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State of the art on chemical sensors for early warning systems

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Early warning systems for rapid detection of deliberated intrusion

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ABSTRACT

STATE OF THE ART ON CHEMICAL SENSORS FOR EARLY WARNING SYSTEMS

This report deals with the different solutions to implement an early warning system in a drinking water network to detect intentional contamination. It is focused on common chemical sensor solutions in a multi-parameter probe. It deals with the environment of the probe and with its specifications. At the end, preliminary tests are made to evaluate 2 solutions with a normalized test protocol.

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REVISIONS

Page 8, paragraph II.2 Turbidity: “This is important to control the long-term stability and the repeatability/reproducibility of these kinds of device must be not forgotten. These parameters are obviously taken in account in the sensor selection after long-term testing. False negative (or type II error) should be considered for the sensor network. And, sensor placement aims to minimize several objectives of which the type II error. Also, the risk for a real contaminant event to pass unnoticed (undetected) is low.”

Page 9, paragraph III.3 UV Analysis: “For example, the performances of the S::CAN device are well known (indeed a large study was done in Techn’Eau European project). This is a good device nevertheless it is quite expensive taking into account our objective to wide spread of sensors network. Moreover, this device is not adapted to in-line measurement; such device could not be inserted directly and easily on the real pipe. Usually it is put in derivation with water losses, contamination risks, power supply constraints.”

Page 10, paragraph IV Specification: “This is the strategy to develop early warning sensors network with numerous and cheap multi-parameter sensors throughout our distribution systems. To follow this strategy, we could take inspiration from other sector like automobile: they succeed to reach a life time of more than 10 years, a high robustness, low cost device and also complex solutions (ABS, pressure sensors) even if measurement principles are simple.”

Page 14, paragraph I. Multi-Parameters probes on the market: “The short duration of the project did not allow us to do important development on sensors. The goal was to find an apparatus almost ready to use for the EWS. The methodology used was to perform a market review in order to find the most fitted multi-parameter probe for the EWS on a real network. It is why simple quotation rules have been chosen (I.12).”

Page 19, paragraph I.6 HORIBA – W20 XD: correction of the reference of the probe.

Page 21, paragraph I.12 Comparison and Selection of the available probes:
“

- Insertion depth linked to the pipe diameter, less it is higher length of network could be addressed (especially end-user pipe). It is important to install easily the probe on the pipe. One of the most important criteria for the installation is the “insertion depth”. This is the length of the probe which must be in contact with water in the pipe. For example, if insertion depth is 5 cm, for canalisation with a diameter under than 10cm you must install a chamber. To install the chamber you must stop the flow and thus the installation cost become very high.
- Price: lower is the price higher is the number of point could be surveyed for the same investment
- Number and importance of measured parameters: linked to the WHO suggestion and the variety of events which can be detected. We could also in addition of security issues address simultaneously safety issues to reinforce the interest of the solution.

“
And

“For each probe, the number of points associated to the selected parameters which can be measured is added. The maximum quotation is 18 points (100%). According to our criteria, the probe which has no one of the most important parameters (Chlorine, optic measurement) has a quotation equal to zero.The maximum score is 100% for the probe which has all the useful parameters (Intellitect). The two most important parameters are Chlorine concentration and turbidity. Some drinking water networks are treated with monochloramines especially in the USA and China markets, in these cases this parameter is as important as chlorine. Nevertheless, the number of this kind of network in the world is lower than the chlorinated ones.”

Page 22, Table 16: Prices are given in k€.

Page 23, paragraph I.12 Comparison and Selection of the available probes: “Despite its low quotation, we wanted to test the probe from Hach because it was widely used in the U.S. project, it could be a reference. For the moment, the supplier was unable to sell it because it was not addressed to the European market. (in addition, the chlorine sensor is not ready yet on the probe).”

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INTRODUCTION

The aim of the SecurEau project is the security and the decontamination of drinking water distribution systems following a deliberate contamination. The size of the system, the difficulty of cleaning pipe walls, the need to rapidly identify the point (s) of intentional contamination, and the extension of the contaminated area represent many bottlenecks to be overcome.

Whole security systems are based on a multi-level approach to improve their efficiency and adapt the response of the system to the risk. This multi-level approach is defined by three main steps:

- early warning system, to detect the deliberate intrusion as soon as possible;
- development of methods, to identify the nature of the contaminants, and to provide a risk analysis. The focus will be based on rapid off-line measurement;
- decontamination procedure, to remove the pollutant from the network. These procedure will be based on a model of contaminant accumulation and on specific methods to control the efficiency of decontamination, especially on deposits. One of the most interesting phase of the SecurEau project is undoubtedly its full scale application within the Work Package 7.

At the end of the project, devices and procedures will be applied in 2 drinking water networks: Veolia Central UK in London (UK) and BWB in Berlin (G).

In this context, the Early Warning System (EWS) is the main way to detect terrorist attack. These attacks could have interruption of water supply as a major consequence. Consequently the EWS has to detect all intrusions and to provide only true alarms (number of false alarms should be minimized) to the operators of water distribution systems. The pertinence and quality of measurement is one of the key issue to succeed. However communication, data processing, operating and maintenance aspects should also be considered.

The present deliverable of the Work Package 2 is the state of the art about early warning systems for rapid detection of deliberate intrusion in drinking water networks. It is roughly a technology review of devices (including principles of measurement) to monitor the water quality. For a full scale application at the end of SecurEau only devices already commercialized are taken into account in this review. After a short description of other projects in the same field, relevant water quality parameters are defined and our own EWS specifications are also described (see Part I). Sanitary aspects and data treatment issues will be introduced. The list of multi-parameter probes available on the market is given in Part II. Protocol to evaluate the probes previously selected and preliminary results on two of them are described Part III.

PART I - CONTEXT OF THE STUDY

I. WP2 PURPOSE

A contamination event should be detected when the water quality parameters change from the "normal" operating conditions. Acquiring information about the correlations between integrated sensor observations and their response (false negative, false positive, measurement uncertainties) with respect to contaminants, is consequently necessary. Use of multiple water quality sensors should provide validated information that may lead to the more appropriate action. First, only commercially available water quality sensors will be used to detect anomalies. Reviews of sensor technologies have already been published [1], [2], [3] and the topic related to "Biofilm monitors" [2] has already been reviewed by few partners involved in a previous European programme (SAFER). In order to make the early warning system efficient, the sensors have to comply with the following characteristics: (i) to be easy to set-up on-line, (ii) to provide a fast response, (iii) to allow a large implementation (*i.e.* low cost, few maintenance and calibration), (iv) to respond to a high number of contaminants. The WP2 purpose is to develop a methodology to set-up networks with sensors providing thus an early warning of intrusion which implies both development/adaptation of relevant sensors and optimal location of these sensors in the distribution system.

CEA, Monitoring System and Veolia Environment are respectively involved in radionuclides, biologicals, and chemicals detection. Each partner is in charge of adaption and/or development of generic or specific sensors within the first three years of the project. Veolia Environnement should provide solutions for chemical sensors.

Results which will be obtained in this Work Package will be used in Work Package 7 in which we have to implement the sensors in real VEOLIA drinking water networks (London and Berlin). That is why:

- sanitary conformity agreement (official control of several organic materials in contact with drinking water – see Part I.V.1) has to be taken into account
- finding a way to settle the measurement devices in the different pipes sizes is necessary
- operational methods to be able to install and to maintain the sensors has to be taken into consideration
- Purchasing price as well as operating costs for a large deployment has to be considered with care.

