Characterization of lubricants and oils by the Thermo Scientific FlashSmart Elemental Analyzer

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Goal

This application note reports data on determination of nitrogen in lubricants and oil samples and shows the performance of the FlashSmart Elemental Analyzer and its reproducibility capabilities.

Introduction

In a typical production process of mineral oils, the nitrogen content is periodically monitored and tested for quality control. The reproducibility of data, which is measured as deviation of results from the mean value, is one of the main targets in all analytical tests for the alternative techniques accepted.

The method for nitrogen analysis in lubricants, based on combustion, is described in ASTM D5291. The ASTM method has been established for samples containing nitrogen in percentages from <0.1% to 2% (mass) with a repeatability of 0.16% (mass). The method is for the determination of carbon, hydrogen and nitrogen in laboratory samples of lubricants and petroleum products. Using the Test method D levels of 0.01 N% in lubricants can be determined.

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As the demand for improved sample throughput, reduction of operational costs and minimization of human errors is steadily increasing, a simple and automated technique, which allows fast analysis with an excellent reproducibility is the key for efficient nitrogen analysis. The Thermo Scientific™ Flash*Smart*™ Elemental Analyzer (Figure 1), which uses the dynamic combustion of the material, requires no sample digestion or toxic chemicals, and provides important advantages in terms of time, automation and quantitative determination of nitrogen in concentrations between 0.01% (100 ppm) to higher than 5% (mass). Simultaneous determinations of nitrogen, carbon, hydrogen and sulfur are also possible with a simple upgrade.

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

Method

The Flash*Smart* Elemental Analyzer uses the dynamic flash combustion of the samples, which are weighed in tin capsules and introduced into the combustion reactor via the Thermo Scientific™ MAS Plus Autosampler with oxygen.

After the combustion, for nitrogen determination only, the produced gases are carried to a second reactor filled with copper by a helium flow, then swept through CO_2 and H_2O traps, a GC column and finally detected by a Thermal Conductivity Detector (TCD). Total run time is less than 5 minutes (Figure 2).

For simultaneous CHNS, after the combustion the resulted gases are carried to a layer containing copper by a helium flow, then swept through a GC column that provides the separation of the combustion gases, and finally, detected by a TCD Detector. Total run time is less than 10 minutes (Figure 3). For NCS or sulfur determination only a water trap is installed between the reactor and the GC column.
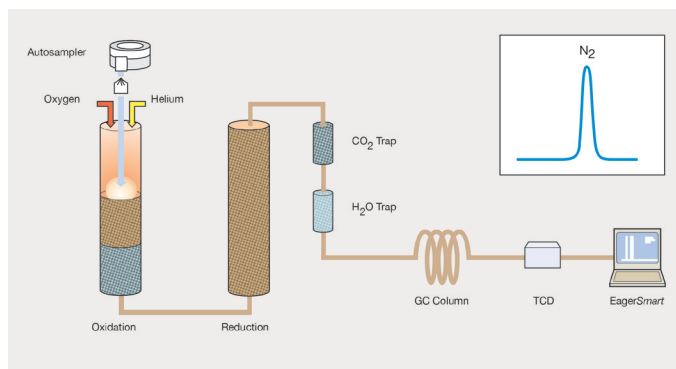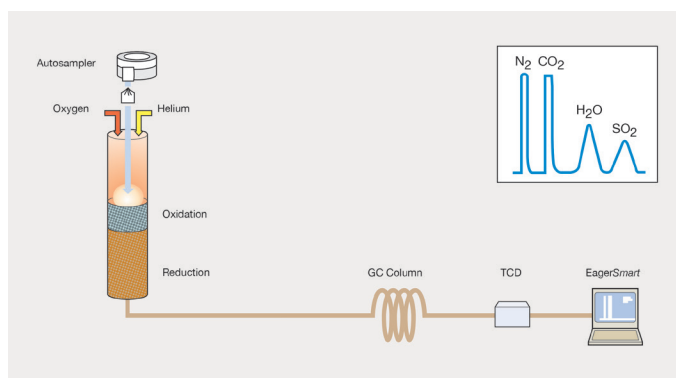

Figure 2. Nitrogen Lubricant configuration.

Figure 3. CHNS configuration.

A report is generated by the Thermo Scientific™ Eager*Smart*™ Data Handling Software.

Results

Different lubricants and oils were analyzed several times to show the reproducibility of nitrogen determination and simultaneous CHNS analysis. Samples were weighed in tin containers without pre-treatment.

