Challenge

Reproducible and reliable determination of TOC and TN_b contents in particle loaded wastewater samples.

Solution

Fully automated and simultaneous TOC/TN_b measurement using direct injection technology providing optimum particle handling and minimized carry-over.

TOC/TN_b Determination in Pulp and Paper Process Effluents

Introduction

The pulp and paper industry generates large volumes of wastewater or effluents that need to be treated before they can be reused or released into natural waterways. According to the European Industrial Emissions Directive (IED) Best Available Techniques (BAT) have to be implemented within the EU for direct wastewater discharges from pulp, paper and card production[1]. The BAT reference document (BREF) indicates that among other parameters, TOC (total organic carbon) and TN_b (total bound nitrogen) are of growing importance. They need to be monitored on a daily or weekly basis. Furthermore, for economic and environmental reasons a preference for the parameter TOC instead of COD is given as it does not require the use of highly toxic compounds like dichromate (Cr VI) and mercury.

In many cases the COD and TN contents are still measured using separate methods. This is a labour and time consuming process and associated with the formation of chromium VI and mercury contaminated waste. By correlation studies an empirical conversion factor for TOC (total organic carbon) to COD conversion can be established for specific emission sources and waste water treatment steps. This allows a fully automated analysis process for TOC/TN_b determination according to EN 1484[2] and EN 12260[3] (or ISO 20236[4] for both parameters) to be applied, which saves resources and time.

analytikjena
An Endress+Hauser Company

Since process effluents from pulp and paper production often contain a large amount of solids (cellulose fibers), direct injection technology has proven particularly effective for TOC/TN_b analysis. The multi N/C 2100S does not require hoses or valve technology, but doses the sample directly into the combustion chamber via a septum-free injection port and a wide bore needle using a microliter syringe. The direct injection technique provides a safe and reproducible particle transfer without the risk of clogging or carryover. This increases instrument availability, reduces wear and tear and increases sample throughput and efficiency.

Materials and Methods

Samples and Reagents

- Samples from different product processing and clean-up stages as well as raw water used in production were analyzed
- 2 M HCl was used for automatic acidification in NPOC mode

Sample Preparation and measurement

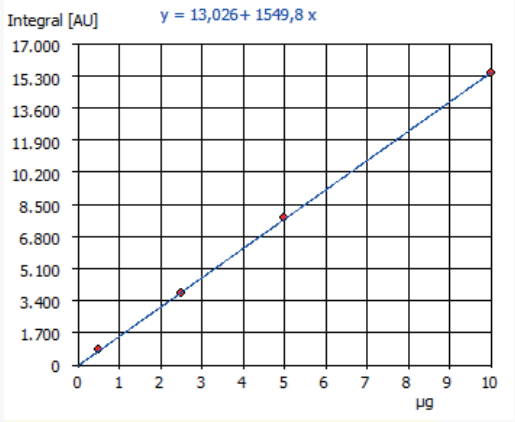
The samples were stored in a refrigerator at 4 °C until analysis. For measurement, the samples were transferred into 8 ml autosampler vials. The wastewater samples were analyzed in direct mode using an NPOC/TN method. The sampler AS 60 with 60 sample positions was used for automated measurement.

The samples were automatically acidified to a pH <2 using 2 M HCl, and subsequently purged to remove any inorganic carbon (TIC). The complete TIC elimination from the sample can be checked by TIC control measurement. A representative injection volume of 500 µL was transferred into the combustion tube for measurement. The samples were completely oxidized at a temperature of 800 °C in an oxygen-rich atmosphere using a platinum catalyst. The formed CO_2 was quantitatively determined by focus radiation none-dispersive infrared detection (FR-NDIR). Simultaneously the nitrogen oxides were detected by means of an electrochemical ChD detector (alternatively, chemiluminescence detector can be used for total bound nitrogen (TN_b) determination.

Calibration

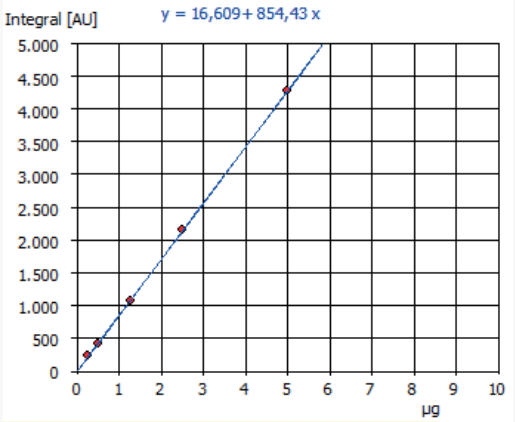
Within the method up to three calibration ranges can be linked to each parameter in order to cover an over-all working range of up to three magnitudes. Detection limits and limits of quantification are depending on the selected working range and can be derived from the method characteristics given above.

