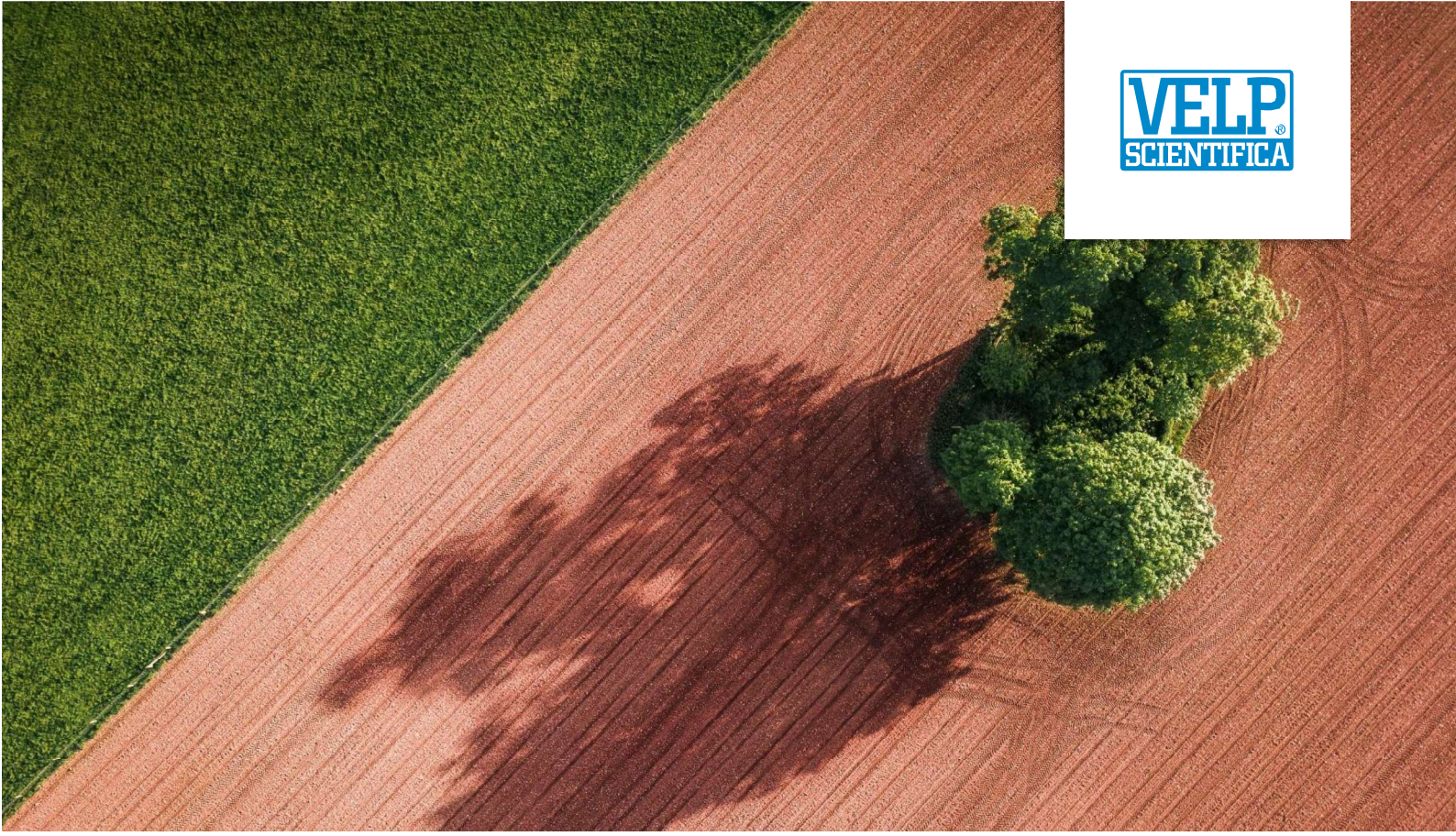


APPLICATION NOTE

Determination of Total Carbon (TC) and Total Organic Carbon (TOC) in reference soils samples: an interlaboratory study

REFERENCE SOLUTIONS

- F30800090 - CN 802 Carbon Nitrogen Elemental Analyzer
- F30800100 - EMA 502 Elemental Analyzer CHNS-O

KEYWORDS

Elemental analysis; Total Carbon Determination; Total Organic Carbon Determination; TOC; Soil; High Temperature Combustion; Repetability

INTRODUCTION

The determination of organic carbon plays a fundamental role in the characterization of soils and sediments as its presence or absence can significantly influence the final characteristics of a soil such as the soil structure, water retention, and nutrient availability. TOC analysis proves indispensable in assessing soil health and fertility by indicating the organic matter's decomposition stage. High organic carbon levels often correlate with enhanced fertility and microbial activity, influencing nutrient availability.

