

THE SKY IS THE LIMIT

Lost water can never be retrieved...especially in petrochemical industry where the costs of discharging can be sky high. Besides the expenses of waste water treatment processing, energy supply, taxes and legal charges, valuable base chemicals or products can be lost. To monitor these effluent streams a TOC analyser can be used that rapidly responds to any change in levels.



Normally, production installations have low waste water discharge levels, mostly within the range of 1,000 ppm TOC (total organic carbon). However, occasionally the installation can suffer failures or process disturbances take place. In this case, the range could very well reach a level of up to 50,000 ppm. If these go unnoticed, various consequences need to be considered:

- Loss of process fluids and base chemicals
- Risk of an influent shock loading in the WWTP
- Increased operating costs of the WWTP e.g. aeration, dosage of extra feed fluids
- Increased effluent discharge costs
- Problems with authorities about exceeding effluent discharge levels.

For safe and efficient plant operation, the online TOC analysis is recommended, if not regulated. The operation of a TOC analyser is standardised (EN 1484:1997): Generally, using a reactor, a portion of the waste water sample is oxidised converting the hydrocarbon content to carbon dioxide (CO₂). A CO₂ gas detector, typically a Non Dispersive Infrared (NDIR) detector, measures the amount of CO₂ formed. Various oxidation methods are available, mainly differing in their oxidation techniques. At high levels of up to 50,000 ppm, the oxidation strength must be outstanding. However, many TOC analysers are not able to measure levels high enough and therefore need to pre-dilute samples. The drawback of dilution is that many types of waste water, for example with particulate, volatile, or oily contents, cannot be accurately diluted.

Oxidation methods

The heart of every TOC analyser is the reactor, where the oxidation to CO₂ takes place. Many manufacturers claim that their design offers the greatest performance. However, the needs and demands of industries are tough and the waste water compositions are diverse and challenging. Especially with high organic loads, where

organics may be present in different states and kinds (dissolved, volatile, mixed, solidified, fats, free floating oils, particulates) many TOC analysers need a sample conditioning system that removes organic particles, algae, fats and/ or slime. Conversely, True TOC analysers determine the total of organic species irrespective of the sample composition and consistency.

UV oxidation

This wet-chemical technique oxidises the sample by use of UV light, a catalyst and a reactor made of quartz glass. It is well known and commonly used, but, however, not a very suitable method for samples containing particles. It is rather known as the DOC analysis method (Dissolved Organic Carbon). The recovery rate of this method differs depending on the type of organic component and on the analyser process parameters such as UV exposure time, UV light intensity, the oxidant concentration and the DOC level. In general, the UV exposure time is about 5 minutes resulting in a relatively slow response. The measuring range is limited to about 1,000 ppm DOC/TOC. Higher ranges are achieved by pre-diluting the sample. Salt, especially sodium chloride (NaCl) has a negative impact on measurements.

High pressure & temperature

This oxidation technique uses the physical phenomena that organic compounds in water are oxidised at a critical stage where both, the temperature and the pressure of the waste water sample are high. Firstly, the sample is mixed with a liquid catalyst and an aliquot of it is then drawn into a small reactor, basically a titanium tube. Secondly, two high pressure valves are activated and the sample is captured and sealed. An electrical heater is powered causing a rapid increase of the reactor temperature to >375°C. Subsequently, the pressure increases (P >215 bar). At this stage, the organics are oxidised to CO₂. The reactor cools down, the high pressure valves open and a carrier gas transfers the CO₂ to a NDIR detector. This oxidation technique can only handle filtrated samples (d < 200 micron) and as a consequence, mainly measures DOC. Particles may block the small reactor, possibly causing fouling of the high pressure valves. Any leak, even the smallest, will directly influence the correct reactor operation causing the oxidation recovery to drop. The oxygen needed for the oxidation of organic species comes from the liquid catalyst only (e.g. persulfate). Therefore, the maximum range is limited to about 1,000 ppm (increased by using pre-dilution). At higher TOC levels the recovery rate gets worse.

