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Elemental Analysis: Nitrogen determination of lubricants with different pure organic calibration standards

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Goal

This technical note reports data on nitrogen determination in lubricants using alternative standards, not included in the ASTM 5291 Method.

Introduction

During production, the nitrogen content of mineral oils is monitored and tested for quality control purposes. Additives with nitrogen give mineral oils that include them desirable features as lubricants, and lubricant manufacturers monitor nitrogen concentrations in their products for its effects on performance and quality.

The ASTM 5291 Method describes the instrumental determination of carbon, hydrogen and nitrogen in laboratory samples of petroleum products and lubricants. This method suggests a list of pure organic compounds, commonly used to calibrate the analytical system. Other pure compounds can also be used. Some of these standards cannot be used for nitrogen determination of lubricants, since they do not contain nitrogen. Atropine is the standard with the lowest nitrogen percentage, though it is classified as toxic (CAS 51558).

As the demand for improved sample throughput and reduction of operational costs, an automated technique, removing the need for toxic chemicals is needed.

The Thermo Scientific™ Flash*Smart*™ Elemental Analyzer (Figure 1), based on the dynamic combustion of the material (modified Dumas method) requires no sample digestion or toxic chemicals, while being a solution for the accurate and reproducible quantitative determination of nitrogen in large range of concentration. Different standards can be used to calibrate the instrument, without affecting the performance of the analytical results.

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

Methods

The Flash*Smart* EA operates with the 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 second reactor filled with copper, then swept through CO_2 and H_2O traps, a GC column. Finally, they are detected by a Thermal Conductivity Detector (Figure 2). The Thermo Scientific™ Eager*Smart*™ Data Handling Software provides a comprehensive analytical report.

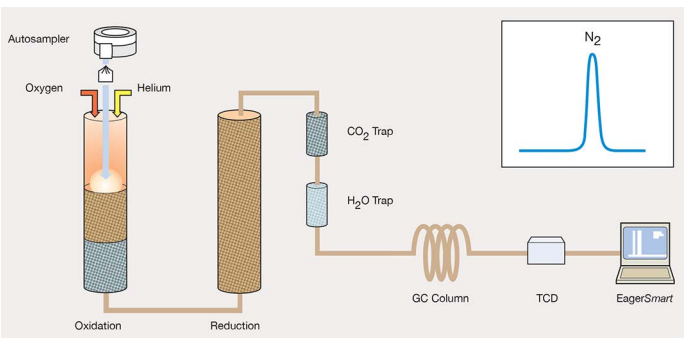

Figure 2. Nitrogen configuration.

Results

The ASTM 5291 Method describes the instrumental determination of carbon, hydrogen and nitrogen in laboratory samples of petroleum products and lubricants. The list of pure organic compounds, commonly used to calibrate the analytical system is showed in Table 1. Other pure compounds can also be used.

Table 1. Calibration Standards suggested by ASTM 5291 Official Method.

Compound	N%	C%	H%
Acetanilide	10.36	71.09	6.71
Atropine	4.84	70.56	8.01
Benzoic acid	-	68.84	4.95
Cyclohexanone-2,4-dinitrophenylhydrazone	20.14	51.79	5.07
Cystine	11.66	29.99	5.03
Diphenyl	-	93.46	6.54
EDTA	9.59	41.10	5.52
Imidazol	41.15	52.92	5.92
Nicotinic acid	11.38	58.53	4.09
Stearic acid	-	75.99	12.76
Succinamide	24.13	41.37	6.94
Sucrose	-	42.10	6.48
Sulphanilamide	16.27	41.84	4.68
Triethanol amine	9.39	48.30	10.13

Other standards not included in Table 1, such as BBOT (2,5-Bis (5-tert-butyl-benzoxazol-2-yl) thiophene) and tocopherol nicotinate were considered as alternatives to atropine. Table 2 shows the theoretical values, the acceptable range according to the technical specification of the Analyzer and the sample weight used for the calibration. The calibration method used was K factor.

