Dow chooses an innovative oxidation technology to monitor TOC/TN online

The Problem

Dow in Bomlitz, Germany, needed a reliable TOC/TN monitoring solution on the influent of their mechanical wastewater treatment plant to get real-time insight. Their difficult sample matrix with a high solids content presented an additional challenge.

The Solution

Following an extensive evaluation, Dow selected the Hach BioTector B7000 TOC/TN online analyser featuring innovative Two Stage Advanced Oxidation (TSAO) technology. Its self-cleaning ability and the 3.2 mm i.d. oversized tubing eliminates the need for delicate filtration, prevents clogging, and overcomes sample cross contamination.

The Benefits

The Bomlitz site now benefits from maximum availability, alongside minimal service and maintenance interventions. In Dow's evaluation, BioTector attained the best: laboratory conformance for TOC and TN; combined monitoring on TOC, TIC, and TN; and guaranteed complete TIC removal prior to TOC and TN measurement.



Industrial Park Walsrode

Background

Since 2007, Dow has owned and operated the Industrial Park in Walsrode. The site's sewage treatment plant receives various types of wastewater from 20 small and medium sized industries. Within the larger Dow Group, Dow Bomlitz is the centre of excellence for cellulose chemistry and, with more than 700 employees, is a key production location in Germany and Europe. The wastewater treatment plant at the industrial park already uses other Hach[®] online monitoring equipment, such as for the determination of solids, nitrate, oxygen, ammonium, and phosphate.

The Dow Bomlitz site

Dow sought the most reliable TOC/TN analyser with minimal to no service intervention needs. This was due to extremely challenging measurement requirements caused by the harsh wastewater matrix in the influent of the mechanical wastewater treatment. The high solids content was a particularly major challenge. Before making a final choice, the BioTector TOC/TN was evaluated against other TOC/TN oxidation technologies.



The acceptance criteria for the eight-week trial were:

- Availability of the measurement data
- Comparability of online measurement with laboratory for TOC and total nitrogen (TN)
- Low need for service and maintenance interventions
- Robustness and reliability in untreated wastewater containing a solids and fibres content

The aim of the evaluation was to select the most reliable oxidation technology for online TOC; technology which also attains best conformance as compared with Dow's laboratory measurement of high-temperature catalytic oxidation TOC/TN. A high maintenance and high manual cleaning effort was expected for analysers on this type of wastewater matrix. In addition to maintaining any analyser technology the staff has to perform many more tasks to ensure a safe operation of the treatment plant. Therefore, the analyser of choice needs to have highest reliability, ease of use, and should require minimal service and maintenance interventions. It must fit seamlessly into their entire workflow and deliver consistently reliable TOC and TN measurement data.

Measurement method of the Hach BioTector

The BioTector removes the Total Inorganic Carbon (TIC) by adding acid directly into the mixer-reactor. The CO_2 produced in the TIC phase is measured and displayed as a TIC measurement value. This is very different from other TOC technologies. The advantage of the TIC being measured in this phase is that the TIC purge is automatically ended as soon as the CO_2 curve has fallen below a given threshold of the NDIR baseline. This is a standard safety check, as incomplete TIC removal might lead to the situation that TIC is carried over into the TOC measurement. This TIC carryover leads to erroneous TOC measurement.

First stage of TOC measurement:

By addition of base, the sample is brought to a pH \geq 11. The built-in ozone generator creates ozone, which is mixed-in continuously with the alkaline sample matrix in the mixer-reactor to form hydroxyl radicals (OH°). As very strong and powerful oxidising agents, these OH° radicals oxidise the organics in the sample, including 2mm of soft particles, to produce carbonates and oxalates.

Second stage of TOC measurement:

By addition of an acid, which includes a small amount of dissolved Mn catalyst, the sample is brought to $pH \leq 1$, and all produced carbonates and oxalates are chemically converted into CO_2 . CO_2 is then quantitatively measured by the NDIR detector and displayed as a TOC measurement value for the sample that was injected.

After the second stage of oxidation, all the TN that was present in the original sample is now oxidised into NO_3 . An optional TN module, which can be built into a BioTector B7000 analyser, can measure this NO_3 optically. The result is displayed as TN measurement value for the sample that was injected. To save precious analysis time, this TN measurement is done while the next TIC and TOC measurement is started again.

After each TIC and TOC measurement, the reactor is emptied, followed by self-cleaning of both sample tubing and the mixer-reactor. This self-cleaning technology prevents clogging and sample cross-contamination and ensures a clean reactor before the next sample measurement is started.



The Solution at the Dow Bomlitz site

Test Set-up

Two widely applied TOC/TN oxidation technologies were tested and compared against each other for a period of eight weeks: One technology uses high-temperature oxidation at 1200°C (without a catalyst), and the second technology uses an innovative two-stage advanced oxidation (TSAO). A BioTector B7000 TOC/TN analyser was used for the TOC and TN measurement.

