ON-LINE MONITORING OF BOD, COD AND TOXIC FLOWS

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Introduction

With ever-tightening constraints and penalties, the need for continuous reliable monitoring of industrial and municipal effluents has become more important. This particularly applies to the effluent from paper maufacture. Many such effluents contain high concentrations of readily degradable organic compounds which make them potentially harmful from an oxygen depletion point of view. The use of reliable monitoring can provide a means for proper management of production and treatment processes in order to maintain compliance with consents and also the reduction of losses from production. This should, allow greater confidence that the aquatic environment can be protected.

The penalties for breaching consent licenses are becoming ever more onerous. In a recent incident a paper manufacturer was fined £20,000 and had to pay £200,000 to re-stock the nearby fish farm. We have got many examples where consent licenses are tightening; one particular discharge has recently had its BOD limit reduced from 30mg/l to 15mg/l. This trend is obviously typical.

The requirement to install on-line instruments to monitor effluents from industrial processes can be viewed by the industrialist as a new, expensive and unwelcome development. However the more enlightened industrialists are viewing the prospect in a much more positive way. By being aware of losses of perhaps valuable products and of their contribution to the problems associated with effluent treatment and disposal, a means is provided to control such losses at source. It also obviously provides a means of more peaceful coexistence with the industrialist's neighbours, as well as regulatory authorities.

What type of instruments are needed?

Reliability is one of the most important characteristics of instrument for use in this kind of application. Instruments designed from the outset, as field instruments, offer the greatest likelihood of reliable trouble-free operation. Instruments which are developments of laboratory systems, in some cases have inherent design limitations.

This limitation is most apparent where sample handling is concerned. The sample must be brought to the instrument as quickly as possible from the sampling point. Sample lines must be large enough diameter to be able to handle real world samples without the danger of line blockage. The system would ideally involve as little sample pre-treatment as possible. Removal of fine solids by the use of ultrafiltration should be avoided. Such removal of solids can change quite dramatically the characteristics of the sample. The effect of this step will obviously vary, depending upon the solids content of the sample stream.

Instruments for use in this type of field application must have very low attendance and maintenance requirements. Experience has shown that with different designs of instrument, maintenance can vary from less than 1 hour per week to what has been described as "a full-time job". Instruments which have requirements for high maintenance may, depending upon the efficiency of the maintenance department, be susceptible to significant periods of down-time. Any instrument which is affected by such down-time could be viewed as not really being on-line.

When considering the costs involved in purchase and ownership of such instruments it should be emphasised that the "overall cost of ownership" should be considered. That is, including:

- the purchase price;
- operational costs;
- maintenance costs;
- cost of consumables.

What parameters should we monitor?

When considering the organic content of an effluent stream there are a number of potential parameters which may be considered:

Biochemical Oxygen Demand (BOD)

The BOD of an effluent stream is the parameter which is in many cases still used to define an effluent flowing into a river. It is the only parameter which is based upon the response of a biological system to the effluent flow. Traditionally it is a very difficult assay to automate. More recent developments have provided a means of accurately assessing BOD as an on-line measurement.

Chemical Oxygen Demand (COD)

The COD of an effluent is traditionally determined as a laboratory test, which provides much more rapid and precise response than the BOD test. It is an important parameter for discharges flowing to sewer. It is being considered as a measurement for control of discharge to rivers. Again, recent developments have resulted in the use of the measurement as an on-line parameter.

Total Organic Carbon (TOC)

The measurement of TOC can in many cases provide an indication of the level of either BOD or COD. However, the relationship between these various parameters is for many waste categories somewhat variable, making the use of one parameter to predict any other an unreliable procedure.

