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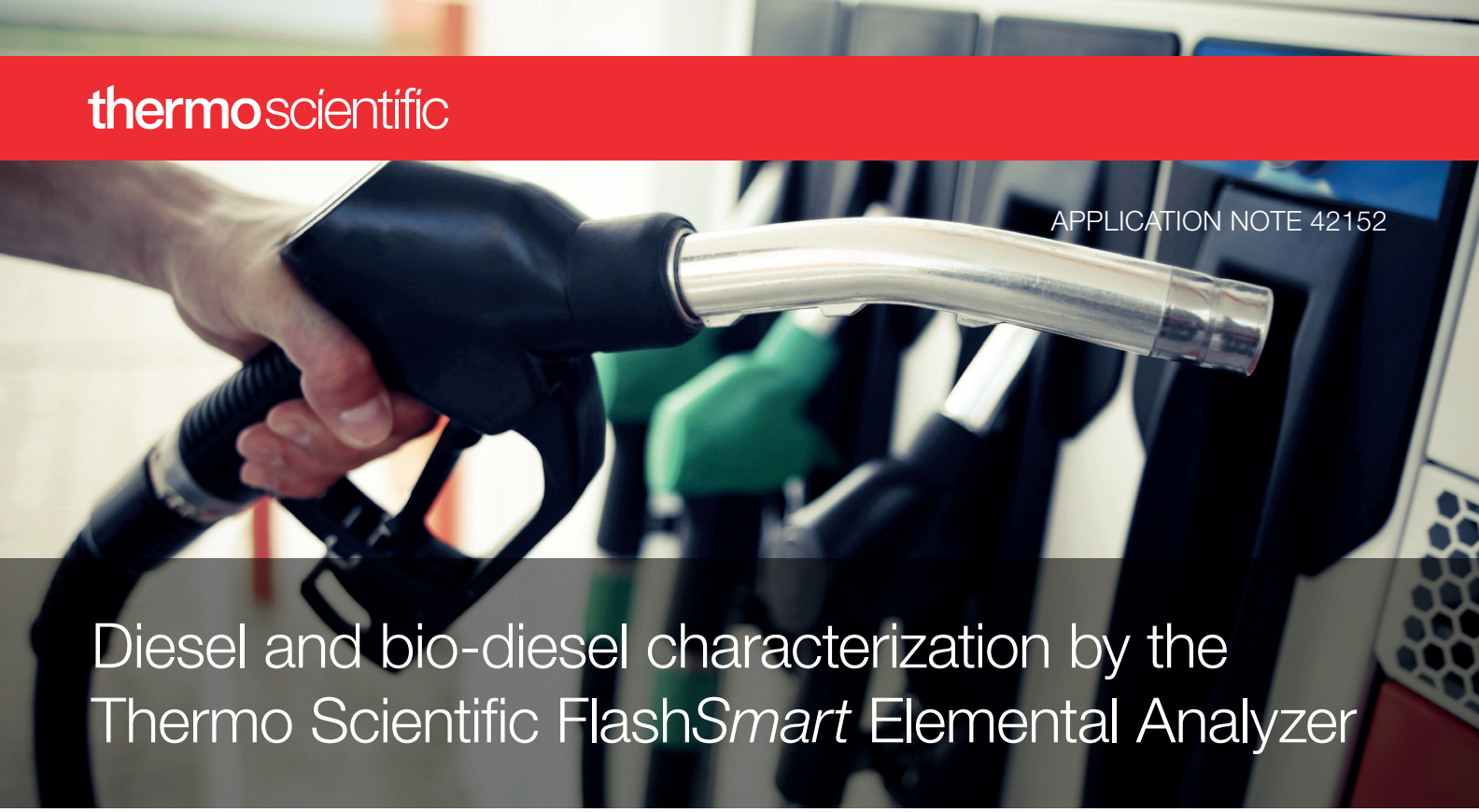

APPLICATION NOTE 42152

# Diesel and bio-diesel characterization by the Thermo Scientific Flash*Smart* Elemental Analyzer


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**Keywords**

Bio-diesel, CHNS, Combustion, Diesel


## Goal

This application note shows the robustness of the Flash*Smart* Elemental Analyzer to perform CHNS/O data for diesel samples and pure organic liquid standards.

## Introduction

Many manufacturing plants and research laboratories are involved in the characterization of diesel and bio-diesel. Their main task is to ensure the products adhere to legislative requirements for production such as carbon dioxide emission levels, impact on water resources, energy balance and efficiency. A way to characterize these materials and to calculate their energetic value is to determine their elemental composition.

Determination of elemental composition requires an accurate and automated analytical solution. The Thermo Scientific™ Flash*Smart*™ Elemental Analyzer, coupled with the Thermo Scientific™ AS 1310 Liquid Autosampler and MAS Plus Autosampler (Figure 1) allows the quantitative determination of carbon, nitrogen, hydrogen, sulfur and oxygen on light and heavy liquids and viscous samples. Dedicated Thermo Scientific™ Eager*Smart*™ Data Handling Software provides an automated calculation of the gross and net heat value (GHV and NHV). The system, which is based on the dynamic combustion of the sample, provides simultaneous CHNS determination in a single run and oxygen determination by pyrolysis in a second run.

