ON-LINE MEASUREMENT IN WASTE WATER TREATMENT PLANTS: SENSOR DEVELOPMENT AND ASSESSMENT OF COMPARABILITY OF ON-LINE SENSORS.

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1. Introduction

Overviews of commercially available sensors (e.g. analysers) for water treatment plants[1] show that many of these require sampling and filtration. Although these sensors are improving[2-3], they still require a good deal of maintenance[4-7] and the installation costs can be considerable. Furthermore, long response times (10 - 25 minutes) may cause difficulties in incorporating them in standard feed-back process control loops.

Thus the need for new principles for sensors for real-time on-line process control seems obvious and some of the major demands to the development work are and have been to design sensors, which can be placed directly in activated sludge (no sampling and filtration) and measure within appropriate ranges with a fast response time (less than 5 minutes) and continue to do that with maintenance only once a month, or more.

Several well known measuring principles can be used to comply with these demands, if the principles are used together with technology now available (such as possibilities for fast and large computations, optical standard components and micro-machined designs). Some of these principles include:

Colorimetry combined with semi-micro mechanics and membrane technology.
Absorbance using photo diode-arrays for spectral information.
Fluorescence with multi-wavelength excitation and scanning for emissions.
Virtual sensors (or software sensors) based on calculations on signals from reliable sensors or installed equipment.

Once the sensors have been developed, the next question to arise is: How is the reliability and quality of measurements obtained from the sensors secured and how is the comparability of different sensors improved.

At the present time neither validation schemes nor standards exist for user needs concerning the in situ on-line measurements of water quality determinands and in consequence, the instrument producers and suppliers set their own specifications, based upon the technology that they possess.

These problems are the basis of a recently started project, financed by the SMT programme, the ETACS (European Testing and Assessment of Comparability of on-line Sensors/analysers) project. The objective of the project is to initialise a process, which will establish a validation scheme, which will have the form of a test protocol, that can be used in two situations :

- in the laboratory for documentation of the instrumentation according to the performance claimed by the producers.
- in situ during operation for documentation of the reliability of results obtained by the users.

The content of a test protocol, which can be the technical basis for further work in European and international standardisation organisations, should be based on the typical performance characteristics of in situ on-line sensors, which include :

- Selectivity & specificity
- Range
- Linearity
- Sensitivity
- Limit of detection
- Limit of quantification
- Ruggedness
- Accuracy
- Precision, repeatability & reproducibility
- Response time, dead time & rise time
- Effective operation time (up time)

The project will suggest precise definitions of these performance characteristics and test the practical use of them, both in the laboratory and in the field.

The paper will concentrate on the two aspects mentioned above. a) Description of a sensor developed using the first of the four measuring principles, although brief description will be given for the other three mentioned principles. b) Further description of the need for a test protocol, to secure the quality and reliability of sensor measurement and to improve the comparability of different sensors/analysers.

2. Sensor development

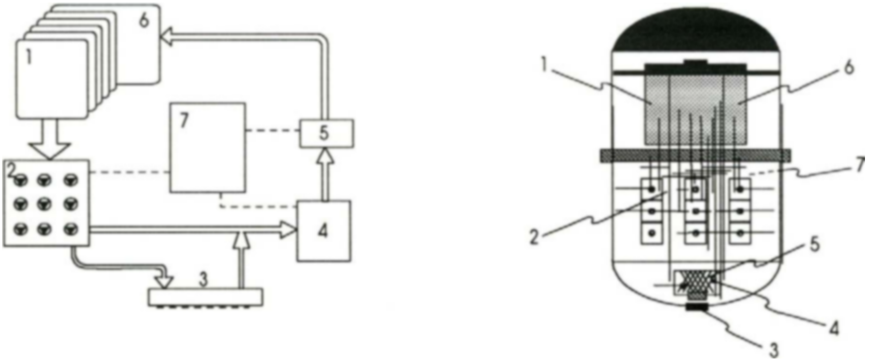
2. 1. Colorimetric sensors

The sensors developed using colorimetric principles, in combination with semi-micro mechanics and membrane technologies, include ammonium, nitrate and phosphate sensors and is defining a concept which now is called µCFA (Micro Continuous Flow Analysis).

