

# Fully Automated Elemental Analysis For Liquid Samples Applications

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## ABSTRACT

**Purpose:** Carbon, nitrogen, hydrogen and sulfur determination by combustion method.

**Methods:** organic liquid solutions and bio-oil sample were analyzed through an elemental analyzer with automatic liquid autosampler.

**Results:** CHNS data of liquid matrices in a large concentration range are presented to evaluate the accuracy, precision and repeatability of the elemental analyzer.

## INTRODUCTION

Elemental analysis of fuels and organic liquids is fundamental in petroleum and organic chemistry for research and quality control. Using an automated analyzer, rapid and accurate percentage of carbon, nitrogen, hydrogen and sulfur (CHNS) can be obtained.

The Thermo Scientific™ FlashSmart™ Elemental Analyzer (Figure 1) operating with the dynamic flash combustion of the sample (modified Dumas method) with the Thermal Conductivity Detector (TCD), meets laboratory requirements, such as accuracy, reproducibility, day to day reproducibility and high sample throughput.

The FlashSmart Elemental Analyzer is equipped with two totally independent furnaces allowing the installation of two analytical circuits which are used alternatively and completely automatic through the Thermo Scientific™ MultiValve™ Control (MVC) Module. Each analytical circuit can receive its own autosampler as the Thermo Scientific™ MAS Plus Autosampler (for solid and liquids samples) weighed in tin containers. Otherwise liquid samples are injected directly by the Thermo Scientific™ AS 1310 Liquid Autosampler.

Figure 1 shows the FlashSmart EA coupled with the MAS Plus and AS 1310 Liquid Autosampler. Figure 4 shows the analyzer coupled with two AS 1310 Liquid Autosamplers.



Figure 1. FlashSmart Elemental Analyzer with MAS Plus and AS 1310 Liquid Autosamplers.

## MATERIALS AND METHODS

For CHNS determination, the FlashSmart Analyzer operates with the dynamic flash combustion of the sample. Liquid samples are injected by a syringe into the combustion reactor via the AS 1310 Liquid Autosampler with oxygen. The volume injected was 2-3 ul.

After combustion the resulted 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. Finally, the gases are detected by a Thermal Conductivity Detector (TCD) (Figure 2).

A complete report is automatically generated by the Thermo Scientific™ EagerSmart™ Data Handling Software and displayed at the end of the analysis.

