Toxicity and Effluent Discharges

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Introduction

The toxicity of an effluent is, unfortunately, not a precise parameter that can be defined like other parameters such as temperature, pH, etc. It is a measure that must be interpreted and defined within the limitations of the method used in it's determination.

In this presentation some consideration will be given to the methods available for the monitoring of toxicity of effluents, both from municipal and industrial sources, particularly as an on-line measurement. The interpretation and value of the information provided will be discussed.

As an on-line measurement, a major aspect to be considered must be what is the information provided required to tell the operator of the system. The impact of wastes upon the receiving system, be this a treatment system or directly to the environment, is a prime reason for carrying out the determination. Where the waste is initially discharged to a treatment plant, the effect upon the plant may be a primary concern, but ultimately the effect of the residual material in the discharge from the plant must be the most important aspect to be considered.

Changes in the form of the consent licences being granted and enforced by the regulatory organisations may mean increased emphasis being placed upon toxicity as a limiting factor used to control discharges. The objectives of this approach are that hopefully improvements will result in the quality of receiving watercourses. This will be particularly relevant in light of changes currently occurring, and those still being proposed, in the structures and organisation of the regulatory authorities in the UK.

Objectives of toxicity monitoring

The toxicity of a material, be it a pure chemical or an industrial effluent containing such chemicals, is obviously a cause for concern, and the handling and ultimate fate of the material must be considered carefully. If we consider this aspect from the viewpoint of industrial and municipal effluent we can arrive at a number of points:

- the potential toxicity of material coming out of a treatment plant into the ecosystem must be at an acceptable level;

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- wastes going into such a treatment plant must not contain any toxic material to such an extent that the treatment process is damaged;
- the receiving ecosystem and the treatment plant should be protected in some way against the ingress of such toxic materials.

Consequently we can view toxicity monitoring as providing a means of protecting the biological system into which the potentially toxic material is to flow.

These two requirements i.e. protection of the environment in general, as opposed to a specific treatment system, can reasonably be viewed separately since the objectives are clearly different. In the case of the discharge from the works there must be an absolute limit on the presence of toxic materials since we must strive to protect our environment. However the criteria as applicable to a treatment plant are different. We must consider the treatment plant as being just that, i.e. a system designed and used to treat materials and to remove, neutralise or mineralise undesirable, possible toxic materials from the effluent flow to be treated. Consequently it is possible, and quite likely that materials that could be strictly defined as "toxic" will be present in the inlet to the plant, most, or even all, of the time. A system installed to monitor the toxicity of the flow entering the works must be able to provide an alarm signal only when the influent is likely to cause a problem to the treatment process.

These two requirements are not of course in any way conflicting, since the inlet monitoring is designed to protect the treatment process, which should allow treatment to carry on as efficiently as possible. There is still the potential danger that the "toxic" material may be accepted by the treatment system without any adverse effect upon the treatment process, but the material is not treated in the process. In this case the material would still be present in the discharge from the works and a potential threat to the receiving environment. Monitoring the discharge is still clearly an important requirement.

Apart from environmental factors mentioned above there may also be financial implications associated with toxic materials. For example if an effluent stream is deemed to be toxic it may require extra, or even completely different forms of treatment prior to discharge. As such costs associated with such treatment may be dramatically greater then those for treatment of a "normal" effluent flow. Therefore some means of detecting those streams which fall into this category and those which do not may be required. This can provide a means of controlling such costs.

Similarly major cost implications can result from entry of toxic material into a treatment works, if the treatment system is damaged as a result. Removal of toxic materials from the system, time required for recovery, tankering-in replacement sludge etc., etc., can amount to huge extra costs to the operators of such plant.

Types of toxicity testing available

As stated above toxicity testing is not an absolute measure as are many other parameters. We cannot define toxicity as a simple number. The measurement has at all times to be qualified by the method by which it was determined.

