MEDIUM

PROCESS WORLDWIDE

RELEASE

ISSUE 2 / 2014

TYPES OF WATER

SURFACE WATER

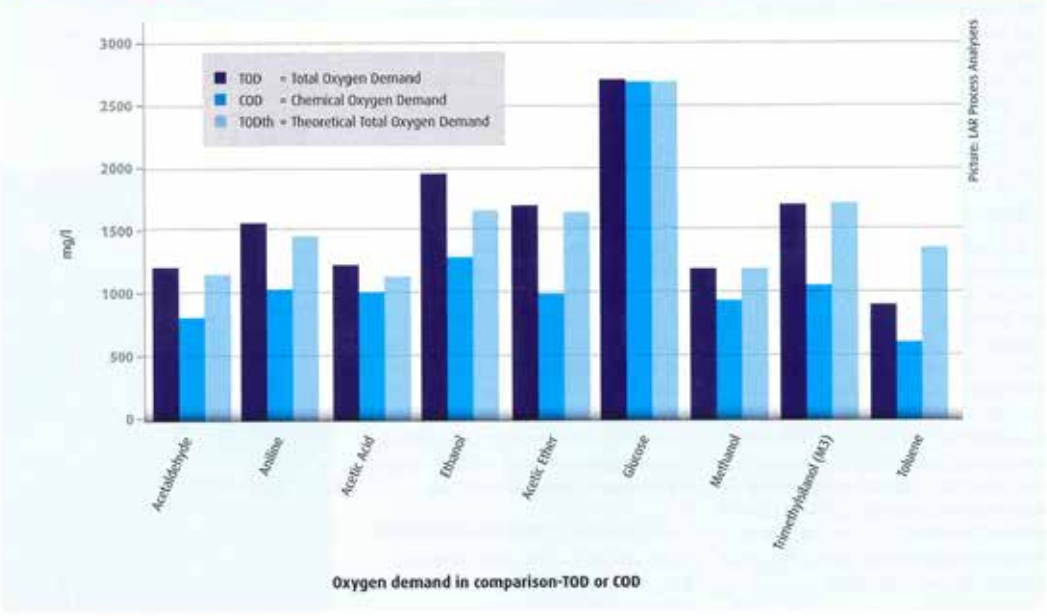
PARAMETERS

COD / TOC / DOC / TOD / TOXICITY

WATER/WASTEWATER

Going Below the Surface

Measuring Organic Sum Parameters for Water Analysis



Oxygen demand in comparison-TOD or COD

Online measuring and monitoring of water quality and purity in rivers, lakes and streams is a centerpiece of environmental protection and water conservation. Especially organic substances threaten the delicate nature of aquatic ecosystems. Due to the diverse contaminants and pollution sources, analysis relies on the measuring of sum parameters. Different approaches feature distinctive characteristics—but what is the best, fastet and most reliable measurement method?

DR. DR. RER. NAT. WOLFGANG GENTHE

River monitoring is an important early warning system to detect any water pollution due to chemical accidents or other causes. As rivers and lakes are sensitive drinking water resources, this task is of utmost importance. Therefore, water monitoring stations have been established along rivers around the world. Today, there is data available of over 30 years of experience.

The author works for LAR Process Analysers.
Contact: Phone +49-30258-95859

It is common knowledge that it is absolutely mandatory to have both the right measurement as well as reliable instruments with low maintenance for this purpose. A suitable measuring method has to guarantee correct data combined with high recovery rates for every thinkable substance. This is especially important as there should be no chemical compound undetected, while the results should be as accurate and reproducible as possible. It is also necessary that the employed monitoring method has a low detection limit to realize even smaller changes on a relatively low concentration level.

Furthermore, the consumption of reagents has to be considered: As monitoring stations are often unattended at remote locations, the necessary maintenance should be as low as possible. Moreover, the employed analytical method itself should not pose the danger of environmental pollution. As most of the risks for operating personal are related to reagents, it is fundamental to choose analytical methods which are safe to work with.

Use of Sum Parameters

Due to the huge number of listed chemicals it is impossible to check for each single substance. Hence, it has become common to use sum parameters to detect any kind of pollution quickly. While this method has the advantage of a fast detection, it must be clear here that it is not possible to get information about what substances are involved.

Therefore, it is common to use a combination of measuring sum parameters for organic matter and for toxicity in river monitoring.

