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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 Flash*Smart* 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.

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The Thermo Scientific™ Flash*Smart*™ 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 Flash*Smart* 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 Flash*Smart* Elemental Analyzer.

Figure 1. Thermo Scientific Flash*Smart* Elemental Analyzer.

Methods

For CHNS or CHN determination the Flash*Smart* 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).

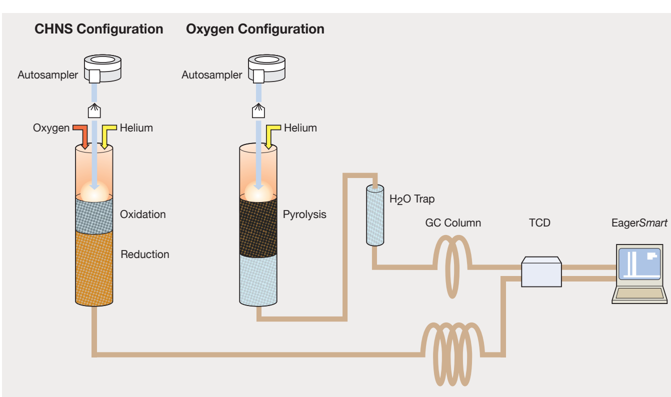

Figure 2. CHNS/O configuration.

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 CO_2 and H_2O traps, and a GC column, and finally, detected by a Thermal Conductivity Detector (TCD). Total run time less than five minutes (Figure 4).

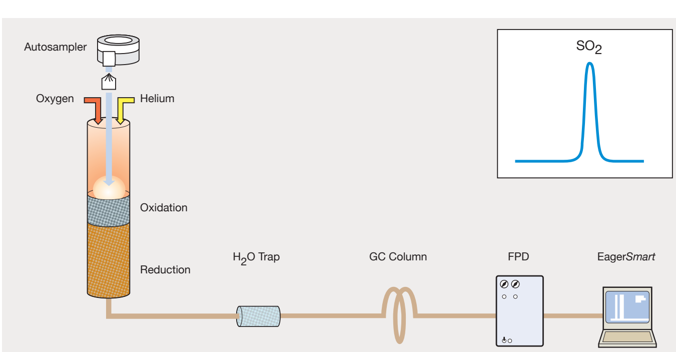

Figure 3. Sulfur configuration by FPD Detector.

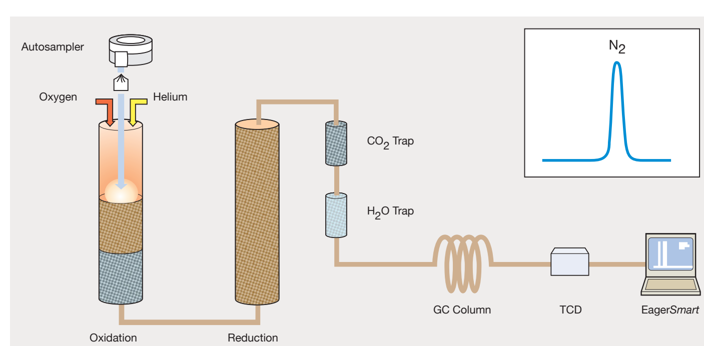

Figure 4. Nitrogen configuration.

A complete report is automatically generated by the Thermo Scientific™ Eager*Smart*™ 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 polyacrilonitriles. The calibration was performed with 2–3 mg of acetanilide using K factor as calibration method, and sample was weighed at 2–3 mg. Acrilonitrile (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 3.494 3.478	61.108 61.092 61.168	2.642 2.629 2.620	3.950 3.910 3.943	20.304 20.213 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 15.770 15.756	0.303	54.983 54.950 54.819	0.158	0.221 0.223 0.223	0.548
2	13.775 13.763 13.777	0.054	49.014 48.889 48.971	0.129	3.266 3.282 3.267	0.270

Table 3. CHN/O data of polyacrilonitriles.

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

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 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 4. Nitrogen data of polymers (pellets).

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

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

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

Table 6. Nitrogen data of polyethylene films.

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

Table 7. Nitrogen data of plastics additives.

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

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%
571 573 540 542 558	2.792

Table 9. Sulfur data of plastic powders.

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

Conclusion

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

The Flash*Smart* Elemental Analyzer meets laboratory requirements in terms of automation, high sample throughput.

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