In agricultural science the quantification of organic carbon influences decisions related to crop management, fertilizer application, and soil amendments. The information derived helps to optimize agricultural productivity while minimizing environmental impacts, striking a balance between yield and sustainability.

Moreover, recent studies leverage TOC analysis to monitor carbon sequestration efforts, guiding initiatives aimed at mitigating climate change. This methodological depth makes TOC analysis a cornerstone in soil science, empowering scientists to make informed decisions for sustainable land management and environmental conservation.

With the goal of testing the performance of the VELP combustion analyzer *CN 802* and *EMA 502* and ensure accuracy and reliability in soil analysis, here we present a study conducted with the participation to the proficiency test programmes WEPAL-QUASIMEME, an Accredited Institution for the organisation of Interlaboratory Studies. These programs are designed to assess the proficiency of participating laboratories by evaluating their analytical capabilities through the analysis of a wide range of sample matrices, like soil and sediments. The analysis was carried out following standard procedures and reporting the results back to WEPAL-QUASIMEME.

The organization then compares the reported values with the true values, providing valuable feedback to each laboratory on their analytical tests, with full performance assessment based on robust statistics.

In this contest, VELP constantly participates in the Proficiency Testing to guarantee the highest quality of the instruments and ensure the best performance in terms of results, reliability and ease of use.

SAMPLE PREPARATION

The samples consisted of four different reference soil, clay and sediments received from WEPAL-QUASIMEME, the samples were sufficiently homogeneous and stable for the purpose of the test. The concentration of TC and TOC were unknown before performing the analysis, the expected values were communicated at the end of the interlaboratory study.

For the determination of total carbon (TC), the sample has to be packed into a tin foil without further pre-treatment, and analysed directly with the *EMA 502* and *CN 802* elemental analyser. For TOC determination carbonates are before destroyed by treating the original sample with acid, the sample preparation procedure for the complete removal of inorganic carbon in the samples is as follows:

1. Weigh the homogenized sample into the conical-shaped silver foil and place it on the VELP Teflon plate (cod. TA00000378) for sample preparation (the samples cannot be acidified in tin foil directly, since the acid will damage the tin packing material);

2. Carefully acidify drop by drop the sample weighed-in in silver foil with diluted hydrochloric acid (e.g. HCl 2 N) until no bubble formation is visible. Add the acid slowly in order to avoid foaming and splashing of the sample;

3. Dry the acidified samples directly in the VELP ARE 5 Hot Plate Stirrer (cod. F20510560) until complete removal of the carbon dioxide just selecting a temperature between 40 to 170 °C. During this procedure acid fumes will evolve from the sample, higher drying temperatures should be avoided in order to discard the possibility of loss of volatile organic compounds;

4. Close the foil over the sample with the aid of tweezers. To avoid the loss of substance and to ensure a complete combustion of the silver cup, wrap and pack the sample into a tin foil and close capsules manually or better by using a solid sample shaper or manual pellet press;

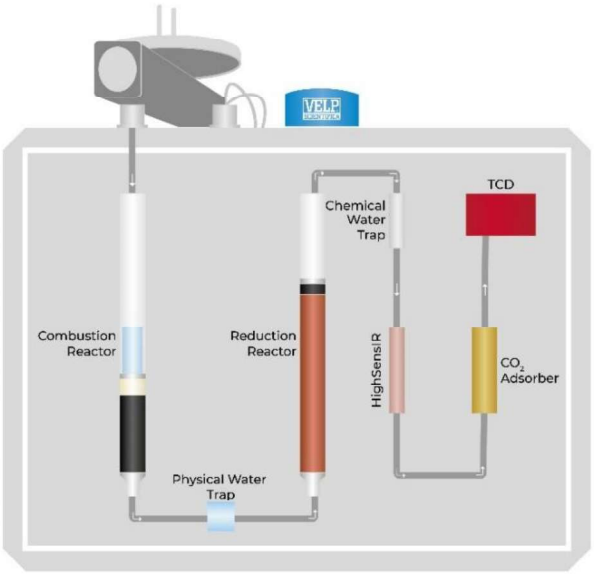
After sample preparation, the sample can be placed into the Autosampler of the *EMA 502* and *CN 802* elemental analyser and carry out the determination directly as TOC in a completely automatic way.

ANALYTICAL METHOD

The analysis was carried out by using two different VELP elemental analysers based on hight-temperature catalytic combustion technology, that has proved to deliver precise, reliable and matrix-independent results in a few minutes. Here the samples are introduced into the combustion furnace at high temperature above 1000 °C, in presence of catalyst and in excess of pure oxygen gas to convert the elemental components into gaseous oxidation products, which are subsequently analysed by means of a suitable detector.

