TOXICITY MONITORING

In recl~nt times the increasing and more and more serious environmental catastrophes which have l.rit Hungary's living waters prove the fact that the water quality of our rivers are exposed to the pollution in the neighbouring countries. *(It is enough to mention the river Tisza which is the most important river after Danube in our country. There were two catastrophes at this river in 2000. The first one was just in February 2000 when an enormous volume of cyanide pollutifon got in river Tisza from Romania. Later in March heary metals pl~llution, first of all lead and some other toxic elements polluted this river again from that country. The pollution of cya,nide was extremely big and the effects of this pollution could be noticed along not only Tisza 47ut along the Danube to the Back Sea.)* II

The Hungarian Environmental Authorities can decrease these damages to a certain extent derived from this defenceless situation by revealing the potential sources of danger, by catasu'ophe-preventing plans or by alann-pools etc. However, it is indispensable to detect the occurrence and the type of pollution the earliest possible. Missing infonnation often hinders the effective measures and one can often have infonnation about pollution only after the occurrence of the environmental catastrophe.
Accorl:ling to the present experiences the infonnation about pollution reaches us very slowly from 1he neighbour country, therefore, it is very important to control the water quality of rivers entering our country continuously by water monitoring systems. The basis of effective infomlation gathering is the determination of the group of examined parameters, since it is imposi)ible to implement continuous analyser separately to each potential polluting component. Toxicity may be perhaps the most significant complex parameter. Any kind of pollution that can be dangerous to living world can be detected by monitoring the toxicity of water. After observing serious pollution the next step is the detailed laboratory analysis of water samples. During analysing the polluting components responsible for toxicity can be detemLined. II

In the: interests of the protection of population, permanent toxicity monitoring has a significant role at such water plants, where water taking-out/gaining-out is directly coming from l:iving waters or from shore-filtering (bank-filtering) wells. In HtLngary the first on-line toxicity analyser was placed at river *lpo~v,* at the Hungarian Slova1::ian border. The water plant ofSalg6tarj£m uses temporarily the water ofIpoly River for filling up the reservoir of Komra-valley for making drinking water. The water quality is monitored by a monitoring system consisted of several on-line monitors. The water toxicity is controlled by a STIPTOX-norm Toxicity Analyser.

Generally the continuous monitoring of toxicity -as an important parameter of water quality -is p(~rformed in a bioreactor by continuous measurement of the life fuIlctions ofbioculture bred in stable conditions.
According to one of the methods, the bioluminescence of the bred culture in the reactor is measured while during the other procedure the oxygen consumption of tile bacteria culture is measured. In the first case usually Photobac. Phosporeum are bred, while in that of the other Pseud,omonas putida. The last procedure is applied by permanent toxicity monitoring instruJnent made by ISCO-STIP GmbH and called STIPTOX-norm (Fig. 1). The instrument is applicable for permanently monitoring the pollution of natural waters, at drinking water- networks and for the protection of biomass at sewage water treatment plant.

