APPLICATION NOTE

Routine determination of Total Organic Carbon (TOC) and Total Nitrogen (TN) in environmental samples

REFERENCE SOLUTIONS

- F30800090 – CN 802 Carbon/Nitrogen Elemental Analyzer

KEYWORDS

Elemental analysis; Waste; Compost; Sludge; Soil; Total Nitrogen (TN) Total carbon (TC); Total organic carbon (TOC); High Temperature Catalytic Combustion

INTRODUCTION

Over the past years, the growth of economic activity's production and consumption has led to a considerable increase in the production of urban and agro-food industry waste, creating complex management challenges. Agricultural residues from food and garden waste as well as residues of consumption like domestic solid waste (biodegradable fraction of municipal waste) and wastewater sewage sludge, are often disposed of in the natural media and therefore constitute a source of potential pollution for the environment.

However, these materials are often rich in organic matter and fertilizing elements, presenting an opportunity to improve agricultural soils depleted by continuous and intensive cropping. Determining Total Nitrogen (TN) in sludge and biowaste, such as compost, is thus associated with the need for nutrient and organic matter recycling. It represents a valuable element of study for soil reinforcement with organic amendment.

In addition, carbon speciation is equally important for the environmental characterization. A primary distinction arises between total inorganic carbon (TIC) and total organic carbon (TOC). TIC, found as carbonates released as CO_2 by acid treatment, is generally harmless and common in most soils, with minimal environmental impact.

TOC, on the other hand, encompasses all carbon forms in organic matter, including readily microbiological degradable fractions and stable compounds like hydrocarbons. TOC can be present in large quantities in environmental samples, it is a good indicator to evaluate soil quality in agriculture, but also represents an extremely rapid and reliable method to assess pollution caused by anthropogenic activities as part of an ecological risk assessment for the evaluation of organic contaminants and the classification of waste for landfills. TOC is determined in agreement with international regulations such as ISO 10694 or EN 15936, between the different procedures the so-called "direct method" can be applied to any sample matrix, providing reliable and accurate results.

In this procedure, the inorganic carbon (TIC) present in the samples is previously eliminated by treating the sample with acid, and then the remaining organic carbon is measured directly after dry combustion with the CN 802 Elemental Analyzer, expressed in % TOC in relation to the dry mass.
This Application Note illustrates the sample preparation procedure and the fast, reliable, and routine determination of TN and TOC of environmental samples using the CN 802 Elemental Analyser, the automatic analyzer designed by VELP to cover an extremely wide carbon and nitrogen concentration range. To this purpose, a variety of different sample types like soil, sludge from sewage plants treating domestic or urban waste waters, biowaste derived from biodegradable fractions of municipal waste, and solid waste of various kinds were analyzed.

SAMPLE PREPARATION

The degree of chemical homogeneity of the test sample is very important to achieve accurate results, samples should be homogenized and finely milled into fine powders with controlled particle size to obtain a representative sample. For solid material dried samples might be used, in this case, determine the dry mass on a sample aliquot and enter the moisture value (Moisture %) in the Software CNSoft™ so that the results will be automatically referred to dry mass.
For the determination of Total Carbon (TC) and Total Nitrogen (TN), the sample has to be packed into a tin foil without further pre-treatment and analyzed directly with the CN 802 elemental analyzer. For Total Organic Carbon (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:

Initial kit for TOC determination, cod TA00000378

1) Weigh the homogenized sample into the conical-shaped silver foil (A00000371) and place it on the VELP Teflon plate for sample preparation (included in the Initial kit for TOC determination, cod. TA00000378). Sample weight for TOC determination shall be lower than classic TC and TN determination, in the way to reduce the amount of chlorine introduced into the analyzer.
2) Carefully acidify drop by drop the sample weighed in a silver foil with diluted hydrochloric acid (example: 4M solution) until no bubble formation is visible. Add the acid slowly to avoid foaming and splashing of the sample. Add as little acid as possible, but enough to soak the entire sample and remove the inorganic carbon completely. Generally, 4 hours of waiting is more than enough time for the complete removal of carbon dioxide.
3) Dry thoroughly the acidified samples directly in the VELP ARE 5 Hot Plate Stirrer (cod. F20500560) according to international standard guidelines. High drying temperatures should be avoided to discard the possibility of loss of volatile organic compounds.