II. DRINKING NETWORK SECURITY, A WORLDWIDE ISSUE

The SecurEau consortium brings together the expertise on drinking water distribution systems gained in many national programmes, the EU framework programmes (e.g. SAFER; Techneau; COCERSI; CAREW, CARE-S and TENAWA), as well as international programmes (e.g. Battle of the water sensor network). In this state of the art, two main projects, funded by US [5](EPA Project) and ISRAELIAN government with Mekorot water company [6], have been especially studied because of their similitude with our present topic. However, few technical details are really available. The most important results and reports are likely to be confidential especially for the Mekorot project.

The United States Environment Protection Agency (EPA) has been working since 2003 on this topic and has got a significant number of results. In this point of view we started 6 years after them, which is why it was necessary to analyse their approach and suggest an innovative working method. For the EPA project, a review of existing technologies for water quality monitoring was performed. A number of analysers manufactured by various companies has been tested, to measure parameters like TOC, UV/VIS spectrum, chlorine, oxygen… Size, operating and maintenance costs weren't a major constraint in their approach. The solutions provided rely on the integration of classic analysers in a large bay [7]. Constraints of implementation, cost (more than 160 k$), energy, water losses, maintenance cost and maintenance frequency, pipe derivation allow this system to be installed only on a few strategic points on the network [7]. This kind of settings is not fitted to the entire network survey. This approach seems to make sense if used for some specific sensitive customers but not on a large scale.

Nevertheless, the EPA project has found very interesting results by testing the sensors' behaviour when a contaminant gets injected within the network. These results gave them a kind of “library of contaminants” [8]. Moreover, several contaminants tend to have an effect [9] on all parameters and prove the interest of using multiparameters measurement for our purpose. The variations observed could be used as a fingerprint for each contaminant. Again, all interesting results and reports on this topic have been classified. Nevertheless, their conclusions give us an idea of what the most important parameters to detect a contaminant’s injection are.

A parallel approach was developed by Mekorot which is the national water supplier and drinking water producer in Israël. In this region, security around the installations of drinking water treatment is reinforced against the deliberated intrusion - compared to the usual situation. They develop tools to centralize all the information with the Israeli firm called Whitewater. For the same reason as in the EPA project few technical data are available. Concerning instrumentation, they plan to have an implementation of quality measurements along the network. The sensor density they used is about 20 units on the 200 km of the feeder pipe (main canalization), Figure 1. For each point [4] they measure free and total chlorine, pH, turbidity, conductivity, NH3, F, biosensors (only fish) and filterability.

Figure 1: Mekorot project - probes implementation

Terrorism is meant to spread terror and in this case it is not necessary to kill. If only a small quantity of contaminant injection is done on some specific places, for instance one building or one residential sector, this might be enough to provoke terror. In the EPA approach only few points are under survey [8], so operator and government can’t prevent this kind of attack. This European project plans to install a large number of non-specific sensors but highly integrated (WP2.2) to have an indicator of water quality level. New progresses made by nano and microelectronic industries allow us to reconsider measurement principles integration with a ‘low-cost’approach. A sensor with lower cost is likely to exhibit lower performance, (lower sensitivity for instance). It is expected that this will be compensated by (1) larger implementation and (2) the creation of a real water quality sensors Network including data treatment to minimize false alarm and to improve rapid detection of the contamination.

III. MAIN WATER QUALITY PARAMETERS

With the vast array of chemical (C), biological (B) and radiological (R) agents available for possible use in an intentional attack, deployment of contaminant-specific monitors that could specifically detect all of the CBR contaminants of concern would be impractical and cost prohibitive. Moreover, the Lethal Dose is often very low (ppb) and it is very difficult to detect this order of magnitude. Thus the goal of the EWS should not be to detect a substance but a change in water quality, and to identify – if it's possible- the substance responsible for this change. In this case, we are dealing with classic water quality parameters. Thus we have to choose the most relevant parameters for this EWS. It's important to consider that the most important source of change in drinking water quality is not due to the terrorist attack – it is due to a non-intentional incident (pipe broken, problem in water treatment…).

The World Health Organization (WHO) gives recommendations [11] about the water quality surveillance in the drinking water network. The WHO recommends doing regular measurements (routine inspection) on tap water for the following main parameters: faecal indicator bacteria and heterotrophic bacteria, E. *coli,* residual of chlorine, temperature, pH, turbidity, colour, oxidation reduction potential (ORP), conductivity… The bacteria survey is not the topic of this state of the art: this report is focus only on chemical measurement.

In this context, the most important parameter is the chlorine **residual [9], [11]**. Chlorine residual monitoring provides a rapid indication of problems that will direct measurement of microbial parameters. A sudden disappearance of an otherwise stable residual can indicate ingress of contamination. Alternatively, difficulties in maintaining residuals at points in a distribution system or a gradual disappearance of residual may indicate that the water or pipework has a high oxidant demand due to growth of bacteria [11]. The **ORP** measurement can also be used in the operational monitoring of disinfection efficacy. It is possible to define a minimum level of ORP necessary to ensure effective disinfection [10]. This value has to be determined on a case-by-case basis; universal values cannot be recommended.

Turbidity is a measure of suspended solids. With chlorine, this is probably the most important non-microbial parameter than can provide significant data about contamination. It is not associated especially with faecal material, but increases in turbidity are often accompanied with increases in pathogen numbers, including cysts or oocysts [10]. It can be useful also to consider the Total Organic Carbon (TOC) parameter approximated by UV/VIS absorption measurement, which characterizes the nutriment concentration in the water, so a potential re-growth rate.

Colour in drinking water may be due to the presence of coloured organic matter, e.g. humic substances, metals such as iron or manganese. The appearance of colour in water is caused by the absorption of certain wavelengths by specific substances. Change in colour from that normally seen can provide warning of possible quality changes linked for instance to corrosion problems.

A decrease of water **pressure** will allow the ingress of contaminated water into the system through breaks, cracks, joints and pinholes. Moreover, contamination could also appear through human error resulting in the unintentional cross-connection of wastewater, backflow from hot water production system or through illegal or unauthorized connections. In this last case, **temperature** will be helpful to analyse the contamination origin. Moreover, the growth speed of biomass is correlated with temperature.

The mineral content of water resource could be approached by the **conductivity**. Indeed, surface and ground water have specific conductivity. A change in this parameter in drinking networks, is usually linked to a modification of the origin of the water: exchange from municipalities, different resource used…

According to the test made by the EPA [9] with the injection of pollutant in water, parameters showing the most significant variation are chlorine and turbidity. Instead of turbidity, we may have to consider the more generic term of "optic measurement".

The table 1 lists the parameters that need to be under survey. A range of their possible values has been added.

Temperature	< 25 °C
Pressure*	3 - 10 bar
pH	6,5 - 9
Turbidity	<2
color	<15
Conductivity	200 - 1100 µS/cm
Free chlorine**	0,1 - 0,3 mg/L
COT (UV/VIS)	2 mg/L
ORP	-

** For water with chlorine - * generaly observed

Table 1: List of parameters

Several measuring principles are detailed below. Adequacy to low cost and online measurement objectives is also analysed.

III.1. CHLORINE

The only way to measure chlorine with a low maintenance (without reagent) is the three electrodes amperometric method [12]. The principle of amperometry [13] is based on the measurement of the current between the working and counter electrode which is induced by a redox reaction of the working electrode. The conditions are chosen in such a way that the current is directly proportional to the concentration of a redox active species in the analyte solution. The electrical potential of the working electrode *versus* the measured solution is achieved by a separate Reference Electrode and is controlled by a tuning (potentiostat) electronic system (figure 2).