Table 1: NPOC and TN_b calibration curves



Residual SD:	73,494AU	Linearity:	OK
Method SD:	94,84µg/l	Variance homogeneity:	OK
Method VC:	1,0538%	Detection limit:	274,8µg/l
Qual. of rep.:	0,99991	Identification limit:	549,5µg/l
Correl. coeff.:	0,99996	Quantification limit:	1,17mg/l

Fig. 1: Example of NPOC calibration and method characteristics



Residual SD:	13,001AU	Linearity:	OK
Method SD:	30,43µg/l	Variance homogeneity:	OK
Method VC:	0,80085%	Detection limit:	59,46µg/l
Qual. of rep.:	0,99995	Identification limit:	118,9µg/l
Correl. coeff.:	0,99998	Quantification limit:	237,3µg/l

Fig. 2: Exampe of TN calibration and method characteristics

Within one 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. Detection limits and limits of quantification are depending on the selected working range and can be derived from the method characteristics given above.

Instrumentation

The analysis was performed on a multi N/C 2100S using an NPOC/TN method.

Method Parameters

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

Table 2: 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. 2, max. 3
Rinse with sample before injection	3 times
Sample purge time	300 sec.
Injection volume	500 µL

Results and Discussion

Table 3 shows blank value corrected mean values from at least two repeat measurements for different real samples and recoveries for TOC and TN_b reference solutions. Dilution ratios are also reported. For informative purposes, the COD contents provided for the respective samples and the TOC-COD correlation factors calculated from them were also given.

Table 3: Results

Sample ID	COD	NPOC ± RSD [mg/L] ± [%]	TN_b ± RSD [mg/L] ± [%]	TOC-COD correlation factor	Dilution factor
Raw Water	8,0	2.79 ± 1.84	3.50 ± 1.02	2.86	-
EVII	8,9	2.99 ± 0.71	3.49 ± 0.68	2.98	-
EX	365	120.5 ± 0.18	4.60 ± 0.26	3.04	-
ZF	4302	1480 ± 0.08	15.36 ± 1.89	2.91	1:10
Sedimat	4450	1580 ± 0.47	15.50 ± 0.08	2.82	1:10
ZA	365	1600 ± 0.04	39.63 ± 1.33	3.17	1:10
AA	4302	956.5 ± 2.01	55.05 ± 1.66	3.27	1:10
BK	4450	3230 ± 0.10	11.97 ± 2.18	2.55	1:100
Check Standard Nicotinic Acid (TOC 20.0 / TN_b 3.88)	365	20.2 ± 0.9	3.97 ± 0.8	-	-

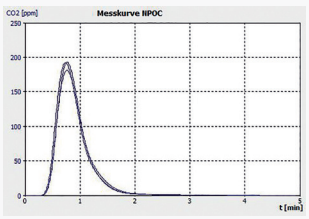


Fig. 3: Peak graph NPOC BK

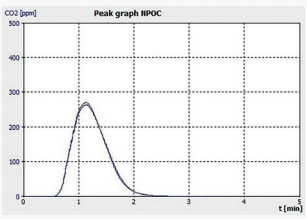


Fig. 4: Peak graph NPOC EX

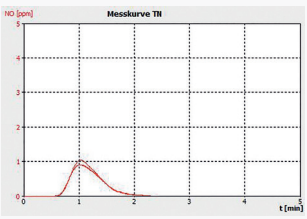


Fig. 5: Peak graph TN_b BK

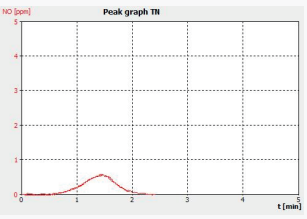


Fig. 6: Peak graph TN_b EX

Conclusion

The analyzed samples represent a typical range of process effluents from different process stages and sampling points in the wastewater treatment process as well as raw water for paper production. Despite the very different TOC and TN_b concentrations, all samples were measured with outstanding accuracy and precision. Nicotinic acid was used as an analytical quality assurance standard (AQA) to simultaneously check for TOC and TN_b recoveries. Very good recoveries were achieved with this reference material for organically bound nitrogen.

This outstanding performance of multi N/C analyzers for such demanding wastewater matrices 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 contribute to this. 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.

The analyzers of the multi N/C series are most suitable for the determination of total organic carbon and total bound nitrogen in process effluents and wastewater from pulp and paper industries.

References

[1] Official Journal of the European Union, L 284/76, 30.09.2014, Commission Implementing Decision of 26. September 2014 “Establishing best available techniques (BAT) conclusions, under Directive 2010/75/EU of the European Parliament and of the Council, for the production of pulp, paper and board”

[2] DIN EN 1484 – Water analysis - Guidelines for the determination of total organic carbon (TOC) and dissolved organic carbon (DOC); German version EN 1484:1997

[3] DIN EN 12260 – Water quality - Determination of nitrogen - Determination of bound nitrogen (TNb), following oxidation to nitrogen oxides; German version EN 12260:200

[4] ISO 20236 – 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

Headquarters
Analytik Jena GmbH
Konrad-Zuse-Strasse 1
07745 Jena · Germany

Phone +49 3641 77 70
Fax +49 3641 77 9279

info@analytik-jena.com
www.analytik-jena.com

Version 1.1 · Author: BeBl
en · 12/2020