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As the liquid samples are directly injected in the elemental analyzer, no sample preparation is required; reducing time and cost per analysis. To perform total sulfur determination at trace levels in diesel the Flash*Smart* Elemental Analyzer is coupled with the Flame Photometric Detector (FPD). This method combines the advantages of the elemental analyzer with the sensitivity, selectivity and robustness of the FPD Detector.

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

Depending of the density and volatility of diesel and bio-diesel, samples can be injected directly or weighed in a tin containers. The improvement in liquid injection allows the proper combution of light diesel samples and the complete quantification of its elements without memory effect. For higher density diesel samples, the use of a hard container and a dedicated sealing device permits the complete characterization of this material.

## Methods

For CHNS determination the Flash*Smart* Elemental Analyzer operates using the dynamic flash combustion technique. Samples, weighed in hard tin containers closed by the sealing device or injected directly, are introduced into the combustion reactor via the MAS Plus Autosampler or AS 1310 Liquid Autosampler with oxygen. After combustion the resulting gases are carried by a helium flow to a layer filled with copper, then swept through a GC column that provides the separation of the combustion gases, and finally, detected by a Thermal Conductivity Detector (TCD) (Figure 2). Total run time is less than 10 minutes.

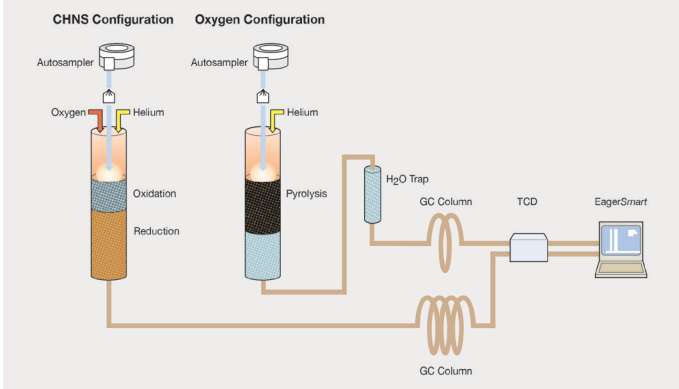


**Figure 2. CHNS/O configuration.**

For trace sulfur determination, samples are weighed in a hard tin container. The gases produced by combustion are carried by a helium flow to a layer filled with copper, then swept through a water trap, a short GC column and finally the sulfur content is measured by the Flame Photometric Detector (FPD). Total sulfur determination run time is 5 minutes (Figure 3).

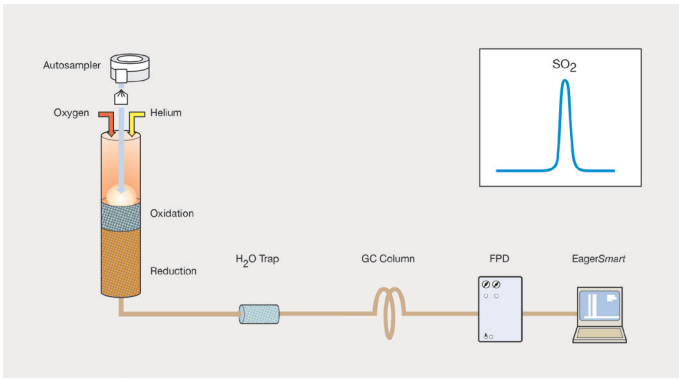


**Figure 3. Sulfur configuration by FPD.**

For oxygen determination, the system operates in pyrolysis mode. Samples are weighed in silver containers or injected directly, and introduced into the pyrolysis chamber via the MAS Plus Autosampler or AS 1310 Liquid Autosamplers. The reactor contains nickel coated carbon at a temperature of 1060 °C. The oxygen in the sample, combined with the carbon, forms carbon monoxide which is then chromatografically separated from other products and detected by the TCD Detector (see Figure 2). Total run time is 5 minutes.

A complete report is automatically generated by the Eager*Smart* Data Handling Software.

## Improvement in liquid injection

Due to the density and volatility of diesel and biodiesel samples, a modification of the injection system was performed in order to achieve a proper introduction of the sample that allows the complete combustion without memory effect. By adding an insulator around the injector and a collar on the top of the reactor, the resultant higher temperature in the injection area allows complete volatilization and combustion of the sample.

## Results

This note shows CHNS/O data for diesel samples and pure organic liquid standards to demonstrate the robustness of the Flash*Smart* EA. The application was performed without matrix effect and shows the reproducibility of the data obtained. Table 1 shows the reproducibility of CH data obtained of n-hexane (83.63 C%, 16.37 H%, density 0.655 g/ml), iso-octane (84.12 C%, 15.88 H%, density 0.692 g/ml) and toluene (91.25 C%, 8.75 H%, density 0.867 g/ml). The instrument was calibrated with iso-octane and the volume injected was 2 ul.

