Characterization of Lubricants and Oils by the Thermo Scientific FLASH 2000 Elemental Analyzer Using Helium and Argon as Carrier Gases

Dr. Liliana Krotz, Dr. Francesco Leone, and Dr. Guido Giazzi
Thermo Fisher Scientific, Milan, Italy

Key Words
Argon, ASTM, Elemental Analyzer, Helium, Lubricants, Nitrogen, Repeatability, Reproducibility

Goal

Demonstrate the performance of the Thermo Scientific FLASH 2000 Elemental Analyzer for the characterization of lubricants and the repeatability and reproducibility of data obtained in compliance with ASTM method.

Introduction

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

The method for nitrogen analysis in lubricants, based on combustion, is described in the ASTM D5291. The method covers the instrumental determination of carbon, hydrogen and nitrogen in laboratory samples of petroleum products and lubricants. Using the Test Method D levels of 0.1 N% in lubricants can be determined.

Figure 1. Thermo Scientific FLASH 2000 N Lubricant Analyzer.

As the demand for improved sample throughput, the reduction of operational costs and the minimization of human errors increases, a simple and automated technique allowing fast analysis with an excellent reproducibility is required. The Thermo Scientific™ FLASH 2000 Organic Elemental Analyzer (Figure 1), based on dynamic combustion (Dumas method), requires no sample digestion or toxic chemicals, while providing important advantages in terms of time, automation and quantitative determination of nitrogen in large concentration. However, to prevent high cost of helium, due to its possible shortage, the FLASH 2000 Analyzer can work with an alternative gas, argon, which is readily available.

Methods

The Elemental Analyzer 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 200R Autosampler together with the proper amount of oxygen. After combustion, the produced gases are carried by a helium flow to a second reactor filled with copper, then swept through CO_2 and H_2O traps, and a GC column. Finally they are detected by a thermal conductivity detector (TCD) (Figure 2). A comprehensive report is generated by the Thermo Scientific™ Eager Xperience Data Handling Software and displayed at the end of the analysis. The dedicated software performs automated calculations of the empirical formula.

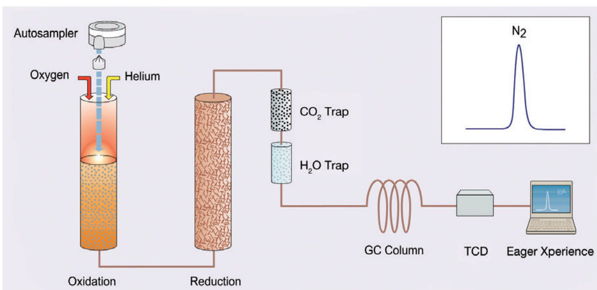

Figure 2. Configuration of the FLASH N Lubricants.

Analytical Conditions

Parameter	Helium gas	Argon gas
Combustion Reactor Temperature	950 °C	950 °C
Reduction Reactor Temperature	840 °C	840 °C
Oven Temperature	50 °C	50 °C
Carrier Gas Flow	140 mL/min	60 mL/min
Reference Gas Flow	100 mL/min	60 mL/min
Sample Delay	10 sec	12 sec
Oxygen Flow	300 mL/min	300 mL/min
Oxygen Injection Time	8 sec	20 sec

Note: The Eager Xperience Eager Xperience Data Handling Software provides a new option AGO (Argon Gas Option) which allows the user to manage the flow of argon gas during the run.

Results

To evaluate the repeatability of the system using helium and argon as carrier gases, the Thermo Scientific Lubricant Reference Material (1.12 N%, accepted range 1.02-1.22 N%) was analyzed several times. Using helium carrier gas, the instrument calibration was performed with about 4-5 mg Atropine (4.84 N%) with K factor as calibration method, the Lubricant Reference Material analyzed as unknown was weighed at 8-10 mg. Using argon as carrier gas, the calibration was performed with 19-21 mg of atropine with K factor as calibration method, the Lubricant Reference Material analyzed as unknown was weighed at 30-35 mg. Table 1 shows the nitrogen data obtained with both gases.

Table 1. Nitrogen repeatability of Thermo Scientific Lubricant Reference Material with helium and argon gases.

Gas	Helium Carrier Gas	Argon Carrier Gas
N%	1.054	1.082
	1.057	1.089
	1.061	1.091
	1.054	1.069
	1.045	1.066
	1.052	1.087
	1.054	1.093
	1.066	1.071
	1.058	1.093
	1.071	1.091
Average N%	1.057	1.083
RSD %	0.698	0.978

The performance of the FLASH 2000 OEA was evaluated through the analysis of lubricant samples coming from an **ASTM International Interlaboratory Program.** ASTM organizes periodic comparison of test results and calculated statistical parameters with the laboratories participants in the petrochemical and analytical community worldwide to help the analytical laboratories monitoring their performance in conducting **ASTM methods.** The participating laboratories receive different lubricant samples every year and are requested to analyze the samples according to their own procedures. The results are collected and processed by ASTM and a complete report is sent to each participants.