2. 1. 1. Sensor design

Basically the principles used are the same for all three kinds of sensors. Fig. 1 shows a diagram of how the sensor is working and how the different parts of the sensor have been built into the prototype construction. Reagents and clean water are stored in bags (1) and transported around the sensor with pumps mounted on a transportation manifold (2). A carrier (clean water) is pumped to the membrane device (3) and flows in a channel on one side of the membrane. The other side is exposed to the measuring media and the carrier is then enriched with ions passing through the membrane. The enriched carrier is mixed with reagents and pumped to the reaction area (4) and further on to the photometer for detection (5). Both the reaction area and the photometer are heated to a constant temperature. From the photometer all liquids are pumped to a waste bag (6). All functions in the sensor are supervised and controlled by a microcomputer (7).

Figure 1: Design and construction of the sensor.



Transport manifold : All transportation of liquids inside the sensor takes place in channels with a width of 0.3 to 1 mm milled directly into the manifold material. Pumps delivering 3 µl/turn, are integrated with the manifold and deliver carrier and reagents from the cooled storage bags with a speed of 5 rpm, resulting in a total consumption of liquids within the sensor of less than 3 litres/month. The length of the channels (also on the analysis manifold) have been minimised in order to obtain the smallest possible volume of flowing liquids, giving the fastest response time as possible.

Membrane device : The membrane functions as an ion sieve with practically no mass transportation of water. This means that the sensors with respect to liquids can be regarded as a closed loop system with all used liquids collected in the waste bag. As the carrier is flowing continuously on one side of the membrane and the other side is in direct contact with the measuring media, the sensors can deliver a true continuous measurement, without the need for any further sample pretreatment (pumps, cross flow filters, etc.). The MW cut-off of the membrane is approximately 100 Daltons and with an approximate thickness of 50 µm, which is the same as for many Dissolved Oxygen sensors. The lifetime of the membrane is tested to be well over 1 month.

Analysis manifold : On the analysis manifold, reagents and carrier are mixed, starting a colorimetric reaction and the resulting colour is measured by the sensor photometer. Transport inside the manifold is performed as in the transport manifold and these two manifold and the membrane device define the μCFA system.

The analysis manifold, together with the sensor photometer (or the wavelength of the photometer), gives the sensor its identity and three different manifolds have been developed for well-known colorimetric reactions: Indophenol Blue method for ammonium determination, hydrazine reduction followed by formation of a Diazo complex for nitrate determination and Molybdenum blue method for phosphate determination. However, the high demand for short response times makes it impossible to allow the reactions to come to an end and this problem has been solved by design of a system with very high repeatability enabling the photometer detection to take place at the exact same time during the colorimetric reaction.

Calibration and measurement : Beside the normal operation mode, the sensors are equipped with an auto-calibration and a cleaning routine, using standard solutions of the ion to be measured and proper cleaning agents. Both the standards and cleaning agents are stored in bags together with the reagents and each bag, for measuring, calibration and cleaning, has its own pump, controlled by the microcomputer. This enables the sensor to operate in different modes (measuring mode, calibration mode, etc.), according to preset criteria. The standards can be used in two different situations: calibration of the chemical system, or determination of the membrane efficiency. Both calibration routines and the cleaning routine are performed with the sensor placed in the measuring media.

For low concentrations of the actual ion to be measured transmission follows Lambert-Beers law. However, for high concentrations this law does not apply and therefore the dynamic range is extended using a calibration involving three standard references and a non-linear relationship between concentration and absorbance for higher concentrations.

