Challenge

Reproducible and reliable determination of TOC and TN_b contents in samples with high particle loads/wastewater.

Solution

Fully automated and simultaneous TOC/TN_b measurement using direct injection technology and catalytic high-temperature combustion, which allow optimum particle handling and a minimized risk of carry-over.

TOC/TN_b Determination in Municipal Sewage Plants

Introduction

In wastewater treatment plants, the organic and nitrogen load have to be measured in the untreated inflow, the pretreated effluent, and the final effluent after the completed treatment process. In many cases, the chemical oxygen demand (COD) and TN contents are measured with separate methods. This is a labor- and time-consuming process often associated with the formation of chromium-VI-contaminated waste. Through correlation studies, an empirical conversion factor for TOC to COD conversion can be established. Hence, a fully automated analytical process for TOC/TN_b determination according to EN 1484 and EN 12260 can be applied to save resources and time.

In order to guarantee accurate and efficient analysis, it is recommendable to use a catalytic high-temperature combustion TOC analyzer for simultaneous determination of NPOC and TN_b from one single injection. According to these standards, TOC is defined as the sum of dissolved and particle-bound organic carbon compounds. Thus, the challenge is to assure a representative sample transfer, including all the particles, into the combustion system and at the same time to guarantee a complete oxidation of both, difficult-to-oxidize substances and particle-bound organics. This requires an effective sample homogenization on the autosampler rack and a sample introduction technique that ensures no particles get lost on the way to the combustion tube or cause any blockages, which may lead to system downtime or to extended wear and tear on sensitive Teflon parts inside the dosing system. A combustion system capable of providing sufficiently high furnace temperatures to assure a complete sample digestion is required as well. This application note describes a method using the multi N/C 2100S TOC/TN_b analyzer. The samples were measured at a customer's site (wastewater treatment plant) in Germany using a direct injection system for optimized particle handling.

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Materials and Methods

Samples and Reagents

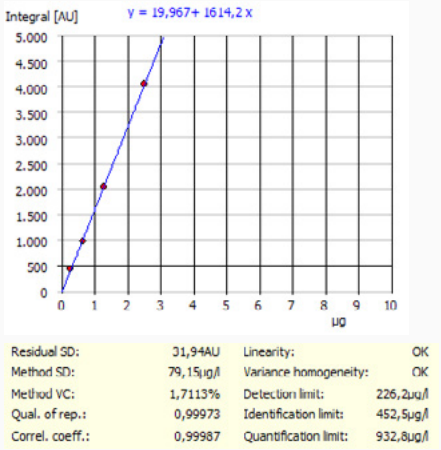
- Wastewater samples were taken from the inflow into the sewage plant as well as intermediate treatment stages
- 2 M HCL was used for automatic sample acidification to a pH < 2

Sample Preparation

The samples were stored in a refrigerator at 4 °C until analysis and then transferred into suitable autosampler vials. The wastewater samples were analyzed in direct mode applying an NPOC/TN$_b$ method. The samples were adjusted to pH < 2 using 2 M HCl, and subsequently purged for a period of 5 minutes. An injection volume of 250 µL was used for these measurement sequences. The samples were catalytically oxidized at a temperature of 800 °C in an oxygen flow. The 16 mm combustion tube, filled with platinum catalyst was used. The formed nitrogen oxides are detected by means of a chemiluminescence detector (alternatively a ChD detector can be utilized), CO_2 detection was done by FR-NDIR.

Calibration

The multi N/C analyzer was calibrated between 1 and 1000 mg/L for total organic carbon (TOC) with a potassium hydrogen phthalate standard solution. A multipoint calibration was used to evaluate the results of the NPOC measurement. For total bound nitrogen a calibration was carried out from 1 to 100 mg/L with an ammonium sulfate and potassium nitrate solution (50:50 mix) according to EN 12260.