Thermo Scientific™ Lubricant Reference Material was analyzed ten times. Data obtained was compared by using different calibration standards (Table 3).

Table 2. Theoretical values, acceptable range and sample weight of the pure organic standards tested.

Standard	Weight	Nitrogen		Carbon		Hydrogen	
	(mg)	%	Range (±)	%	Range (±)	%	Range (±)
Atropine	4–5	4.84	0.07	70.56	0.30	8.01	0.10
BBOT	4–4.2	6.51	0.10	72.53	0.30	6.09	0.10
Tocopherol Nicotinate	9.5–10	2.61	0.03	78.46	0.30	9.97	0.10

Table 3. Nitrogen data of Thermo Scientific Lubricant Reference Material.

Run	TS Lubricant Ref. Mat.	Atropine Std.	BBOT Std.	Tocopherol Nicotinate Std.
	Weight (mg)	N%	N%	N%
1	8.105	1.11	1.10	1.10
2	8.856	1.10	1.09	1.09
3	8.848	1.11	1.10	1.10
4	8.901	1.11	1.10	1.10
5	8.585	1.11	1.10	1.10
6	9.001	1.10	1.10	1.10
7	8.698	1.10	1.09	1.09
8	9.836	1.11	1.10	1.10
9	12.529	1.10	1.10	1.10
10	9.313	1.09	1.09	1.09
	Average N%	**1.10**	**1.10**	**1.10**
	Std. Dev.	**0.007**	**0.005**	**0.005**
	RSD%	**0.63**	**0.44**	**0.44**

The performance of the Flash*Smart* EA was evaluated through the analysis of lubricant samples provided by the ASTM International Interlaboratory Program. Periodic comparisons of test results are performed with laboratories within the petrochemical and analytical community worldwide, to monitor their performances in fulfilling ASTM Methods.

The participating laboratories receive different lubricants samples every year and are required to analyze them. The results are collected and processed by ASTM and shared with a report.

Table 4 shows a comparison of the data obtained with the Flash*Smart* EA with the different calibration standards and the ASTM range. All data obtained fall within the range indicated in the ASTM reports. The samples were weighed at 8–10 mg.

Table 4. Nitrogen data of ASTM lubricant samples.

Calibration Standard	Atropine	BBOT	Tocopherol Nicotinate	ASTM Range
Sample Name	N%	N%	N%	N%
1	0.941	0.944	0.942	0.854–0.974 N%
	0.944	0.947	0.945	
	0.944	0.947	0.945	
Average	0.943	0.946	0.944	
RSD%	0.19	0.18	0.22	
2	0.776	0.779	0.777	0.748–0.848 N%
	0.780	0.783	0.781	
	0.777	0.780	0.778	
Average	0.778	0.781	0.779	
RSD%	0.27	0.26	0.27	
3	0.706	0.708	0.708	0.669–0.769 N%
	0.710	0.712	0.711	
	0.708	0.711	0.710	
Average	0.708	0.710	0.710	
RSD%	0.28	0.29	0.22	
4	0.956	0.959	0.957	0.912–1.010 N%
	0.952	0.955	0.954	
	0.951	0.955	0.953	
Average	0.953	0.956	0.955	
RSD%	0.28	0.24	0.22	
5	0.730	0.733	0.731	0.650–0.747 N%
	0.728	0.730	0.728	
	0.729	0.731	0.730	
Average	0.729	0.731	0.730	
RSD%	0.14	0.21	0.21	
6	0.555	0.557	0.556	0.500–0.606 N%
	0.558	0.560	0.560	
	0.556	0.558	0.558	
Average	0.556	0.558	0.558	
RSD%	0.27	0.27	0.27	

Table 5 shows the nitrogen data of other lubricants obtained with the Flash*Smart* Analyzer with the different calibration standards. Table 6 shows the nitrogen data of low-nitrogen-content sample, which was analyzed 10 times to evaluate its repeatability. The samples were weighed at 8–10 mg.

