



Challenge

TOC determination in cellulose suspension with undissolved particles at a size of up to 100 μm according to DIN EN 1484 or DIN EN ISO 20236

Solution

Fast, reliable, and cost-efficient measurement in highly particle loaded samples thanks to the excellent particle handling of the combustion-based analyzers of the multi N/C x300 series

TOC Recovery in Particle-Containing Samples with the Cellulose Test According to DIN EN ISO 20236 and DIN EN 1484

Introduction

When monitoring total organic carbon (TOC) and total bound nitrogen (TN_b) in environmental samples like surface or waste water, by definition not only the dissolved organic carbon and nitrogen compounds have to be measured, but also the particle-bound fraction of these compounds have to be fully detected. According to DIN EN 1484^[1] and DIN EN ISO 20236^[2], the TOC is defined as the sum of all organically bound carbon present in water, both in dissolved and suspended matter. On the other hand, the dissolved organic carbon (DOC) is defined as the sum of the organically bound carbon in water originating from compounds passing through a membrane filter of 0.45 μm pore size. Accordingly, a TOC/ TN_b analyzer used for the determination of particulate environmental samples has to prove that both sample homogenization and sample handling in the analyzer from sample vial up to the combustion process ensures complete transfer and oxidation of a representative aliquot of the particulate sample.

To verify this, Annex C of DIN EN 1484 and chapter 8.2 of DIN EN ISO 20236 include a specific test to determine the recovery and variation of replicate determination for particle processing of a cellulose suspension with up to 100 μm particle size at a 100 mg/L TOC concentration. The mean value from a triplicate measurement must not exceed $\pm 10\%$ of the theoretical value. The repeatability variation coefficient must be $\leq 10\%$.

In addition to the necessary sample homogenization and sample processing preconditions of a TOC/ TN_b system, the oxidation power of the analyzer is also critical to pass this so-called cellulose test. At this point it has to be mentioned that conventional wet-chemical and/or UV-based TOC analyzers show only low recovery rates on this cellulose test and are therefore not suitable for the TOC measurement of typical particle-containing environmental water samples.

Materials and Methods

Samples and reagents

To prepare a 100 mg/L C suspension solution, 225 mg cellulose (particle size between 20 µm and 100 µm) is placed in a 1000 mL volumetric flask and made up to the mark with water. For proper homogenization, the solution should then be stirred on a magnetic stirring plate, possibly overnight to allow the micro cellulose to swell. Before each use, the suspension must be stirred again in order to prepare for a homogeneous solution. The filling of the respective sample vessel plays a very important role. It is absolutely necessary that the suspension solution is shaken vigorously immediately before filling and then transferred into the vessel relatively quickly with a large volume surge until the vessel overflows. Alternatively, a large 5 or 10 mL micropipette can be used to transfer the thoroughly mixed suspension into sampler vials.

- Wastewater samples were taken from the inlet as well as from an intermediate treatment stage of a sewage plant
- 2 M HCl was used for automatic sample acidification to a pH value < 2

Sample preparation and measurement

The samples were stored in a refrigerator at 4 °C until analysis and then transferred into suitable autosampler vials after appropriate stirring. The wastewater samples and the cellulose test suspensions were analyzed in direct mode applying an NPOC method. The samples were adjusted to pH < 2 using 2 M HCl, and subsequently purged for a period of 5 minutes. Using an autosampler, representative sample aliquots were transferred into the combustion tube. The samples were catalytically oxidized at a furnace temperature of 800 °C in an oxygen-rich atmosphere. A 16 mm combustion tube filled with platinum catalyst was used. The CO₂ formed was quantitatively detected by the focus radiation non-dispersive infrared detector (FR-NDIR). Optionally, the formed nitrogen oxides can be detected by means of a chemiluminescence detector (CLD) or an electrochemical detector (ChD).

