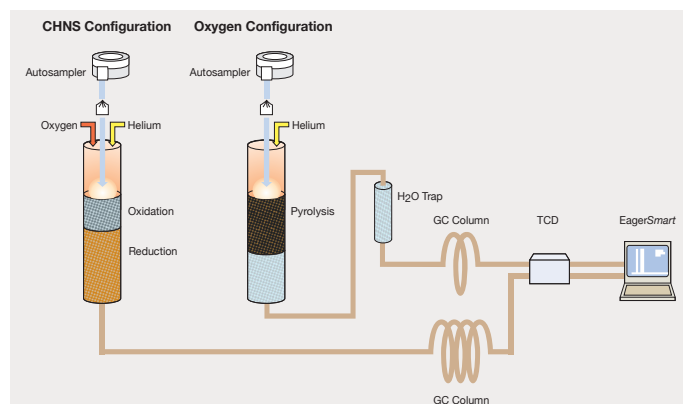


Figure 2. CHNS/O configuration.

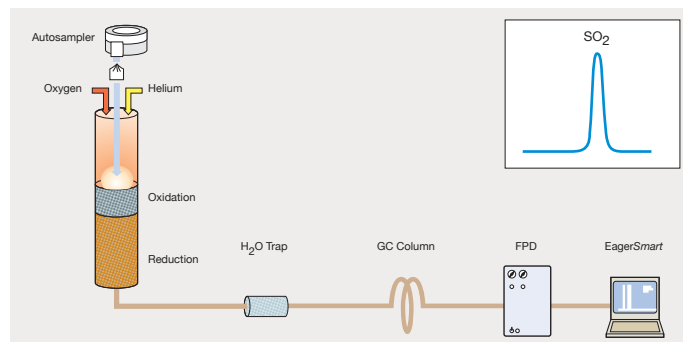


Figure 3. Sulfur configuration by FPD Detector.



Figure 1. Thermo Scientific FlashSmart Elemental Analyzer.

Total run time less than 10 minutes (Figure 2). For trace sulfur determination, the gases produced by combustion are carried by a helium flow to a layer containing 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 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. The reactor contains nickel coated carbon at a temperature of 1060 °C. The oxygen in the sample, combined with the carbon, forms carbon monoxide which is chromatographically separated from other products and detected by the TCD Detector (Figure 2).

For nitrogen determination, the Elemental Analyzer operates by dynamic flash combustion of the sample. Samples are weighed in tin containers and introduced into the combustion reactor via the MAS Plus Autosampler with oxygen. After combustion, the produced gases are carried by a helium flow to a second reactor containing copper, then swept through CO₂ and H₂O traps, and a GC column, and finally, detected by a Thermal Conductivity Detector (TCD). Total run time less than five minutes (Figure 4).

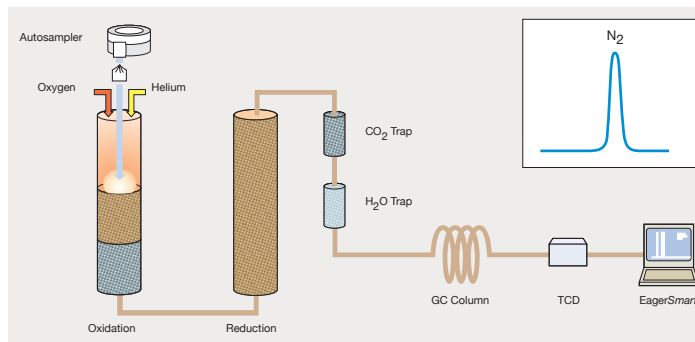


Figure 4. Nitrogen configuration.

A complete report is automatically generated by the Thermo Scientific™ EagerSmart™ Data Handling Software.

Results

Different types of polymers and plastics, raw materials and additives, with different content and aspect (pellets, powders and films), were analyzed.

Table 1 shows the repeatability of CHNS/O determination in polyimide sample and Table 2 shows the repeatability of NCS determination in polymers powders. For CHNS and NCS analysis, the system was calibrated with 2–3 mg of BBOT* standard using K factor as calibration method. The sample were weighed at 1–2 mg. For oxygen determination, 1–2 mg of benzoic acid was analyzed as standard using K factor. The sample were weighed at 1–2 mg.

Table 3 shows the CHN/O data of polyacrylonitriles. The calibration was performed with 2–3 mg of acetanilide using K factor as calibration method, and sample was weighed at 2–3 mg. Acrylonitrile (monomer) is the main component of many types of compounds (polyacrylonitriles) such as plastics.

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

Table 1. CHNS/O data of polyimide.

Element	N%	C%	H%	S%	O%
	3.483	61.108	2.642	3.950	20.304
	3.494	61.092	2.629	3.910	20.213
	3.478	61.168	2.620	3.943	20.236
Average	3.485	61.123	2.630	3.934	20.251
RSD%	0.235	0.066	0.421	0.543	0.234

Table 2. NCS data of polymers powders.

Sample	N%	RSD%	C%	RSD%	S%	RSD%
1	15.829		54.983		0.221	
	15.770	0.303	54.950	0.158	0.223	0.548
	15.756		54.819		0.223	
2	13.775		49.014		3.266	
	13.763	0.054	48.889	0.129	3.282	0.270
	13.777		48.971		3.267	

Table 3. CHN/O data of polyacrylonitriles.

