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APPLICATION NOTE 42216

# Characterization of lubricants and oils by the Thermo Scientific Flash*Smart* 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 Flash*Smart* 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.

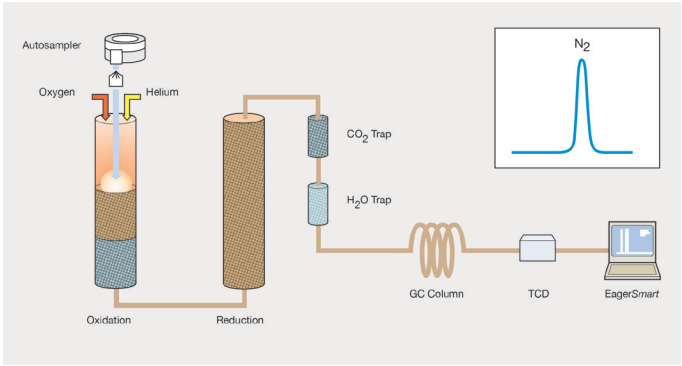


**Figure 2. Nitrogen Lubricant configuration.**

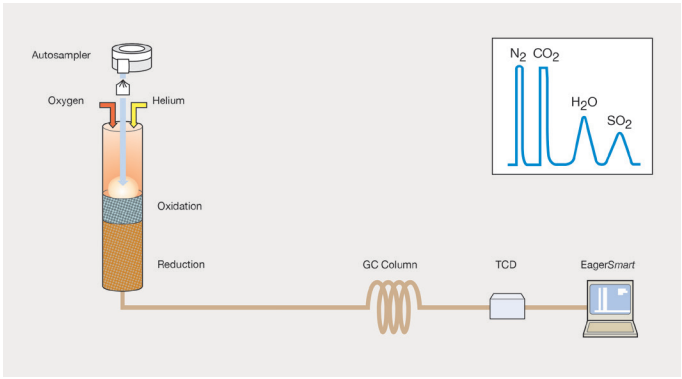


**Figure 3. CHNS configuration.**

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.

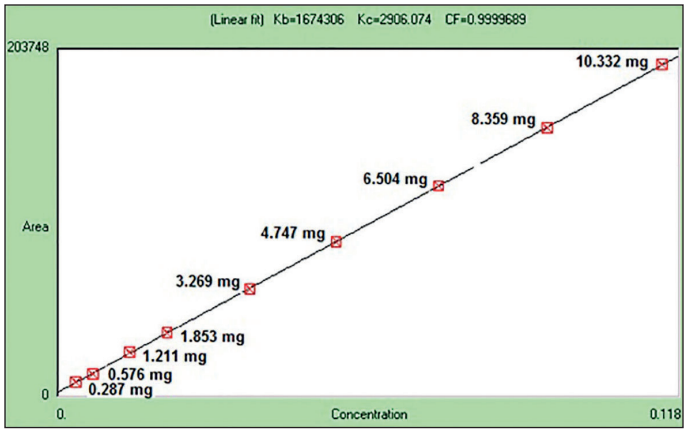


Figure 4. Nitrogen Linear Fit Calibration Curve.

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<br>0.3065<br>0.3062 |
| 2 | 0.6253 | 0.4580<br>0.4539<br>0.4594 |
| 3 | 0.9414 | 0.4700<br>0.4788<br>0.4727 |
| 4 | 0.4275 | 0.5200<br>0.5237<br>0.5197 |
| 5 | 0.7969 | 0.6400<br>0.6349<br>0.6451 |
| 6 | 0.7908 | 0.8461<br>0.8420<br>0.8331 |
| 7 | 0.5825 | 1.4617<br>1.4664<br>1.4783 |
| 8 | 0.3135 | 3.9927<br>3.9683<br>3.9760 |

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

| Sample | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| N% | 0.0347<br>0.0323<br>0.0309<br>0.0298<br>0.0358<br>0.0323<br>0.0316<br>0.0304<br>0.0329<br>0.0292 | 0.0468<br>0.0446<br>0.0465<br>0.0493<br>0.0495<br>0.0463<br>0.0450<br>0.0469<br>0.0476<br>0.0431 | 0.1051<br>0.1147<br>0.1158<br>0.1078<br>0.1147<br>0.1059<br>0.1084<br>0.1177<br>0.1089<br>0.1121 | 0.1456<br>0.1488<br>0.1482<br>0.1507<br>0.1424<br>0.1535<br>0.1436<br>0.1535<br>0.1494<br>0.1514 | 0.1800<br>0.1819<br>0.1849<br>0.1860<br>0.1811<br>0.1849<br>0.1858<br>0.1894<br>0.1834<br>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<br>191<br>209<br>194<br>175<br>182<br>179<br>187<br>192<br>186 | 189 | 5.03 |
| 2 | 126<br>138<br>110<br>134<br>132<br>127<br>135<br>134<br>121<br>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<br>0.280<br>0.273 | 1.5851 |
| Heavy Gas Oil 2 | 0.242<br>0.247<br>0.247 | 1.1767 |
| Heavy Gas Oil 3 | 0.069<br>0.073<br>0.072 | 2.9182 |
| Slurry Oil | 0.213<br>0.212<br>0.217 | 1.2363 |
| Residual Oil | 0.276<br>0.274<br>0.266 | 1.9454 |
| Vacuum Gas Oil | 0.098<br>0.093<br>0.099 | 3.3254 |

To verify the performance of the Flash*Smart* 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 Flash*Smart* 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<br>0.222<br>0.200<br>0.212<br>0.214 | 4.312 | 85.270<br>85.370<br>85.359<br>85.102<br>85.283 | 0.126 | 13.395<br>13.308<br>13.319<br>13.289<br>13.355 | 0.316 | 0.289<br>0.290<br>0.283<br>0.291<br>0.297 | 1.724 |
| Crude Oil 2 | 0.270<br>0.282<br>0.271<br>0.279<br>0.270 | 2.071 | 85.425<br>85.770<br>85.547<br>85.377<br>85.752 | 0.212 | 11.919<br>11.925<br>11.894<br>11.794<br>11.870 | 0.446 | 2.028<br>2.018<br>2.015<br>1.985<br>2.018 | 0.810 |

Table 9. NCS repeatability of lubricants.

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

Table 10. Sulfur repeatability of oils.

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