Application Note

CHNS/O Characterization of Municipal and Industrial Waste Using the EMA 502 Elemental Analyzer

Reference Solutions
• **EMA 502** CHNS-O Elemental Analyzer (F30800100)

Keywords
Elemental analysis; Solid Waste; Waste Oil; Alternative Fuels; Carbon, Nitrogen, Hydrogen, Sulphur, Oxygen; Net Calorific Value; Catalytic Combustion and Pyrolysis

Introduction

In light of the ever-expanding population, waste management has become one of today's most pressing environmental challenges. Traditionally, landfills have been used to store waste from households and businesses. Still, nowadays municipal and industrial waste are considered a resource, with certain fractions being recycled and others used in recovery operations such as energy conversion. Many industries are shifting toward the use of "alternative fuels" to replace expensive, high-emission fossil fuels. As a consequence, the alternative fuel industry is also evolving, processing energy-rich resources such as non-recyclable plastics, paper and cardboard residues, chemically treated wood, textile waste, and sewage sludge into higher-quality fuels.

Waste-derived fuels qualified as Solid Recovered Fuels (SRF) can be used directly in energy conversion processes, such as in incineration, combustion, and pyrolysis, where energy is used for supplying heat and/or electric power. For instance, the cement industry is widely adopting SRF to lower greenhouse gas emissions, preserve natural resources, and promote sustainable waste management practices.

Understanding the composition of the organic elements in SRF, particularly Carbon (C), Hydrogen (H), Nitrogen (N), Sulfur (S), and Oxygen (O), is essential for evaluating its combustion efficiency, energy potential, and environmental impact. Carbon, Nitrogen, and Sulfur contents are particularly significant when applying thermal treatments due to the formation of CO_2, NO_X, and SO_2, which contribute to the greenhouse effect, acid rain, and photochemical smog. Moreover, monitoring elevated levels of Nitrogen and Sulfur aids in preventive maintenance by minimizing corrosion in boilers and combustion systems.

Hydrogen content is a key parameter in fuel characterization, as it is required to calculate the net calorific value (NCV), also known as the lower heating value (LHV). The NCV represents the amount of usable energy released as heat during complete combustion with oxygen and serves as a direct indicator of fuel efficiency.

Knowing the oxygen content is also important in samples like waste oil or pyrolysis products, as it provides insight into the chemical structure of the fuel and helps to model combustion behaviour, stability, and industrial processing. In this application note, we present results obtained using the VELP EMA 502 Elemental Analyzer on the most common solid and liquid waste intended for incineration in waste-to-energy plants, offering a fast and fully automated solution for the simultaneous determination of the CHNS/O elemental composition and the subsequent calculation of the net caloric value.

Sample Preparation

Accurate CHNS analysis begins with proper sample preparation, as the degree of chemical homogeneity significantly affects the reliability of the results. Municipal and industrial waste are materials with an extremely heterogeneous composition, and must be thoroughly homogenized and finely ground by using laboratory cutting mills to obtain a consistent powder with controlled particle size, ensuring the sample is truly representative.
For the determination of CHNS, the sample has to be packed into a tin foil cup and analysed directly with the EMA 502 Elemental Analyzer. To enhance combustion efficiency and elemental recovery, vanadium pentoxide (V_2O_5, code A00000457) was frequently used as an additive in a 5:1 ratio (V_2O_5:sample). Liquid samples, such as waste oils, have been dispensed into the tin foil cups using a syringe or a glass pipette. For Oxygen determination, the sample has to be packed into a tin foil without additives. In some cases, waste samples may contain a high percentage of halogenated compounds like chlorine and fluorine, which are known to be highly aggressive for combustion analyzers.

Fig. 1. Municipal waste ground to a final particle size of less than 1 mm

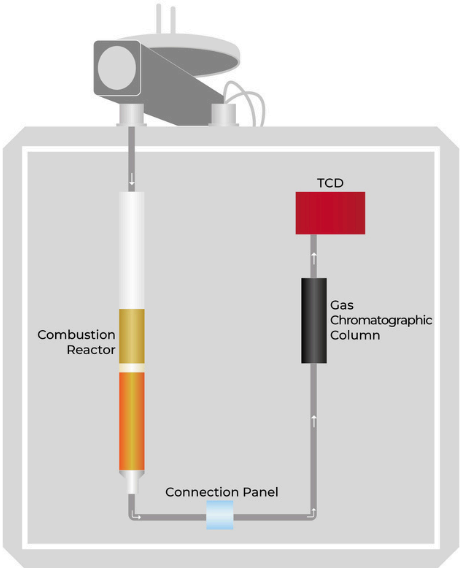
For frequent analysis of highly halogenated samples (> 10 % halogens), special precautions are recommended to minimize potential problems caused by the presence of aggressive compounds, such as the use of the quartz ash collector (cod. A00000445), the addition of additives to absorb halogens (cod. A00000456), the use of silver foils for sample weighing, maintenance, and cleaning is best practice. Weighing accuracy is an essential part of the analytical process. When dealing with sample weights less than 10 mg, a microbalance (0,001 mg resolution) is recommended. After weighing, the samples are then loaded into the Autosampler of the EMA 502 for simultaneous CHNS determination in a single run, or for oxygen analysis.