$C^* = \mathrm{Log}(Tr/a)/b$ (for low concentrations) and $C^* = c/(Tr-d)$ (for high concentrations) (1)

where C^* is the resulting concentration measured by the chemical system, Tr is the measured transmission and a, b, c and d are the constants calculated from the measured transmission with low and medium reference concentrations, respectively medium and high reference concentrations.

As the membrane efficiency M_{eff}, can be lower than 100% and can vary from one membrane to another, it is essential that the sensor automatically determines this efficiency, in order to be able to calculate the correct concentration of the ion in the measuring media, defined as $C = C^*/M_{eff}$. It can be shown that[8]:

$M_{eff} = 1+[(C^*-C_s^*)/C_s]$ (2)

where C_s is the concentration of the reference in the carrier before passage of the membrane and C_s^* is the concentration of the reference after passage of the membrane.

Signal conditioning: The raw analogue photometer signal is sampled and digitised with a frequency of 10 Hz and is then filtered for peaks caused by noise or air bubbles passing through the photometer. Finally a moving average is calculated with a time period of 12 seconds (which equals one turn of the pumps and 120 sampled values), in order to remove the effect of oscillation of the signal caused by the pumps. This averaged value is then used by equation (1) and finally divided by the membrane efficiency.

2. 1. 2. Laboratory tests

Laboratory tests were designed to give information regarding the sensor performance according to the definitions given in EN45001[9], of performance characteristics of an instrument. Calibration curves for each of the three sensor types were determined using standard solutions and each sensor, in turn, was placed in these standard solutions for an hour, logging every 5 seconds, giving 720 measurements for each sensor in each standard solution. Response times for the sensors were determined using standard solutions, as the sensors were moved rapidly from a blank solution to a standard solution and were defined as the time it takes the sensor to reach 90% of a new concentration, caused by a step change. Table 1 shows the result of the laboratory tests for some performance characteristics.

Table 1. Sensor performance according to laboratory tests.

	Unit	**NO_3^- - N**	**NH_4^+ - N**	**PO_4^{3-} - P**
Range	mg/l	0 - 10	0 - 25	0 - 10
Sensitivity	mg/l	0.05	0.05	0.025
Limit of quantification	mg/l	0.05	0.05	0.025
Limit of detection	mg/l	0.075	0.1	0.2
Accuracy*	mg/l	±(0.1 + 10%)	±(0.1 + 5%)	±(0.1 + 5%)
Repeatability*	mg/l	±(0.1 + 5%)	±(0.1 + 3%)	±(0.2 + 3%)
Response time	min.	3	2½	5

*percentage is given of the actual measured concentrations.

2. 1. 3. Wastewater Treatment Plant Tests

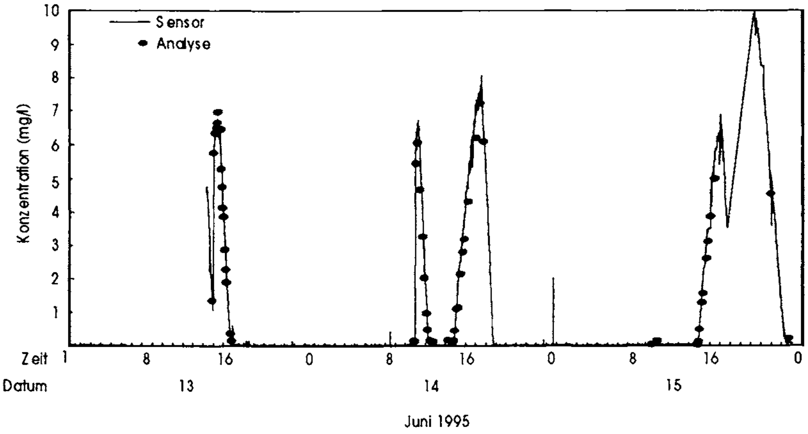
The sensor prototypes have been tested in a pilot scale waste water treatment plant operating with recirculation nitrogen removal and in a full scale biodenitro waste water treatment plant. The pilot scale plant was loaded with real wastewater and both treatment plants had extended nitrogen removal.