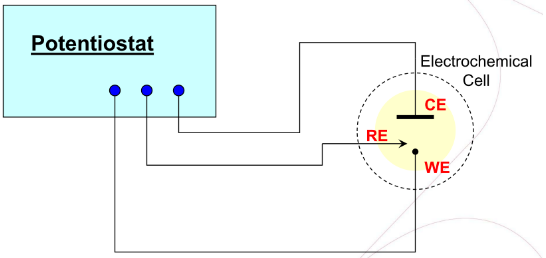

Figure 2: Amperometric 3 electrodes principle

It's important to keep in mind that the amperometric method measures the Free Active Chlorine. When chlorine is added in water, it is dissociated into 2 species [14]: potential chlorine (ClO^-) and free active chlorine ($HClO$) in equilibrium with pH dependency. The addition of potential chlorine and free active chlorine is the Free Chlorine. However, the water quality management is achieved with the concentration of free chlorine. The figure 3 shows the equilibrium [14] between the 2 chlorine species:

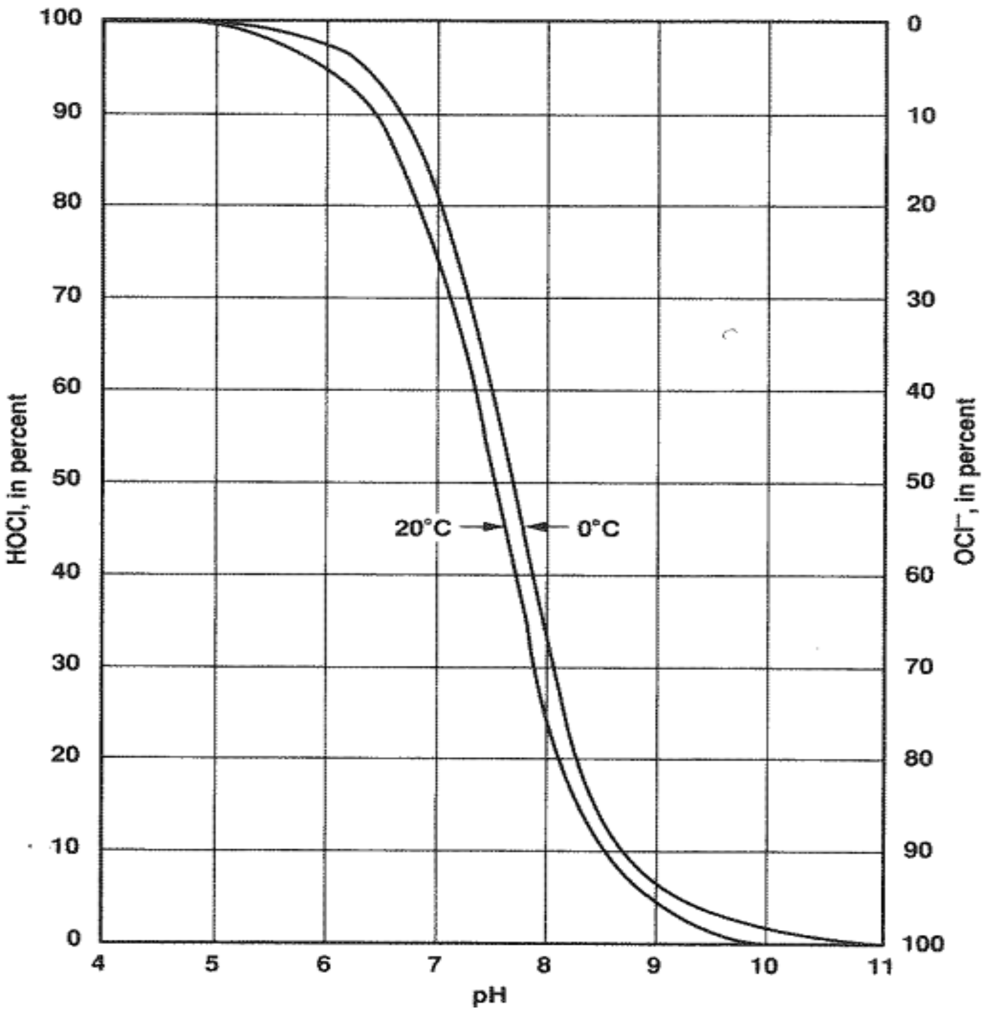

Figure 3: Molar fractions for the three compositions of free chlorine in water as a PH function

The concentration of free chlorine is measured by the DPD method, which is the reference measurement. The measurement principle is a colorimetric measure with reagent. Measurement is made according to norm ISO 7393-2 [15]. It uses the diethyl-p-phenylene diamine (DPD) in an acid medium (pH = 6.5) which colours the sample in red proportionally to the free chlorine concentration. To compare the DPD measurement to the amperometric electrode one, it is necessary to convert the free chlorine in free active chlorine. To achieve that you need to know pH and temperature of the water. The formula for the conversion [14] is:

$$[FC] = [HOCl] + [ClO-]$$

$$[FC] = [HOCl] \times (1 + 10^{pH-pKa})$$

$$\text{with } pKa = 5.43 + \frac{616.25}{T}$$

Where [FC] is the Free Chlorine and [HOCl] is the free Active chlorine.

For our application, pH measurement would be impractical and cost prohibitive due to the maintenance operation more or less close to one month. Nevertheless, the power of disinfection of the free active chlorine is about twenty five times more than that of the potential chlorine [16]. One explanation is that bacterial membranes are lipid media with a negative charge in which negatively charged ions are not soluble (ClO-) while the chemical structure of hypochlorous acid allows it to penetrate the cytoplasmic membranes of micro-organisms [17]. Thus the concentration of the Free active chlorine seems to be objectively a more satisfactory quality parameter. Moreover, pH is quite stable in the drinking water network (controlled water treatment parameter), so it would be easily possible to calculate free active chlorine.

III.2. TURBIDITY

DIN/EN 27027 (ISO 7027) [18] is the standard method to measure turbidity in drinking water in Europe. This norm is very important and provides a common language about a measure, the interpretation of which is not always obvious. The measurement of turbidity is related to the weight reported by volume (g/L) of material suspended in a liquid. In spite of what might be the common opinion or what information instrument manufacturers might give, the link between turbidity and quantity of suspended matter is not trivial. Turbidity is measured by observing the reaction of a light beam passing through a sample (transmission, diffusion…). ISO 7027 defines the procedure and the nature of the light beam: we need to measure the intensity of the beam with an angle of 90 degrees (±2.5 °) compared to its source. This source has a wavelength of 860 nm (± 30 nm). The results obtained with this procedure depend heavily on the nature - especially the size- of particles. If we take 2 samples with the same weight of suspended matter (g/L) but with particles of different sizes – the sample which contains smaller particles returns a stronger signal. ISO 7027 solves this problem by imposing a protocol for the calibration based on Formazine whose particle size is controlled. Thus, each measure is given in FNU (Formazine Nephelometric Unit) which provides a common language.