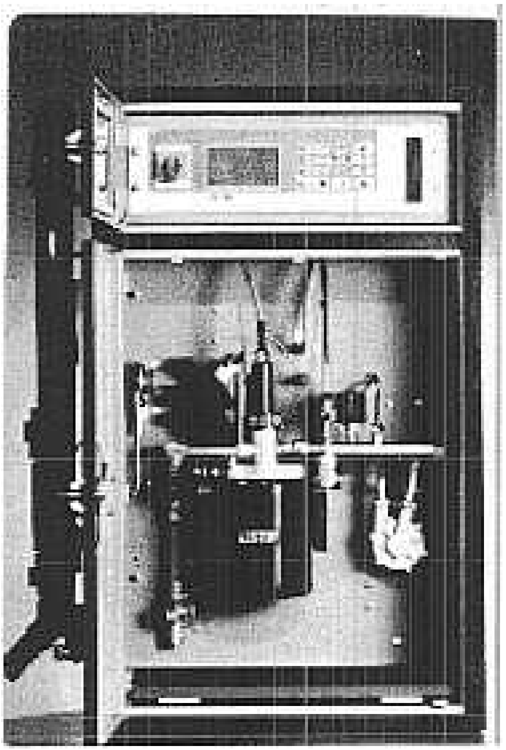

Fig. 1: *STIPTOX-norm Toxicity Analyser*

How j~TIPTOX-norm Analyser operates

The main part of the analyser is the bioreactor. The oxygen consumption ofbioculture immobilised is measured at constant conditions. The water sample before getting into the bioreactor is diluted with fresh water saturated with oxygen. The toxicity of water sample decrea.ses/impedes the life circumstances and population of the biomass and as a result the oxyge:l1 consumption decreases. If the sample is strongly toxic the oxygen consumption can be lower then a certain limit which was programmed (alarm level). Evaluating the result the compl1ter increases the rate/volume of diluting fresh water keeping the total quantity of water led into the bioreactor at a constant volume. The rate of toxic sample is decreased in this way and SOl the bioculture in the reactor is protected. If the toxicity decreases tile computer decreases the dilution automatically while the initial dilution is reached.

The s~lffiple is continuously flowing through the sample tube placed on th(~ left side of the analy~:er (Fig.2). The small volume of the sample is taken by the peristaltic pump PI and so the saJmple can get into the bioreactor BR. The sample taking is controlled by the computer placecL in the upper part of the analyser.

It is important to emphasise that there is *no need any ultrafiltration.* Parti(~les with max. 20mIrL diameter can flow in the water sample. There is a genious solution for taking sample by thf: analyser patented by STIP. *(Let us, please to illustrate the advanta,ge of this sampling solutil1n. Where this STIPTOX-norm Analyser is working there are some other analysers (ammonium, nitrate etc.) but not from STIP. Once there was a bigflood on this river where*

this m!onitoring system is operating. While the other analysers were broken down because of the water with full of particles but STIPTOX-norm analyser was working excellently as if anything would not have been happened.) There is no need any ultrafiltration but only a coars~~ corrosion proof filter is placed at the sampling stump. This filter is automatically clean~:d with fresh water stream. The automatic cleaning period can be programmed and it is controlled by the computer.

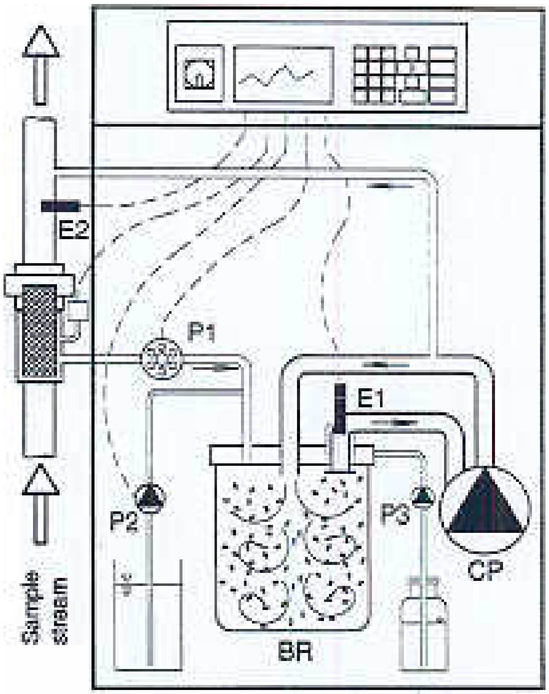

Fig. 2: *The principle of operation of STIPTOX-norm*

The pllInp P2 dilutes the sample with thennostated fresh water which is saturated with oxygen. This stream is added to the sample and introduced into the bioreac~tor.

The diluting water is prepared in a container placed in the back of the analyser. Drinking water :is introduced into the reservoir. The water level is regulated by a swimming valve, while 'the temperature is hold at a constant value by a controller. Air is int1~oduced (in bubbles) into the reservoir. In this way the diluting water will be saturated with oxygen and its temperature will be constant.

In the bioreactor which is themostated a great number of small rings can be found. The bacteria culture is immobilized on the inner surface of the rings. The oxygen demand of bacteria is ensured by the saturated fresh water and by the nutrient introduced by the perist~L1tic pump P3. The flow rate by this pump P3 ensures the sufficient nutrient for the biology even if the water sample does not contain any nutrient for them. 1'his is very impor1tantas in this way any change in the value of BOD (Biochemical Oxygen Demand) of sampLe does not influence the result of measurements.