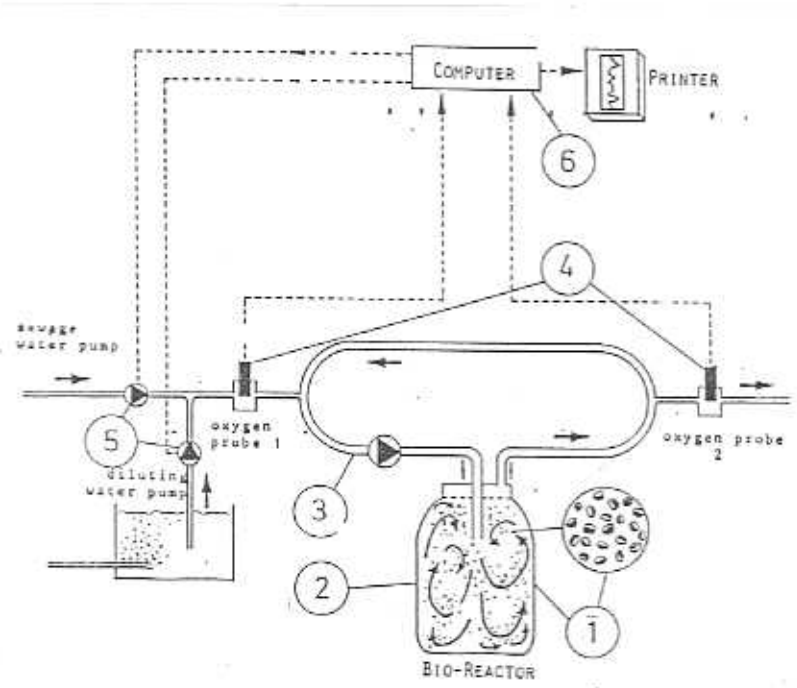
The Envitech STIP instruments

- **The BIOX 1000**

  This instrument provides a means of continuously and accurately measuring the Biochemical Oxygen Demand of an effluent stream. It, for the first time, offers the use of this parameter for control purposes. The instrument operates as a truly continuous on-line measurement. It incorporates a simple yet proven sample handling system which requires no pre-treatment of the sample being analysed. The method of operation of the instrument is as follows (see also Figure 1):

  - Sample is pumped into a bypass loop within the instrument at a high rate ensuring that solids remain in suspension, sample reaches the instrument quickly and that the sampling system is as representative as can be achieved.
  - A small flow from this bypass loop enters the analytical system. It is diluted with heated and oxygenated dilution water. This flow enters a circulating system which contains a bioreactor. Within the bioreactor a natural culture of bacteria is maintained. The oxygen content of the flow is monitored at the inlet to the circulating system and at the outlet. The difference between these two measurements is the oxygen consumed in response to the BOD in the sample. A steady state system is maintained within the circulating system by maintaining the oxygen consumption at a constant level. This is achieved by controlling the dilution of the incoming sample. The BOD value displayed by the instrument is calculated on the level of dilution necessary to maintain the steady state.

Figure 1: BIOX 1000 - Method of Operation



1 Plastic growth rings

2 Bioreactor

3 Circulation system

4 Oxygen Electrodes

5 Sample and Dilution Water pumps

6 Computer

- The instrument provides a 4-20mA signal proportional to the BOD plus system failure alarms and limit alarm. An RS 232 output is also provided.
- For most applications this instrument does not require the use of any consumables, such as expensive chemicals. It also does not involve the use of any toxic materials.

- **Phoenix On-line COD monitor**

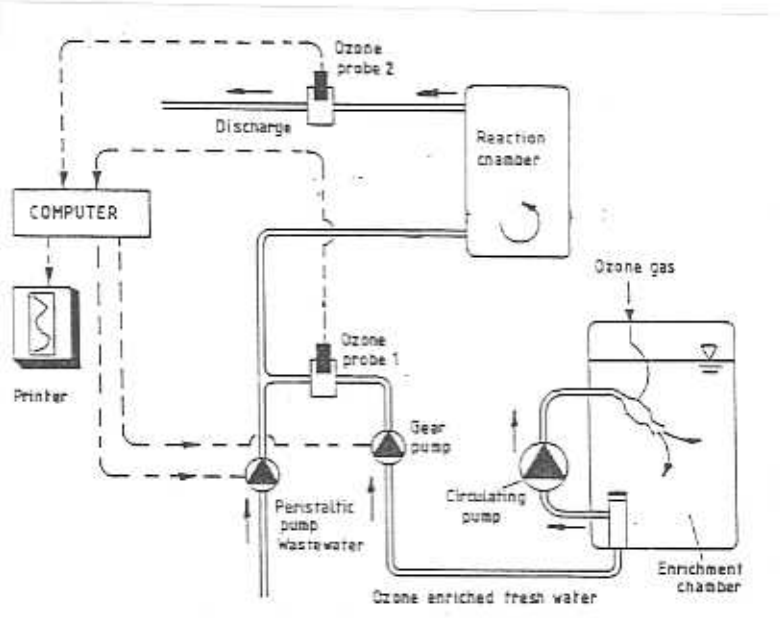
  This instrument provides a means of continuously monitoring the COD of an effluent stream. It uses a different analytical technique from the DIN COD method. It does not use the toxic chemical involved in that test, nor does it require the extremely aggressive reaction conditions. The oxidant used is ozone and the reaction is carried out at 30°C and at pH 3.2. pH adjustment is achieved using phosphoric acid. Ozone is generated within the instrument from a supply of technical grade oxygen. The method of operation is in essence very closely related to that of the BIOX instrument:

  - The sampling handing system is exactly the same as for the BIOX.
  - The small sample flow taken for analyses is mixed with heated, pH adjusted, ozonated dilution water. The diluted flow enters a

reaction vessel and then flows to waste. The ozone concentrations at the inlet and the outlet of the reaction vessel are continuously monitored. Again, as in the BIOX, a steady state system is maintained by feedback adjustment of the necessary dilution in order to maintain the steady state.