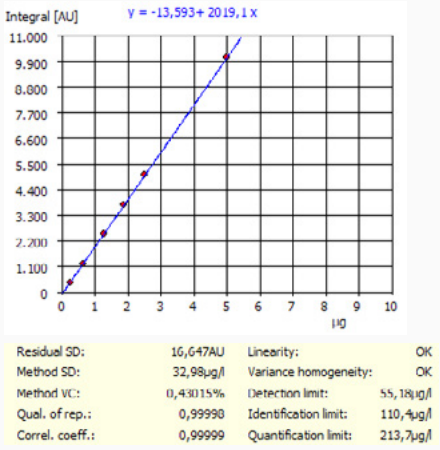
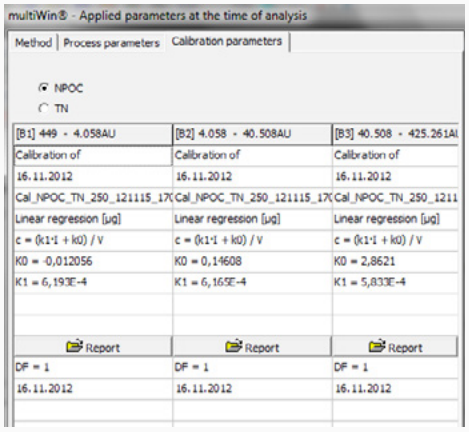


Figure 1 and 2: Example of TC and TN calibration and method characteristics

Within the method up to three calibration ranges can be linked to each parameter in order to cover an over-all working range of up to three magnitudes. With the NPOC/TN$_b$ method three NPOC and two TN$_b$ multi-point calibration ranges were linked as follows:



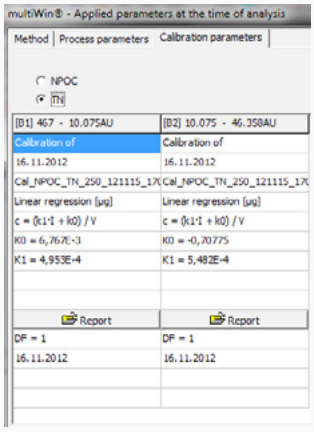


Figure 3 and 4: NPOC and TN$_b$ calibration ranges used with the combined NPOC/TN method

Instrumentation

The following method settings were used to determine the NPOC and TN_b contents:

Table 1: Method settings

Parameter	multi N/C 2100S
Measurement parameter	NPOC / TN_b
Digestion	High temperature digestion at 800° C with platinum catalyst
Number of repetitions	min. 3, max. 4
Rinse with sample before injection	3 times
Sample purge time	300 sec.
Injection volume	250 µL

Results and Discussion

The table below shows the mean values of three replicate injections with relative standard deviations for different real samples (anonymized) and various recovery checks for different TN, TOC and particle suspension reference solutions (cellulose according to EN 1484, annex C), respectively.