With this method it is at least possible to obtain information whether the increase in organics is caused by a more dangerous or harmless substance. The following sum parameters should be taken into account:

- 1. Chemical Oxygen Demand – COD
- 2. Total Organic Carbon – TOC
- 3. Dissolved Organic Carbon – DOC
- 4. Total Oxygen Demand – TOD
- 5. Toxicity

Chemical Oxygen Demand COD

Although the permanganate method is still used widely, it is internationally approved that this method is definitely not suitable for this river monitoring. In a survey of the „Institute for water, soil and air of the German EPA" dating back to 1983, it was established that the oxidation power of this method is much too low. Test results show that there are too many substances which go undetected. Also the recovery rates of many other substances are somewhere between 0 and 100 %. For the survey the institute analyzed the recovery rates of approx. 600 substances, the majority of which could not be detected.

The so-called COD di-chromate method may not be left unmentioned. However, its most considerable disadvantage is the necessity of extremely dangerous reagents that produce hazardous waste. Despite the fact that the recovery rates are not always 100 %, the slow response time alone makes this method unsuitable for river monitoring.

The electrochemical determination of COD by OH-radicals can be used as an alternative. The advantages of this method are a short response time combined with relatively high recovery rates while using completely harmless reagents. To reach the necessary stable conductivity, the sample is normally diluted in an electrolyte of sodium sulfate (a normal neutral salt). For the real COD determination, the analyzers have to be correlated with a standard method. The response time of this method is approx. one minute and the frequency of determinations can be as low as two minutes. Nearly no additional reagents are required, making this method quite suitable for environmental monitoring.

	Measuring	Recovery Rates	Detection Limit	Response Time	Consumption of Reagents	Danger for Operator	Danger for Environment
1	COD permanganate	--	+	-	-	-	-
2	COD electrochemical	-	+	+	O	+	+
3	TOC/DOC UV-persulfate	O	++	-	-	O	O
4	TOC catalytic high-temp.	(++)	++	+	++	++	++
5	TOC non-cat. high-temp.	++	++	+	++	++	++
6	TOD non-cat. High-temp.	++	+/O	+	++	++	++

Picture: LAR Process Analysers

Comparison of parameters and methods — Non catalytic, high temperature methods not only provide accurate results, they are also safer for operator and environment.

TOD and TOC Determination

TOD measurement is based on the same idea as COD: All organic compounds are oxidized completely to determine the required oxygen demand. However, using thermal oxidation at 1,200 °C, a complete consumption of all organics is guaranteed and no chloride disturbances occurs (as with the di-chromate method). For this method, the sample is thermally oxidized in an inert reactor with the oxygen consumption measured directly in the gas phase. A similar measurement is used for TOC analysis, where CO_2 is detected instead of O_2 by an NDIR detector.

In the furnace, the water of the injected sample is evaporated immediately while organic compounds are oxidized. Currently, there are several so called high-temperature methods available, with LAR's oxidation at 1,200 °C among the most efficient ones. Unlike other approaches (such as the catalytic high-temperature methods which usually do not reach a higher temperature than 900 °C) the LAR test does not need catalysts. This is not only easier, but also eliminates the risk of catalyst poisoning, which may cause a malfunction of the whole pro-cess. With the non-catalytic high-temperature method at 1,200°C, the process takes only about one or two minutes, so that measurements can be carried out as frequent as every three to five minutes.

The TOD method may be considered as the second best option for river water monitoring, as it provides 100 % recovery rates. As no use of reagents is required, this method is well suited for environmental monitoring. In accordance to the US standard by ASTM D6238, LAR is currently the only company manufacturing a reliable online analyzer for TOD which is successfully in operation throughout the world.

Another issue is toxicity: Although the nitrification inhibition test has not seen much consideration, its results are remarkable: Studies demonstrated the significantly lower EC20 and EC50 values of the determined substances in comparison to tests with luminescent bacteria (the common biomass for online toxicity tests). For Cyanide for example, the EC50 value in the nitrification respiration inhibition test is ≤ 0.15mg/l compared to 8.5 mg/l with luminescent bacteria.

Testing Toxicity Online

Important criteria for online toxicity measurements are an easy handling as well as a fast determination. Latest innovations allow to constantly grow nitrifying bacteria in a fermenter within the analyzer, providing enough biomass at any time. A small amount of this self-sustaining biomass is mixed with the sample in the measuring cell where subsequently the actual respiration measurement takes place by monitoring the oxygen consumption. This method stands out through its high reproducibility, as the measuring cell is flushed with a cleaning solution after each measurement, avoiding any cross contamination or memory effects of previous samples.

A Proven Alternative

Based on the above mentioned criteria, the best choice for sum parameter monitoring of organic matter in water are high-temperature TOC and TOD analyzers. The online determination of TOD is a clean and fast method to define the oxygen demand of a water sample that is both relatively environmentally friendly and a suitable alternative for COD measurements.

Additionally, innovative online toxicity analyzers offer a reliable and fast detection of pollutants: Using highly sensitive nitrifiers as test organisms, these units show, how toxic substances affect the biology of public waters. In several international project these innovative solutions are used to monitor reliably the condition of rivers and lakes.