Hydroxyl radicals

With this oxidation technique samples are oxidised in a wet fluid state. The heart of the analyser is a closed loop circuit consisting of a reactor, a circulation pump, a 4-port filling valve and tubing. A fixed volume of reagent(s) and an aliquot of the sample are pumped into this loop. Furthermore, oxygen (O₂) is converted to ozone use a high voltage corona reactor. By exposing the high pH reagents to a heavy concentration of ozone, hydroxyl radicals are created which oxidise the organics and produce CO₂.

The maximum range of this method depends on the hydroxyl radicals' oxidation strengths, the concentration of the catalyst as well as the composition and consistency of the hydrocarbon organics in the sample. The less of the sample there is, the higher the range. Additionally, oils and fats can foul the complete circulation system causing absorption and adsorption effects and slowing down the response time.

COMPARISON of the 5 described oxidation methods	PF	RL	CT	SR	SA
UV OXIDATION Photochemical UV persulfate oxidation	Red	Red	Red	Red	Red
HIGH PRESSURE & TEMPERATURE Oxidation by use of high P & T and a liquid catalyst	Red	Red	Red	Green	Green
HYDROXYL RADICALS Oxidation by use of ozone and hydroxyl radicals	Green	Green	Red	Red	Green
CATALYTIC COMBUSTION Thermal catalytic oxidation at ~850°C	Red	Red	Red	Green	Red
NON-CATALYTIC COMBUSTION Thermal oxidation at 1,200°C	Green	Green	Green	Green	Green
PF = Particle filtration is needed, measures only DOC					Yes
RL = Range limitation, sample pre-dilution with water is needed					
CT = Liquid or solid catalyst / oxidiser is needed					No
SR = Relative slow response					
SA = Salt (NaCl) interferes with the TOC measurements and/or blocks the reactor					

Figure 1: Comparison of different oxidation methods.

Rangeability of TOC-analysers with different Oxidation Techniques without the use of diluting the sample with water

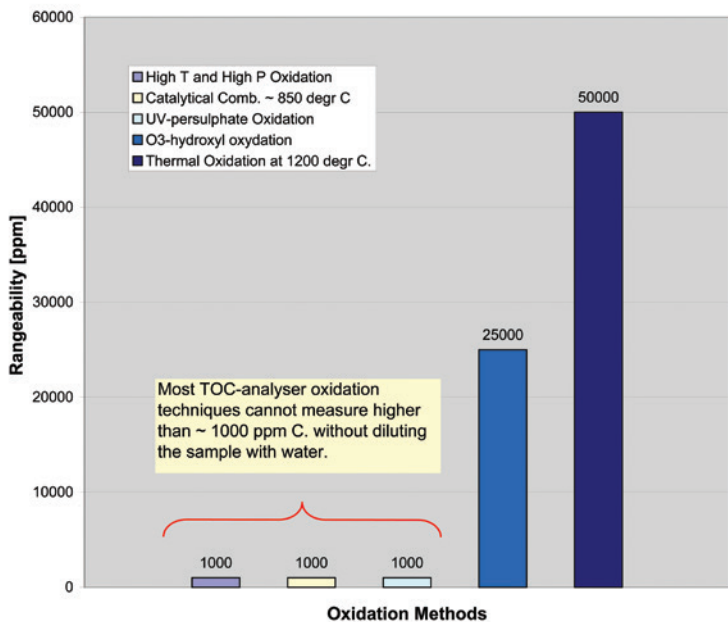


Figure 2: Rangeability of TOC-analysers with different Oxidation Techniques without the use of diluting the sample with water