Fouling of the sensors: To investigate the fouling of the membrane devices, ten devices were placed in the pilot scale treatment plant for a period over half a year and laboratory analyses were carried out periodically on the carrier from each of the membrane devices and from the tank of the pilot scale treatment plant.

During the period the pilot scale treatment plant was operated as close to steady state as possible and the feed to the plant consisted of raw waste water. The mass transfer coefficient for the membranes was calculated from the experimental results[8] and it was found that the ion transport over the membrane was practically unaffected during the period. This result was confirmed by visual inspection of the membranes during the period, which showed no bacterial growth at all.

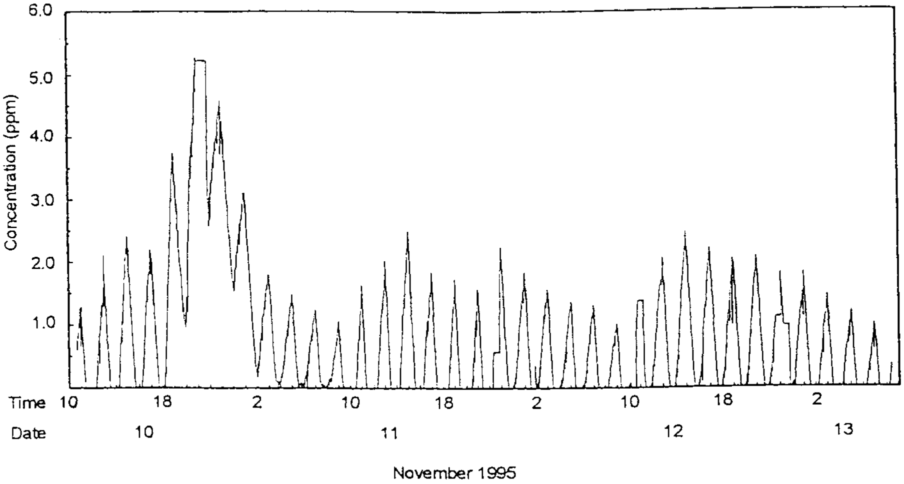
Sensor responses to the process in the pilot scale treatment plant: The sensors were installed in the aeration tank of the pilot scale treatment plant and several experiments performed over a longer time period with determination of process rates were conducted using the sensor responses and laboratory analyses on grab samples from the tank. The tank functioned as a batch container, due to stop of the inflow of feed during the experimental period.
All recorded sensor responses are in good agreement with the laboratory analyses and the sensor response times are very close to follow real time changes in the pilot scale treatment plant. Fig. 2 shows that the calibration and response of the sensors (ammonium sensor) do not change over several days, compared with laboratory analyses and that the pilot scale treatment plant is normally operated with a very low concentration of ammonium in the nitrification tank. The figure shows several experiments with adding of ammonium chloride (first and second peak) or stop/start of the aeration.

Figure 2. Ammonium measurement in the pilot scale treatment plant.



Sensor response to the process in the full scale biodenitro waste water treatment plant: Figure 3 shows the ammonium sensor response during three days of test, in the full scale waste water treatment plant (from Friday afternoon to Monday morning). Responses are as expected both the very high load (which is partly because a nearby slaughterhouse cleaned up for the weekend) and the low load during weekend. Autocalibration periods can easily be seen as periods of constant signal around midnight and it is obvious that calibration every night is not needed. Furthermore, it can easily be seen that the control scheme of the plant can be optimised, because aeration periods are clearly too long in the weekend and maybe too short during periods of high load.

Figure 3. Ammonium measurements in the full scale waste water treatment plant.