Calibration

For the determination of the cellulose suspensions and the samples, the TOC/TN_b analyzer was calibrated with potassium hydrogen phthalate. Standards with the following concentrations were prepared and measured: 50 mg/L, 100 mg/L, 250 mg/L, and 500 mg/L. Each calibration point was injected with three replicates as agreed in the method. The method characteristics resulting from the linear regression are shown in the following diagram.

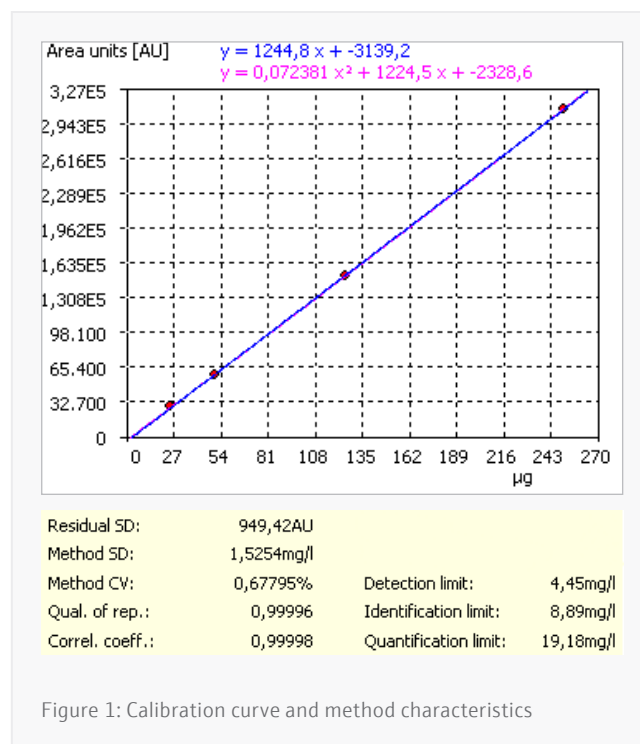


Figure 1: Calibration curve and method characteristics

Instrumentation

The TOC measurements were performed on multi N/C 2300 and multi N/C 3300. Following method settings were used to determine the TOC content.

The proper alignment of the sample aspiration needle on the autosampler is important for a representative sample aspiration of particle-containing samples, as magnetically stirred water sample forms a stirring funnel. Sample take-up

is optimized when the sample aspiration needle is located outside the center of the vial and, depending on the vial size, at least 5 to 7 mm above the magnetic stirring bar. It is also important to set the correct stirring speed in the method in order to achieve good homogenization on the one hand, but not to create a large stirring funnel at the same time. Therefore, depending on the sample vessel size, the settings recommended in the table above should be used.

Table 1: Method settings

	multi N/C 2300	multi N/C 3300
Parameter	NPOC (direct TOC measurement)	NPOC (direct TOC measurement)
Digestion	High temperature combustion with Pt catalyst at 800 °C	High temperature combustion with Pt catalyst at 800 °C
Number of repetitions	Min. 3, max. 3	Min. 3, max. 3
Autosampler and vial sizes	AS 60, 8 mL vials, 250 µL syringe	AS vario ER, 72 pos. rack, 40 mL vials
Sample rinses before injection	3	3
Reverse rinses	-	1
Sample injection volume	250 µL	500 µL
Stirring speed	5	7
NPOC purge time	300 s	300 s

Results and Discussion

The analysis results of all samples and cellulose test suspensions are summarized in Table 2. Measurements were performed as triplicates. The achieved measurement reproducibility was within the expected range. A typical measuring curve of a cellulose suspension with the corresponding replicate results is shown in Figure 2.