- The COD value displayed is calculated on the level of dilution needed to maintain this steady state.
- The only consumables required for the system are phosphoric acid (2-3 litres per week) and oxygen (8 litres per week). Again, no toxic materials are used.

Figure 2: Phoenix on-line COD monitor - method of operation



Examples of application

These instruments are being used for a wide range of functions throughout both municipal and industrial applications. These range from simply monitoring and reporting through to full control of the treatment plant in response to the characteristics of the incoming flow. Concentrating on the paper industry the following serve as illustrations of their potential uses:

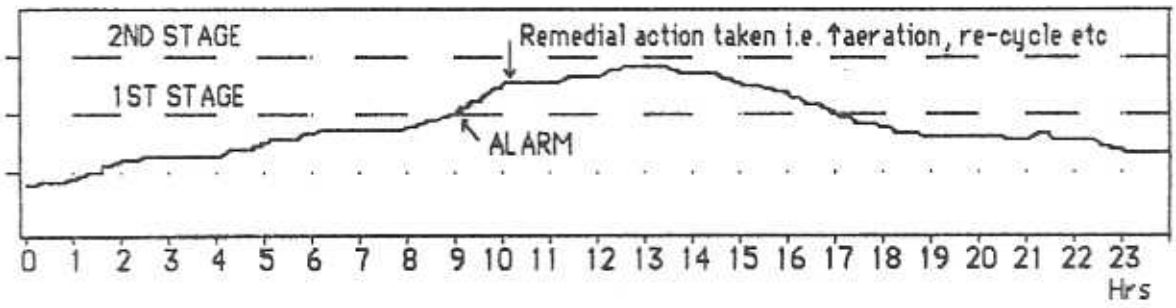
- <u>Consent compliance</u>

  Where a paper mill discharges its effluent after treatment to a river the NRA has required the installation of a continuous on-line monitor of BOD. This system operates as follows (see also Figure 3):

  - If the level of BOD is the effluent rises to 75% of the consent limit, the NRA must be notified and corrective measures implemented to reverse the trend.

- If in spite of this the BOD continues to rise and reaches the consent limit, the discharge flow must be stopped.

Figure 3: Use of BIOX 1000 for Consent Compliance monitoring



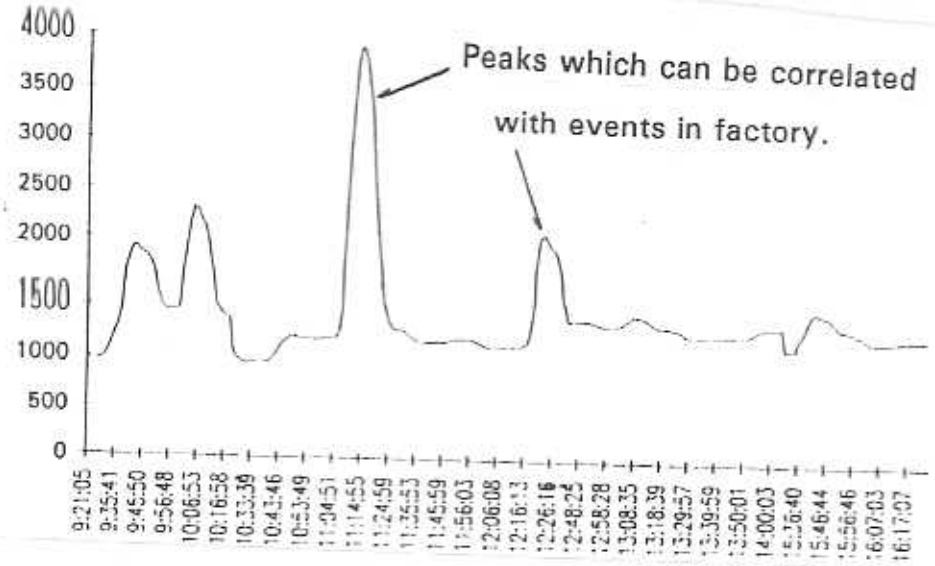
This system has been in operation now for nearly 2 years. It has meant that the mill operators are much more aware of the quality of their effluent on a continuous basis and the treatment plant can be managed more realistically in order to avoid breaches of consent. One of the other great advantages is that the arrival of the NRA inspector to take a sample is no longer a major source of concern. The quality of the sample he is going to take is known beforehand. On one occasion, on the basis of the BOD displayed by the instrument, an NRA analysis was contested and the instrument's value subsequently substantiated.