The sample was taken by the BioTector analyser directly out of the wastewater channel, without any additional need for further sample preparation. With the high-temperature oxidation TOC/TN analyser setup, samples were taken using a submersible pump.

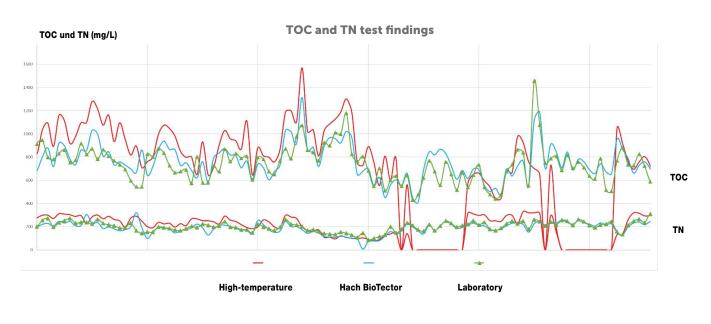


Diagram shows 26/08 to 21/09; density of measurement frequency due to presence of on-site laboratory



Test results

Measurement values from the BioTector B7000 TOC/TN analyser have been reported to be correct and comparable for both TOC and TN from the beginning. They showed only the slightest deviation from Dow's high-temperature catalytic oxidation TOC/TN lab analyser. For the B7000 TOC/TN analyser, no downtime has occurred in the evaluation period.

Unlike the Hach BioTector with its innovative TSAO TOC technology, the setup using high-temperature oxidation TOC technology at 1200°C did not monitor the TIC removal. As a result, the high-temperature TOC/TN setup resulted in TIC not being removed completely, leading in turn to erroneous TOC measurements.

Based on the outstanding test results, Dow opted for the BioTector from Hach. Dow also plans to implement additional Hach TOC analysers at its site in future.

Technical features of the Hach BioTector in challenging applications

The Two Stage Advanced Oxidation (TSAO) TOC technology specifically has been designed to handle the harshest, most demanding wastewater and process applications, to ensure good stability and availability, and to compare most favourably to laboratory measurement.

Its operation takes place at ambient temperature and pressure and it can be stopped and restarted at will for maintenance reasons. Thus, no time is lost waiting for the reactor to cool down, and no safety measures need to be considered concerning high temperature conditions. This technology is also extremely advantageous for use in hazardous zone applications.

The automatic self-cleaning of the reactor and the reverse sample line cleaning after each measurement, in combination with oversized sample tubes, prevents clogging and sample cross-contamination of subsequent measurement values even in challenging sample matrices containing grease and fibres. Reaction residues such as salts are removed from the instrument in the liquid phase.

The 3.2 mm diameter oversized sample tubing gives the BioTector analyser a larger particle size range compared with any other conventional TOC technology. Soft organic particles measuring up to 2 mm actually can be measured without the need to be filtered out, as is usually required with conventional TOC analyser technologies.

In addition, the well-proven and powerful TSAO TOC technology allows the analysis of large sample volumes of up to 8-10 mL, which typically is a 1,000 times bigger sample volume when compared with conventional TOC technologies, thus achieving a much more representative measurement.



Hach BioTector B7000i

The BioTector benefits at a glance:

- Excellent certified analyser up-time of 99.86% (MCert.)
- Best laboratory conformance for TOC/TN vs. high-temp. catalytic oxidation lab TOC/TN analysis
- Automatic self-cleaning of the reactor and reverse sample line cleaning between each analysis
- Up to 10 mL representative sample quantity analysed
- Oversized 3.2 mm sample tubes eliminate the need for delicate filtration
- Resistant to contaminations such as oils, greases, and fibres
- Able to handle salt contents of up to 30%



Conclusion

Hach as a wastewater partner

Industrial applications present significant challenges, and many TOC analysers struggle to deliver reliable functionality under these tough conditions. Increased quantities of chloride, greases, oils, particulates, and a host of other contaminants frequently result in problems for measurement technology, leading to low levels of reliability, erratic breakdowns, high maintenance costs, and a lack of confidence in the measurement technology.

Hach BioTector B7000 TOC analysers have been designed to withstand and overcome these challenges presented by industrial process water and wastewater. It delivers reliable, accurate data for many types of industrial water cycles, including wastewater treatment plants.

Hach is a leading global partner for water analysis providing customised solutions for all water cycles. Hach welcomes feedback from customers and uses this data for subsequent product development.

Outlook

The Team at Dow has put its faith and full trust in TOC/TN determination from Hach.

Quote from Dow Operations Leader, I-Park Operations, and department head for wastewater treatment, Marco Dollinger:

"The BioTector had the best sample recovery and the best comparability with our laboratory measurement."

Following the successful evaluation phase, Dow Bomlitz intends to deepen its collaboration with Hach. Additional projects are aimed to increase accuracy and insight through reliable online monitoring of the individual production wastewater sources from the various businesses. Dow is committed to implementing a comprehensive support concept from Hach.

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About the customer

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