2. 1. 4. Conclusions

The tests of the prototypes of the sensors demonstrate that it is possible to design and construct real-time on-line in-situ sensors (without any pretreatment of samples and without any spill of chemicals (closed loop system)), with response times less than 5 minutes for ammonium, nitrate and phosphate. Furthermore, the sensors have an effective auto-calibration routine and no fouling of the membranes used is observed and finally maintenance periods of a month is possible, due to the low chemical consumption. The sensors have now been brought from prototypes to commercially available sensors and are now available on the market.

The µCFA and membrane technology developed for the prototype sensors are believed to have a large potential for further refinements, such as extension of the dynamic range and faster response times. Furthermore, it should be possible, without too much difficulty, to extend the types of ions to be measured by the sensors.

It has been demonstrated[10] that this type of sensors supports the use of set-point control by simple rule based control schemes and it is believed that there is a great potential for optimisation of treatment processes even with these simple control schemes.

2. 2. *Absorbance, Fluorescence and Software Sensors*

2. 2. 1. Absorbance sensors

The sensors presented in the previous section measure absorbance at one specific wavelength, specified by the developed colour. However, it is also possible to measure the absorbance spectrum of a sample by sending light through the sample and measure the absorbance at the different wavelength. As every constituent in the sample, which have molecular energy levels, which are able to absorb the light used will absorb the light with different absorbances, due to the specific energy levels for the specific constituents, complex samples can give very complex spectra.

Absorbance measurements is usually obtained in the UV-VIS (Ultraviolet and Visible light) region of the spectrum. This region has a lower limit due to the strong absorbance of water itself below 200 nm. Nitrate is a good example of a constituent that has a specific absorbance (at 205 nm), but in waste water samples this absorbance is very often hidden by strong absorbances from organic substances. Nevertheless, nitrate sensors, based on the absorbance at 205 nm, are available on the market, all of them trying to compensate for the interference from organic substances.

Figure 4. Absorbance spectra in the UV region of samples from a waste water treatment plant.

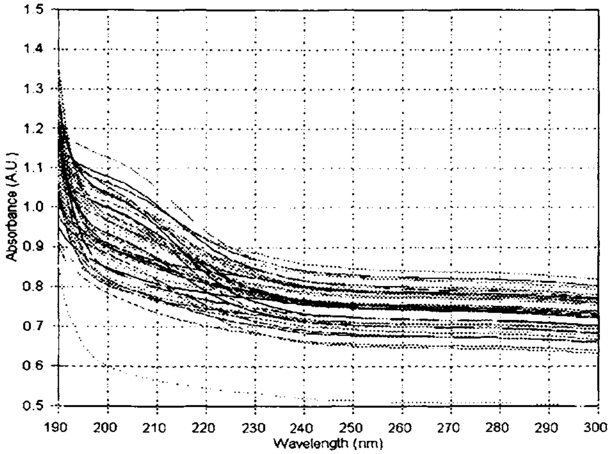


Figure 4 shows absorbance spectra of samples of activated sludge at different times during the cycle of a biodenitro waste water treatment plant and as can be seen from the figure, these samples are all very complicated. However, the samples can be analysed for different substances, using multivariate calibration and this calibration can be used to give the concentrations of the substances, of spectra recorded at a later time. This principle is clearly demonstrated for nitrate by Karlsson et at.[11], who also showed that it would be possible to measure total-P, total-N, ammonium and iron simultaneously with the nitrate. This methodology is also known as chemometrics and together with the development of micro-scale spectrophotometers (diode arrays) it will be possible to develop small integrated multiparameter absorbance sensors.

2. 2. 2. Fluorescence sensors

As described above, absorbance is caused by substances absorbing light. The substances, which are now in a higher and more unstable energy state, release the energy surplus. This release is normally done by molecular processes like rotation, vibration or transfer of energy to other molecules. However, in some substances this release can happen as emission of light and this is known as fluorescence. The wavelength of the fluorescent light is specific for a given substance and will always be at a longer wavelength than the light absorbed, because some of the energy surplus always will be released as vibration and rotation.
A typical design of a single channel fluorimeter (sensor based on fluorescence) is described by Nørgaard et al.[12] This fluorimeter measures the NADH concentration by the fluorescence at 460 nm (excitation at 340 nm), thereby giving a measure of the biological activity, as the corresponding oxidised state, NAD^+, is not excitated at 340 nm. This fact has been known for several years in the fermentation industry.