Where a specific material has a known biological effect the limits to be permitted in an effluent discharge can be defined in terms of the concentration of that specific material. Such methods can be applied to heavy metals and specific organic materials where perhaps they are known to be present, e.g. if a factory discharging into the catchment system is involved in production of that chemical. However for the most part monitoring effluent for the presence of specific chemical species is difficult, and expensive. This is particularly so where an on-line measurement is required. Mostly such limits are policed retrospectively, and occasionally prosecutions result. However the early warning and control of such discharges is very difficult to achieve.

One aspect about the latter approach i.e. monitoring and limiting specific chemicals, is that no account can be reasonably taken of synergistic effects. One group of chemicals may have a minimal effect in isolation, but in combination with another group, the effect may become dramatically increased.

There are examples where the chemical approach is used. In one case where an effluent is discharged into a river used for significant abstraction of drinking water, the consent licence requires very close monitoring with sophisticated analytical instruments, including HPLC.

An alternative approach is to use a model of the receiving ecosystem in order to test for a positive effect upon a biological/biochemical process. This approach looks at a relevant system and once exposure to the sample has occurred, an easily detected gross effect is looked for.

This approach is widely used in a batch/laboratory type role. A biological system is exposed to the sample under defined and controlled conditions, for a defined time. The response is then monitored. The response often obtained is death of a number of unfortunate members of the original population. This system is used for certain effluents known to be likely to contain toxins.

The test organism used may be selected and defined on the basis of those animals likely to come into contact with the effluent once discharged. This may be illustrated by an example where the effluent from a chemical factory which manufactures herbicides discharges into an area of sea famous for it's shellfish. In this case the effluent must be regularly tested for it's effect upon crustaceans, specifically crayfish. If less than 50% of the population dies in 96 hours the effluent is deemed to be acceptable for discharge. This regular testing is a requirement of the licence allowing the factory to discharge it's effluent to the sea.

Other systems using animals have been developed, some even as on-line systems. A monitoring instrument was developed some years ago based upon the response of fish to effluent stream. A population of specific fish species is maintained in a controlled environment and the water in which they live is either dosed with a specific material or replaced with the water being tested. The fish are monitored for a change which may have been caused by any toxic material. The response used in the current version of the instrument is their breathing rate. Apparently a change in this is a common response to toxins. The instrument has been applied to drinking water intakes where water quality must be high. Few examples have been used for effluent applications.

Other tests have been developed using other animals and plants including Daphnia and algae.

Microbiologically based systems

The use of model systems based upon the responses of microbial cultures is currently seen as offering more realistic means of operating toxicity detecting systems. The approach offers the possibility of lower cost, more compact systems, which can provide very rapid responses and where the systems can be operated automatically, and with lower demands on their operators.

Again there is a number of different approaches being developed. One that is quite widely used is based upon the response of a bioluminescent marine bacterium, *Photobacterium phosphoreum*. This test has the advantage that it provides a rapid and reproducible response. The system has been developed from the initial laboratory system to a new on-line system. The possible disadvantages of the approach include the fact that no account of acclimatisation can be included. The test is based upon a single pure culture of one organism and variations in the response of different organisms cannot be extrapolated. The system is quite expensive to install and requires the constant consumption of high cost consumables. However the system does appear to be becoming accepted as a measurement by some of the regulatory authorities.

Toxicity instrument based upon response of natural mixed bacterial culture

An alternative approach which offers benefits for many applications is to use a naturally occurring mixed bacterial population and monitoring the response of this to the effluent stream. This is the system as used in the StipTox on-line toxicity monitor. Much of the following relates to applications and experience with this particular instrument.