- <u>Process control in response to effluent characteristics</u>

By monitoring the characteristics of the effluent leaving the site and relating peaks with events within the mill, sources of high organic losses can be pin-pointed and possibly controlled. This is an approach which can bring major benefits with comparatively low capital outlay Figure 4 shows a typical trace which shows BOD peaks which can be tied in to events within the factory.

The ultimate objective of this type of approach is to move towards zero wastage from production. Perhaps a half-way benefit would be to manage events within the mill in order to reduce losses to such a level that existing or future consent limits can be lived within without the need for the installation of full-scale biological treatment plant.

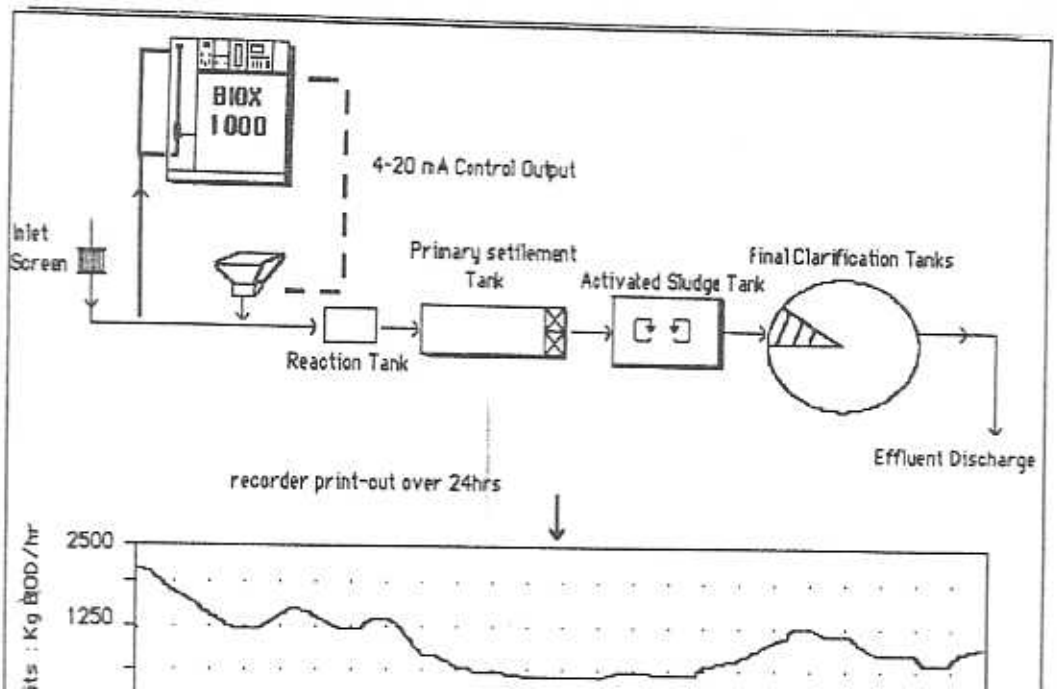
Figure 4: Process control in response to effluent characteristics



- Control of the treatment plant in response to incoming load

If a treatment plant is in operation on a trade effluent by monitoring the characteristics of the incoming flow it may be possible to provide very significant cost-savings in running costs of the plant. This can be achieved by relating such high cost consumables as electricity, oxygen, nutrient additions directly to the incoming load rather than being related to design figure.