The new optic technologies are compatible with the low cost approach. The LED (Light-Emitting Diode) are an optoelectronic compounds thus they are managed by the Moore law [15] and the price much decreases with the quantity of pieces. An example is the turbidity sensor which appears in the apparatus for private consumption in washing machine application. Even if the conditions are very different in our application (turbidity sensor is calibrated at each cycle of the washing machine), a transfer of technology must be possible. This is important to control the long-term stability and the repeatability/reproducibility of these kinds of device must be not forgotten. These parameters are obviously taken in account in the sensor selection after long-term testing. False negative (or type II error) should be considered for the sensor network. And, sensor placement aims to minimize several objectives of which the type II error. Also, the risk for a real contaminant event to pass unnoticed (undetected) is low.

III.3. UV ANALYSIS

The UV analysis is an alternative measurement method to estimate the concentration of organic compound in water. The most common wavelength is 254 nm. At this wavelength, turbidity is highly influent and the result needs to be compensated with the Turbidity measurement as shown in the figure 4 [19].

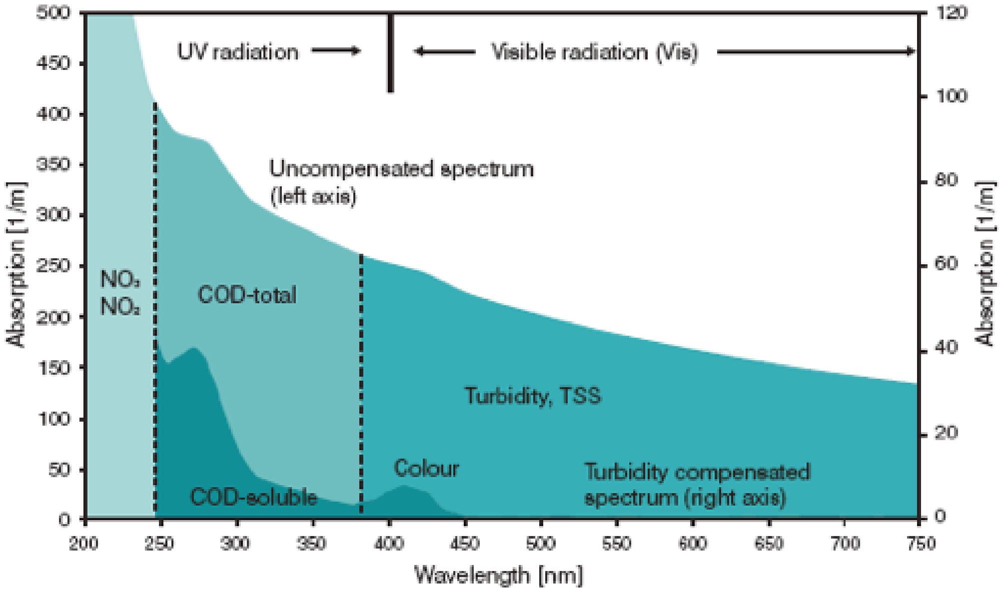

Figure 4: Influence of turbidity in a UV/VIS spectrum

The wavelength of 254 nm is the most important one to estimate organic compounds in water; nevertheless as we said previously, it is essential to compensate it (influence of solid particles) with a wavelength in visible domain. Most of the sensors on the market to measure UV/VIS are very expensive and not fitted with the in-pipe direct insertion (Spectrolyser from S: CAN, Trios, UVAS from HACH). For example, the performances of the S::CAN device are well known (indeed a large study was done in Techn'Eau European project). This is a good device nevertheless it is quite expensive taking into account our objective to wide spread of sensors network. Moreover, this device is not adapted to in-line measurement; such device could not be inserted directly and easily on the real pipe. Usually it is put in derivation with water losses, contamination risks, power supply constraints. The essential gap between the existing technologies and technologies fitted with our specifications are the energy consumption, the design of the probe for a direct insertion in the pipe and the price.

III.4. CONDUCTIVITY

The conductivity is the ability of a material to conduct electric current. The basic principle [12](2 electrodes) by which instruments measure conductivity is simple - two plates are placed in the sample, a potential is applied across the plates (usually a sine wave voltage), and the current is measured. Conductivity, the inverse of resistivity is determined from the voltage and current values according to Ohm's law.

The measurement principle of a four electrodes conductivity is to inject a voltage in phase opposition in the 2 couples of electrodes and measure the voltage of the two internal electrodes and the current generated. The conductivity (S/cm) of the solution is the inverse of resistivity:

$$1/R = I/U.$$

(R: Ohms - I: Ampere U -: Volt)

This measurement principle allows compensating the fouling of the conductivity electrode by a monitoring of the electrode potential. The current which is injected in the electronic system to regulate the potential is considered as a fouling indicator. With this monitoring of the potential and compensation of the fouling, the maintenance period is much longer than with a 2-electrodes principle. More than an increase of maintenance period time, this measurement principle gives a validation of the conductivity measurement.

III.5. PRESSURE

The Pressure parameter is easy to measure and cost effective, thanks to micro-electronic technologies. The measurement principle is that a piezoresistive material changes its electrical resistance when a mechanical stress is applied, in our case the water pressure. Piezoresistive sensors [12] are made with silicium component and can be produced by micro-electronic industries: large and automatic production on wafer (silicium disk) (Figure 5). These kinds of processes are often used in different sectors like the car industry, aeronautics, diving material etc. This technology allows a very low production cost, high accuracy and a long lifetime. Moreover, due to the component size, a high integration is permitted; this is a huge advantage for a multi-parameters probe development.

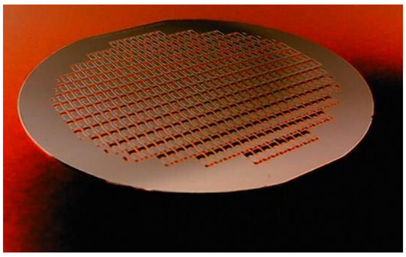

Figure 5: 4 inches Wafer of Piezoresistive sensors

IV. SPECIFICATIONS

Considering that we want to install a large number of sensors, any constraints which would seem insignificant when sensors are used normally can become really important in a large deployment of measurement points.

- Costs
  It is time to start the revolution of 'low cost'in environmental instrumentation. Today you can buy a car for 10k€ with about 50 sensors. You often buy a sensor for a single parameter for water analysis no less than 10k€… there is a huge difference! This is the strategy to develop early warning sensors network with numerous and cheap multi-parameter sensors throughout our distribution systems. To follow this strategy, we could take inspiration from other sector like automobile: they succeed to reach a life time of more than 10 years, a high robustness, low cost device and also complex solutions (ABS, pressure sensors) even if measurement principles are simple. Price should be targeted less than 1 k€ for a complete multi-parameters probe. The goal is to have an Early Warning System which can be bought by a collectivity.

- Life-Time and Maintenance
  For this kind of large-scale deployment sensors, if the period of maintenance is too short, soon the probe becomes unmanageable for the operators. It is important not to increase the operational costs dramatically. The highest maintenance period is of 1 year for the first step and we wish to reach the ambitious target of 5 years. These 2 notions of lifetime and maintenance are to be considered together: another important notion is the training level of the worker who will be in charge of maintenance. The more the maintenance is complex, the more it can become expensive. Thus, the acceptable maintenance which is chosen is to change the multi-parameters probe or just clean it – Thus the life time should be equal to the maintenance period.

- Energetic independence
  Only a few measurement points will be near a power supply and it would be too difficult to implement a power source near each probe. For example, a standard lithium battery can have a capacity of 13 Ah (LSH20 from Saft). More, we have to consider the environmental aspect and the decree D3E [20] which requires special and controlled a waste treatment. Thus, this low consumption aspect is directly linked to the operation costs. The energy consumption can be divided in 2 parts: the measurement and the communication system.