Table 2: Results

Sample ID	Method	TC/NPOC	TN
TC_10mgl	NPOC_TN_250	10.07mg/l ± 0.50%	283.0µg/l ± 1.79%
Cellulose	NPOC_TN_250	99.29mg/l ± 0.13%	113.6µg/l ± 2.26%
TC_150mgl	NPOC_TN_250	150.0mg/l ± 0.09%	174.2µg/l ± 3.11%
NO3_NH4_6mgl	NPOC_TN_250	815.0µg/l ± 9.50%	5.96mg/l ± 0.35%
TN_6mgl	NPOC_TN_250	11.68mg/l ± 0.83%	5.96mg/l ± 0.11%
TN_30mgl	NPOC_TN_250	51.17mg/l ± 0.30%	29.29mg/l ± 1.31%
[redacted]	NPOC_TN_250	93.79mg/l ± 2.08%	25.37mg/l ± 1.21%
[redacted]	NPOC_TN_250	250.7mg/l ± 0.68%	116.3mg/l ± 0.54%
[redacted]	NPOC_TN_250	160.2mg/l ± 1.41%	12.12mg/l ± 0.92%
[redacted]	NPOC_TN_250	125.2mg/l ± 1.44%	28.53mg/l ± 0.51%
TC_10mgl	NPOC_TN_250	10.40mg/l ± 0.49%	196.2µg/l ± 3.17%
Cellulose	NPOC_TN_250	106.6mg/l ± 0.48%	97.80µg/l ± 7.26%
TC_150mgl	NPOC_TN_250	151.4mg/l ± 0.17%	136.2µg/l ± 3.93%
NO3_NH4_6mgl	NPOC_TN_250	432.0µg/l ± 17.45%	6.07mg/l ± 0.34%
TN_6mgl	NPOC_TN_250	11.78mg/l ± 0.96%	6.01mg/l ± 0.93%
TN_30mgl	NPOC_TN_250	51.82mg/l ± 0.07%	29.71mg/l ± 0.94%
[redacted]	NPOC_TN_250	49.34mg/l ± 0.74%	22.52mg/l ± 1.33%
[redacted]	NPOC_TN_250	230.1mg/l ± 0.47%	93.07mg/l ± 0.71%
[redacted]	NPOC_TN_250	887.8mg/l ± 0.35%	59.52mg/l ± 0.75%
[redacted]	NPOC_TN_250	221.2mg/l ± 0.64%	116.2mg/l ± 0.51%
TC_10mgl	NPOC_TN_250	9.89mg/l ± 0.11%	145.4µg/l ± 5.26%
Cellulose	NPOC_TN_250	100.1mg/l ± 0.65%	141.3µg/l ± 1.91%
TC_150mgl	NPOC_TN_250	150.3mg/l ± 0.10%	93.88µg/l ± 2.42%
NO3_NH4_6mgl	NPOC_TN_250	375.6µg/l ± 5.64%	6.01mg/l ± 0.34%
NO3_NH4_30mgl	NPOC_TN_250	340.3µg/l ± 5.13%	29.40mg/l ± 0.06%
TN_6mgl	NPOC_TN_250	11.64mg/l ± 0.62%	6.02mg/l ± 0.90%
TN_30mgl	NPOC_TN_250	52.02mg/l ± 0.47%	29.76mg/l ± 0.67%
[redacted]	NPOC_TN_250	1.04g/l ± 0.30%	23.53mg/l ± 0.59%
[redacted]	NPOC_TN_250	104.5mg/l ± 2.25%	90.65mg/l ± 0.67%
[redacted]	NPOC_TN_250	996.7mg/l ± 0.77%	13.59mg/l ± 1.26%
[redacted]	NPOC_TN_250	284.7mg/l ± 0.86%	158.4mg/l ± 0.81%

Conclusion

The measurements covered the analysis of undiluted wastewater samples with TOC concentrations up to almost 1 g/L and TN_b concentrations up to 160 mg/L. The analyses were performed with outstanding accuracy and precision. The cellulose test to check for particle handling according to EN 1484, as well as measurements of analytical quality assurance (AQA) standards for TOC and TN_b were performed frequently and showed convincing recovery rates. Especially the recoveries for 6 mg/L and 30 mg/L nicotinic acid TN_b standards prove a high performance for organically bound nitrogen.

This outstanding performance of multi N/C analyzers for such matrices, as wastewater is based on the optimized combustion process with freely selectable combustion temperatures up to 950 °C. The direct injection with a septum-free pneumatic injection head in combination with a wide-bore needle of 0.7 µm inner diameter, as well as proper sample homogenization on the auto sampler rack and the valve- and tubing-free sample transfer into the combustion system further contribute to this performance. An operation mode keeping the stainless-steel injection needle in the oven head at elevated temperatures during peak integration time to assure complete evaporation of TOC components and a clean needle for further sample processing in combination with an effective rinsing of the microliter injection syringe minimize carry-over effects.

A high degree of automation combined with the well-proven Self Check System for trouble free unattended system operation make light work of TOC/TN_b analyses even in challenging samples. In addition, the patented VITA flow management system compensates flow fluctuations inside the system caused by sample evaporation, providing TOC calibration stability for up to one year and saving valuable measurement time.

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