APPLICATION NOTE

Total Carbon (TC) and Total Organic Carbon (TOC) determination in wastewater with CN 802 Elemental Analyzer

REFERENCE SOLUTIONS

- F30800090 – CN 802 Carbon/Nitrogen Elemental Analyzer

KEYWORDS

Elemental analysis; Wastewater samples; Total carbon (TC); Total organic carbon (TOC); High Temperature Catalytic Combustion; Repeatability

INTRODUCTION

Total organic carbon (TOC) in water samples is an important indicator of the organic contamination level and has become one of the most important parameters used to measure the organic pollution and water quality. These organic compounds originate from diverse sources such as decaying plant matter, agricultural runoff, industrial discharge, and domestic sewage. While many organic compounds are harmless, some can pose significant risks to human health and the environment.

The determination of TOC in waste water samples is a very widespread analysis, and plays an essential role in regulatory compliance and environmental management. International organizations developed official methods for TOC analysis, such as EN ISO 20236:2021, which involve the catalytic oxidation of the waste samples in an oxygen containing atmosphere at a temperature ≥ 680 °C to carbon dioxide, and subsequent analytical detection by means of an infrared spectrometry (IR). These standardized methodologies ensure the reliability and integrity of water quality data across different laboratories and facilitates the comparison of results between regions and countries, supporting sustainable water resource management practices worldwide.

The innovative *HighSensIR* detection system of the *VELP CN 802 Elemental Analyzer* can cover an extremely wide carbon concentration range, which make it suitable for the TOC determination of waste water samples according to official methods. Liquids and aqueous samples can be automatically analyzed in long routine series in the same analysis run as with solids, simply preparing the samples by means of tin capsules. As an alternative, the use of the new manual dosing sample kit accessory enables the direct injection of liquid samples in the combustion furnace, showing an extremely high sensitivity in the ppm range. This application note describes the procedure for the routine determination of Total Organic Carbon (TOC) in waste water samples using different methods depending on the carbon concentration of interest.

SAMPLE PREPARATION

Waste water samples were stored at a temperature of 4 °C and analysed within 48 h of sampling; as an alternative sample can be stabilized by the addition of Hydrochloric acid to achieve a pH of ≤ 2, stored at 4 °C in the dark, and analysed within 8 days. If the sample contain suspended particles matter, homogenise the sample and reduce the particle size according to standardized methods by means of a rotor- stator homogenizer such as the VELP disperser OV 625 Digital System (code SA20900470) equipped with a proper dispersing tool able to achieve the required fineness. For the determination of total carbon (TC), the sample has to be analysed directly with the *CN 802 Elemental Analyser* without further pre-treatment. For TOC determination carbonates are before destroyed by treating the original sample with acid; inorganic carbon (e.g. dissolved CO_2 or ions of carbonic acid) present in the sample is removed by acidification with diluted Hydrochloric acid (e.g. HCl 3 mol/l) under stirring and purged with a carrier gas.

The *CN 802 Elemental Analyzer* offers dedicated solutions to perform accurate analysis of liquids samples:

Method 1: Tin capsules with disc for autosampler

For laboratories handling high-throughput analysis of liquid samples the tin capsules (code A00000482) with dedicated discs for capsules (code A00000390) allow to seamlessly integrate liquid samples analysis into the autosampler workflow, alongside solid samples.

Before analysis, liquids samples are homogenised by means of a VELP magnetic stirrer (code F203A0450), and directly pipetted and weighed into the tin capsules. Capsules are closed with the aid of tweezers or by using a closing device for capsules (code A00000217). Subsequently, samples are placed into the Autosampler disc of the *CN 802 Elemental Analyser* to carry out the determination directly as TOC in a completely automatic way. Watch a VIDEO

Disc for capsules for autosampler code A00000390

Tin capsules 6x18 mm, 100 pcs code A00000482

Method 2: Direct injection by syringe

For analyses requiring the highest sensitivity the manual dosing by direct injection with the syringe is the method of choice. The versatility of the *CN 802 Elemental Analyser* allows to switch from the analysis of solids to liquid samples in few minutes, the manual dosing liquids samples kit (code A00000486) can be easily mounted in place of the Autosampler and by activating the manual dosing mode through the new functionality in the CNSoft™ Software.

The manual dosing kit allows to inject up to 1 ml of liquid sample directly into the combustion area bypassing traditional encapsulation, allowing for the analysis of samples with very low concentration levels of carbon. Before analysis, liquids samples are homogenised by means of a VELP magnetic stirrer (code F203A0450) and then accurately injected in the combustion furnace by means of a precision syringe (not included in the standard supply). Watch a VIDEO