In nitrogen determination only, the calibration can be performed with 4-5 mg atropine (4.84 N%) using K factor as calibration method, or by Linear Fit using a Lubricant Reference Material. Figure 4 shows a Linear Fit calibration curve. The SPX Lubricant Reference Material (1.11 N%) weighted between 0.2 mg and 10 mg. Table 1 shows the nitrogen repeatability of SPX lubricant analyzed as unknown and another lubricant at 0.08 N% analyzed in five days.
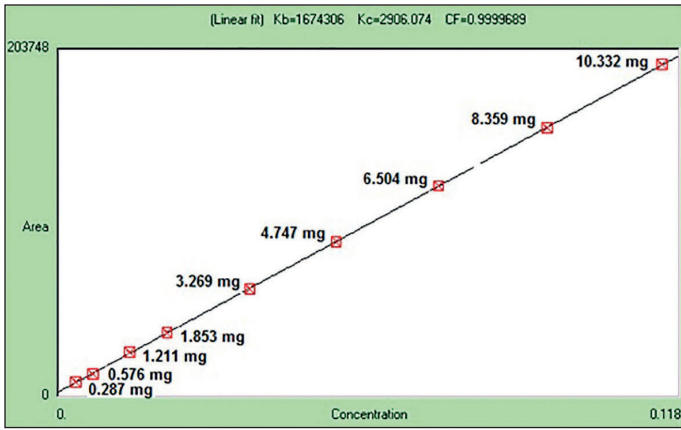
Figure 4. Nitrogen Linear Fit Calibration Curve.

Table 1. Day by day reproducibility in N determination of lubricants.

Sample	Day 1	Day 2	Day 3	Day 4	Day 5	Average N%	RSD%
SPX 1.11 N%	1.1076	1.0978	1.0994	1.0994	1.1137	1.1036	0.6
Lub 0.08 N%	0.0779	0.0815	0.0785	0.0818	0.0787	0.0797	2.2

Table 2 shows the nitrogen repeatability of lubricant samples in a wide range of concentrations analyzed in two days. No matrix effect was observed when changing sample.

Table 2. Day-by-day reproducibility in N determinations of several lubricant 3 samples.

Sample	Day 1 – N%	Day 2 – N%
1	1.130	1.130
2	1.073	1.073
3	1.596	1.594
4	1.173	1.163
5	0.874	0.866
6	1.198	1.210
7	1.123	1.117
8	0.579	0.573
9	0.878	0.888

Table 3 shows the nitrogen repeatability of three determinations of lubricant samples, containing more than 0.3% nitrogen. Table 4 shows the nitrogen repeatability of 10 determinations of lubricant samples with a nitrogen content between 300 ppm N and 0.20 N%.

Table 3. Nitrogen reproducibility of three determinations of lubricant samples.

Sample	RSD%	N%
1	0.3154	0.3047 0.3065 0.3062
2	0.6253	0.4580 0.4539 0.4594
3	0.9414	0.4700 0.4788 0.4727
4	0.4275	0.5200 0.5237 0.5197
5	0.7969	0.6400 0.6349 0.6451
6	0.7908	0.8461 0.8420 0.8331
7	0.5825	1.4617 1.4664 1.4783
8	0.3135	3.9927 3.9683 3.9760

Table 4. Nitrogen reproducibility of 10 determinations of lubricant samples.

Sample	1	2	3	4	5
N%	0.0347 0.0323 0.0309 0.0298 0.0358 0.0323 0.0316 0.0304 0.0329 0.0292	0.0468 0.0446 0.0465 0.0493 0.0495 0.0463 0.0450 0.0469 0.0476 0.0431	0.1051 0.1147 0.1158 0.1078 0.1147 0.1059 0.1084 0.1177 0.1089 0.1121	0.1456 0.1488 0.1482 0.1507 0.1424 0.1535 0.1436 0.1535 0.1494 0.1514	0.1800 0.1819 0.1849 0.1860 0.1811 0.1849 0.1858 0.1894 0.1834 0.1886
Average N%	0.0320	0.0466	0.1101	0.1487	0.1846
RSD%	6.54	4.28	3.54	2.58	1.66

Table 5 shows the nitrogen repeatability of 10 determinations in lubricant samples. The content is to be found at trace level (less than 200 ppm N).

Table 5. Reproducibility in trace N determination of lubricant samples.

Sample	ppm N	Average ppm%	RSD%
1	193 191 209 194 175 182 179 187 192 186	189	5.03
2	126 138 110 134 132 127 135 134 121 136	129	6.63

Table 6 shows the nitrogen repeatability of three determinations of different oil samples.

Table 6. Nitrogen reproducibility of three determinations of oil samples.