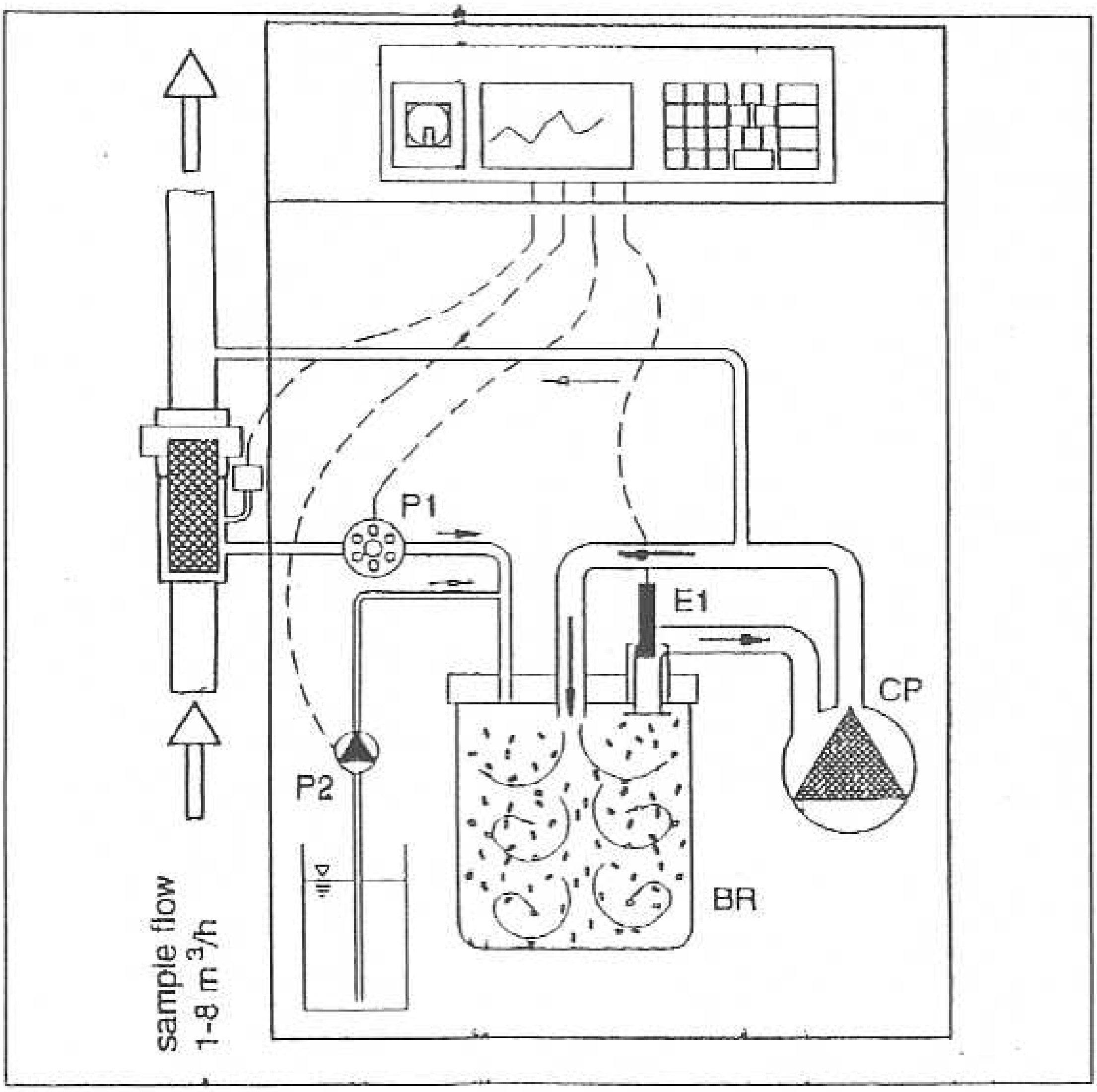


Figure 1 - Schematic of BIOX-1010 BOD and toxicity analyser

The system is based upon another instrument from the same manufacturer, the BIOX-1010 continuous on-line BOD analyser generating results within 3 minutes. The BOD M3 procedure utilises microbes which are growing in a turbulent mixed bioreactor within small plastic rings where they are protected from mechanical abrasion. Biomass respiration is kept constant by a feedback control system that dilutes waste water to a constant LOW BOD level. If the BOD increases, the dilution will increase correspondingly, and vice versa. In the schematic relation of MICHAELIS/MENTEN as shown in figure 2 the operational point is shown at a constant low concentration of only 5mg BOD/l. When used as a BOD analyser in crude waste water, a very high dilution rate protects the adapted biomass from toxic effects. The respiration rate then only depends on the substrate concentration.