Sample	N%	RSD%	C%	RSD%	H%	RSD%	O%	RSD%
A	23.17		64.26		5.73		4.79	
	23.35	0.45	64.35	0.12	5.76	0.71	4.59	2.25
	23.17		64.42		5.68		4.63	
B	22.77		64.65		5.73		5.31	
	22.54	0.75	64.23	0.33	5.66	0.98	5.37	0.71
	22.44		64.41		5.62		5.30	
C	24.97		64.88		5.67		2.99	
	24.88	0.21	65.20	0.30	5.66	0.37	3.01	0.51
	24.88		65.23		5.70		2.98	

Table 4 shows the nitrogen data of polymers in pellets. The system was calibrated with 10–12 mg atropine standard using K factor as calibration method. Samples 1 and 2 were weighed at 200–250 mg. For samples 3 to 5 the calibration was performed with 5–6 mg atropine and samples were weighed at 30–40 mg. Table 5 shows the nitrogen data of polycarbonate polymers in pellets analyzed in duplicate. The system was calibrated with 25–30 mg atropine using K factor as calibration method. Sample was weighed at 150–170 mg.

Table 6 shows nitrogen data of polyethylene films. As standard, 3–4 mg atropine was analyzed using K factor as calibration method. Samples were weighed at 20–25 mg. Table 7 shows the nitrogen data of plastics

Table 4. Nitrogen data of polymers (pellets).

Sample	N (ppm)	RSD%
1	985	1.589
	998	
	982	
	1002	
	1029	
	999	
	1005	
	1001	
	1008	
	1031	
2	331	1.236
	332	
	324	
	328	
	326	
	334	
	346	
	335	
	327	
	339	
3	967	0.206
	971	
	969	
4	439	2.300
	427	
	447	
5	91	1.111
	89	
	90	

Table 5. Nitrogen data of polycarbonate polymers (pellets).

Sample	1	2	3	4	5
N%	0.675	0.656	0.617	0.113	0.110
	0.678	0.651	0.622	0.111	0.111
RSD%	0.314	0.541	0.571	1.263	0.640

additives. The calibration was performed with 25–30 mg of atropine using K factor as calibration method. Samples were weighed at 25–30 mg.

Table 6. Nitrogen data of polyethylene films.

Sample	N (ppm)	RSD%
1	2410	0.312
	2410	
	2397	
2	1569	1.212
	1590	
	1552	
3	1072	1.573
	1040	
	1064	
4	781	0.604
	779	
	788	
5	492	0.841
	500	
	494	
6	266	5.556
	252	
	238	
7	220	1.646
	213	
	218	
8	114	5.038
	103	
	107	

Table 7. Nitrogen data of plastics additives.

Sample	N%	RSD%
Raw Material 1	18.141	0.022
	18.136	
	18.144	
Raw Material 2	19.639	0.087
	19.631	
	19.606	
Raw Material 3	13.414	0.039
	13.407	
	13.417	
Raw Material 4	2.242	0.569
	2.241	
	2.219	
Raw Material (Dimeric Benzotriazole)	12.799	0.057
	12.808	
	12.814	
Polycarbonate + Dimeric Benzotriazole	0.642	0.483
	0.645	
	0.639	
Raw Material (Hindered Amine Light Stabilizer)	5.767	0.231
	5.753	
	5.740	
White Polystyrene Granules (Contains Hindered Amine Light Stabilizer)	0.506	0.808
	0.501	
	0.509	

For trace sulfur determination by FPD Detector, the system was calibrated with Thermo Scientific Pasta and Soil Reference Materials with 0.135 S% and 0.032 S%, respectively using quadratic fit as calibration method.

Table 8 shows the sulfur data of a polyethylene film sample. Table 9 shows the sulfur data of plastic powders while Table 10 shows the sulfur data of polymers. The samples were cut into small pieces and the samples were weighed at 0.5–3 mg.

Table 8. Sulfur data of polyethylene film sample.

S (ppm)	RSD%
571	2.792
573	
540	
542	
558	

Table 9. Sulfur data of plastic powders.

Sample	S (ppm)	RSD%
1	562	1.857
	582	
	566	
2	58	5.329
	54	
	60	
3	39	10.657
	42	
	48	
4	2366	0.813
	2335	
	2370	

Conclusion

The Thermo Scientific FlashSmart Elemental Analyzer enables to perform accurate and reproducible CHNS/O determination in polymers and plastics samples.

No matrix effect was observed when changing the sample and element content indicating the complete combustion of the samples.

Nitrogen only analyses, simultaneous CHNS, NCS, CHN and oxygen can be performed on the Thermo Scientific FlashSmart Elemental Analyzer with a simple upgrade. Trace sulfur determination can also be performed when coupled to the FPD Detector

Table 10. Sulfur data of polymers.

Sample	S (ppm)	Av. S (ppm)	RSD%
A	495	466	3.87
	466		
	467		
	456		
	447		
B	876	869	4.01
	902		
	820		
	879		
C	1369	1419	3.03
	1442		
	1445		
D	1866	1867	2.61
	1856		
	1813		
	1931		
E	2969	2894	4.02
	2772		
	3016		
	2821		
F	350	329	3.80
	328		
	317		
	321		
	320		
	336		
G	178	182	2.20
	176		
	182		
H	59	57	6.11
	59		
	52		
	61		
	56		
I	41	39	6.11
	40		
	42		
	36		
J	38	27	14.79
	25		
	32		
	29		
	23		

The FlashSmart Elemental Analyzer meets laboratory requirements in terms of automation, high sample throughput.

Find out more at thermofisher.com/OEA

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