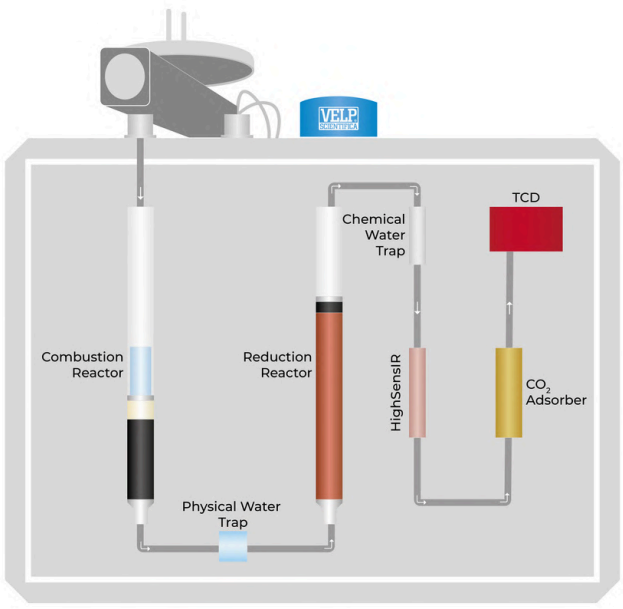
Manual dosing liquids samples kit code A00000486

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. 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 according to Method 1, or by means of the manual dosing liquids sample kit as described in Method 2. 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. 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). 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 halogenated acid vapours. The gas stream reaches a chemical trap for fine removal of water and pass 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. The sample gas is led to a 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 daily preliminary operations involve conditioning the instrument before starting the analysis of water samples. The maintenance operations to stabilize the working condition in the low carbon range are described in detail in the operating manual.

Prior to performing testing, perfect calibration of the instrument is a key condition for achieving correct analysis results. A standard solution of KHP (Potassium hydrogen phthalate, $C_8H_5KO_4$) with a carbon concentration of 76,8 mg/l was used for the creation of the calibration curve.

For method 1 a calibration curve was created dispensing the KHP standard solution with a syringe into the tin capsules, after sample weighing the sealed capsules were placed into the autosampler and measured automatically. Figure 1 reports the calibration curve obtained using tin capsules technology, showing a lower value of about 5 µg C abs. as the minimum absolute amount of carbon accurately detectable with this method.

For method 2 samples were introduced in the combustion area through the manual dosing liquids sample kit, and a calibration curve was created gradually increasing the injection volume from 6 µl up to 100 µl, corresponding to an absolute amount of carbon between 0,5 µg and 7,9 µg C abs. The 6-point lowest range calibration curve reported in Figure 1 for direct injection by syringe showed the possibility to achieve accurate results even at carbon concentration 10 times lower than method 1, obtaining a linear calibration curve with a value of R^2 = 0,9995.

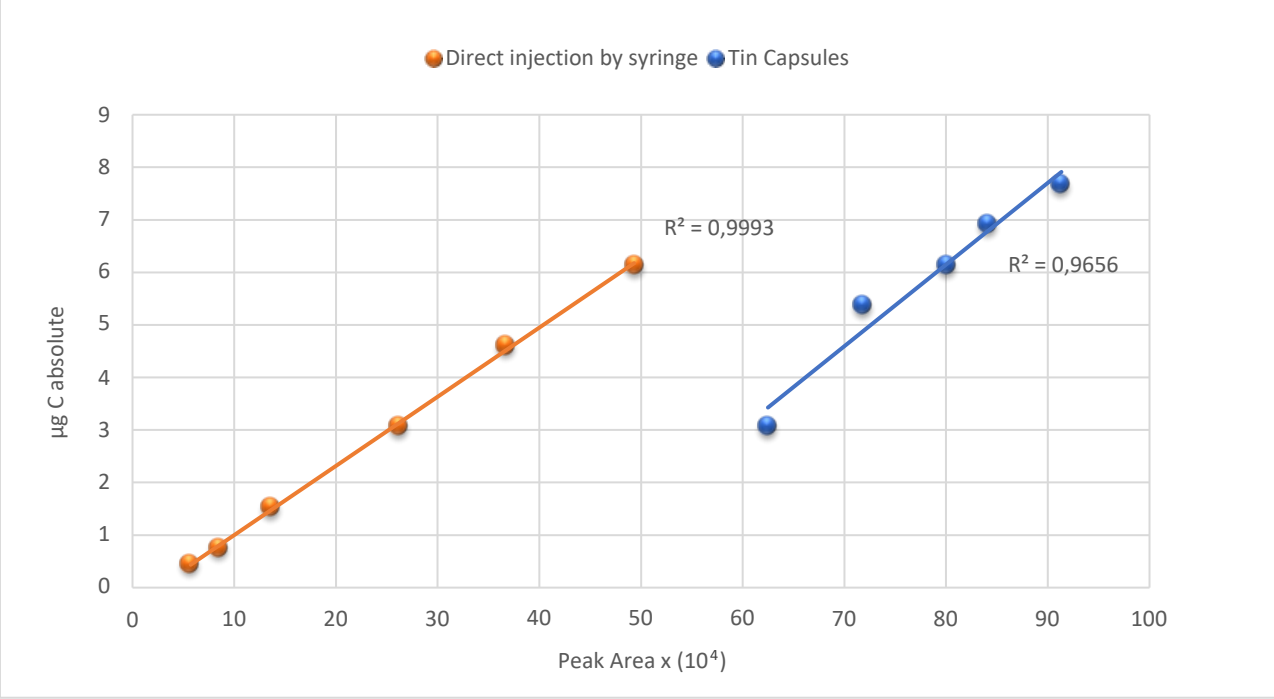


Figure 1. Calibration curves performed with a KHP standard solution obtained with method 1 and method 2.

