New Methods For Determining Unknown Pollutants

Jens-Uwe Schroeter, LAR Process Analysers AG
Dr. Werner Arts
www.lar.com

When determining unknown pollutants, it should be considered that it is impossible to detect all possible trace substances. The analysis of all known substances within a single sample is too expensive and time consuming. However, there must be a process to determine the existence of pollutants in water or sewage water promptly or at least within a few minutes.

Therefore, quantitative parameters have been introduced to increase the efficiency of water analysis. Normally these parameters cannot differentiate between unwanted or harmful substances. Typically, unwanted substances are any water pollutants that do not result in significant harmful effects. In comparison, harmful substances have direct or long-term poisonous effects on the environment, even in very low concentrations. We could, in this respect, use the terms toxic and less toxic substances.

In this article we will focus on the possibilities for determining unknown substances by quantitatively measuring toxicity.

Background Information

Harmful substances should preferably be detected with responding on-line analysis equipment as soon as possible after their discharge into a given medium. Most of the known parameters are available as on-line measurement today. The appropriate combination of parameters such as TOC, TN, TP and others with adequate toxicity measurement is of great significance. It is essential that the toxicity measurement is as manageable and representative as possible. The collection of toxicity parameters, being quantitative, should be relatively simple without requiring a specialised laboratory for growing test organisms.

By combining TOC, DOC, TN, (optional TP) with ammonia and nitrate as well as an UV-spectrum or UV-absorption and by using adequate evaluations and comparisons, it is possible to draw conclusions on the pollution by harmful substances and their possible origin. However, it is still difficult to detect toxic substances in low concentrations. They do not necessarily stand out by a significant concentration increase of the parameters stated above even though there may have been toxic effects already.

As a simple example we may consider cyanide, a well-known highly toxic substance which is toxic even at low concentrations. At low concentrations it would not be easily detected by the above-mentioned parameters. Suitable toxicity measurement methods, however, detect cyanide even at low concentrations immediately.

Appropriate Measurements of Toxicity

To determine unknown substances efficiently, it becomes increasingly important to use an appropriate toxicity measurement method; this measurement should provide a sufficiently high sensitivity towards pollutants. If necessary, several toxicity measurements could be performed simultaneously because different organisms react differently towards toxic or harmful substances.

If one toxicity measurement is applicable, there should to be an evaluation of the most likely groups of substances at the effluent. The chosen toxicity measurement should provide a high sensitivity towards a wide spectrum of pollutants, giving a significant reaction

Substances	Inhibition of Nitrification		Inhibition of luminescent bacteria	
	EC20 (µg/liter)	EC50 (µg/liter)	EC20 (µg/liter)	EC20 (µg/liter)
Phenol	100	1,000	9,000	29,000
3-Chlorphenol	200	900	1,000	7,000
2.3-Dichlorphenol	7	90	1,000	4,000
2.4-Dichlorphenol	7	150	1,000	3,000
2.5-Dichlorphenol	10	380	2,000	6,000
3.4-Dichlorphenol	250	800	<1,000	1,000
3.5-Dichlorphenol	100	500	3,000	5,000
2.4-Dinitrophenol	10.000	70,000	6,000	29,000

Chart 1: Toxicity of phenolic compounds (Uwe J. Strotmann u. Heike Eglsäer BASF AG, Ludwigshafen Germany, 1995)

of the test organisms to low concentrations of pollutants. The common values EC20 or EC50 equal a reaction or inhibition of organisms of 20% or 50%. EC values must show a high reproducibility, using toxicity measurement methods for the determination of harmful substances.

Additionally, it is important that taking the sample and measuring the discharge streams is carried out as early and undiluted as possible. More polluted water, getting diluted by adding less contaminated water, makes it more difficult to detect unknown harmful substances. For a reliable pollution determination, a sampling device is required that automatically allows for a later single-substance determination.

Nitrification Respiration Inhibition Test

Although the nitrification inhibition test has not yet been considered in great detail, results demonstrate that they meet previously discussed requirements in this article. Studies by Uwe J. Strotmann (BASF AG Ludwigshafen, Laboratory for Environmental Protection) show that nitrification inhibition tests have a special sensitivity towards chlorinated phenols.

Strotmann has demonstrated significantly lower EC20 and EC50 values of the determined substances in nitrification inhibition tests, compared to tests with luminescent bacteria.

Tests with nitrifying bacteria confirm their very sensitive response towards numerous chemicals or harmful substances providing a good foundation as test organisms for more extensive toxicity tests. However, it must be noted that a single toxicity measurement test cannot determine all possible substances in low concentrations. A combination of different suitable tests is preferred.

An important criteria for on-line toxicity measurements is easy handling. It is now possible to continuously grow nitrifying bacteria in a fermenter over a long period of time by supplying suitable nutrients. Each measurement can be performed with fresh bacteria within minutes.

Another requirement for on-line monitoring has been fulfilled by successful chronological tracking of harmful events, without periodically or completely disturbing the biomass or test organisms after exposure to stronger toxicity.