CN 802 Carbon Nitrogen Elemental Analyzer

The *CN 802* is a Carbon and Nitrogen analyzer able to cover an extremely wide elemental concentration range and applications, with the ability to analyse high sample weight and volume for samples that have inhomogeneities or low concentration levels. *CN 802* Elemental Analyzer is operated with a series of solutions designed to tackle all possible issues caused by the routine measurement of aggressive samples like the chlorine and acid vapours introduced by the acidification process, and thus represent the ideal solution for routine long-term determination of TOC in any kind of sample matrix.

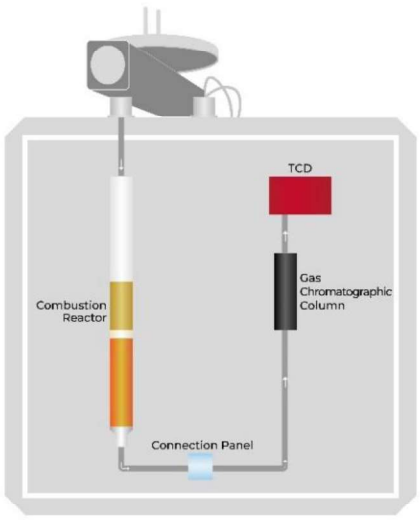


VELP CN 802 Carbon Nitrogen Elemental Analyzer workflow

The samples are introduced into the combustion reactor via the electronic Autosampler after purging with carrier gas. During combustion the carbon present in the sample is quantitatively converted to carbon dioxide (CO_2) while nitrogen compounds will oxidize to nitrogen oxides (NOx). When measuring acidified samples for TOC determination, the use of resistant **ceramic ash crucible** (cod. A00000198) is recommended to avoid that sample residues enter the combustion tube. After combustion of the sample, the gases produced are carried by a helium flow to the **DriStep™electronic physical trap** able to condense more than 99 % of water and acidic impurities, and then into a dedicated **Halogen Adsorber** to trap more acid vapours and halogens. The gas stream reaches the reduction furnace where a formulation of highly active copper powder VELP Vcopper™ helps the reduction of NO_X into molecular nitrogen N_2. Prior to detection, the gas pass through a chemical trap for fine removal of water and moisture. The sample gas is led to the highly sensitive **HighSensIR**, where the formed Carbon dioxide (CO_2) is measured. Then, the chemical-free auto-regenerative CO_2 absorbers let pass only the elemental nitrogen that is detected 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 CNSoft™, results are displayed in 3 – 5 minutes.

EMA 502 Elemental Analyzer CHNS-O

The *EMA 502* is a very sensitive micro elemental analyzer designed for simultaneous carbon, hydrogen, nitrogen, and sulphur by combustion analysis, and oxygen determination by pyrolysis. The high degree of automation, low operating cost, easy design and flexibility in determining the elements make it suitable for a large variety of application, including few numbers of daily samples for TOC determination.



VELP EMA 502 Elemental Analyzer CHNS-O workflow

The samples are introduced into the combustion reactor via the electronic Autosampler after purging with carrier 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 complete the process by reducing nitrogen oxides NO_X into molecular nitrogen N_2. When measuring acidified samples for TOC determination, the use of the quartz ash crucible (cod. A00000445) is recommended to avoid that sample residues enter the combustion tube. The gas stream then reaches the gas chromatographic column, which ensures homogenous and complete separation of all the elements prior to 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.

EXPERIMENTAL RESULTS

Total carbon (TC) and total organic carbon (TOC) content were performed in four different soil, clay and sediments samples coming from the WEPAL-QUASIMEME proficiency test circuit. The TC and TOC content were unknown before performing the analysis, and the expected values were communicated to VELP at the end of the interlaboratory study. In the following table are reported the results provided by the proficiency test programmes WEPAL-QUASIMEME:

Sample	TC [%] (Average ± SD %)	TOC [%] (Average ± SD %)
Sandy soil	2.639 ± 0.102	0.673 ± 0.098
Clay_1	2.865 ± 0.101	1.730 ± 0.114
Clay_2	1.774 ± 0.099	1.334 ± 0.142
Clay soil	2.100 ± 0.135	1.967 ± 0.127

Table 1. Experimental results provided by the proficiency test programs WEPAL – QUASIMEME.