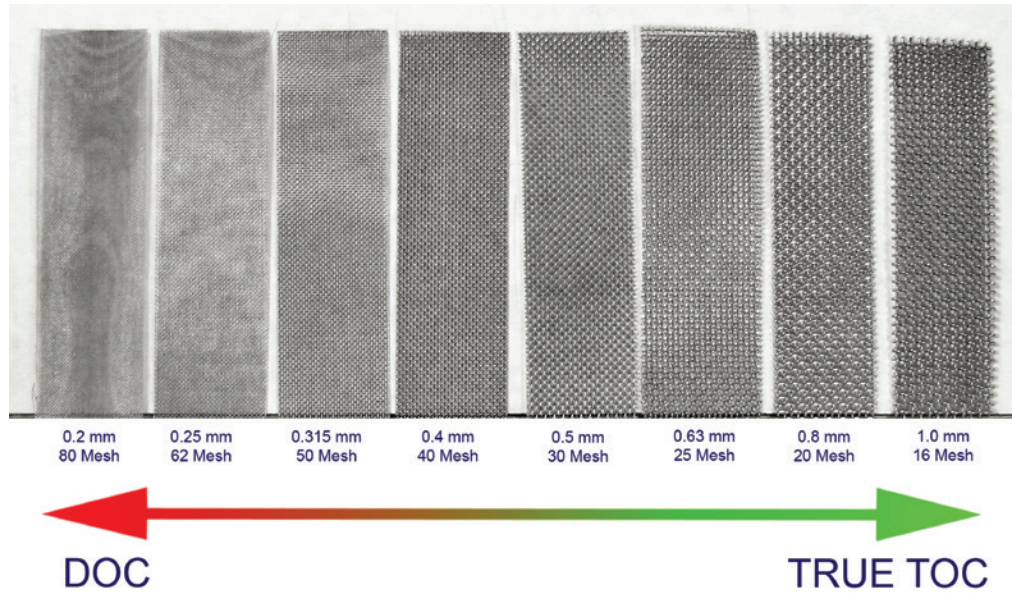


Figure 3: Filter mesh

Catalytic combustion

This method oxidises organic compounds using a catalyst within a reactor that is maintained at a temperature of about 850°C. An aliquot of the sample is injected onto the catalyst. At this relatively low temperature, the catalyst (e.g. platinum pellets) is essential to be able to oxidise as many organic compounds as possible. For salty samples the reactor is maintained at a temperature lower than the melting point of NaCl (m.p. 800.4°C). The drawback is that the oxidation strength is not sufficient enough to fully oxidise all organic species resulting in a reduced recovery rate, especially at higher TOC levels. Even when using a very small injection volume (e.g. 50 micro litre), the maximum analyser range is approximately 2,000 ppm. Higher ranges are achieved by sample dilution. Moreover, the oxidation recovery is affected by ageing, coating and poisoning of the catalyst. Generally, these catalytic oxidation methods cannot handle organic particles larger than 50 microns and hence, measure mainly the DOC rather than TOC.

Non-catalytic combustion

The raw sample is injected into an inert ceramic reactor packed with ceramic beads. The reactor is placed in an electrically controlled oven maintained at a temperature of 1,200°C. This high temperature guarantees that all organics - regardless of their state (dissolved, particulate, volatile) - are oxidised completely. By-products such as salts and sulphur will sublimate keeping the reactor clean and unblocked. For high salt concentrations, the reactor is designed in such a way that the salts are spat out into a special reactor foot, where they can be easily removed. The CO₂ formed is measured by a NDIR detector. This True TOC analyser design can easily handle undiluted raw waste water samples with a level up to 50,000 ppm TOC.

Drawback of pre-dilution

Three of the above mentioned oxidation methods have a TOC range limitation of approx. 1,000 to 2,000 ppm, ranges above may be achieved by sample pre-dilution. Even without considering the technical consequences of adding a complex dilution system, we can conclude from an analytical perspective that the accuracy of the measurements is disputable. It is of the utmost importance that the sample remains representative in its composition of the original raw waste water despite having been diluted. Many types of water are difficult to dilute, or hard, even impossible to mix into a homogeneous solution. Furthermore, whilst diluting and mixing the sample with demineralised water, VOC could be lost into the ambient atmosphere resulting in a less exact TOC measurement.

Drawback of sample filtration

Three of the five described oxidation methods have problems with raw waste water that contains particles bigger than 50 to 200 micrometer. These analysers need an additional conditioning system to filter out the particulate matter. Highly contaminated waste water normally contain a lot of particulates like slimes, algae and other suspended organic solids. If these particulate organics are filtered out, then the measured TOC results will be much too low. Instead of measuring the True TOC of the raw waste water, these analysers measure more or less only the DOC content.