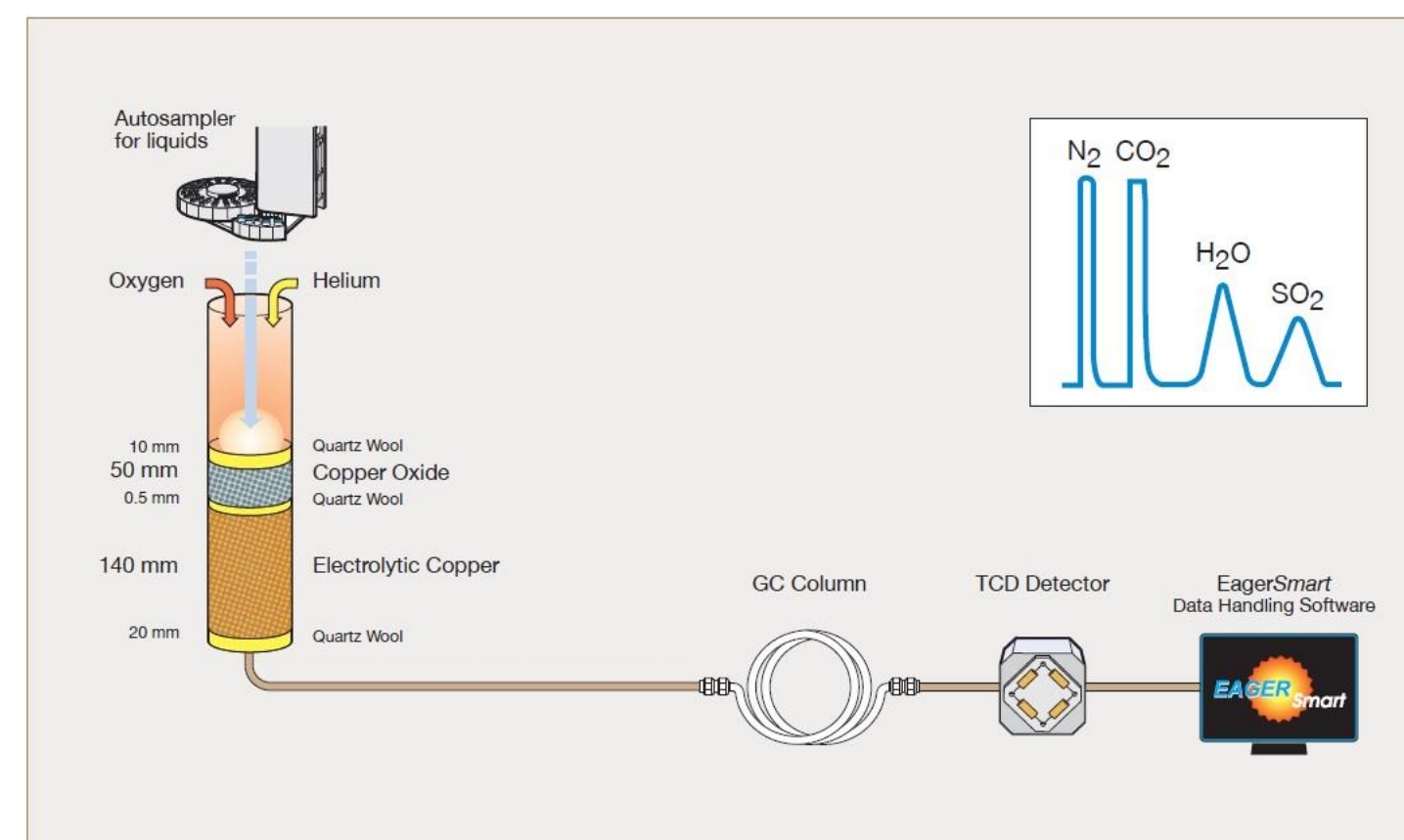


Figure 2. CHNS configuration.

Table 1 shows the pure organic solvents and Thermo Scientific Reference Material used to prepare the liquid solutions, the theoretical values and the density.

Table 1. Pure organic solvents and reference material information.

	Theoretical Values				
	N%	C%	H%	S%	Density (g/mL)
Acetonitrile	34.12	58.51	7.37	0.00	0.786
DMSO*	0.00	43.83	15.15	41.02	1.100
Ethanol	0.00	52.14	13.12	0.00	0.789
Iso-octane	0.00	84.12	15.88	0.00	0.692
Lubricant Ref. Mat.	1.12	82.32	13.82	2.54	n.a.

\* DMSO: Dimethyl sulfoxide

## RESULTS

Two tests were performed preparing different solutions across a large range of concentrations to demonstrate the performance of the FlashSmart Elemental Analyzer.

### • Test A: CHNS determination of solutions containing about 52 C%

Six solutions using Acetonitrile – DMSO – ethanol were prepared at different concentrations (solutions 1 to 6). Table 2 shows the expected percentages, the accepted range ( $\pm$ ) according to the technical specification of the Elemental Analyzer and the resultant density of the solutions. The instrument calibration was performed with the solutions 5 and 6 as standard using K factor as calibration method. Then, all solutions were analyzed as unknown 10 times to evaluate the repeatability. Table 3 shows the CHNS data obtained and the relative statistical values.

Table 2. Acetonitrile-DMSO-ethanol solutions information.

Solution	Expected Concentrations								
	N%	Range ( $\pm$ )	C%	Range ( $\pm$ )	H%	Range ( $\pm$ )	S%	Range ( $\pm$ )	Density (g/mL)
1	0.0620	0.01	52.16	0.30	13.12	0.14	0.0860	0.01	0.789
2	0.0710	0.01	52.11	0.30	13.13	0.14	0.1140	0.02	0.789
3	0.1120	0.02	52.19	0.30	13.13	0.14	0.1430	0.02	0.789
4	0.1430	0.02	52.10	0.30	13.13	0.14	0.172	0.02	0.790
5	0.2300	0.02	52.14	0.30	13.13	0.14	0.2870	0.02	0.790
6	0.2860	0.02	52.07	0.30	13.14	0.14	0.3440	0.02	0.790

Table 3. CHNS data and statistical values.