- Wireless communication
  It's obvious that we cannot install a network cable throughout the city. Different ways of managing these issues are available. Constraints must taken into account, frequency of communication (impact on energy consumption), existing infrastructure (GSM, 3G…), cost of the transmission. The choice of communication solution and the communication frequency is linked to the intelligence in the multiparameter probe. Indeed, if the intelligence is in the probe it communicates when it chooses - or the intelligence is in the central processing unit and the probe communicates regularly (with a higher frequency).

- Water loss
  Some measurement techniques use reagent, in this case, pipe derivation (source of permanent leak) and waste collection must be planned. Environmental, economical and sanitary impact should be taken into account. Several hundred leaks (from 5 to 50L/h each) provoke an increase in operating cost which is not sustainable. Derivation pipe increases the risk of contamination, leak (broken pipe) and operating issues. For these reasons no derivation and no water loss should allowed.

- Easy Installation
  The probe must be installed without stopping the pipe flow. One solution is to install a water saddle tee with a shut off valve. The difficulty is then to set the probe in the flow with pressure. Since there is pressure and considering the relatively large diameter of the probe, the strength to insert the probe in the pipe is about equivalent to a weight of 130 kg (10 bars for a probe with a diameter of 4 cm). One solution is to design the bottom of the probe to install it like a screw with a spanner. Then the sealing is due to the screw thread and to an O-ring (Figure 6).

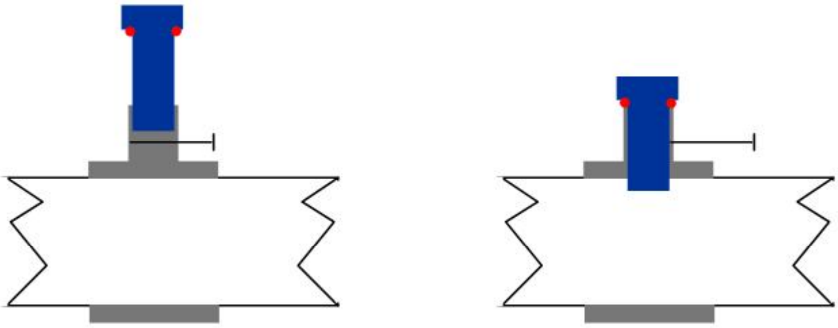

Figure 6: Installation scheme for the probe insertion

- Canalization diameter
  On Work Package WP2.2, the probes will be placed on the network with an optimization strategy. Thus, we don’t know yet the diameter of the pipe. It is important that the installation method is fitted with all the canalization diameters – from 15 mm diameter for the smallest end user connexion to the biggest diameter of a feeder.

V. OTHER IMPORTANT ASPECTS

V.1. SANITARY CONFORMITY AGREEMENT FOR DRINKING NETWORKS

The goal of the Work Package is to develop an EWS. For this purpose sensors must be installed directly in the pipe. In order to put a device in the drinking water distribution network, proof must be given that there is no danger for the consumer. Several agreements are imposed in Europe. The French one remains one of the strictest. ACS (Agrément de Conformité Sanitaire) is the French Sanitary conformity agreement for all apparatus in contact with drinking water. There are 3 kinds of agreements: Process, Material and accessories [21]. If the probe is made of at least 2 components – one of them being of organic nature – it will have to get the agreement that is made for accessories. This agreement is divided into 2 phases. The first one is an investigation on the major organic compounds. This investigation is meant to find out exactly all the molecules that exist in the material. All suppliers who have contributed to the production of the material are contacted. The second phase is the “migration study”: the part of the probe which will be in contact with water is placed in EVIAN™ water with 1ppm of free chlorine during 24 hours. The water volume is proportional to the surface of the probe in contact with water ($3cm^2/L$).

In Germany, the agreement is the KTW (Kunststoffe und Trinkwasser) [22] and deals with plastic materials. The first phase is similar to the French one and the most important difference with migration study is the type of water which is used – tap water with no imposed chlorine concentration. In England, the agreement is the WRAS (Water Regulations Advisory Scheme) [23] - English norm BS 6920 (2000). This agreement concerns the non metallic materials and is built around 5 tests: taste and odour, colour and turbidity, migration of heavy metals, toxicity test of the residual in water in contact, development of aerobic flora.

The Commission of the European Union initiated the establishment of a European system for the acceptability of materials in contact with water called EAS (European Acceptance Scheme). Since the directive 98/83/CE [24] was signed in 1998, the European commission has been trying to homogenize the rules and the protocol of tests to obtain the agreement. Today there is no common protocol in Europe. Nevertheless, countries are bound together and when the agreement has been signed in one of them, it will be easier to sign it in another country. Considering that the French agreement is rigorous and internationally recognised, we shall start working on this project to get this one first.

V.2. DATA ANALYSIS

Considering all the events that we have to detect (that are more numerous than the variables we are dealing with) and the non-specific measures that we have access to, data treatment is significant. We can easily say that the data treatment is as important as the sensors' performances. We know from the beginning of the project that it is impossible to have a specific measurement for each attack agent (maybe excepted for the radiological attack). In this case the goal is to have a large number of independent variables. Of course, each parameter of the multi-parameters probe is a variable but – if the performance of the sensor is satisfactory- , we can consider for instance the first order derivative function as another independent variable (for instance: the chlorine concentration and the kinetics of chlorine concentration decrease). We will illustrate different ways of data mining in the following chapters.

There are two methods to classify an event with the non-parametric measurements: the non supervised classification and the supervised classification. The first one is based on information extraction – an example is the PCA. The Principal Components Analysis (PCA) is a very well known technique to analyse and interpret a multivariable dataset. We use this method to reduce the dimension (number of variables) in the dataset, without reducing too much the information given by this dataset. It can be considered as a projection of the variable on an axis. The new variables (often 2 or 3 to have a graphic representation) are linear combinations of the raw variables. This axis is emphasized to obtain the best possible variability.

The supervised classification is based on a learning phase which is the construction of a model that describes a set of predetermined classes. The algorithm EVE (Effluent Variation Evaluation) is a good example of a supervised classification. This method has been developed to help in the management of the industrial Waste Water Plant to start an alarm when the quality of the influent changes and can damage the process of wastewater treatment. The detection consists in evaluating the variation of values compared to a historical data set, and computing the variations together to detect abnormal changes [25]. This detection algorithm is applied to a UV-VIS spectrometer – thus parameters are the absorption at several wavelengths. The figure 7 shows the data treatment principle. It is based on the study of the cross derivative values. This method is more focused on the variation of parameters than on the values of parameters themselves.