Case study

At a huge petrochemical site, different factories are in operation, producing mainly liquid chemical base products for the production of specialised plastics. The discharged waste water of each factory flows into a single sewer system transferring the water to the main waste water treatment plant. When the processing operation is disrupted the waste water load may rapidly rise up to 10,000 and even 50,000 ppm TOC. However, under normal operational circumstances the TOC level is <500 ppm. Peak loads needed to be prevented, as costly products were being lost raising the waste water treatment costs on top. So, in the 1990ies, six TOC analysers were installed to continuously monitor the discharge loads of these streams. These analysers were based on batch injection and catalytic oxidation. The composition and consistency of the waste water were problematic since organic particles, slimes, algae and chlorinated hydrocarbons were present in high concentrations. As a consequence, the analysers' wetted parts fouled and blocked, requiring almost daily maintenance. To achieve a better performance a special paper tape particle filter was installed and the particulate matter was filtered out. However, with not much effect.

It got to a point where the operators made the decision to select and install a new TOC analyser. Their goal was to really achieve improvements meaning less maintenance, a higher availability and better analytical performance. Finally, they selected the QuickTOCultra of LAR Process Analysers, whose principle is based on the non-catalytic combustion at 1,200°C. As they did not want to take any risks a 3 month trial period was agreed upon. To be able to compare the analysers performances, the new QuickTOCultra was installed at the most problematic waste water stream, side by side with the old analyser. The trial was a great success: Perfect analytical performance, no failures, no problems and naturally without needing the paper tape particle filter! LAR's QuickTOCultra was directly measuring the TRUE TOC of the untreated raw waste water. The analyser proved not only to rapidly monitor peak levels of up to 50,000 ppm, it also showed that it has no memory effects meaning that it will return to low normal values quickly and easily. This was a breakthrough for the site operators. There are currently six single and two-stream QuickTOCultra analysers installed on this petrochemical site.

Unique features

LAR's QuickTOCultra uses a straightforward technique with only three wetted parts. Its oxidation technique is based on the non-catalytic thermal combustion at 1,200°C which proved to fully oxidise all types of organic carbon. Even the carbon compounds that are difficult to oxidise are completely cracked at this high temperature. The recovery is without a doubt, 100 percent. The range of this analyser is unique: Without using any dilution technique, it is able to measure from low ppm levels, all the way up to a level of 50,000 ppm TOC. Furthermore, the analyser uses an advanced robot operated injection system. Its simplicity is evident. The raw waste water sample flows through an overflow vessel where it is thoroughly mixed. A thick rugged needle sucks up an aliquot of the sample, including organic particles. It then injects a precise volume of that sample into the reactor. The organics in the waste water are fully combusted at the high temperature of 1,200°C. The amount of CO₂ formed is directly proportional to the TRUE TOC concentration in the waste water.

Another feature is the explosion-proof housing used. Normally, water analysing equipment will be installed into analyser shelters with climate control. LAR offers stand-alone measuring equipment with special explosion-proof housings providing a easy-to-manage and easy-to-operate solution compared to analyser shelters. The protection housings are in accordance with the latest ATEX and IECEx standards. The protective housings are classified as protection type Ex-p, with analyser housing under controlled overpressure. The analyser systems can be used in ATEX Zone 1 and Zone 2 (T3/T4) as well as in IECEx Zone 1 T4.

Summary

A well-designed TRUE TOC analyser is capable to handle waste water with a high load of suspended organic particles. Not only can it easily process waste water, it also completely oxidises all organics, including particles. An advanced robot driven injection technique, in combination with the non-catalytic 1,200°C thermal oxidation, make this possible. This method and analysis technique is known as the TRUE TOC. An excellent example of such a TRUE TOC measurement system, is the LAR QuickTOCultra analyser. Using the same approach, LAR offers also analysers for the determination of COD, TOD and TNb - combinations of these parameters are possible. These analysers are easy to maintain and measure the complete organic content of waste water and are characterised by exceptionally low operational costs.



Figure 4: Online TOC analyser in an ex-zone housing

Author Details

Dr. Werner Arts, President, LAR Process Analysers AG
Neukoellnische Allee 134, 12507 Berlin, Germany

- Tel: +49 30 2789580
- Email: sales@lar.com
- Web: www.lar.com