Table 2: Results

Sample ID	Result: NPOC [mg/L]	RSD [%]
Sewage plant inflow	284.7	0.86
1st Cellulose test at 100 mg/L	94.9	0.41
Intermediate treatment	125.2	1.44
2nd Cellulose test at 100 mg/L	99.3	0.48
KHP check standard at 150 mg/L	150.3	0.10

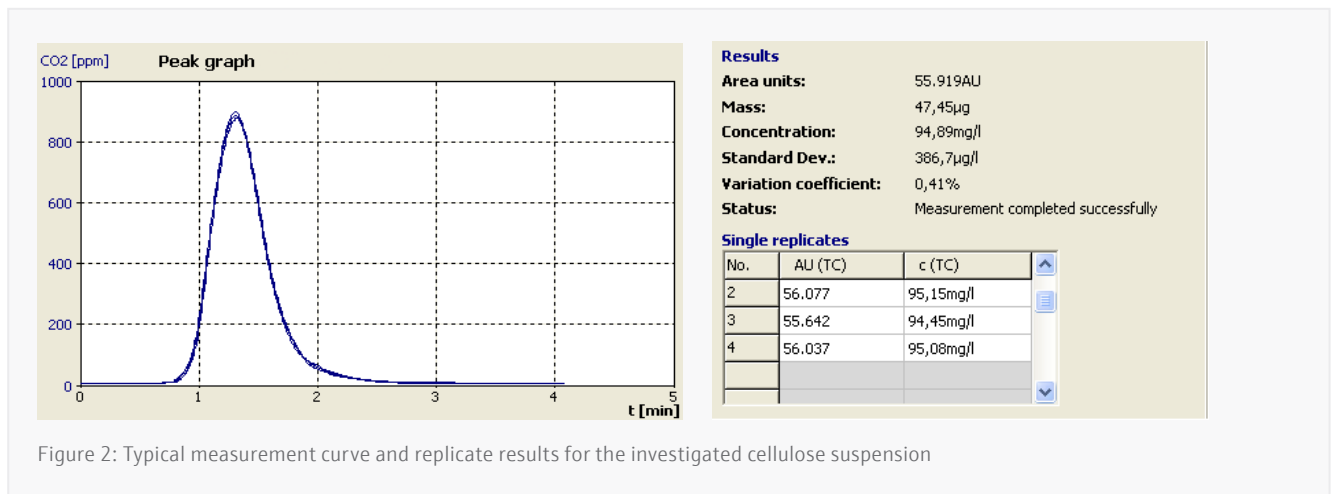


Figure 2: Typical measurement curve and replicate results for the investigated cellulose suspension

Summary

The measurement results of the cellulose suspensions exceed the required expectations of a recovery in the range from 90 to 110% with results of 95% and 99%. Likewise, the coefficients of variation at 0.41% and 0.48% exceed the requirements of DIN EN 1484 or DIN EN ISO 20236, respectively. Decisive for these good results are the excellent particle handling capabilities of the multi N/C analyzers. With the multi N/C 2300, this is achieved by the 0.7 mm inner diameter of the aspiration needle in combination with the ultra-short sample dosage line. The sample transfer needles, tubing, and the rotary valve of the multi N/C 3300 with an inner diameter of 0.8 mm and, in combination with the proven, fast sample loop injection principle, are perfectly suited for samples containing particles. Additionally, the high furnace temperatures guarantee 100% sample oxidation. The use of large sample injection volumes and the routine filling of the sample vessels further support a successful cellulose particle test.

Real wastewater samples taken from the sewage treatment process also show excellent reproducibility. A fully



Figure 3: multi NC 3300 with autosampler AS vario

automated measurement process for large sample sequences is supported by a wide range of available autosamplers with integrated sample homogenization, ranging from 21 sample positions (AS 21hp) to 147 sample positions with the AS vario and AS vario ER for the multi N/C 3300. The AS 60 autosampler for the multi N/C 2300 also offers a very good level of automation for sewage plant testing laboratories.

References

- [1] DIN EN 1484 Water analysis – Guidelines for the determination of total organic carbon (TOC) and dissolved organic carbon (DOC)
- [2] DIN EN ISO 20236: Water quality – Determination of total organic carbon (TOC), dissolved organic carbon (DOC) total bound nitrogen (TN_t) and dissolved bound nitrogen (DN_t) after high temperature catalytic oxidative combustion

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