Element	Data	Acetonitrile-DMSO-ethanol solutions					
		1	2	3	4	5	6
N	Av. %	0.0598	0.0698	0.109	0.141	0.2360	0.282
	Std.Dev.	0.0008	0.0008	0.0016	0.0019	0.0025	0.0029
	RSD%	1.32	1.18	1.45	1.34	1.04	1.04
C	Av. %	52.14	52.14	52.18	52.09	52.22	52.06
	Std.Dev.	0.0820	0.0707	0.0280	0.0878	0.0706	0.0509
	RSD%	0.16	0.14	0.05	0.17	0.14	0.10
H	Av. %	13.11	13.11	13.13	13.12	13.11	13.12
	Std.Dev.	0.0189	0.0189	0.0250	0.0250	0.0211	0.0169
	RSD%	0.14	0.14	0.19	0.19	0.16	0.13
S	Av. %	0.0878	0.1110	0.140	0.1700	0.285	0.341
	Std.Dev.	0.0013	0.0012	0.0015	0.0019	0.0018	0.0021
	RSD%	1.43	1.06	1.08	1.12	0.65	0.61

### • Test B: CHNS determination of solutions containing about 83 C%

Four solutions (A to D) at higher carbon content were prepared with Lubricant Reference Material dissolved in iso-octane. Table 4 shows the expected percentages, the accepted range ( $\pm$ ) according to the technical specification of the Elemental Analyzer and the resultant density of the solutions. The instrument calibration was performed with the solutions C and D as standard using K factor as calibration method. Then, all solutions were analyzed as unknown 10 times to evaluate the repeatability. Table 5 shows the CHNS data obtained and the relative statistical values.

Table 4. Lubricant/iso-octane solutions information.

Solution	Expected Concentrations								
	N%	Range ( $\pm$ )	C%	Range ( $\pm$ )	H%	Range ( $\pm$ )	S%	Range ( $\pm$ )	Density (g/mL)
A	0.0540	0.01	84.03	0.30	15.78	0.15	0.122	0.02	0.703
B	0.103	0.02	83.95	0.30	15.63	0.15	0.239	0.02	0.735
C	0.143	0.02	83.89	0.30	15.62	0.15	0.325	0.02	0.755
D	0.144	0.02	83.91	0.30	15.64	0.15	0.295	0.02	0.751

Table 5. CHNS data and statistical values.

Element	Data	Lubricant/iso-octane solutions			
		A	B	C	D
N	Av. %	0.0569	0.0981	0.143	0.143
	Std.Dev.	0.0009	0.0015	0.0016	0.0014
	RSD%	1.27	1.42	1.11	0.98
C	Av. %	84.18	83.94	84.00	83.96
	Std.Dev.	0.0786	0.0627	0.1546	0.0793
	RSD%	0.09	0.07	0.18	0.09
H	Av. %	15.76	15.69	15.65	15.64
	Std.Dev.	0.0117	0.0114	0.0488	0.0221
	RSD%	0.07	0.07	0.31	0.14
S	Av. %	0.119	0.235	0.326	0.292
	Std.Dev.	0.0016	0.0032	0.0035	0.0021
	RSD%	1.34	1.37	1.08	0.70

Finally, a light bio-oil was analyzed. The instrument calibration was performed with the solutions C and D of test B as standard using K factor as calibration method. The light bio-oil was analyzed 10 times. Table 6 shows the CHNS data obtained and the relative statistical values.

Table 6. CHNS data and statistical values of light bio-oil.

Element	N%	C%	H%	S%
Data	0.102	70.11	13.42	0.105
	0.101	70.02	13.40	0.106
	0.101	70.05	13.41	0.106
	0.103	70.15	13.45	0.105
	0.103	70.12	13.45	0.105
	0.102	70.11	13.40	0.104
	0.102	70.15	13.45	0.105
	0.101	70.08	12.41	0.106
	0.100	70.10	13.43	0.105
	0.100	70.08	13.43	0.104
Average	0.101	70.10	13.43	0.105
Std.Dev.	0.0011	0.0411	0.0201	0.0007
RSD%	1.06	0.06	0.15	0.70

## CONCLUSIONS

- The FlashSmart Elemental Analyzer is the optimal solution for the analysis of CHNS for liquid samples in vary application fields, in terms of accuracy, repeatability, automation, speed of analysis and cost per analysis.
- The EagerSmart Data Handling Software controls the analytical conditions of the FlashSmart Elemental Analyzer and the AS 1310 Liquid Autosampler conditions as the volume injected, the washing of the syringe and the timing of injection to get the proper combustion of the sample.
- The AS 1310 Liquid Autosampler allows the automated injection of 105 samples.
- No memory effect was observed changing the sample matrix, indicating complete combustion and detection of all elements.



Figure 4. FlashSmart Elemental Analyzer with two AS 1310 Liquid Autosamplers.

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## TRADEMARKS/LICENSES

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