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Elemental analysis

# Analysis of liquids by Flash*Smart* Elemental Analyzer with a liquid autosampler

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## Goal

To assess data precision and repeatability using the Thermo Scientific™ Flash*Smart*™ Elemental Analyzer (EA) for automatic injection of liquid samples.

## Introduction

Carbon, nitrogen, hydrogen, sulfur determination by combustion, and oxygen determination by pyrolysis are commonly used for the characterization of a variety of liquid samples such as beverages, organic solutions, diesel, gasoline or liquid fertilizers. The Flash*Smart* Elemental Analyzer (EA) provides highly accurate elemental analysis of liquid samples while supporting high productivity through automation delivered by the Thermo Scientific™ AS 1310 Liquid Autosampler.

The Flash*Smart* EA is equipped with two fully independent furnaces allowing the installation of one or two analytical circuits that can be used sequentially. Each analytical circuit can be equipped with an AS 1310 Liquid Autosampler that is fully controlled by the Thermo Scientific™ Eager*Smart*™ Data Handling Software. Optionally, the system can be used with a combination of a liquid and solid autosampler. The flexibility of the Flash*Smart* EA allows several analytical configurations to be used for elemental analysis, from nitrogen analysis to NC, CH, CHN, CHNS, NCS and oxygen determination. The injection volume can be in micro (2-3 µl) or macro (100 to 250 µl) range.

## Methods

The Flash*Smart* EA (Figure 1) operates with the dynamic flash combustion of the sample. The Eager*Smart* Data Handling Software controls all analytical parameters of the instrument including the liquid autosampler, the oxygen flow and the timing of oxygen injection.