On-line Nitrification Inhibition Test

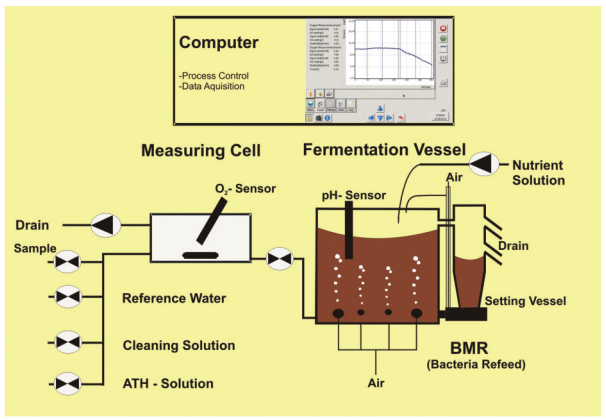

Fig. 1: Operation of an on-line toxicity analyser

In the following on-line toxicity analyser, nitrifying bacteria is continuously grown in a fermenter by providing special nutrients and using several control strategies. In the measuring cell a small amount of this self-sustaining biomass is mixed with the sample to be measured, subsequently the actual respiration measurement takes place by measuring the oxygen.

Fig. 1 shows the simplified working principle. Separating the fermenter from the measuring cell by using a valve combined with

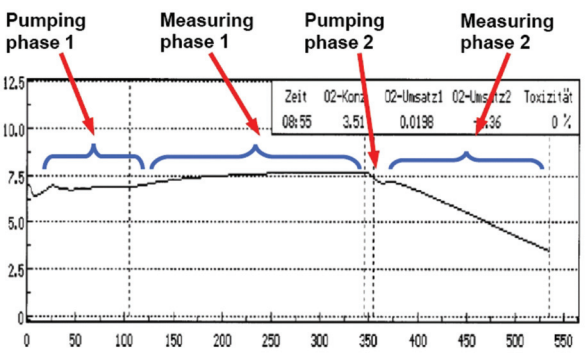

Fig. 2: Chart of a non-toxic event (high consumption rate)

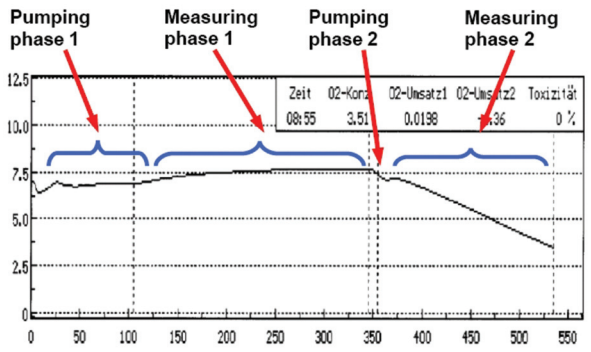

*Fig. 3: Chart of a toxic event (100% toxicity, consumption rate 0.0 mg/l*min)*

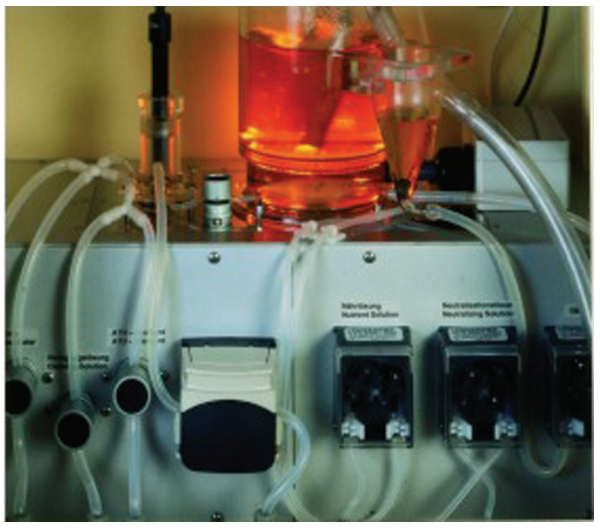

Fig. 4: Interior view of patented on-line toxicity analyser

the drawing principle of the sample pump, there is no contamination of the biomass in the fermenter.

Fig. 2 and 3 illustrate the detailed analysis steps. During the first pumping phase a sample is drawn into the measuring cell. In measuring phase 1 the sample's own oxygen consumption is measured. Potential micro-organisms within the sample will be detected that may be causing a consumption of oxygen, but being resistant towards toxic substances. In the second pumping phase a certain amount of nitrifying bacteria is pumped into the measuring cell. The actual measurement of toxicity is taking place in measuring phase 2. By measuring the respiration rate (mg/l*min), the gradient of the inclining curve, the measurement and the respiration rate are independent of any fixed initial oxygen concentrations. However, for correct results an oxygen concentration of min. 2 mg/l must remain within the measuring cell after the measurement. To illustrate the method fig. 2 and 3 show intervals of 10 minutes. In practice they can be reduced to < 5 minutes.

The analyser shown in fig. 4 provides continuously self-sustaining biomass for months and years. The only significant maintenance requires the provision of nutrient solution every 1 to 2 weeks depending on the container's size. General analyser inspections on a bi-weekly basis proved to be sufficient in practice.

Summary

For a timely and reliable detection of unknown pollutants at a discharge point the waste water streams should be measured in an undiluted form as possible. Measuring the common quantitative parameters, the on-line measurement of toxicity with its high sensitivity towards a great spectrum of harmful substances is of particular importance. The introduced nitrification respiration inhibition test is suitable for a wide range of applications, as stand-alone method or in combination with other toxicity tests.
It provides accurate and prompt results requiring low maintenance efforts and little costs.