**Table 1. Reproducibility of CH determination in n-hexane, iso-Octane and Toluene.**

| Sample name | No. of runs | Theoretical values | | Experimental data | | | |
|---|---|---|---|---|---|---|---|
| | | C% | H% | C% | RSD% | H% | RSD% |
| n-Hexane | 10 | 83.63 | 16.37 | 83.51 | 0.17 | 16.29 | 0.18 |
| iso-Octane | 30 | 84.12 | 15.88 | 83.98 | 0.23 | 15.91 | 0.41 |
| Toluene | 12 | 91.25 | 8.75 | 90.98 | 0.25 | 8.75 | 0.53 |

Table 2 shows the reproducibility of CH determination in diesel samples obtained with the AS 1310 Autosampler direct liquid injection.

**Table 2. Reproducibility of CH determination of diesel samples.**

| Sample | Diesel 1 | | Diesel 2 | | Diesel 3 | |
|---|---|---|---|---|---|---|
| Element | C% | H% | C% | H% | C% | H% |
| % | 85.34<br>85.35<br>85.64<br>85.67<br>85.72<br>85.73<br>85.61<br>85.25<br>85.26<br>85.67 | 14.32<br>14.31<br>14.39<br>14.37<br>14.38<br>14.38<br>14.37<br>14.34<br>14.37<br>14.39 | 84.67<br>84.72<br>84.49<br>84.62<br>84.53<br>84.71<br>84.60<br>84.55<br>84.37<br>84.43 | 15.37<br>15.39<br>15.32<br>15.34<br>15.36<br>15.36<br>15.36<br>15.32<br>15.35<br>15.33 | 86.45<br>86.51<br>86.26<br>86.32<br>86.41<br>86.59<br>86.57<br>86.52<br>86.67<br>86.47 | 13.87<br>13.92<br>13.82<br>13.86<br>13.90<br>13.88<br>13.90<br>13.93<br>13.85<br>13.88 |
| RSD% | 0.23 | 0.20 | 0.14 | 0.14 | 0.02 | 0.05 |

Table 3 shows the reproducibility of oxygen determination of diesel samples obtained by direct liquid injection.

**Table 3. Reproducibility of oxygen determination of diesel samples.**

| Sample | O% | RSD% |
|---|---|---|
| A | 0.0265<br>0.0224<br>0.0214<br>0.0233<br>0.0233 | 8.179 |
| B | 0.0191<br>0.0192<br>0.0181<br>0.0196<br>0.0201 | 3.848 |

High density diesel samples were weighed in tin containers for CHNS analysis and in silver containers for oxygen determination. The Eager*Smart* Data Handling Software automatically calculates the GHV (Gross Heat Value in kcal/kg) and NHV (Net Heat Value in kcal/kg). Table 4 shows the CHNS/O data and the Heat Values of two diesel samples.

**Table 4. CHNS/O and Heat Value calculation of diesel samples.**

| Sample | N% | C% | H% | S% | O% | GHV | NHV |
|---|---|---|---|---|---|---|---|
| 1 | 0.0618<br>0.0644<br>0.0657 | 90.54<br>90.20<br>90.15 | 9.39<br>9.39<br>9.38 | 0.0587<br>0.0585<br>0.0596 | 0.3002<br>0.2711<br>0.2862 | 10211<br>10212<br>10212 | 9709<br>9710<br>9710 |
| 2 | 0.0579<br>0.0681<br>0.0614 | 90.06<br>90.06<br>90.02 | 9.70<br>9.72<br>9.71 | 0.0342<br>0.0398<br>0.0381 | 0.2259<br>0.2560<br>0.2431 | 10289<br>10288<br>10288 | 9770<br>9769<br>9769 |

Table 5 shows the sulfur data of two diesel samples obtained with the FPD Detector, where the sulfur content is at trace levels. Samples were weighed in hard tin containers. Instrument calibration was performed with a solution of a lubricant in iso-octane at 100 ppm sulfur.

**Table 5. Sulfur determination in diesel samples by FPD Detector.**

| Sample | S ppm | RSD% |
|---|---|---|
| A | 25<br>22<br>21<br>22 | 8.179 |
| B | 58<br>56<br>52<br>57 | 3.848 |

## Conclusions

The Flash*Smart* Elemental Analyzer allows the quantitative recovery of the elements from any matrix by direct liquid injection or by weighing, and no memory effect is observed when changing the sample.

With the Flash*Smart* EA CHNS determination in a single run followed by oxygen determination can be performed, without changing the configuration at extra cost and time loss. Furthermore, with a simple modification of the configuration, the analysis of trace sulfur by the FPD Detector can be performed.

Analysis is made simple thanks to the automated calculations performed by the Eager*Smart* Data Handling Software which determines complete characterisation of the sample, including the calorific power. Additionally, with single analytical runs and no change of configuration for CHNS/O determinations alongside direct injection, laboratories benefit from time savings, safer environments without the use of hazardous chemicals and low cost per analysis.

Find out more at **thermofisher.com/OEA**


**AN42152-EN 0417**

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