Furthermore, it can be shown[13] that the NADH fluorescence can be used to detect the end of the denitrification in an alternating activated sludge plant and that some correlation exists between fluorimeter output and the peak oxygen uptake rate.

As with absorbance, also fluorescence can be measured as a spectrum. This spectrum has a 3-dimensional structure and is the fluorescence as a function of both excitation and emission. Until today only very little work has been done in the field of multi-channel fluorescence and chemocmetrics[14] and almost nothing on waste water samples.

2. 2. 3. Software sensors

Software sensors, or virtual sensors, is a term used for "signals" from calculations based on signals from reliable, available sensors in combination with other signals like on/off indications and time counters.

As an example of a software sensor, consider the rate of change of the dissolved oxygen concentration, $d(C_{ox})/dt$. This rate change can be calculated from the oxygen concentration measurements, C_{ox}, done at time n and n-1

$$d(C_{ox})/dt = (C_{ox,n}-C_{ox,n-1})/(t_n-t_{n-1}) \quad (3)$$

Furthermore, the rate change can also be expressed in terms of respiration

$$D(C_{ox})/dt = K_la(C_{ox,m}-C_{ox})-OUR \quad (4)$$

As the oxygen transfer coefficient, K_la, can be written as a new constant multiplied with the airflow, Q_{air}, to the aeration tank and as the oxygen saturation concentration, $C_{ox,m}$, can be calculated as

$$C_{ox,m} = C_{ox,20}\ 1.02^{(20-T)} \quad (5)$$

then the oxygen uptake rate, OUR, can be written as

$$OUR = K \cdot Q_{air}(9.07 \cdot 1.02^{(20-T)}-C_{ox})-d(C_{ox})/dt \quad (6)$$

K is determined by setting $Q_{air} = 0$, ($OUR = d(C_{ox})/dt$) and following this by trial and error setting a Q_{air} giving a constant oxygen concentration, ($d(C_{0x})/dt = 0$). Hereafter the OUR can be calculated from measurements done by the oxygen sensor, the temperature and the airflow.

Other kinds of software sensors are for example filters, to be used in real time in order to avoid outliers in the signal from the real sensors or different types of real time quality control/sensor validation procedures. These software sensors are in fact sensors on the sensors and can be useful to follow.

3. Assessment of comparability of sensors, the ETACS[15] project

In order to support the protection of the environment, there is an urgent need for improvement of comparability, reliability and quality of measurements obtained from in situ on-line sensors/analysers, used to determine the composition of and flow of effluents from waste water treatment plants and industries.

Therefore a new project, the ETACS[15] (European Testing and Assessment of Comparability of on-line Sensors/analysers) project has recently been initiated. The purpose of the project is to carry out a pre-normative work on standardised validation of methods for in situ on-line measurements of water quality determinands, such as ammonium, nitrate, phosphate, BOD, COD and TOC. The key objectives of the project are:

The development of a test protocol for validation of the performance of in situ on-line sensors/analysers and how these can be compared.
Practical testing of the test protocol to access its applicability to provide experience to form a final test protocol.
Widespread acceptance of the test protocol by producers/suppliers, users and relevant authorities, to assist its early adoption as an agreed European standard.

These objectives will secure that in situ on-line water quality measurements will be of sufficiently known and documented quality, in order to be used for real time process control, regulatory monitoring and harmonised environmental databases.

