Challenge

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

Solution

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

TOC/TN_b Determination in Refinery Effluents

Introduction

The petrochemical industry generates large volumes of wastewater or effluents that need to be treated before they can be reused or released into natural waterways. Total organic carbon (TOC) and the total nitrogen bound (TN_b) content is routinely determined, as these contaminants lead to eutrophication of surface water recourses, endangering aquatic life and groundwater supplies.

According to the European Industrial Emissions Directive (IED), Best Available Techniques (BAT) have to be implemented within the EU for direct wastewater discharges from the refining of mineral oil and gas.[1] The BAT reference document (BREF) indicates that, among other parameters, TOC and TN_b are of growing importance. They need to be monitored on a daily basis. Furthermore, a preference for the parameter TOC instead of COD is given, as TOC does not require the use of highly toxic compounds, such as dichromate (Cr VI) and mercury.

In many cases, the COD and TN contents are still measured using separate methods. This is a labor- and time-consuming process and is 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 (also the planned new ISO 20236 for both parameters) can be applied to save resources and time.

Effluent waters from refining processes usually represent demanding samples for TOC/TN_b analyzers, since tubing and valve technique feeding the sample into the combustion process are prone to carry-over. Direct injection as applied in the multi N/C 2100S using a septum-free injection port and a wide-bore needle for optimum particle handling can overcome this problem. Direct injection ensures a sample transfer without particle losses and prevents blockages, hence increasing system uptime and reducing wear and tear on sensitive Teflon parts inside the dosing system. In addition, the injection needle is fully thermally cleaned before injecting the next sample, since it stays in the hot furnace inlet zone during analysis time, thus reliably avoiding carry-over. multi N/C 2100S thus offers a robust solution for simultaneous TOC/TN_b analysis of particulate or oily samples.

Materials and Methods

Samples and Reagents

Samples from different prozess streams and clean-up stages have been collected and measured alongside with a reference standard.

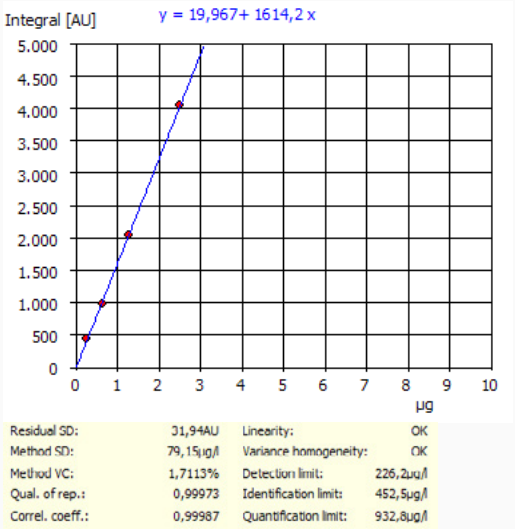
Sample Preparation and measurement

The samples were stored in a refridgerator at 4 degrees Celsius until analysis. For measurement, the samples were transferred into suitable autosampler vials. The wastewater samples were analyzed in direct mode using an NPOC/TN method.

Using 2 M HCl, the samples were adjusted to pH < 2 and subsequently purged for 5 minutes. An injection volume of 250 µL was used for these measurement sequences. The samples were catalytically oxidized at a temperature of 800 degrees Celsius in an oxygen-rich atmosphere. A combustion tube filled with platinum catalyst was used for complete sample oxidation. The formed nitrogen oxides were detected by means of a chemiluminescence detector (alternatively ChD detector can be utilized), CO_2 detection was done by focus radiation none-dispersive infrared detection (FR-NDIR).

Calibration

The multi N/C analyzer was calibrated between 1 and 500 mg/L with a potassium hydrogen phthalate standard solution for TOC determination. A multi-point calibration was used to evaluate the results of NPOC measurement. For total bound nitrogen a calibration was carried out from 1 to 50 mg/L using an ammonium sulfate and a potassium nitrate (50:50 mix) solution according to the standard EN 12260.