Fig. 2. Velp EMA 502 in action

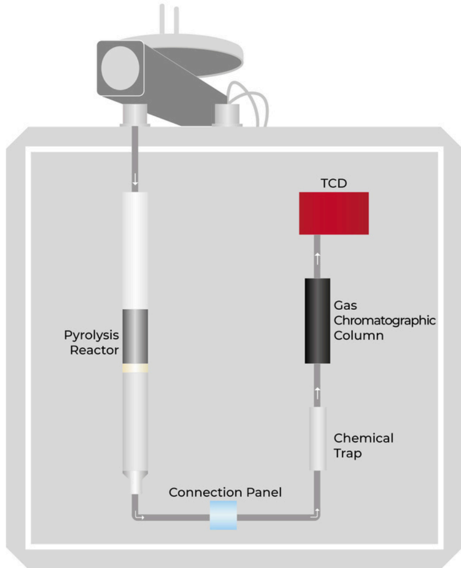
Analytical Method

The analysis was carried out by using the EMA 502 CHNS/O Elemental Analyzer, a very sensitive micro elemental analyzer designed for simultaneous carbon, hydrogen, nitrogen, and sulfur by combustion analysis, and oxygen determination by pyrolysis.
The analysis is based on high-temperature catalytic combustion technology, which has proved to deliver precise, reliable, and matrix-independent results. The samples are introduced into the combustion reactor via the electronic Autosampler after purging with carrier gas. Here, the samples are introduced into the combustion furnace at high temperature above 1000 °C, in the presence of a catalyst and in excess of pure oxygen gas. During combustion, the elemental components of the sample are quantitatively converted into gaseous oxidation products (CO_2, H_2O, NO_x, and SO_2), and a formulation of highly active copper powder Velp Vcopper™ placed in the lower part of the combustion reactor completes the process by reducing nitrogen oxides NO_X into molecular nitrogen N_2. The gas stream then reaches the gas chromatographic column, which ensures homogenous and complete separation of all the elements before the final detection by the innovative LoGas™ Thermal Conductivity Detector (TCD), with no requirement for a reference gas.

The signals from the detectors are transferred to the PC for further calculation by the software package EMASoft™; the full CHNS determination is completed in 12 minutes.
The EMA 502 elemental analyzer can be converted within a few minutes to determine oxygen content in pyrolysis mode, a method of analysis carried out in the complete absence of oxygen. Before starting the analysis, the standard reaction tube must be replaced with a pyrolysis tube containing nickel wool as an active catalyst, and the chromatographic column must be replaced with a dedicated oxygen-analysis column.
Once the sample is introduced into the pyrolysis tube at a temperature above 1000 °C, the oxygen is quantitatively converted into CO. The gas is then stripped of acidic pyrolysis products using a chemical trap. The resulting carbon monoxide is subsequently separated from other products by gas chromatography and detected by the TCD detector. A complete report is automatically displayed at the end of the analysis by the EMASoft™ software package; the oxygen determination is completed in just 6 minutes.



Flow diagram - CNHS mode (EMA 502 Elemental Analyzer)



Flow diagram - O mode (EMA 502 Elemental Analyzer)

Experimental Results

This study carried out the analysis of different sample types, representing the wide variability of environmental samples that are daily analyzed in the laboratory.
Accurate calibration of the instrument is a fundamental requirement for obtaining reliable analytical results. The EMA 502 Elemental Analyzer can be calibrated using either a single- or multiple-standard in order to extend the calibration range as much as possible towards both the high and low ends. Given the low nitrogen concentrations typically found in some types of waste samples, a multi-standard calibration was performed using a BBOT standard containing the four elements of interest (C = 72.5%; H = 6.1%; N = 6.5%; S = 7.4%), and an Oatmeal standard (N = 2.01%), which allowed the calibration to be extended to significantly lower nitrogen concentrations.
This strategy ensured a robust calibration curve, with the thermal conductivity detector (TCD) providing a linear response for all elements of interest. A regression coefficient of at least 0.999 was adopted as the quality criterion for the CHNS calibration curves.
The software includes a comprehensive database of easily selectable oxygen dosing methods to ensure complete combustion of the samples, a key requirement for obtaining fully matrix-independent results. In this study, the pre-installed “coal” method, designed to deliver the highest oxygen dosage, was used for samples with extremely high carbon content, such as Used Cooking Oil and Pyrolysis Oil (approx. 90% carbon). For solid waste materials, such as municipal and industrial waste, a customized “Waste” method with a medium-high oxygen dosage was employed (O_2 Factor = 2,5 ml/mg; O_2 Flow Rate = 300 ml/min; min oxy volume: 10 ml).