Table 2 shows a comparison of the statistical results obtained by the ASTM and the FLASH 2000 OEA data using helium and argon carrier gases. All data obtained fall within the range indicated in the ASTM reports. The samples were analyzed as received. The Sample Code includes the name ALA followed by the year and the month in which the sample was analyzed and evaluated by ASTM. Using helium carrier gas, the instrument calibration was performed with 4-5 mg atropine (4.84 N%) with K factor as calibration method, the ASTM Lubricants were weighed at 8-10 mg. While using argon carrier gas, the calibration was performed with atropine (13-14 mg, 4.84 N%), ALA 0902 (9-35 mg, 0.561 N%) and Thermo Scientific Lubricant Reference Material (36-37 mg) with linear fit as calibration method. The ASTM Lubricants were weighed at 30-35 mg. Table 2 shows the ASTM data and Table 3 shows the nitrogen data obtained by the FLASH 2000 OEA using both gases and Table 4 shows the nitrogen data of other type of lubricants.

Table 2. ASTM information.

Sample Denomination	Number of laboratories participants	ASTM Robust Mean N%	ASTM Range accepted N%
ALA 0702	26	0.708	0.669 – 0.769
ALA 0706	31	0.788	0.748 – 0.848
ALA 0802	25	0.701	0.650 – 0.747
ALA 0902	31	0.561	0.500 – 0.606
ALA 1102	32	0.931	0.854 – 0.974

Table 3. Nitrogen reproducibility of ASTM lubricants with helium and argon carrier gas.

Sample Denomination	Helium Carrier Gas			Argon Carrier Gas		
	N%	Average N%	RSD %	N%	Average N%	RSD %
ALA 0702	0.729 0.727 0.721	0.726	0.59	0.710 0.721 0.727	0.719	1.20
ALA 0706	0.785 0.780 0.779	0.781	0.41	0.784 0.783 0.775	0.781	0.63
ALA 0802	0.716 0.729 0.724	0.723	0.91	0.718 0.708 0.714	0.712	1.01
ALA 0902	0.565 0.563 0.564	0.564	0.14	0.574 0.571 0.568	0.578	0.61
ALA 1102	0.941 0.933 0.941	0.939	0.49	0.947 0.950 0.940	0.946	0.54

Table 4. Nitrogen reproducibility of lubricants with helium and argon carrier gas.

Sample	Helium Carrier gas			Argon carrier gas		
	N%	Average N%	RSD %	N%	Average N%	RSD %
1	0.436 0.440 0.436	0.437	0.52	0.454 0.455 0.457	0.455	0.34
2	0.470 0.479 0.473	0.474	0.95	0.495 0.489 0.506	0.497	1.74
3	0.520 0.524 0.520	0.521	0.43	0.529 0.522 0.526	0.526	0.67
4	0.186 0.189 0.189	0.188	0.92	0.191 0.195 0.195	0.194	1.19
5	0.147 0.147 0.144	0.146	1.19	0.148 0.148 0.153	0.152	2.18
6	0.640 0.635 0.645	0.640	0.80	0.645 0.648 0.658	0.65	1.05

The stability of the system using argon carrier gas was verified though the analysis of 19-21 mg of atropine standard (4.84 N%, accepted range 4.79-4.91 N%) and 30-35 mg of Thermo Scientific Lubricant Reference Material (accepted range 1.184-1.224 N%) analyzed as unknown over a 12 day period. Calibration was performed with 19-21 mg of atropine using K factor as calibration method. During a 12 day period, maintenance was performed as follows:

- Day 3: the argon cylinder was replaced
- Day 8: oxygen cylinder was replaced
- Day 11: the ash crucible was cleaned and the CO_2 and H_2O trap fillings were replaced.

Every evening and every weekend the instrument was placed into Stand-By mode to reduce the consumption of argon gas. Table 5 shows the data obtained which were inside the accepted range according to the technical specifications of the analyzer, indicating the stability of the analyzer.

Table 5. Day by day reproducibility in N determination using argon as carrier gas.

Run Day	February Date	Sample	N%	Av. N%	RSD %	Sample	N%	Av. N%	RSD %
1	10	Atropine	4.868	4.87	0.560	Lubricant	1.178	1.186	0.999
2	11		4.894				1.177		
3	12		4.888				1.178		
4	13		4.885				1.188		
5	14		4.895				1.182		
6	17		4.886				1.184		
7	18		4.900				1.198		
8	19		4.836				1.187		
9	20		4.893				1.204		
10	21		4.816				1.188		
11	24		4.895				1.182		
12	25		4.789				1.195		

Conclusion

The Thermo Scientific FLASH 2000 N Lubricant Analyzer is a valuable solution for the analysis of nitrogen in lubricants in terms of accuracy, reproducibility, sensitivity, automation and speed of analysis. Thanks to the minimal need of sample preparation processes, the cost per analysis was reduced.

All data were obtained with an excellent repeatability and no matrix effect was observed when changing the sample. The repeatability was confirmed when argon carrier gas was used and data proved to be comparable with the data obtained under helium used as carrier gas.

The FLASH 2000 OEA enables the characterization of the different lubricant samples according to the nitrogen content coming from the additive. The information of its concentration can be used to judge its future performance.

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