Nitrogen Determination in Lubricants by Flash Combustion using Argon as Carrier Gas

Liliana Krotz, Francesco Leone, and Guido Giazzi
Thermo Fisher Scientific, Milano, Italy

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Overview

Purpose: Demonstrate nitrogen determination in lubricants by Organic Elemental Analysis

Methods: Lubricant samples were analyzed using an elemental analyzer with automated autosampler using helium and argon as carrier gas.

Results: Nitrogen data from different lubricant samples are presented to demonstrate the performance of the Elementar Analyzer.

Introduction

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

The method for Nitrogen analysis in lubricants, based on combustion, is described in 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 0.01 N% in lubricants can be determined.

As the demand for improved sample throughput, reduction of operational costs and minimization of human errors is increasing, it is very important to have a simple and automated technique which allows fast analysis with excellent reproducibility.

The Thermo Scientific™ FLASH™ 2000 Elemental Analyzer (Figure 1), based on the dynamic combustion of the material (Dumas method), requires no sample digestion or toxic chemicals, while providing important advantages in terms of time, automation and quantitative determination of nitrogen in a large range of concentration. However, as there is a possible worldwide shortage and an increase in costs for helium, the FLASH 2000 Analyzer can work with an alternative gas, argon which is readily available.

FIGURE 1. The Thermo Scientific FLASH 2000 Ntrogen Lubricant Analyzer.

Methods

The FLASH 2000 Organic Elemental Analyzer operates according to the dynamic flash combustion of the sample. Samples are weighed into tin capsules and introduced into the combustion reactor via the Thermo Scientific™ MAS 200R Autosampler together with oxygen.

After combustion, the produced gases are carried by a argon flow to a second reactor filled with copper, then swept through CO_2 and H_2O traps, a GC column and finally detected by a thermal conductivity detector. (Figure 2).

A report is automatically generated by the Thermo Scientific™ Eager Xperience Data Handling Software and displayed at the end of the analysis. The dedicated software allows the automatic calculation of the empirical formula.

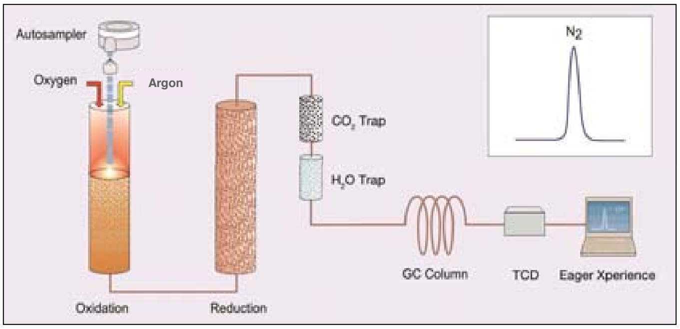

FIGURE 2. Nitrogen/Lubricant configuration.

Table 1 shows the analytical conditions using helium and argon as carrier gas.

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

TABLE 1. Analytical Conditions.

Note: The 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.

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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 as 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 between 8 and 10 mg. While 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 between 30- 35 mg. Table 2 shows the Nitrogen data obtained with both gases.

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

TABLE 2. Nitrogen repeatability of Thermo Scientific Lubricant Reference Material with helium and argon gases.

The performance of the FLASH 2000 Analyzer was evaluated through the analysis of lubricant samples coming from an ASTM International Interlaboratory Program. The participating laboratories receive different lubricants samples by year and they 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 3 shows the comparison of the calculated statistical results obtained by ASTM while Table 4 shows the FLASH 2000 data using helium and argon as carrier gases. All data obtained are inside in the range indicated in the ASTM reports. The samples were analyzed as received. The Sample Code include the name ALA follow by the year and the month in which the sample was analyzed and evaluated by ASTM.

Using helium as carrier gas, the instrument calibration was performed with about 4-5 mg atropine (4.84 N%) with K factor as calibration method, the ASTM Lubricants were weighed between 8 and 10 mg.

While using argon as 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 between 30-35 mg.

Table 5 shows the nitrogen data of other lubricant samples obtained using helium and argon as carrier gas.

Sample Name –Year-Month	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. ASTM information.

Sample	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 ASTM lubricants with helium and argon gases.

Sample	Helium Carrier Gas			Argon Carrier Gas		
Number	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

TABLE 5. Nitrogen reproducibility of lubricants with helium and argon gases.

The stability of the FLASH 2000 Analyzer using argon as 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 for 12 days. Calibration was performed with 19-21 mg of atropine using K factor as calibration method. During these 12 days maintenance was performed as follows:

- on day 3: the argon cylinder was replaced.
- on day 8: oxygen cylinder was replaced
- on day 11: the crucible was cleaned and the CO_2 and H_2O traps filling were replaced

Every evening and every weekend the instrument was set in Stand-By mode to reduce the consumption of argon gas. Table 6 shows the data obtained which falls within the accepted range of the technical specification of the analyzer, meaning excellent stability of the FLASH 2000 Elemental Analyzer.

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		

TABLE 6. Day by day reproducibility in N determination using argon as carrier gas.

All data showed were obtained with an acceptable repeatability and no matrix effect was observed when changing the sample. Good repeatability was obtained with the FLASH 2000 Analyzer using argon as carrier gas. The data are comparable with those obtained when using helium.

By using the FLASH 2000 Analyzer it is possible to characterize the different lubricant samples according to the nitrogen content coming from the additive. Knowledge of its concentration can be used to predict performance.

Conclusion

The FLASH 2000 N Lubricant Analyzer is an excellent solution for the analysis of nitrogen in lubricant in terms of:

- accuracy,
- reproducibility,
- sensitivity,
- automation,
- speed of analysis,
- cost per analysis.

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