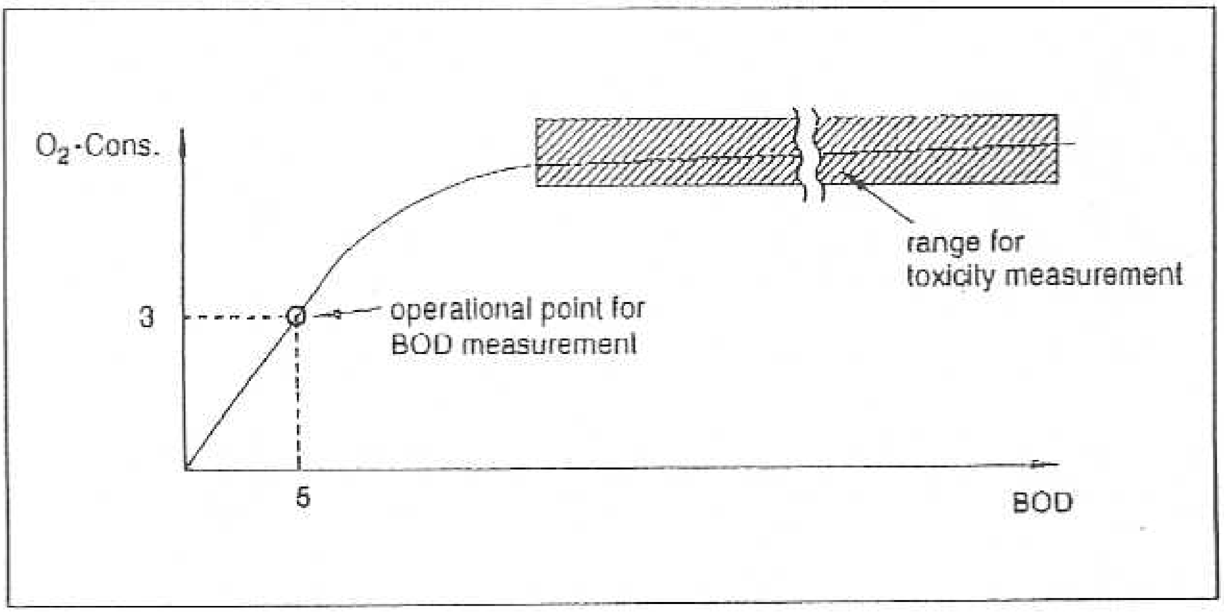


Figure 2 - Relation of substrate concentration versus respiration rate

(Michaelis/Menten)

Procedure of Toxicity Measurement with Turbulent Bed Bioreactor

The identical measuring system can be used as a toxicity analyser by moving the operational point to a high level of BOD where substrate concentration has reached a level of saturation. By this, a sample stream is supplied to the bioreactor at a pre-set low dilution rate and therefore toxic loads also are applied almost undiluted. At the high level of substrate supply a maximum respiration rate will be reached and will only be diminished by toxic effects or inhibition. Taking a constant base line of oxygen consumption applicable for a non-toxic sample, any relative reduction of respiration is automatically evaluated as a toxic effect. A result can be given as respiration rate or as toxicity (%) related to the normal (non-toxic) level.