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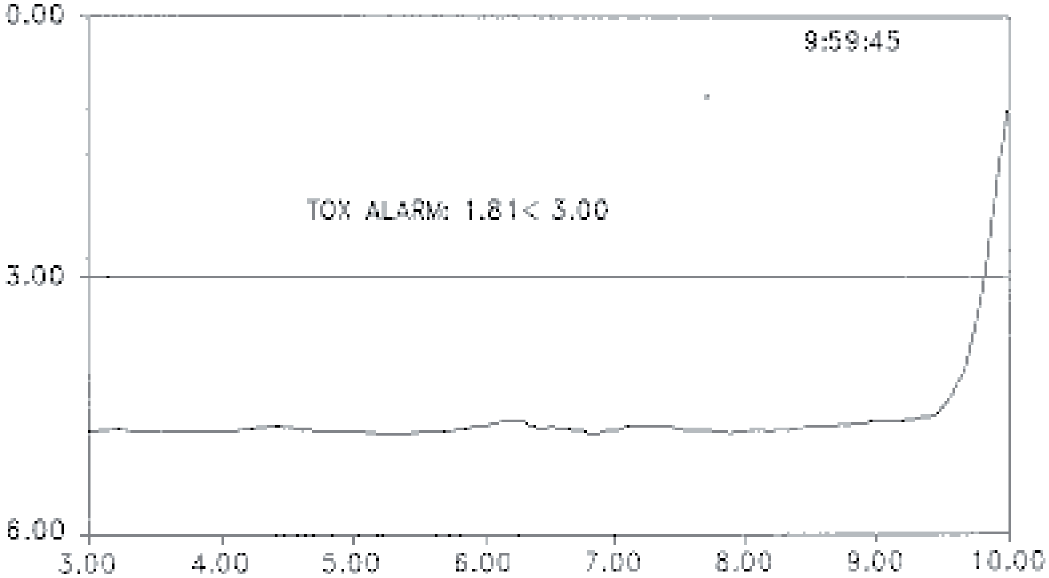
In the' bioreactor the sample and the rings are intensively stirred by a centrifugal pump CP. On the sulcking side there is a filter to prevent rings getting out from the reactor into the pump. The oxygen sensor is placed here (EI). The calibration of this sensor is done automatically after programming by the end-user. The temperature sensor as well as the heating unit (for the thermostatically controlled bioreactor can be also found in this part of the analyser. The water getting out from the reactor is led out from the analyser. There is a possibility to built in anothl~r oxygen sensor E2 into the sample stream if we want to increase the accuracy/reliability of the measurements and if the oxygen concentration of the sample may fluctuate within a short period.

DatalrJgging system

The aJ1alyser gives a great deal of data which can be handled very easily. 'The microcomputer placec[in the upper part of the analyser can accept the signals from the oxygen sensor(s) and from 1he temperature and pressure sensors as wellfas it controls the pumps, magnet valves and heating elements. The measuring process is fully automatized and it does not need any outer
help.

The d.lta just measured and the actual operating infonnation (parameters) and data can be read at the large LCD display (Fig.3) which can be sent e.g. *to* a central computer though the serial port R.S232. The analyser can store the data measured in the last 14 days but these information can al:so be stored on a floppy disk and it can be evaluated by any computc~r program. There are outputs 0-4/20mA programmable and error messages and an alann contact.



EO = 7.93 mg/l **E1** = 6.12 mg/l

:--i02
mg/l

Fig. 3: *Data on the display*

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The menu system of control program is very Wel
tdesigned, easy handle and well organized. The main menu files are the measurement, the se .ce and maintenance, programming and help function. In measuring mode the actual resul s and operating parameters can be notice:d/read. In the service menu the end-user can find the all infonnation for the temporary infornllation, too. The all steps of maintenance can be read on the display with detailed interpretations. In this main menu the next operations including the maintenance can be carrie,d out: cleaning and calibration of the oxygen sensor(s) and the pumps, deairing of the analyser as well as some other operation function.li

Under the Programming Menu the basic parameters can be set. These are input and output data, ~L1arm and protection levels, datalogging and datatransfer. As the setting of these parameters can influence the operation of analysef basically these menu files can be protected with a (personal) code. !