At the present time neither validation schemes nor standards exist concerning the in situ on-line measurement of water quality determinands and in consequence the producers and suppliers set their own specifications, based upon the technology that they possess. This approach to measurements is very unsatisfactory, since it provides no basis for users to either specify or compare performance of the sensors. In addition to this, producer supported data are often based on laboratory tests, carried out off-line and therefore not carried out on genuine on-line samples.

Therefore the ETACS project shall initialise a process, which will establish a validation scheme, which will have the form of a test protocol and which eventually can form the basis of a system for accredited certification of in situ on-line sensors/analysers, enabling reliable and comparable measurements. The validation scheme can be used in two situations :

- in the laboratory for documentation of the instrumentation according to the performance claimed by the producers.
- in situ during operation for documentation of the reliability of results obtained by the users.

The test protocol shall be independent of both specific in situ on-line sensors/analysers and specific determinands and during the project period it will be tested and documented as the technical basis for further work in the standardisation organisations.

The content of the test protocol shall be based upon the typical performance characteristics of in situ on-line sensors/analysers and include:

Selectivity & specificity :

- Range.
- Linearity.
- Sensitivity.
- Limit of detection.
- Limit of quantification.
- Ruggedness.
- Accuracy.
- Precision, repeatability & reproducibility.
- Response time, dead time & rise time.
- Effective operation time (up-time).

The project will suggest precise definitions of these performance parameters and test the practical use of them both in the laboratory and in the field.

The project will fall into three phases :

Phase 1

The development of a test protocol for validation of the performance of in situ on-line sensors/analysers and how these can be compared.
Collection of information about existing standards and certification- /accreditation arrangements in Europe.
Information to the European Standard Organisations - with the possibility to form groups for discussion and information dissemination.
Detailed description of the procedures and design of methods to be used for laboratory tests and field test, based on a review of existing work and experience.
Identification of determinands and producers/suppliers of sensors/analysers, to be considered to be covered by the test protocol.
Identification of at least three different types of on-line sensors/analysers, which will be the best representatives for testing the developed procedures and methods.
Preparations of a draft test protocol for laboratory and field tests of on-line sensors/analysers.
Information to the European producers/suppliers and laboratories about the work and the possibilities for participation in phase 3 of the project.

Phase 2

Practical testing of the test protocol to access its applicability to provide experience to form a final test protocol.
Selection of determinands and sensor/analyser classes.
Purchase of sensors/analyser and development of the logistics, “test bench facilities” and standard samples.
Commissioning of the chosen types of sensors/analysers.
Laboratory and field test of the draft test protocol on at least two different types of on-line sensors/analysers. Test is performed by the project participants.
Review of the protocol with revision of the procedures and methods, according to the experience obtained after both laboratory testing and field testing.
Meetings with a group of European Standard Organisations.
Production of a summary report, the final test protocol and other information to be used in phase 3 of the project.

Phase 3

Widespread acceptance of the test protocol by producers/suppliers, users and relevant authorities, to assist its early adoption as an agreed European standard.
Extension of the number of laboratories and offer European producers/suppliers of on-line sensors/analysers the opportunity to have there product tested at these laboratories, according to the protocol.
Formation of a network of laboratories and producers/suppliers, in order to be able to collect and disseminate the results and experience obtained.

Organise a series of workshops for end users in different countries, with presentations performed by participants, laboratories and producers/suppliers and with participation of different standardisation organisations.
Production and dissemination of a final report to all interested partners.

Currently we are in the beginning of phase 1 and collecting information about the current state of art, regarding existing standards of the above mentioned performance characteristics. Two searches have been conducted in all major databases, world-wide and the result showed that there is no standard available at all, covering the above mentioned performance characteristics, sensors and water/wastewater and that only a few of them have been defined.

This result confirms the basis of the ETACS project, that is to produce a test protocol that can be used to secure the quality and reliability of sensor measurements and used to improve to comparability of different sensors. This test protocol shall form the basis of further work in international standardisation organisations.

4. Acknowledgement

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