To prevent a total kill of the micro-organisms due to strong toxic effects, a sample dilution system is automatically implemented. After a reduction of the respiration rate by e.g. 20% a continuously controlled increasing dilution of the sample will stop a further reduction of respiration. The dilution rate then is directly taken into account to calculate the corresponding respiration rate. Thus, even under strong toxic shocks the biomass will not be killed but maintain the ability to respond to the decrease of the toxic concentration and will regain its normal activity level. The sensitivity of the analyser can be easily adjusted to the requirements by setting of the standard dilution rate. For some applications a higher dilution rate could be necessary, as with a relatively small test biomass the reaction will always be more sensitive compared to the biological stage in a treatment plant which is buffered by its huge tank capacity.

With a 20mA output, a serial computer interface or an alarm contact the toxicity signal can be directly transmitted to a central control or monitoring system.

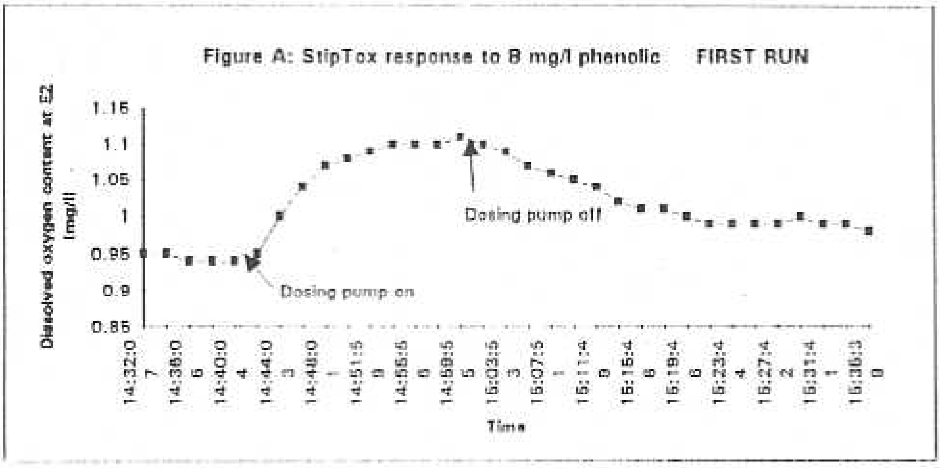
The effect of acclimatisation

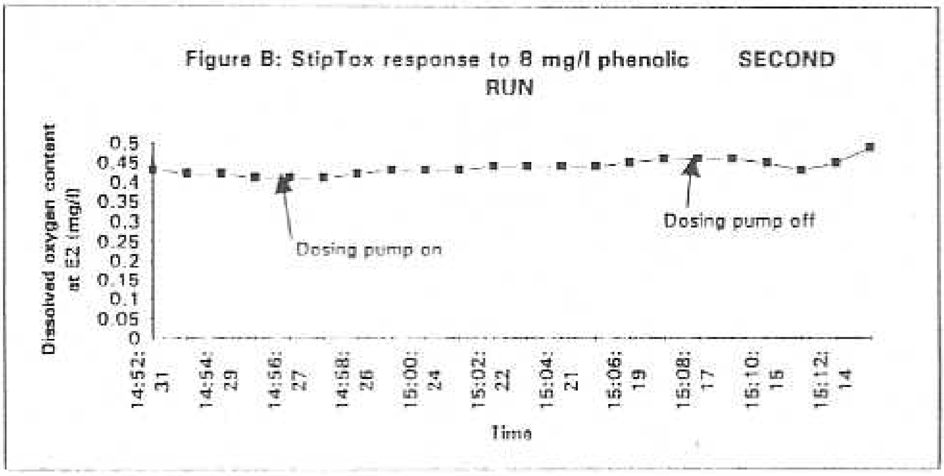
The above instrument provides a means of detecting potentially harmful materials in the effluent stream being monitored. However the response of the microbial culture within the instrument will be dependent upon a number of factors. One of the main sources of variability in response is caused by the level of acclimatisation which the culture has acquired to the specific toxin. If a culture is exposed to a chemical for the first time, a strong response may be expected. If a culture is exposed to a chemical, albeit a "toxic" chemical, but one which is normally present in the effluent, the tolerance of the culture to that chemical may be much higher. This point is very important when considering the different classes of application, to which the instrument may be applied, e.g. protection of a treatment plant as opposed to protection of the environment.