Experiences

In Hungary the fisrt *STIPTOX-norm* Toxicity Analyser was installed on a border river to control the water toxicity as this water is taken ou~ and led into a large reservoir and later it is used tor making drinking water as written above. I
The bacteria *Pseudomonas Putida* were bred at laboratory conditions and then they were placed! into the bioreactor on the rings. The result was excellent. SwitchinJ~ on the analyser after one hour stabile baseline could be got. The analyser begun its work.
The aIlalyser was very sensitive to the change of water quality. Some more experiments were carried out to simulate and to control a toxic pollution and to show the answer of the analyser iftherl~ would have been a toxic component in the water. For this purpose different toxic compounds were added to the water. The effect o~ a double toxic pollution simulated experiments are shown in Fig.4. i

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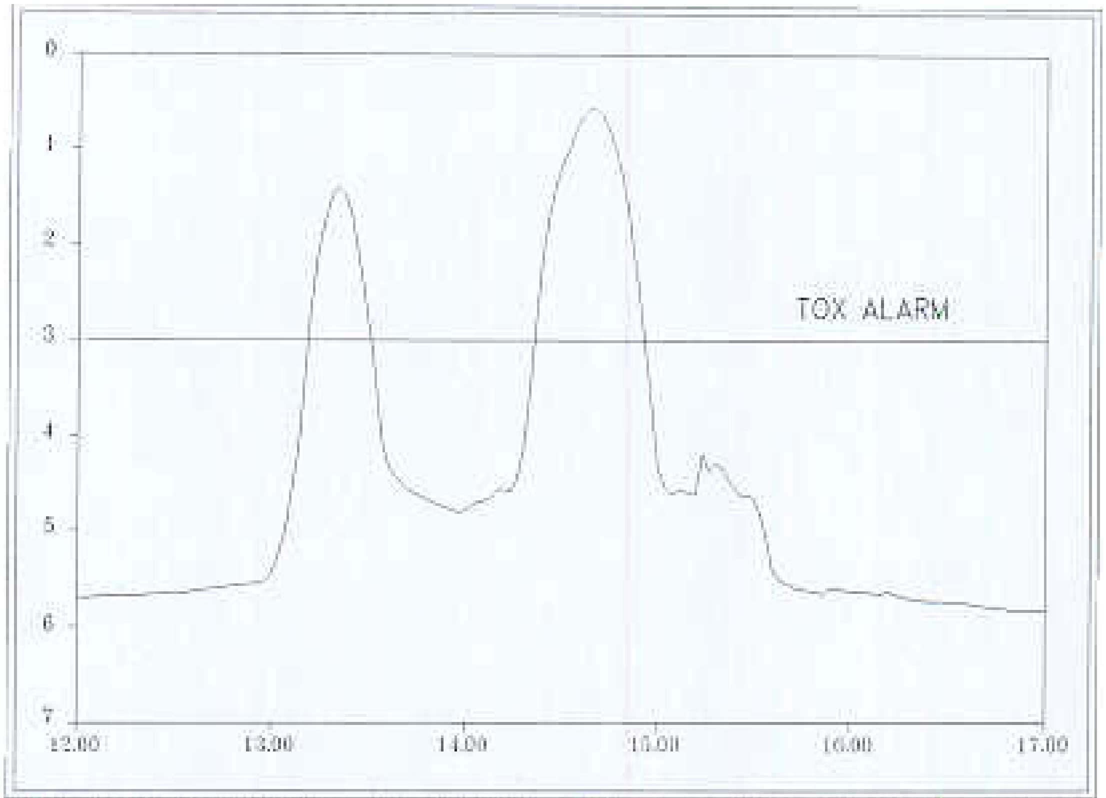

Fig. 4.: *The effect of cyanide and phenol pollution*

The phenol pollution was introduced into the water sample at 13.00 and lasted till 13.15. Within a few minutes the toxicity values increased and soon the programnled alann level was reach~:d. (Lower alann level could have been chosen, too, of course.). The cyanide pollution (as poltassium-cyanide) was simulated between 14.15 and 14.30. In both cases a very quick answer was obtained. We would like to emphasise the very quick reaction time the analyser gave *tl?x-alarm* within 3-5 minutes after the pollution. (The level of alann can be reprog;rammed at any time.)
After 1he stopping the pollution the **tox-alarm** was also stopped in both cases and soon, after 20-40 minutes the base line was reached. This means that the protection ofbioculture is excelli~nt. Without the protection mentioned above the biocu1ture would have become extinct totally. On the other hand this curve (Fig.4) shows that the biocu1ture could manage to survive the two very toxic pollution without any damage.
As we mentioned this analyser is controlling the toxicity of a river (its water is used for produc;ing drinking water). If there is an alann signal the analyser stops th,e taking-out of the water immediately and if the toxicity alarm has been over the analyser gives a command to continue the taking-out of water again.

On th(~ basis of our experiences the STIPTOX-Nonn Toxicity Analyser is very suitable and recommended for applications as the toxicity may be important parameter everywhere where water is applied, treated and used.

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