Sample	N%	RSD%
Heavy Gas Oil 1	0.272 0.280 0.273	1.5851
Heavy Gas Oil 2	0.242 0.247 0.247	1.1767
Heavy Gas Oil 3	0.069 0.073 0.072	2.9182
Slurry Oil	0.213 0.212 0.217	1.2363
Residual Oil	0.276 0.274 0.266	1.9454
Vacuum Gas Oil	0.098 0.093 0.099	3.3254

To verify the performance of the FlashSmart EA results were compared with data provided by the **ASTM International Interlaboratory Program**. ASTM periodically compares test results and calculated statistical parameters with data provided by laboratories of the global petrochemical and analytical community, in order to help laboratories monitoring their performance when running **ASTM methods**. Laboratories involved in the program receive different lubricants samples and they are requested to analyze the samples according to ASTM methods. Results are first collected and then processed by ASTM and reports are sent out to each participant.

Table 7 shows the comparison of the FlashSmart EA data and the statistical results obtained by ASTM. All data obtained fall within the range indicated by the ASTM reports. The calibration of the system was performed with atropine (4.84%N) using K factor as calibration method. The samples were analyzed as received.

Table 7. Nitrogen reproducibility of ASTM lubricants.

Sample	Thermo Fisher	ASTM	ASTM Reproducibility
	N% value	Robust Mean N%	These Test Data
1	0.675	0.6685	0.0604
2	0.700	0.7088	0.0471
3	0.576	0.5790	0.0604
4	0.760	0.7916	0.0634
5	0.522	0.5272	0.0518
6	0.774	0.7937	0.0460
7	0.608	0.6516	0.0601
8	0.707	0.7166	0.0363
9	0.791	0.7923	0.0723
10	0.786	0.7843	0.0740
11	0.716	0.7182	0.0515
12	0.788	0.7738	0.0596
13	0.643	0.6466	0.0537
14	0.687	0.7079	0.0712
15	0.784	0.7875	0.0607
16	0.929	0.9431	0.0618

For the simultaneous CHNS determination, K factor was used as calibration method with BBOT* as standard. Standard and samples weighted between 2-3 mg.

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

Table 8 shows the CHNS results with crude oil samples. Table 9 shows the NCS repeatability of lubricants while Table 10 shows the repeatability of sulfur determination in oils. No memory effect was observed changing the sample nature, meaning the combustion of all samples followed by the quantitative determination of the elements.

Table 8. CHNS repeatability of crude oils.

Sample	N%	RSD%	C%	RSD%	H%	RSD%	S%	RSD%
Crude Oil 1	0.202 0.222 0.200 0.212 0.214	4.312	85.270 85.370 85.359 85.102 85.283	0.126	13.395 13.308 13.319 13.289 13.355	0.316	0.289 0.290 0.283 0.291 0.297	1.724
Crude Oil 2	0.270 0.282 0.271 0.279 0.270	2.071	85.425 85.770 85.547 85.377 85.752	0.212	11.919 11.925 11.894 11.794 11.870	0.446	2.028 2.018 2.015 1.985 2.018	0.810

Table 9. NCS repeatability of lubricants.

Sample	N%	RSD%	C%	RSD%	S%	RSD%
1	1.9692 1.9533 1.9623	0.4065	83.5652 83.3596 83.3495	0.1459	0.0334 0.0360 0.0340	3.9498
2	0.0848 0.0825 0.0823	1.6698	84.3010 84.7778 84.8720	0.3616	0.2373 0.2316 0.2324	1.3201
3	0.1205 0.1185 0.1208	1.0425	84.5046 84.5403 84.4177	0.0746	0.6492 0.6477 0.6536	0.4716

Table 10. Sulfur repeatability of oils.

Sample	S%	RSD%
Model Oil	11.461 11.514 11.520 11.632 11.531	0.540
Crude Oil 1	8.534 8.573 8.499 8.645 8.471	0.796
Crude Oil 2	4.146 4.165 4.091 4.125 4.144	0.677
Residual Oil A	2.061 2.086 2.095 2.093	0.751
Residual Oil B	2.937 2.960 2.904 2.962	0.918
Residual Oil C	4.534 4.541 4.534 4.558	0.249

Conclusion

The Thermo Scientific Flash*Smart* N Lubricant Analyzer proved to be a valuable solution for the analysis of nitrogen in lubricants in terms of accuracy, reproducibility, and sensitivity of results. Its automation, high speed of analysis and the elimination of sample preparation process allow efficient analysis and help reduce overall operational costs.

The nitrogen analysis for petroleum products and lubricants, using the Dumas method, is described in ASTM D5291. The ASTM standard has been established for samples with percentage of nitrogen from <0.1 to 2% (mass). In this demonstration the range of applicability of the technique has been extended to samples with nitrogen in trace content, up to 0.01 N% as indicated in the Test Method D.

The Flash*Smart* Elemental Analyzer performs the analysis without matrix effect when changing the sample and nitrogen content. With a simple upgrade the Flash*Smart* EA can determine CHNS, NCS or sulfur simultaneously.

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