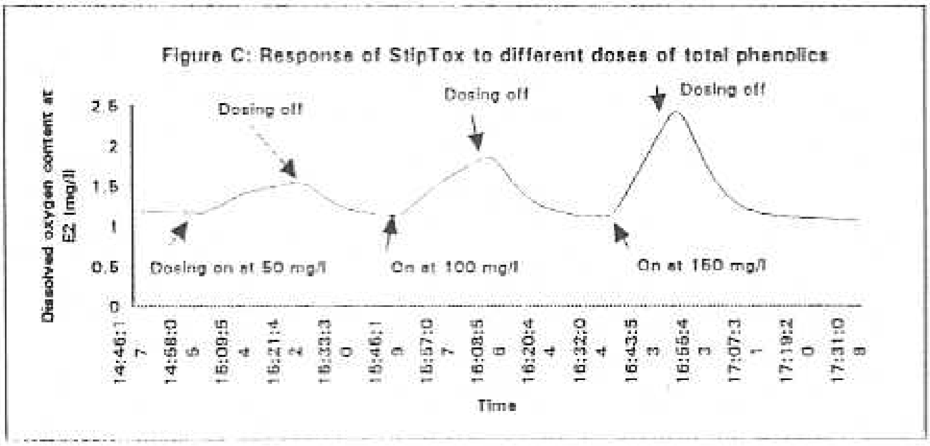
This aspect is demonstrated by the following experiments.

A StipTox was set up to operate in a laboratory mode. It was operated on a standard nutrient feed with a balanced organic content and supplemented inorganic content in order to allow a natural bacterial population to develop within the bioreactor. This developed quite quickly (2 days) when the programme of tests could begin.

The nutrient feed to the instrument was supplemented by a pumped supply of a solution containing chlorinated phenols. The results shown are expressed in terms of dosing concentration entering the bioreactor within the instrument.







Results from StipTox instrument and different concentrations of chlorinated phenolic compounds

The graphs presented as Figures A, B and C demonstrate the effect of a toxic material upon the bacterial population within the bioreactor. The population was not acclimatised to the phenolic compounds, there having been no phenolic content in the standard nutrient feed. Upon exposing the culture to quite a low concentration of phenolic (8 mg/l) a strong response was shown (fig A). However upon repeating the experiment at the same concentration a very different response was obtained as shown in Figure B. The second "challenge" at this concentration produced no detectable inhibition response at all, suggesting that a change in the bacterial culture and/or a change in the biochemical response of members of the population had occurred.

This may simply have been caused by the removal from the population of bacteria susceptible to the toxic effect of the chemical, thereby removing those components which were sensitive to it. The alternative explanation is that acclimatisation has been caused by the first exposure to the chemical allowing the rapid development of resistance within the population. The explanation for this effect is probably a combination of the two effects.

The dose was increased until strong responses were again detected. The results obtained are shown in Figure C. This dosing experiment was repeated several times and the same result obtained. The acclimatisation of the biomass had therefore been completed and reproducible results obtained.

In this case the system had developed which would be analogous with an effluent plant receiving an effluent which often contains such compounds. The biomass would be acclimatised and consequently not as sensitive as a culture which had never been exposed to that compound. In order to protect such a plant the instrument must be based upon the response of an acclimatised biomass if any sensible data, and system protection are to be achieved.

From these results we can conclude:

- The StipTox instrument responds well to the type of phenolic compound likely to be present in an industrial effluent.
- The level of response depends upon the "normal" level of these compounds within the effluent, i.e. the level of adaptation/acclimatisation. A high "normal" concentration can affect the response by maintaining a bacterial culture within the bioreactor which has resistance to the toxic chemicals.
- The level of sensitivity of the culture within the bioreactor should "mirror" the sensitivity of the culture within the treatment plant since both should be similarly adapted/acclimatised. This is after all the design purpose of the instrument in this type of application, i.e. to act as an

early warning so that action may be implemented to protect the culture within the plant. Too sensitive a response would only generate many "false positives".