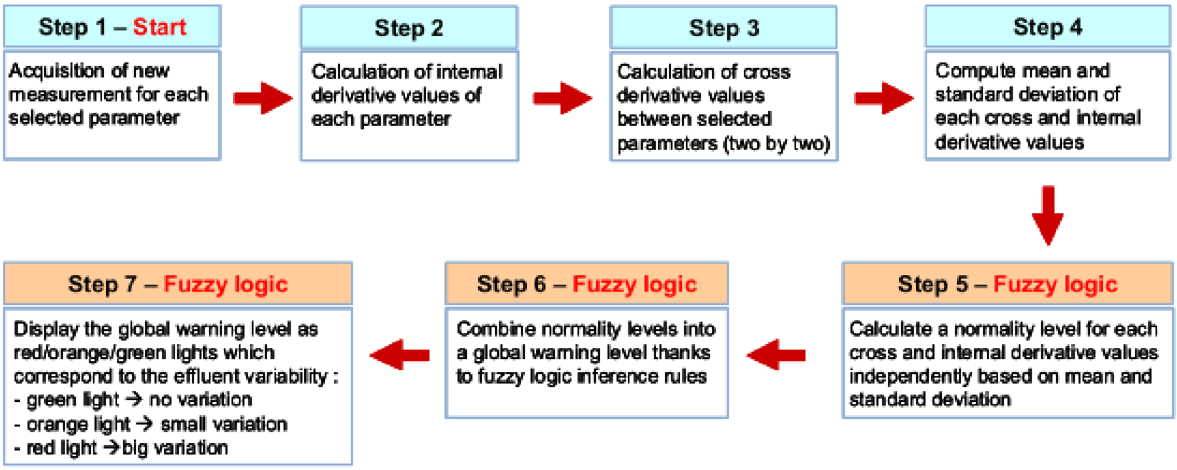

Figure 7: Protocol for data treatment and abnormal change detection [23]

PART II - MATERIAL & METHOD

I. MULTI-PARAMETERS PROBES ON THE MARKET

The short duration of the project did not allow us to do important development on sensors. The goal was to find an apparatus almost ready to use for the EWS. The methodology used was to perform a market review in order to find the most fitted multi-parameter probe for the EWS on a real network. It is why simple quotation rules have been chosen (I.12).

The table 2 shows the suppliers who propose a commercially suitable solution. We have listed all the multi-parameters probes available on the market. These probes are not only dedicated to drinking water. This exhaustive list shows us the several solutions that suppliers can offer. The chapter below will list the pros and cons of each proposed solution. Criteria are accuracy of measurement, maintenance needs and costs. We have contacted most of the suppliers to discuss their product performances and the possibility to adapt them to our specifications.

This time, we decided not to consider the multi-parameters solution formed by a monitoring panel like it has been done in the EPA approach (see chapter about specifications) – and chose to consider only multi-parameters probes. Many solutions are not fitted to the drinking water network application but to the environmental survey (lake, oceanographic studies) but this list of multi-parameters probes technology gives us an overview of several technologies fitted to this kind of applications.

	Intellisonde	Six cense	Pipesonde	Mesm3000	W-20xd	Troll9500	Ysi	Quanta g	Ms 5	Manta	Cs304
Manufacturer	Intellitec	Censar	Hach lange	Silsens	Horiba	In-situ inc.	Ysi	Hydrolab		Eureka	Greenspan
Price	6 K€	9 K€	9 K€	1,5 K€	20 K€	4 K€	6 K€	-	-	3,5 K€	-
Diameter	36 mm	37 mm	43 mm	42 mm	46 mm	47 mm	42	44 mm	44 mm	-	60 mm
Temperature	X	X	X	X	X	X	X	X	X	X	X
Turbidity	X		X		X	X	X		X		
Conductivity	X	X	X	X	X	X	X	X	X	X	X
pH	X	X	X		X	X	X	X	X	X	X
ORP	X	X	X		X	X	X		X	X	
Chlorine	X	X		X			X				
Monochloramine	X	X								X	
Oxygen	X		X			X		X	X		X
Color	X										
Pressure	X		X	X	X	X		X			

Table 2: Multi-parameters probes on the market

I.1. HACH – THE IN-PIPE PROBE.

Figure 8: Hach - In Pipe Probe

PARAMETER	RANGE	ACCURACY
pH	0 - 14	0,2
ORP	-999 to 999 mV	20 mV
Conductivity	100µS/cm	1% of reading
Turbidity	0 to 100 NTU	5% of range
Dissolved Oxygen	0 to 20 mg/L	0,1 mg/L up to 8 mg/L 0,2 mg/L above
Line Pressure	0 to 20 bar	0,03 bar
Temperature	-5 to 50°C	0,1°C

Table 3: Hach In Pipe Probe - specifications

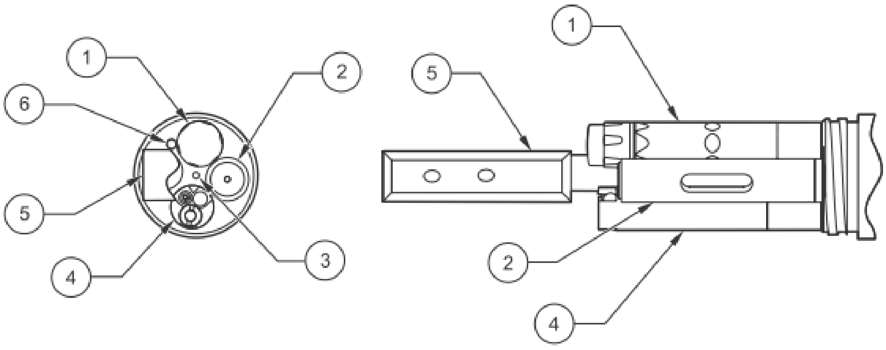

Figure 9: In Pipe Probe design - sensors' locations

1. LDO	3. Pressure	5. Turbidity
2. Conductivity	4. pH/ORP/Reference	6. Temperature

Contacts:

Mitchell Thomas	Product Manager (USA)
Mickael Haeck	Product Manager (Germany)

This probe is only available in the USA and cannot be sold in Europe for the moment because they don't have the EU agreement. This probe is integrated in a complete solution for the detection of incident in the drinking water network: other sensors (Cl17 for chlorine concentration, COT meter…) and a SCADA system (Supervisory Control and Data Acquisition): the Guardian Blue. It is an automate containing a library with the behaviour of all sensors during the incident or attack. With this kind of finger print library, the Guardian Blue can detect and identify several incidents.
The minimum diameter of the pipe is 8 inch (20 cm) because of the turbidity sensor (length: 14 cm).

Dissolved Oxygen concentration is measured following the LDO measurement principle (Luminescent Dissolved Oxygen). The sensor cap is coated with a luminescent material. Blue light from a LED is transmitted to the sensor surface. The blue light excites the luminescent material. As the luminescent material relaxes, it emits red light. The period of time between the moment when the blue light was sent and the red light is emitted is measured. The time it takes for the red light to be emitted depends on the amount of oxygen. This time is measured and correlated to the oxygen concentration.

I.2. CENSAR – SIX CENSE

Figure 10: Censar - Six Cense

PARAMETER	RANGE	ACCURACY
pH	0 - 14	0,3
ORP	-1,4 V to 1,4 V	1% of range
Conductivity	0,1 to 10 mS/cm	0,01 mS/cm
Dissolved Oxygen	0 to 20 mg/L	0,1 mg/L
Temperature	0 to 50°C	0,25°C
Chlorine	0 to 5 mg/L	0,04 mg/L
Monochloramine	0 to 20 mg/L	0,1 mg/L

Table 4; Six cense - specifications

Contact:

Roy Moore	Director

Censar (**C**hemical **EN**vironmental **S**ensing **Ar**ray) Technologies was founded in the year 2002 in order to acquire key technology from Water Security and Technology, which owns a former division of Siemens - Siemens Environmental Systems Labs (SESL).