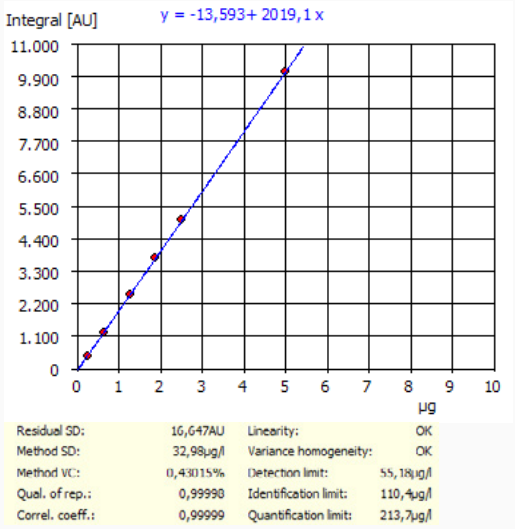


Figure 1 and 2: Example of NPOC and TN calibration and method characteristics

Within the method up to 3 calibration ranges can be linked to each parameter in order to cover an over-all working range of up to 3 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 done on a multi N/C 2100S using an NPOC/TN method.

Parameter	Specification Analyzer
Analytical Parameters	TC, TOC, NPOC, NPOC+, POC, TIC and TN_b
Norm compliance	EN 1484, US EPA 9060,US EPA 415, ASTM G144, EN 12260
User confidence and comfort	multiWin control and evaluation software, VITA technology, self-check system, etc.
Sample feeding	Direct injection at variable volumes 50 – 500 µL
Automation	AS 60 up to 112 pos. (8 mL / 2 mL vials)
Digestion	Thermocatalytic up to 950 °C
Detection	Focus Radiation NDIR, Chemilumineszenz Detection (CLD) or electrochemical detection (ChD)
Measuring range	Carbon: 50 ppb–30000 ppm, Nitrogen: 5 ppb – 200 ppm (CLD) or 50 ppb – 100 ppm (ChD)
Measuring time	appr. 3 - 5 min.
Gas supply	Oxygen 4.5 or better, alternatively: HC- and CO_2-free synthetic / cleaned-up air

Method Parameters

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

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 recoveries for TOC and TN_b reference solutions. According to the Best Available Techniques (BAT) reference document issued under the Industrial emission directive 2010 / 75 / EU[1)], the associated average emission levels (BAT-AEL) for direct waste water discharges from refining processes can be expected as in the following ranges:

COD: 30 – 125 mg/L equals to: TOC: 7 – 32 mg/L

TN_b: 1 – 25 mg/L

Table 2: Results

Sample ID	NPOC Average [mg/L]	TOC RSD [%]	TN_b [mg/L]	TN_b RSD [%]
Sample 1	26.2	2.1	19.5	1.4
Sample 2	161	0.9	41.3	1.1
Sample 3	12.9	1.2	5.38	0.8
Check Standard Nicotinic Acid (TOC 20.0 / TN_b 3.88)	19.8	0.6	4.06	0.7

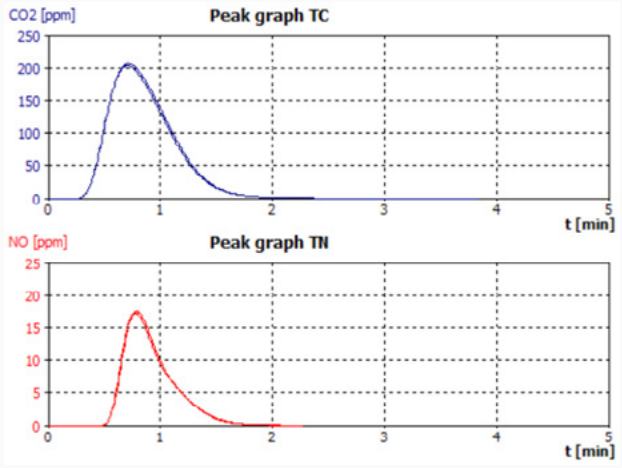


Fig. 3: example for a TOC and TN_b measurement curve of sample 3

Conclusion

The data analyzed covered undiluted wastewater samples from different sampling points in the wastewater treatment process and with varying 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 for the 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 degrees Celsius. 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 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.

References

1) Official Journal of the European Union, L 307/38, 28.10.2014, Commission Implementing Decision of 09. October 2014 "Establishing vest available techniques (BAT) conclusions, under Directive 2010/75/EU of the European Parliament and of the Council on industrial emissions, for the refining of mineral oil and gas"

Headquarters
Analytik Jena AG
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

en · 02/2018