- The adjustment of certain factors within the instrument such as the sample pump rate, and the dilution rate can be used to adjust the sensitivity.

A Typical Application Controlling Holding Tanks at Chemical Factory

Environmental incidents today are not only assessed by the direct costs that result but also for the severe damage to the public reputation of a company. Therefore many industrial companies are undertaking serious efforts for environmental protection.

After the accident at SANDOZ in Switzerland, which caused a heavy toxic pollution of the Rhine down to Holland, big holding tanks became obligatory for all major chemical industrial plants in Germany. Automatic control by toxicity monitors is required.

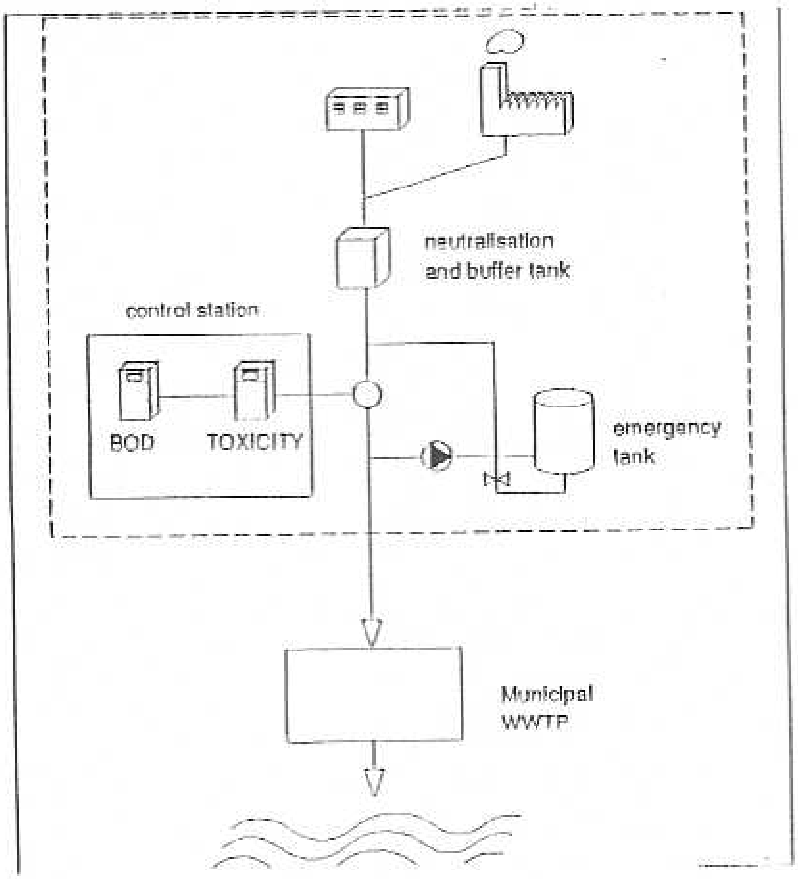
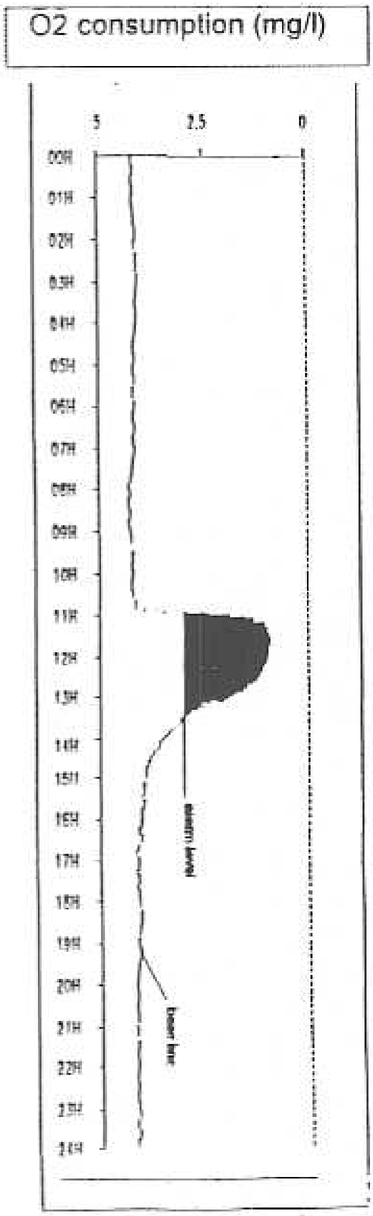