Sample preparation station for TOC determination in solids samples

4) Wrap the silver foil over the sample and close it gas-tight. To avoid the loss of substance and to ensure a complete combustion of the silver foil, it might be helpful to further wrap and pack the sample into a tin foil. In the case of large samples, the use of the closing device for tin foil cups (code A00000217) facilitates the wrapping of the sample into a pellet.

After sample preparation, the sample can be placed into the Autosampler of the CN 802 Carbon/Nitrogen Elemental Analyzer and carried out the determination directly as TOC in a completely automatic way. If the value of Total Inorganic Carbon (TIC) is also needed, the TIC value can then be calculated using the formula: TIC = TC - TOC.

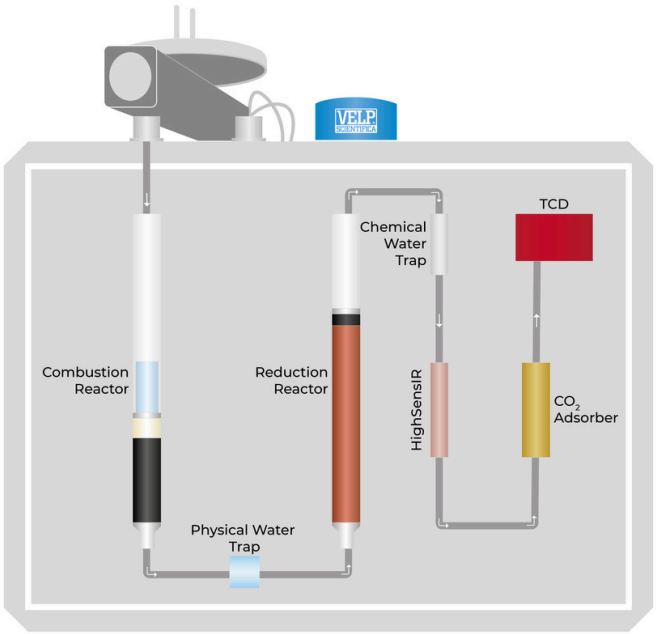
ANALYTICAL METHOD

The analysis was carried out by using the VELP CN 802 Carbon/Nitrogen Analyzer able to cover an extremely wide elemental concentration range and applications, operated with a series of solutions designed to tackle possible issues caused by the routine measurement of acidified aggressive samples. The analysis is based on high-temperature catalytic combustion technology, that 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 a high temperature above 1000 °C, in the presence of a catalyst and in excess of pure oxygen 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 (NO_x). When measuring acidified samples, the use of a resistant ceramic ash crucible is recommended to avoid sample residues entering the combustion tube. Moreover, after the combustion of the sample, the gases produced are carried by a helium flow to the maintenance-free DriStep™ electronic physical trap able to condense more than 99 % of water and acid vapors with high efficiency. Then the gas stream passes through a reduction furnace where a formulation of highly active copper powder VELP Vcopper™ helps the reduction of NO_x into molecular nitrogen N_2.

After passing through a last chemical trap for fine removal of water and moisture residues, 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.



VELP CN 802 Carbon and Nitrogen Elemental analyzer workflow

EXPERIMENTAL RESULTS

The Total Nitrogen (TN) and Total Organic Carbon (TOC) determination applies to a large variety of environmental samples. In this study, four different categories of environmental samples were considered, most of the samples were naturally inhomogeneous and could exhibit a wide concentration range:

- Sewage sludge from municipal wastewater treatment plant,
- Fresh compost from biodegradable fraction of municipal solid waste,
- Agricultural Soil,
- Municipal solid waste.

The CN 802 Elemental Analyzer's ability to handle large sample weights and volumes ensures repeatable and reproducible results even for samples with low homogeneity. In addition, it enables precise measurement of completely unknown samples, eliminating the need for re-measurement.

Perfect calibration of the instrument is a basic condition for achieving correct analysis results. The calibration has been performed on a wide range using EDTA-certified standards (C = 41 %; N = 9,6 %) and does not require the use of matrix-specific standards.

The high-temperature technology employed in the CN 802 analyzer ensures the complete combustion of a large variety of samples, a key condition for achieving a fully matrix-independent calibration.

All the different types of samples have been analyzed in sequence in the same analysis run.

The software includes an extensive library of pre-defined methods that automatically determine the optimal oxygen dosage needed to achieve complete combustion of different sample matrices, based on the sample's nature and weight. It turns out that the analysis of samples that typically show high carbon content (i.e. solid waste) is automatically completed with more oxygen during combustion, while the measurements of soil samples are conducted with lower oxygen dosing due to the poor elemental contents.