Figure 5: Control of nutrient additions in response to waste characteristics

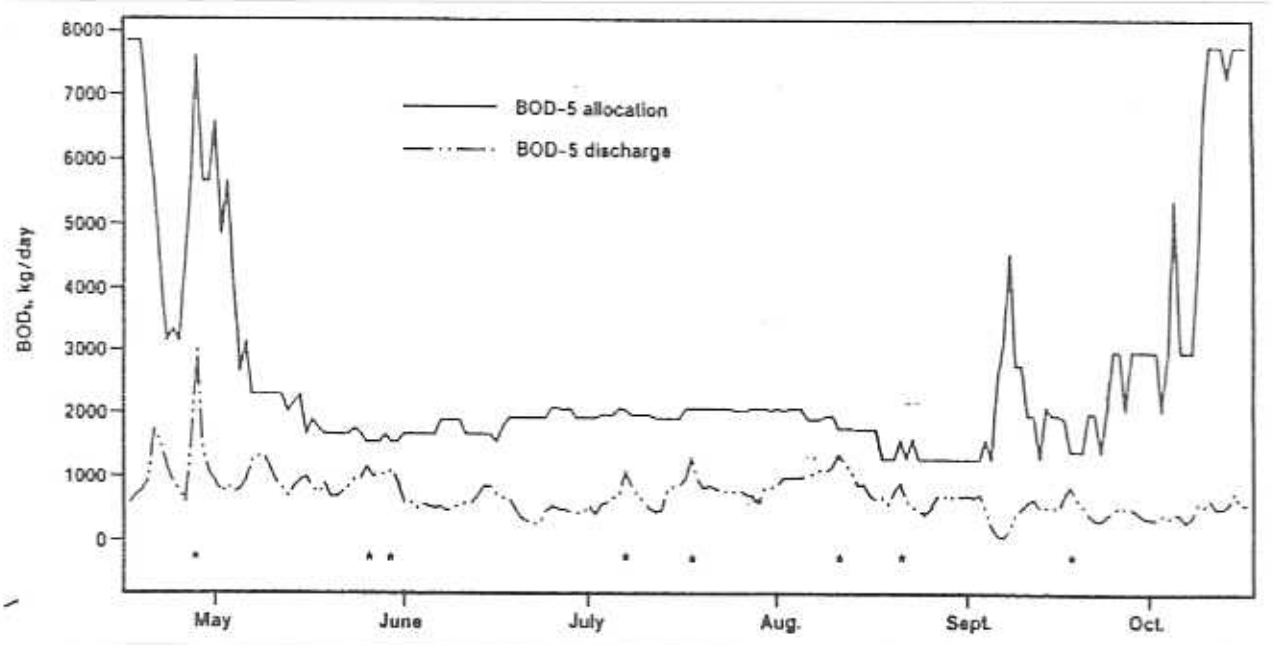


Other aspects of plant operation can also be optimised by this approach. By controlling the rate of sludge recycle and wastage a plant can be operated precisely at its design capacity.

- Operation of a variable consent

Discharge to a river is for the most part related and limited to the capacity of the river to accept the flow under dry weather conditions. Such a consent could be viewed as being unreasonably limiting during periods of flood, or when the river level is high. Under these conditions the capacity of the river to accept organic waste is much higher. There are examples where consent licenses have been designed to relate the admissible discharge to the level of water in the river (1).

Figure 6: Operational control of variable BOD river consent



Such a system requires continuous measurement of the level of water in the river and also the level of organic pollutant being discharged. The latter can be used as a control parameter. A BIOX 1000 has been used to provide a measurement of the BOD to be discharged to the river is response to the water level. The system has allowed the mill the maximise the discharge whilst avoiding the danger of breaching the consent.

More recent developments

The manufacturers of these instruments have a policy of constant development and uprating of the devices. This has resulted in the following:

- **StipTox Toxicity Monitors**

  These are essentially developments of the BIOX 1000 BOD monitor. They are truly on-line instruments which provide a measure of the toxicity of an effluent stream to a naturally occurring microbial culture. Sample handling is the same proven system as in the existing instruments. The parameter monitored is inhibition of the respiration rate of the culture caused by the effluent flow. They provide the means of early warning of potential damage to the environment, or if applicable, to an on-site treatment plant.

- **Phoenix III On-line COD Instrument**

  This is a very new instrument. It is a development of the original Phoenix instrument. It provides a lower cost version whilst maintaining virtually all of the design features of the original. It's only limitation is the range over which it can measure. It is limited to a range of 0 to 1000 mg/l COD. However it should have many applications for monitoring effluent flows in this range, particularly where high solids contents make the use of alternative designs of instrument potentially problematic.

Conclusion

These instruments provide:

- reliable operation requiring no problematic sample pre-treatment;
- minimal operating costs;
- low or no consumable requirement;
- no use of toxic chemicals;
- measurements which are very closely related to the actual parameter requirement by the consent license;
- very competitive cost of ownership.

The use of this type of instrumentation should provide a means of achieving greater process and environmental awareness and, through that, a means of more responsible control. If industrialists can accept the introduction of these types of instruments with this outlook rather than viewing it as some form of unnecessary imposition the better it will be for all.

References

1) Firth, B. K. and Cieslek, P. R., Tappi Journal, Vol. 73, No.4, April 1990, pp92-95.