Figure 4 -Control system for divert tank at pharmaceutical plant

At a pharmaceutical industrial plant in Germany the waste water is collected in a neutralisation tank. Discharge from the neutralisation tank of a pH of 6-7.5 is fed to the municipal waste water treatment plant at a distance of about 2.5km. Sited on the industrial site is a monitoring control station, including a continuous measurement of BOD and Toxicity. The BOD concentration, combined with the measured flowrate, is used for automatic limitation of the BOD load by using the retention capacity of the neutralisation tank. In case of an alarm given by the toxicity analyser the complete effluent flow can be pumped into a holding tank which has a holding capacity of more than 4 hours. During this time the toxic discharge can be identified and halted or all waste water from production be stopped.



Once the toxic level is reduced, the waste water can be diverted back to the municipal treatment plant.

The toxic effluent contained in the divert tank now can be analysed, directly treated and the run-off to the main sewer, where it again passes the control station.

If direct treatment within the divert tank is not possible, the toxic effluent has to be transported by tanker to a specialised treatment facility.

Hence this installation ensures that continuous monitoring of all plant effluents is always guaranteed and toxic effluents beyond a significant level can be diverted from the municipal waste water treatment plant.

Various tests have also been made by connecting the toxicity analyser to a 50 l container to which a constant flow of normal plant effluent is pumped. By addition of special toxic components of certain quantities of production water for which a toxic discharge is suspected, accidents can be simulated or the real effect of production waters can be examined. An example of such a test is shown in figure 5.

Figure 5 Continuous trace showing effect of toxic component.

Different Versions of Analysers for Special Applications

Other measuring procedures can be used depending the requirements of special applicants.

If the direct use of activated sludge from the treatment plant is necessary a continuous feed of activated sludge into the bioreactor can be made. The plastic rings for the immobilised biomass then have to be removed (version STIPTOX-adapt B). Normal variation in the concentration or in the specific activity of the activated sludge would result in a baseline of basic respiration which will indicate a non-toxic sample.

Biomass with selective sensitivity can be created by additional dosage of substrate solutions to the bioreactor (version STIPTOX-norm). This version can be used for applications where an especially higher sensitivity is required, for example in river monitoring. This arrangement provides a system where no possibility of acclimatisation exists, and so very sensitive response of a virgin culture will be obtained.

Conclusions

Over the next few years the controls imposed upon industrial dischargers are going to become increasingly severe. This will be in terms of the chemical and physical makeup of the effluent but also in terms of it's potential effect upon the environment. There is currently an increased emphasis being placed upon the toxicity of an effluent and of the inclusion of clauses concerning this in the consent licences under which such discharges are permitted. The exact form that such constraints will be expressed and controlled will require careful consideration.

The experience gained with the on-line instruments discussed above show that there are many potential applications where they can provide valuable benefits to the user and ultimately to the environment. The two specific application areas discussed i.e. plant inlet protection, and final discharge monitoring, present different challenges and objectives. The instruments can fulfil both of these roles.

References

Teutscher, M., and Grosser, J., "Experiences with on-line Toxicity Analysers in Municipal and Industrial Waste Water Treatment Plants" Presented at European Symposium on Biological Systems for Continuous Water Quality Monitoring, 13-14 Oct. 1994, Nancy, France.