**Figure 1. Thermo Scientific Flash*Smart* EA with AS 1310 Liquid Autosampler**

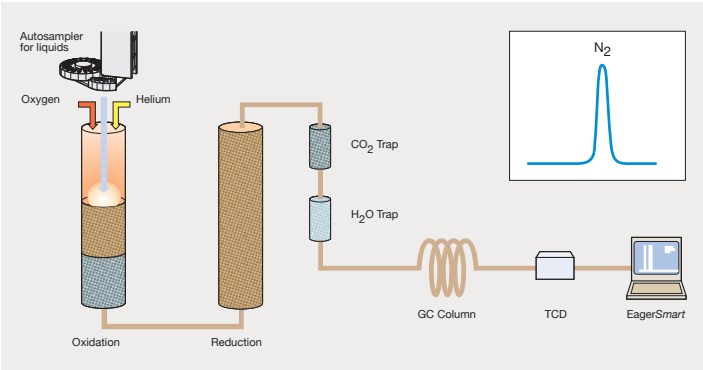


**Figure 2. Flash*Smart* EA N configuration**

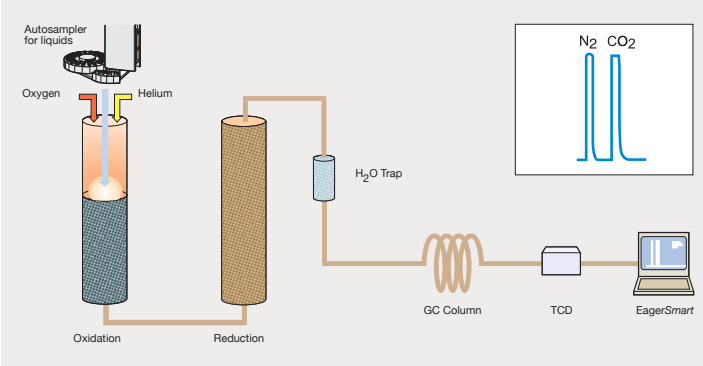


**Figure 3. Flash*Smart* EA NC configuration**

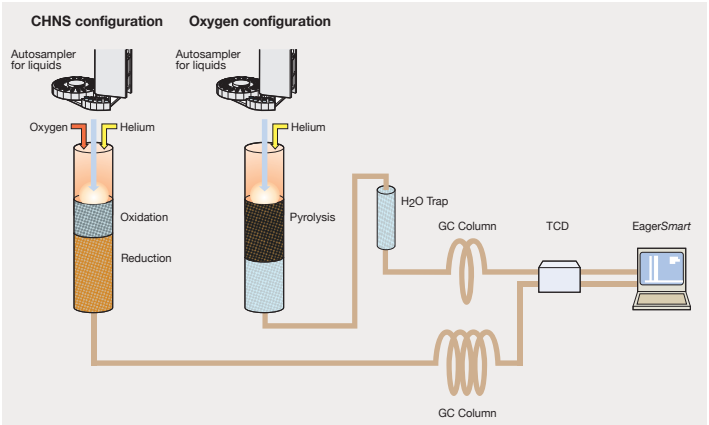


**Figure 4. Flash*Smart* EA CHNS/O configuration**

For nitrogen and NC determination, the gases produced in the combustion reactor are carried by a helium flow to a second reactor filled with copper, then swept through the $H_2O$ trap (and $CO_2$ trap for nitrogen configuration), a GC column and finally detected by a Thermal Conductivity Detector (TCD) (Figures 2 and 3). For CH, CHN and CHNS determination, a single reactor setup is used for combustion as the second circuit is used for oxygen determination by pyrolysis (Figure 4). Each analytical circuit uses a dedicated AS 1310 Liquid Autosampler for sample injection. Pyrolysis operating mode (right furnace, Figure 4) includes a reactor with nickel coated carbon maintained at 1060 °C. The oxygen present in the sample, combined with the carbon, forms carbon monoxide which is then chromatographically separated from other products and detected by the TCD.

A complete report is automatically generated by the Eager*Smart* Data Handling Software and displayed at the end of the analysis. The dedicated software automatically converts the nitrogen % in protein content using a specific protein factor for food and beverages.

The analytical conditions for liquid samples analysis using the AS 1310 Liquid Autosampler depend on the configuration, syringe, and sample matrix, as indicated in Table 1.

**Table 1. Thermo Scientific Flash*Smart* EA with AS 1310 Liquid Autosampler - analytical setup**

| Configuration | Standard and blank | Analytical setup |
|---|---|---|
| Nitrogen or NC | • Urea water solutions at different concentrations<br>• Blank: bidistilled or HPLC Plus water | • Calibration method: K factor<br>• Oxygen injection time: 3 seconds<br>• Oxygen flow: 300 ml/min (for N) or 250 ml/min (for NC)<br>• Standard volume: 50 to 125 µl<br>• Sample volume: 50 to 125 µl<br>• Samples are injected at 8 seconds after the start<br>• Solvent: bidistilled or HPLC Plus water |
| CHN | • Solutions of di-ethylamine in heptane and acetonitrile in ethanol at different concentrations | • Calibration method: K factor<br>• Oxygen injection time: 3 seconds<br>• Oxygen flow: 250 ml/min<br>• Standard volume :2 µl<br>• Sample volume: 2 µl<br>• Samples are injected at 8 seconds after the start<br>• Solvent: heptane (for CHN) or ethanol (for CHNS) |
| CHNS | • Solutions of dimethyl sulfoxide (DMSO) and acetonitrile in ethanol at different concentrations | |
| Oxygen | • Solutions of ethanol and iso-octane at different concentrations | • Calibration method: K factor<br>• Standard volume :2 µl<br>• Sample volume: 2 µl<br>• Samples are injected at 8 seconds after the start<br>• Solvent: ethanol |

## Results

Different sample matrices were analyzed in a large range of concentrations to demonstrate precision and repeatability of the Flash*Smart* EA for the analysis of liquids by direct automatic injection.

Table 2 shows the nitrogen determination of food, environmental, agronomy and biological liquid samples in a large range of concentrations from ppm to percentage level.

Beer samples were degassed prior to analysis to eliminate the carbon dioxide. Wort samples are rather viscous due to the high sugar content but can be analyzed without any pre-treatment or dilution.

Table 3 shows NC data obtained from beverages and agronomy samples. Table 4 shows total carbon (TC) and total organic carbon (TOC) of water samples. The TOC analyses were done after the acidification of the water samples with hydrochloric acid to eliminate the inorganic carbon.

**Table 2. Nitrogen data of liquid samples**

| Sample | Repetitions | N% | SD | RSD% |
|---|---|---|---|---|
| Beer | 20 | 0.0634 | 0.00053 | 0.83 |
| Wort | 16 | 0.1242 | 0.00135 | 1.09 |
| Wine | 20 | 0.0274 | 0.00031 | 1.12 |
| Juice | 20 | 0.0109 | 0.00017 | 1.55 |
| Cheese extract | 20 | 0.0120 | 0.00021 | 1.71 |
| Milk protein fraction | 20 | 0.1340 | 0.00056 | 0.42 |
| Soluble protein in fodder | 20 | 0.0870 | 0.00169 | 1.95 |
| Liquid fertilizer | 3 | 10.17 | 0.01569 | 0.15 |
| Sugar solution | 3 | 0.0109 | 0.00011 | 1.06 |
| Urine | 4 | 0.7400 | 0.00414 | 0.56 |
| Water solution | 3 | 0.0019 | 0.00006 | 2.99 |
| High containing urea water solution | 10 | 14.40 | 0.06336 | 0.44 |