Four replicate injections of the KHP solution obtained with the direct injection by syringe (method 2) were carried out to identify any deviations of the response values obtained during the combustion stage. The calculated repeatability variation coefficient (relative standard deviation) have been evaluated and reported in the following table showing a good repeatability.

TC [ppm]	Average ± SD %	RSD %
76,65	76,33 ± 0,34	0,44
76,35		
76,45		
75,86		

Table 1. System check determination carried out by multiple injection (injection volume = 60 µl) of the KHP standard solution (TC = 76,8 ppm)

SAMPLE 1: TC and TOC determination of wastewater sample

For the analysis of the first wastewater sample the manual direct injection by syringe (method 2) was preferred, due to the low TOC concentration expected (Sample concentration determined by external laboratory: TC = 110,4 ppm, TOC = 54,4 ppm).

In general, the direct dosage allows to reach higher accuracy and reproducibility of the results when deals with samples with a carbon concentration lower than 100 ppm. Four replicate injections have been carried out on the sample as received for Total Carbon (TC) determination, and after acidification and purging for TOC determination. Results are reported in table 2 along with the calculated repeatability variation coefficient (RSD % of replicate injection).

SAMPLE 2: TC and TOC determination of wastewater sample

A second wastewater sample with a higher carbon content have been tested, the preliminary results provided by an external laboratory have given the following results for TC = 490,6 ppm and TOC = 80,4 ppm. The analysis of the wastewater sample was conducted through a comparison with traditional method 1 by weighing the sample into tin capsules, and the determination by direct sample injection according to method 2. Table 3 shows the differences in TC and TOC analysis obtained by the *CN 802 Elemental Analyzer* with different methods for sample introduction.

TC [ppm]	Average ± SD %	RSD %	TOC [ppm]	Average ± SD %	RSD %
112,16	111,35 ± 0,87	0,78	55,26	54,55 ± 0,56	1,03
111,72			54,25		
110,21			53,98		
111,83			54,69		

Table 2. TC and TOC determination of the wastewater sample 1 (Expected concentration: TC = 110,4 ppm, TOC = 54,4 ppm) obtained with method 1

Method	TC [ppm]	Average ± SD %	RSD %	TC [ppm]	Average ± SD %	RSD %
Direct Injection	80,53	80,48 ± 0,38	0,47	487,96	489,84 ± 5,99	1,22
	80,86			492,59		
	80,56			482,47		
	79,96			496,35		
Tin Capsules	81,86	82,05 ± 1,21	1,47	482,36	493,27 ± 9,16	1,86
	81,61			499,73		
	83,77			489,12		
	80,96			501,85		

Table 3. TC and TOC determination of wastewater sample 2 (Expected concentration: TC = 490,6 ppm, TOC = 80,4 ppm) obtained with method 1 and method 2.

CONCLUSIONS

The improved sensitivity of the *CN 802 Elemental Analyzer* with the innovative *HighSensIR* detection system has made the TOC determination of waste water samples according to official methods possible. Thanks to the presence of the *DriStep™* electronic physical trap, able to condense almost all water and acidic impurities coming from the combustion, liquids and aqueous sample material can be automatically analysed in long routine series without the operator intervention.

The two methods for sample introduction tested clearly demonstrate the higher precision and accuracy of the manual sample injection by syringe when measuring samples with very low carbon content. From the calibration comparison is therefore possible to notice, by evaluating the R^2 values (R^2 correspond to the goodness of fit of a model), an important difference in the accuracy of the calibration when measuring samples with very low carbon content. It is clear that the closer we get to low concentrations (and consequently to very low amount of carbon within the sample) the greater the accuracy of the result obtained with manual dosing.

The results obtained on waste water samples suggest that for samples with a carbon concentration above 100 ppm the use of tin capsules for sample introduction may be preferred, as it offer the advantage to perform totally automatic measurements with Autosampler.

Tin capsules have proven to be an excellent choice in terms of reproducibility and speed of analysis. On the other hand, for carbon concentrations below 100 ppm, manual sample injection by syringe is recommended to obtain high reproducibility and accuracy of the result.

This study shows the great versatility of the *CN 802 Elemental Analyzer* as a unique solution to perform long routine analysis of both solid and liquids samples. As an additional feature, the dedicated software package *CNSoft™* allow the unique connection option to the Ermes Cloud Platform, the new Smart Lab solution from VELP to improve your laboratory experience.

STANDARD REFERENCES

- EN ISO 20236:2021. Water quality - Determination of total organic carbon (TOC), dissolved organic carbon (DOC), total bound nitrogen (TNb) and dissolved bound nitrogen (DNb) after high temperature catalytic oxidative combustion.

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