Prior to performing testing, perfect calibration of the instrument is a key condition for achieving correct analysis results. The high temperature technology of the elemental analysers employed in this study ensures complete combustion of a large variety of samples, a key condition to obtain a fully matrix-independent calibration. The *CN 802* analyzer has been calibrated over the whole range using EDTA certified standard, while the multi-elemental analyzer *EMA 502* was calibrated using a single standard of Sulfanilic Acid containing all the elements of interest. The software can create and manage a variety of calibration curves and contains a full database of methods for various sample types optimization. Weighing accuracy is an essential part of the analytical process, when weighing large samples amount in

the order of hundreds of milligrams a standard analytical balance with 0.1 mg resolution is sufficient, while when sample weights of less than 20 mg are desired a balance 0.001 mg resolution is recommended.

Sample	Analyzer	Weight [mg]	TC [%]	Mean ± SD	Weight [mg]	TOC [%]	Mean ± SD
Sandy Soil	CN 802	400,7	2,714	2,668 ± 0,039	399,0	0,668	0,678 ± 0,013
		401,1	2,620		401,9	0,694	
		402,1	2,673		402,1	0,665	
		403,3	2,664		401,8	0,684	
	EMA 502	19,953	2,517	2,770 ± 0,221	10,500	0,598	0,685 ± 0,062
		20,058	3,027		10,110	0,726	
		19,918	2,677		10,054	0,734	
		19,999	2,860		12,335	0,684	
Clay_1	CN 802	400,8	2,881	2,867 ± 0,015	402,4	1,759	1,759 ± 0,014
		399,7	2,851		401,7	1,778	
		402,4	2,879		399,8	1,745	
		399,1	2,857		401,7	1,752	
	EMA 502	20,710	2,840	2,854 ± 0,040	10,335	1,767	1,780 ± 0,027
		20,204	2,912		10,270	1,755	
		20,729	2,821		10,985	1,779	
		20,048	2,843		10,888	1,818	
Clay_2	CN 802	403,5	1,759	1,769 ± 0,037	401,8	1,481	1,455 ± 0,018
		402,5	1,765		401,7	1,447	
		402,5	1,731		400,7	1,446	
		401,4	1,820		401,5	1,444	
	EMA 502	20,868	1,804	1,858 ± 0,228	11,928	1,402	1,376 ± 0,044
		21,595	1,717		10,207	1,421	
		19,866	2,194		10,480	1,325	
		20,912	1,719		11,070	1,355	
Clay Soil	CN 802	402,9	2,206	2,185 ± 0,017	400,5	2,156	2,127 ± 0,023
		401,1	2,165		401,6	2,113	
		400,3	2,179		400,8	2,103	
		402,8	2,188		400,4	2,135	
	EMA 502	21,444	2,352	2,229 ± 0,085	11,362	2,144	2,051 ± 0,131
		19,940	2,217		10,666	2,182	
		20,003	2,193		10,677	1,957	
		20,623	2,155		11,224	1,921	

Table 2. Experimental results of the WEPAL samples obtained with the CN 802 and EMA 502 elemental analyzer, analysed in four series to evaluate the repeatability, accuracy and precision.

CONCLUSIONS

The results demonstrate an excellent correspondence between the experimental data obtained with both *CN 802* and *EMA 502* analysers and the theoretical data coming from the WEPAL-QUASIMEME interlaboratory comparison, showing good repeatability and accuracy with no memory effect.

In this study has been shown how both VELP elemental analysers are perfectly suited for the analysis of soils samples for the determination of total carbon (TC) and total organic carbon (TOC) according to international official methods such as ISO 10694 and EN 15936.

The carbon/nitrogen analyzer model *CN 802* has shown an unmatched repeatability of the results due to the ability to analyse macro sample weight, of the order of hundreds of milligrams. Thanks to the numerous technical solutions specially designed for aggressive samples management, represent the ideal solution for routine long-term determination of TOC in any kind of sample matrix.

On the other hand, *EMA 502* elemental analyzer is a very sensitive micro elemental analyzer designed for simultaneous carbon, hydrogen, nitrogen, and sulphur determination of small sample quantities.

In this study has proven to deliver reliable quantitative analysis of soils samples, and represent a versatile solution for laboratories that needs to measure few numbers of daily TOC samples. Both instruments can work continuously, being able to analyse a large number of samples in a totally automatic way. Moreover, the dedicated software package CNSoft™ and EMASoft™ allow the unique connection option to the Ermes Cloud Platform, the new Smart Lab solution from VELP to improve your laboratory experience.

STANDARD REFERENCES

- ISO 10694 - Soil quality - Determination of organic and total carbon after dry combustion (elementary analysis);
- EN 15936 - Soil, waste, treated biowaste and sludge – determination of total organic carbon (TOC) by dry combustion.

TAILOR-MADE ANALYTICAL SUPPORT

VELP's strong analytical specialist team is available to provide comprehensive coverage of both your application and protocols, to ensure qualified consultation. Be sure to include in your request all the relevant details about your application, sample specifications, official reference method (if available) and any available documentation. For further information, visit **www.velp.com**

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