Table 3. NC data of liquid samples

| Sample | Repetitions | Av. N% | SD | RSD% | Av. C% | SD | RSD% |
|---|---|---|---|---|---|---|---|
| Coffee | 10 | 0.188 | 0.00147 | 0.78 | 3.22 | 0.02701 | 0.84 |
| Liquid fertilizer (low NC %) | 3 | 0.209 | 0.00231 | 1.10 | 15.87 | 0.02517 | 0.16 |
| Liquid fertilizer (high NC %) | 3 | 9.723 | 0.02886 | 0.30 | 26.12 | 0.07637 | 0.29 |
| Water | 10 | 0.0024 | 0.00004 | 1.88 | 0.0011 | 0.00002 | 2.15 |

Table 4. TC and TOC data of water samples

| Sample | Total Carbon (TC) | | | | Total Organic Carbon (TOC) | | | |
|---|---|---|---|---|---|---|---|---|
| | Repetitions | Av. TC ppm | SD | RSD% | Repetitions | Av. TOC ppm | SD | RSD% |
| Water 1 | 2 | 33.0 | 0.00008 | 2.59 | 3 | 4.0 | 0.00001 | 3.19 |
| Water 2 | 2 | 154.5 | 0.00049 | 2.05 | 3 | 45.3 | 0.00015 | 2.50 |

The organic liquid solutions and diesel samples CH, CHN and CHNS data is shown in Table 5. For CH determination pure organic solvents and diesel samples were analyzed. For CHN determination, a solution of di-ethylamine in heptane was prepared, while for CHNS determination, a solution of DMSO/ acetonitrile/ethanol was prepared.

The oxygen data of petrochemical and organic liquid samples are presented in Table 6. All the samples were analyzed in triplicate without any pre-treatment.

Table 5. CH, CHN and CHNS data of liquid samples

| Sample | Repetitions | Av. N% | SD | Av. C% | SD | Av. H% | SD | Av. S% | SD |
|---|---|---|---|---|---|---|---|---|---|
| | | | RSD% | | RSD% | | RSD% | | RSD% |
| n-Hexane | 10 | - | - | 83.51 | 0.142<br>0.17 | 16.29 | 0.029<br>0.18 | - | - |
| Isooctane | 5 | - | - | 84.20 | 0.144<br>0.17 | 15.87 | 0.087<br>0.54 | - | - |
| Diesel | 10 | - | - | 86.48 | 0.124<br>0.02 | 13.88 | 0.033<br>0.05 | - | - |
| Solution CHN | 5 | 0.393 | 0.001<br>0.38 | 83.48 | 0.108<br>0.13 | 16.09 | 0.008<br>0.05 | - | - |
| Solution CHNS | 5 | 2.65 | 0.007 | 51.49 | 0.026<br>0.05 | 12.39 | 0.005<br>0.04 | 2.27 | 0.020<br>0.90 |

Table 6. Oxygen data of liquid samples (n=3)

| Sample | Av. O% | SD | RSD% |
|---|---|---|---|
| Ethanol | 34.79 | 0.03786 | 0.11 |
| Gasoline | 2.016 | 0.00451 | 0.22 |
| Diesel | 0.605 | 0.00473 | 0.78 |
| Biodiesel | 0.103 | 0.00100 | 0.97 |

## Conclusions

The Flash*Smart* Elemental Analyzer is a reliable solution for N, NC, CHNS and O weight% analysis of liquid samples. All data presented were obtained with an excellent repeatability and no matrix effect was observed when changing the sample type.

The all-in-one Flash*Smart* Elemental Analyzer modular design offers full flexibility of system configurations such as CHN/O, CHN/S, CHNS/CHNS, CHN/CHN, NC/S, NCS, N-Protein, etc. Moreover, the system's capability to host two AS 1310 Liquid Autosamplers increases productivity and cost-efficiency of the Flash*Smart* Elemental Analyzer.

By using automated liquid injection configurations, your laboratory gains:

- High efficiency through simplified sample preparation
- Cost-efficient analysis with low maintenance needs (no ashes are produced)
- Reduced oxygen consumption for the combustion process
- High lifetime of consumables (reactors)
- Possibility to determine CHNS/O weight% from few ppm to high element percentage

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