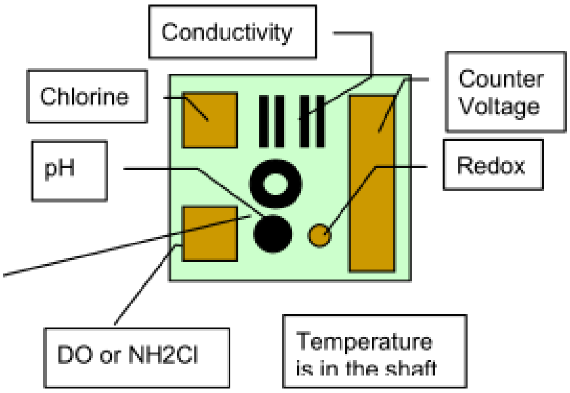

Figure 12: Six Cense - sensors' locations

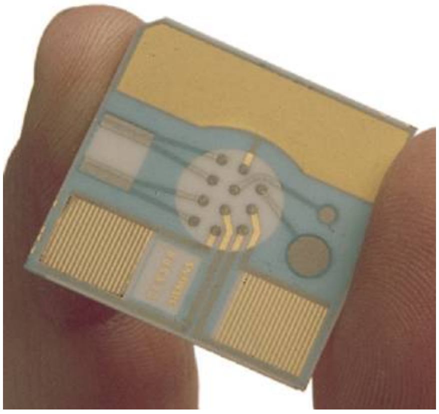

Figure 12: six cense chip

Chlorine sensor measurement principle is the Voltametric technique. It uses proton generator and microlines to measure chlorine and monochloramine, independently from flow and pH. Proton generator produces acid pH in the sensor's environment. pH is maintained acid and the chlorine measurement is independent of pH (free chlorine is measured). Conductivity is measured using a 4-point Alternative Current method to minimize the effect of fouling on the chip electrodes. This parameter has temperature compensation and can be filtered (damped) to reduce noise, although this is not usually necessary. Dissolved Oxygen Measurement principle is the Voltametric technique, using the same basic technology as the chlorine sensor, but with different operating parameters. ORP Is measured with the Galvanometric technique is used and can measure the voltage between the reference electrode and a platinum electrode.

I.3. INTELLITECT – INTELLISONDE

Figure 13: Intellitect - Intellisonde

PARAMETER	RANGE	ACCURACY
pH	0 - 14	0,1
ORP	-1,4 V to 1,4 V	1 mV
Conductivity	0 to 100 mS/cm	0,001 mS/cm
Turbidity	0 to 100 NTU	0,1 NTU
Dissolved Oxygen	0 to 20 mg/L	0,2 mg/L
Line Pressure	0 to 30 bar	0,03 bar
Temperature	-5 to 50°C	0,1°C
Chlorine	0 to 5 mg/L	5%
Monochloramine	0 to 5 mg/L	0,2 mg/L
Color	0 - 50 Hazen	0,2 Hazen
Flow	0 to 2 m/s	5%

Table 5: Intellisonde specifications

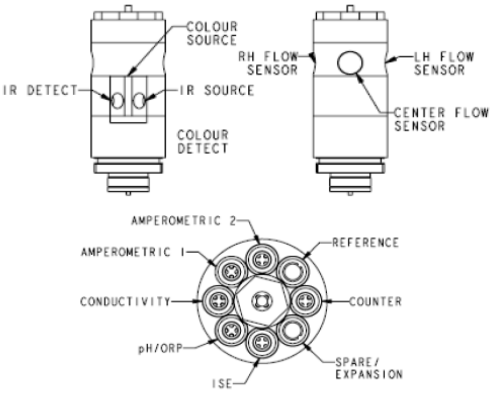

Figure 14: Intellitect - sensors' locations

Contacts:

John Howell	Director
David Vincent	Technical director
Steve Gill	Marketing Manager
Sanath Ediriweera	Engineer

Each sensing element is easily removable from the probe.
To enable the measurement when the water flow is too low, a stirrer mixes the sample in the environment of the sensing elements.

The chlorine sensor is the same as the Censar one. A flat pH standard electrode made of glass is custom designed in a small sensor body. A very high input impedance measures the pH electrode potential. Lifetime is limited by the reference electrode or fouling (less than 6 months – supplier data)._ORP is measured with a small platinum wire which is included in the pH sensor body. The voltage that this wire maintains in the water, is measured by the same design circuit as the pH sensor, and the voltage reported with no further processing._For the temperature a thick film printed Pt1000 temperature sensitive resistor, housed behind a stainless steel housing in close contact with the water, measured with a constant current. The supplier manufactures a printed, platinum 4-electrodes conductivity sensor. Measurement is done by a constant voltage alternative Current. Turbidity is measured with a single source (LED emitting at 860nm as required by the standard, ISO 7027) and a 90° detector measures the light scattered from particulates in the water in front of the probe (the detector faces upstream, maximising flow against the sapphire windows to minimise fouling). Closed-loop control of LED brightness and phase sensitive detection of the scattered light is used to maximise stability and sensitivity. A conventional, current driven external pressure will be used. The pressure sensor is external to the system; a 4-20 mA signal is connected with the probe electronic box. A single LED light source (410 nm) and in-line detector are used to measure apparent colour of the water. Absorbency is a measure of the light that has been lost in transmission which is proportional to colour.

I.4. SILSENS

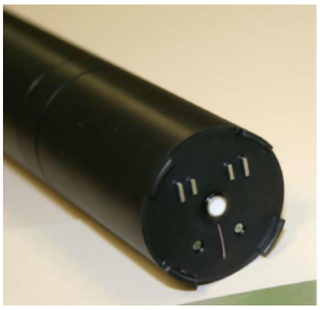

Figure 15: Silsens - MEMS3000

PARAMETER	RANGE	ACCURACY
Chlorine	0 to 2 mg/L	0,01
Pressure	0 to 10 bars	0,05 bar
Temperature	0 to 40 °C	0,1 °C
Conductivity	100 to 600 µS/cm	5 µS/cm

Table 6: MEMS 3000 - specifications

Contacts:

Yves De Coulon	Technical Director
Carine Beriet	Product Manager

Silsens SA is a private company which was founded in January 2006, in Neuchâtel, Switzerland, after having acquired Microsens Products SA (founded in 1991). The company develops, produces and distributes gas and electrochemical sensor products for air and water security and quality applications. Silsens sensor technology has started in the 1980s when a close collaboration with CSEM, the Swiss Center for Electronics and Microtechnology, began.

The chlorine concentration is measured with a 3 electrodes amperometric sensor.The working and the counter electrodes are platinum thin film layers manufactured on Si-wafer. Furthermore, the reference electrode is manufactured in a thin layer of Ag/AgCl, which is manufactured by a similar process. Organic membranes are photopolymerized on the working electrode surface from the measured solution leading to reproducible diffusion conditions. The selectivity is increased by the photopolymerized membrane.

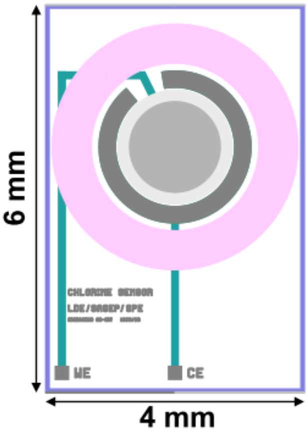

Figure 16: Silsens - Chlorine sensor dimensions

Figure 17: MEMS3000 - Chlorine sensor

Conductivity sensor is a 4 electrodes measurement principle. Electrodes are made in stainless steal. There is a temperature compensation of 2%/°C. This measurement principle enables to compensate the fouling state of the sensor by a regulation of the voltage between the electrodes. The current which is injected to maintain the right voltage is analysed and used to have a fouling index of the conductivity sensor. Pressure sensor is a Piezoresistive silicon micro-machined sensor

I.5. YSI – PROBE 600DW B

Figure 18: YSI - 600DW B

PARAMETER	RANGE	ACCURACY
Chlorine	0 to 3 mg/L	0,05 mg/L
pH	0 - 14	20%
Temperature	0 to 40°C	0,1°C
Conductivity	0 to 100 mS/cm	0,001 mS/cm

Table 7: 600 DW B - specifications

Contact:
Christian HARITCHABALET Anhydre (Distributor)

YSI (Yellow Spring Instrument Company) is a firm which was founded in USA, OHIO in 1948. They are specialized in instrumentation for environmental measurement with number of multi-parameter probes for environmental applications (ocean survey, ground water, lake…).
This probe has a diameter of 4,2 cm.