The tables below present the experimental results for Total Nitrogen (TN), Total Carbon (TC), and Total Organic Carbon (TOC) determination.

All the samples have been analyzed multiple times and the average elemental content together with standard deviation have been calculated.
The results showed a wide carbon concentration range, from a minimum of about 1% for soil samples up to 68% for solid waste, while the value of total nitrogen was always below 1% for all types of samples analyzed. The TOC determination showed repeatable results which means that the amount of weighed samples was representative of the original sample and that the practical procedure in sample preparation, especially the acidification step, allows to achieve high-quality results.

Sample name	Weight (mg)	TC (%)	TN (%)	Weight (mg)	TOC [%]
Waste	50,5	69,17	0,81	50,4	69,10
	50,9	68,86	0,72	50,4	68,35
	51,5	68,86	0,85	51,4	68,65
	50,6	68,54	0,75	51,0	68,49
	Average ± SD %	**68,86 ± 0,26**	**0,78 ± 0,06**	**Average ± SD %**	**68,64 ± 0,32**

Sample name	Weight (mg)	TC (%)	TN (%)	Weight (mg)	TOC [%]
Compost	150,5	29,58	0,93	100,3	27,38
	150,4	29,28	0,94	100,0	26,59
	151,1	29,90	0,96	99,8	28,19
	150,7	29,31	0,94	100,2	27,79
	Average ± SD %	**29,52 ± 0,29**	**0,94 ± 0,01**	**Average ± SD %**	**27,49 ± 0,69**

Sample name	Weight (mg)	TC (%)	TN (%)	Weight (mg)	TOC [%]
Sludge	100,2	18,60	0,40	80,4	18,12
	100,8	18,51	0,38	80,0	18,10
	100,9	18,47	0,39	81,5	18,08
	99,0	18,34	0,39	81,7	18,07
	Average ± SD %	**18,48 ± 0,11**	**0,39 ± 0,01**	**Average ± SD %**	**18,09 ± 0,02**

Sample name	Weight (mg)	TC (%)	TN (%)	Weight (mg)	TOC [%]
Soil	400,3	2,71	0,15	99,3	1,41
	400,6	2,62	0,14	100,6	1,13
	400,0	2,72	0,15	100,1	1,11
	400,5	2,67	0,16	99,5	1,36
	Average ± SD %	**2,68 ± 0,05**	**0,15 ± 0,01**	**Average ± SD %**	**1,25 ± 0,16**

Table 1. Experimental results for TC, TN and TOC determination of different environmental sample types

CONCLUSION

This study carried out the analysis of different sample types like soil, sludge, compost, and solid waste, representing the wide variability of environmental samples that are daily analyzed in the laboratory. Through a detailed sample preparation procedure, it has been shown how to eliminate the inorganic fraction from carbonates, to obtain directly the percentage of Total Organic Carbon (TOC) with good precision and repeatability, respecting international standard regulations. The inhomogeneous nature of the samples was apparent, and the samples showed a wide concentration range. Thanks to the CN 802 elemental analyzer's ability to analyze macro sample weight, repeatable results were obtained for both carbon and nitrogen determination, indicating that the amount of weighed samples was representative of the original sample.
The CN 802 Carbon/Nitrogen Elemental Analyzer has proved to be a reliable solution for the routine analysis of Total Carbon (TC), Total Nitrogen (TN), and Total Organic Carbon (TOC) in environmental samples.

All the different sample types have been analyzed in sequence in the same analysis run, with no memory effect, and with high sample throughput due to fast analysis time and easy maintenance. Moreover, the dedicated software package CNSoft™ allows the unique connection option to the Ermes Cloud Platform, the new Smart Lab solution from VELP to improve your laboratory experience.

REFERENCE METHODS

EN 15936:2022 - Soil, waste, treated biowaste, and sludge - Determination of total organic carbon (TOC) by dry combustion.
EN 16168:2012 - Sludge, treated biowaste and soil - Determination of total nitrogen using dry combustion method.
ISO 10694:1995 - Soil quality - Determination of organic and total carbon after dry combustion (elementary analysis)
ISO 13878:1998 - Soil quality - Determination of total nitrogen content by dry combustion (elemental analysis).

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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