All samples were analysed using vanadium pentoxide as a combustion additive to optimize the combustion and maximize elemental recoveries.
Table 1 reports the experimental results obtained from the full CHNS characterization; all samples have been analysed multiple times, and the average elemental content, together with standard deviation, has been calculated.

Sample name	Weight [mg]	C [%]	H [%]	N [%]	S [%]
Municipal waste	3,254	80,76	12,31	0,40	NA
	3,869	81,52	12,58	0,36	NA
	3,448	81,97	12,70	0,42	NA
	Average ± SD %	**81,42 ± 0,61**	**12,53 ± 0,20**	**0,39 ± 0,03**	**NA**
Industrial waste	4,976	36,19	5,83	5,00	1,49
	5,249	36,13	5,82	5,04	1,51
	4,977	35,95	5,73	5,03	1,33
	Average ± SD %	**36,09 ± 0,12**	**5,79 ± 0,05**	**5,02 ± 0,02**	**1,45 ± 0,10**
Dry Sludge	3,587	53,32	7,73	9,68	0,19
	3,528	53,28	7,76	9,50	0,10
	3,135	53,46	7,60	10,11	0,14
	Average ± SD %	**53,35 ± 0,09**	**7,70 ± 0,09**	**9,76 ± 0,31**	**0,13 ± 0,01**
Used cooking oil	2,290	77,17	11,99	0,35	NA
	2,103	77,10	11,99	0,34	NA
	3,413	79,06	12,01	0,33	NA
	Average ± SD %	**77,77 ± 1,11**	**12,00 ± 0,01**	**0,34 ± 0,01**	**NA**
Pyrolysis oil	2,050	89,39	12,80	0,48	NA
	4,929	88,38	11,89	0,66	NA
	4,322	84,83	11,83	0,74	NA
	Average ± SD %	**87,53 ± 2,40**	**12,17 ± 0,54**	**0,63 ± 0,14**	**NA**

Table 1. CHNS elemental analysis experimental results of the investigated waste samples

Municipal solid waste was collected by municipalities, mainly from households and similar sources such as shops and small businesses. These wastes are highly heterogeneous, containing materials such as plastics, paper, metals, textiles, and more. The results showed a very high carbon content, exceeding 80%, likely due to the high proportion of plastics. Despite the heterogeneous nature of these samples, the results were highly repeatable thanks to effective and thorough sample preparation to a very fine fineness. Nitrogen content is generally very low, while sulfur is often completely absent in municipal waste. Industrial waste is generated by industrial or manufacturing activities, and includes materials that are no longer useful in production processes, such as chemicals, packaging, ashes, solvents, wood, and other by-products. The sample analyzed showed a relatively low carbon content, but a significant sulfur amount of 1.45%.

Sewage sludge is becoming an increasingly common type of urban waste, especially in areas with large urban populations, since it is produced as a by-product during sewage treatment of industrial or municipal wastewater. As expected, this material resulted rich in organic matter, showing a high carbon and nitrogen content of 9,76 %. To ensure maximum accuracy in quantifying the low sulfur content of 0,13 %, a separate analysis was conducted using an increased sample weight of up to 30 mg.
Used cooking oil represents a common type of liquid waste. It typically does not contain sulfur and has a high carbon content, making it an ideal energy-rich feedstock for waste-to-energy power plants, as confirmed by the high carbon content of 77,77 %.
The CHNS elemental composition of the Pyrolysis Oil is typical of oils derived from the pyrolysis of plastic or mixed waste with a high polymer content.

Plastic pyrolysis technology converts post-industrial plastic waste into valuable oil, which can be used in existing petrochemical facilities to produce new plastics for a fully circular solution, or blended to create sustainable fuels. The results in Table 3 show that this type of sample can be analyzed with good repeatability.
The EMA 502 analyzer can be converted in just a few minutes to pyrolysis mode for oxygen determination.
Considering the very low concentration of oxygen to be determined in the pyrolysis oils, the calibration was performed using a low-oxygen standard (Bitumen asphalt with O = 1,26 %).
The TCD detector provides a linear response for oxygen detection, with a regression coefficient of at least 0.999. The experimental results reported in Table 2 showed very different oxygen concentrations, ranging from 10.67% for the waste cooking oil sample to the extremely low concentration of 0.45% for the Pyrolysis Oil. The excellent repeatability of the results implies that the analysed sample is representative of the original material and that the practical sample preparation procedure enables the achievement of high-quality results.