Table 5. Repeatability of nitrogen analysis on lubricants.

Sample Name		N%	N%	N%
A		0.183	0.184	0.183
		0.186	0.187	0.186
		0.185	0.186	0.186
	Average	0.185	0.186	0.185
	RSD%	0.83	0.82	0.83
B		0.514	0.516	0.516
		0.516	0.517	0.517
		0.516	0.518	0.518
	Average	0.515	0.517	0.517
	RSD%	0.23	0.19	0.19
C		0.627	0.629	0.628
		0.628	0.630	0.628
		0.631	0.633	0.632
	Average	0.629	0.631	0.629
	RSD%	0.33	0.33	0.37
D		0.459	0.460	0.459
		0.457	0.458	0.457
		0.457	0.458	0.458
	Average	0.458	0.459	0.458
	RSD%	0.25	0.25	0.22

Table 6. Repeatability of analysis on low nitrogen-content sample.

Calibration Standard	Atropine	BBOT	Tocopherol Nicotinate
Element	N%	N%	N%
	0.109	0.110	0.109
	0.109	0.109	0.109
	0.107	0.108	0.107
	0.110	0.110	0.110
	0.109	0.110	0.109
	0.108	0.108	0.108
	0.109	0.110	0.109
	0.110	0.110	0.110
	0.107	0.108	0.107
	0.108	0.108	0.108
Average	0.109	0.109	0.108
RSD%	0.98	0.91	0.98

A day-by-day stability test was performed analyzing tocopherol nicotinate as standard to calibrate the Analyzer using K factor as the calibration method. Then, tocopherol nicotinate (2.61 N%, ±0.03) and Thermo Scientific Lubricant Reference Material (1.12 N%, ±0.10) were analyzed twice in a time range of 10 days. The nitrogen data fall within the technical specification of the Flash*Smart* EA, indicating complete combustion of the sample. The repeatability of the data demonstrates the stability of the system. Table 7 shows the data obtained during 10 days.

Table 7. 10-day stability of nitrogen analysis day-day using tocopherol nicotinate as calibration standard.

Day	Tocopherol Nicotinate				Lubricant Reference Material			
	W (mg)	N%	Av. N%	RSD%	W (mg)	N%	Av. N%	RSD%
1	4.460	2.61	2.61	0.74	8.707	1.10	1.12	1.52
	4.227	2.59			9.445	1.11		
2	4.939	2.61			8.468	1.13		
	4.679	2.62			9.083	1.16		
3	4.766	2.61			10.316	1.14		
	4.351	2.62			9.247	1.12		
4	5.103	2.63			8.833	1.12		
	4.681	2.63			9.330	1.11		
5	4.879	2.62			8.513	1.09		
	4.609	2.61			9.237	1.13		
6	4.308	2.60			9.568	1.12		
	4.999	2.61			10.255	1.12		
7	4.740	2.60			8.223	1.10		
	4.827	2.61			8.767	1.10		
8	4.215	2.59			9.318	1.13		
	4.620	2.62			8.868	1.13		
9	4.112	2.59			9.473	1.13		
	4.787	2.60			8.741	1.14		
10	4.444	2.60			9.992	1.12		
	4.536	2.61			9.541	1.13		

Conclusions

With the Flash*Smart* EA the nitrogen content of different lubricant samples according to ASTM 5291 Method can be characterized with excellent reproducibility, if compared with the ASTM method requirements.

No matrix effect was observed when changing the sample. The values are comparable to the ASTM accepted range indicating that the three standards, atropine, BBOT and tocopherol nicotinate can be used for the calibration of the Elemental Analyzer.

In particular, tocopherol nicotinate can be a valuable alternative to other standards for lubricant analysis: its content is made of low nitrogen, high carbon and hydrogen amounts, and the element concentration is similar to the element concentration of lubricants. Besides, tocopherol nicotinate is not classified as hazardous standard, allowing to reducing toxicity.

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