Sample name	Weight [mg]	O [%]
Used cooking oil	2,11	10,56
	2,36	10,73
	2,82	10,72
	Average ± SD %	**10,67 ± 0,10**
Pyrolysis oil	21,535	0,46
	21,930	0,44
	21,861	0,45
	Average ± SD %	**0,45 ± 0,01**

Table 2. Oxygen experimental results of waste samples determined by pyrolysis analysis

In the current global energy landscape, where increasing energy demand must be balanced with the reduction of greenhouse gas emissions, waste material stands out as a promising renewable fuel. Wastes are extremely energy-rich, combusting with remarkable power that often exceeds that of coal, making them particularly attractive for power generation. Elemental analysis plays a key role in this context, especially for determining the net calorific values of a fuel, a critical indicator of its energy potential. While the gross calorific value (GCV) is measured experimentally using a bomb calorimeter under ideal conditions, the net calorific value (NCV) reflects real-world performance by accounting for energy lost to water vaporization during combustion. This correction requires precise measurement of the hydrogen content, which is directly linked to the amount of water formed. According to international standards, hydrogen content must be determined through elemental analysis to ensure accurate NCV calculation, making it a fundamental parameter in alternative fuel characterization and efficiency assessment.
Table 3 reports the calculated net calorific values obtained from the tabulated gross calorific values of the waste samples under study. It is worth noting how a higher hydrogen content, as observed in municipal waste and oil samples (H » 12 %), has a significant impact on the NCV, resulting in a substantial reduction in the usable energy of that particular fuel when employed, for example, in a waste-to-energy facility, cement plant, or pyrolysis plant.

Sample name	GCV [MJ/Kg]	H [%]	NCV [MJ/Kg]
Municipal waste	29,66	12,53	**26,84**
Industrial waste	12,31	9,99	**10,62**
Dry Sludge	23,72	7,70	**21,99**
Used cooking oil	41,21	12,00	**38,51**
Pyrolysis Oil	45,46	12,17	**42,72**

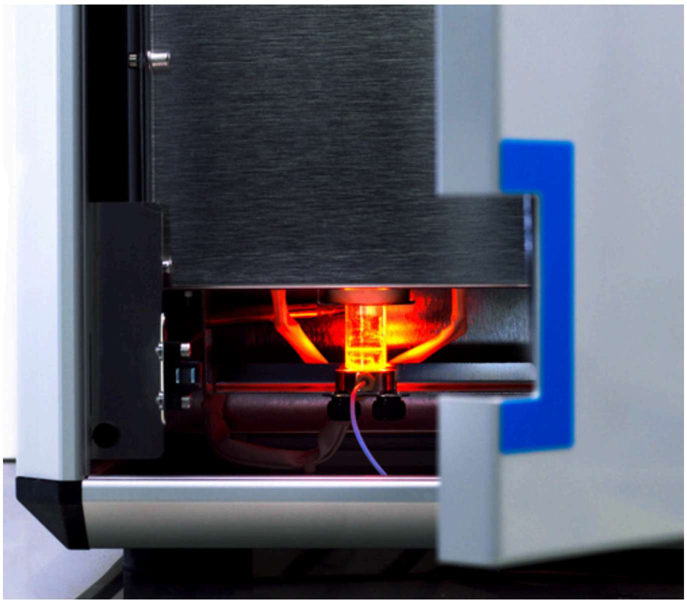
Table 3. Net calorific value (NCV) calculation of alternative fuel samples using hydrogen value correction obtained from elemental analysis

Conclusions

In this application note, we demonstrated that the EMA 502 Elemental Analyzer is a reliable and highly versatile solution for characterizing a wide range of waste materials commonly used as alternative fuels.
The instrument's ability to provide accurate and reproducible CHNS/O data for complex and heterogeneous samples—such as municipal waste, sludges, and waste oils—demonstrates the robustness of the catalytic combustion and pyrolysis method.
The analytical results are crucial for both assessing the energy potential and predicting the environmental impact of these fuels.
Specifically, the accurate determination of hydrogen content is crucial for calculating the Net Calorific Value (NCV), representing the fuel's actual usable energy. Furthermore, the quantification of carbon, nitrogen, and sulfur helps anticipate greenhouse emissions, which is essential for compliance and process optimization in waste-to-energy plants.
Overall, the Velp EMA 502 provides a fast and comprehensive analytical solution for modern laboratories. It plays a fundamental role in the quality control and development of alternative fuels, thereby supporting the transition to sustainable waste management and a circular economy.

Standard References

- EN ISO 21663:2020 Solid recovered fuels - Methods for the determination of carbon (C), hydrogen (H), nitrogen (N) and sulphur (S) by the instrumental method.
- ISO 21654:2021 Solid recovered fuels — Determination of calorific value.



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