Chlorine measurement principle is a 3 electrodes amperometric with membrane. Electrodes are in silver and platinum. The membrane is cut and installed by the operator. The time between 2 maintenance actions recommended by the operator is 2 weeks. The pH electrode is a classical pH measurement principle with a glass electrode and with a reference containing gelled buffer solution (pH=7). A cell with four pure nickel electrodes measures it. This four-electrode measurement gives the possibility to compensate the fouling on the conductivity sensor.

I.6. HORIBA – W20 XD

Figure 19: Horiba – W20 XD

PARAMETER	RANGE	ACCURACY
ORP	-1999 to 1999	15 mV
Line Pressure	0 to 10 bar	5%
Turbidity	0 to 800 NTU	0,1 NTU
Temperature	0 to 55°C	1°C
Dissolved Oxygen	0 to 20 mg/L	0,2 mg/L
Conductivity	0 to 10 S/cm	5%
pH	0 - 14	0,1

Table 8: W20 XD - specifications

Horiba is a Japanese company which is famous for its optic sensors and gasses analyzer.

Measurement principles are very usual: platinum electrode and glass electrode for respectively the ORP and pH sensor, a 4 alternative current electrode for conductivity and a galvanometric sensor for the oxygen sensor.

Contact:

Jean Pierre Ballot	Marketing Director (France)
Takeshi Kobayashi	Product Manager (Japan)

I.7. EUREKA - MANTA BIG4

Figure 20: Manta - Big 4

PARAMETER	RANGE	ACCURACY
Temperature	-5 to 50°C	0,01°C
pH	2 to 12	20%
ORP	-999 to 999 mV	20 mV
Conductivity	0 to 112 µS/cm	5%
Dissolved Oxygen	0 to 200%	2,4%
Ammonium	0 to 200 mg-N/L	10%

Table 9: Big 4 - specifications

Eureka was founded in 2002 by Hydrolab and YSI veterans. Products are dedicated to the environment survey.

Measurement principle for pH, ORP and conductivity are the same than the U22XD. Oxygen sensor is a optical sensor (see I.1.). Ammonium is measured with a Ion Specific Electrode (ISE) Sensor (pH electrode with a ammonium selective membrane).

I.8. HYDROLAB – QUANTA G

Since 1968, Hydrolab has been specialized in multi-parameters probes' conception. They are involved in resource protection measurement. Since 2002, they have joined the Hach Company and relocated operations to Loveland, Colorado.

Figure 21: Hydrolab - Quanta G

PARAMETER	RANGE	ACCURACY
Temperature	-5 to 50°C	0,2°C
Dissolved Oxygen	0 to 50 mg/L	0,2 mg/L for 0 to 20mg/L and 0,6 after
Conductivity	0 to 100 mS/cm	1%
pH	2 to 12	0,2
ORP	-999 to 999 mV	25 mV
Pressure	0 to 10 bar	0,03 bar

Table 10: Quanta G - Specifications

Dissolved Oxygen concentration is measured with a clarck electrode. Conductivity sensor is a 4-graphite electrode conductivity, platinum electrode and glass electrode for respectively the ORP and pH sensor.

I.9. HYDROLAB - MS 5

Figure 22; Hydrolab - MS5

PARAMETER	RANGE	ACCURACY
Temperature	-5 to 50°C	0,1°C
Dissolved Oxygen	0 to 60 mg/L	10%
Conductivity	0 to 100 mS/cm	0,5%
pH	0 - 14	0,2
ORP	-999 to 999 mV	20 mV
Pressure	0 to 20 bar	0,01 bar
Turbidity	0 to 100 NFU	1%

Table 11: MS 5 - specifications

The 4 first parameters in the table 11 are plugged originally on the probe. 2 of the 3 others can be optionally added. The measurement principles are the same than the quanta G. The turbidity measurement is consistent with the norm ISO7027 (see Part 1 – III.2) with a self-cleaning system (brush).

I.10. GREENSPAN – CS304

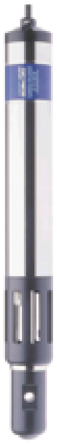

Figure 23: GreenSpan - CS304

PARAMETER	RANGE	ACCURACY
Temperature	0 to 50°C	0,2°C
Dissolved Oxygen	0 to 20 mg/L	0,2 mg/L
Conductivity	0 to 60 mS/cm	0,5%
pH	0 - 14	0,2

Table 12: CS 304 - Specifications

pH is measured with a glass electrode and dissolved oxygen with a clarck electrode. The conductivity is measured with an inductive conductivity sensor. Here, two inductively-coupled coils are used. One is the driving coil producing a magnetic field and it is supplied with accurately-known voltage. The other forms a secondary coil of a transformer. The liquid passing through a channel in the sensor forms one turn in the secondary winding of the transformer. The induced current is the output of the sensor.

I.11. IN-SITU INC – TROLL 9500

In-situ Inc manufactures and sales scientific equipment for the environmental and water-monitoring markets. They have instruments that monitor groundwater, surface water, and coastal waters. They are based in Colorado (USA).

Figure 24: In-Situ Inc - TROLL 9500

PARAMETER	RANGE	ACCURACY
pH	0 - 12	0,1
ORP	-1,4 V to 1,4 V	4 mV
Conductivity	5 - 20 000 µS/cm	2 µS/cm
Turbidity	0 - 2000 NTU	2 NTU
Dissolved Oxygen	0 to 20 mg/L	0,2 mg/L
Line Pressure	0 - 20	0,05%
Temperature	-5 - 50°C	0,1°C
Nitrate	0,14 - 14 000 ppm (N)	10%
Ammonium	0,14 - 14 000 ppm (N)	10%
Chloride	0,35 - 35 500 ppm (Cl)	15%

table 13: TROLL 9500 - Specifications

The Dissolved oxygen is measured with a LDO sensor (see I.1). Turbidity is measured according to the ISO7027 norm. Nitrate, Ammonium and chloride are measured with a Ion Selective Electrode sensor. pH and ORP are measured on the same electrode (platinum disc on the pH electrode). Pressure is measured with a piezoresistive sensor.

I.12. COMPARISON AND SELECTION OF THE AVAILABLE PROBES

To compare all these probes, we have defined 3 criteria:

- Insertion depth linked to the pipe diameter, less it is higher length of network could be addressed (especially end-user pipe). It is important to install easily the probe on the pipe. One of the most important criteria for the installation is the “insertion depth”. This is the length of the probe which must be in contact with water in the pipe. For example, if insertion depth is 5 cm, for canalisation with a diameter under than 10cm you must install a chamber. To install the chamber you must stop the flow and thus the installation cost become very high.
- Price: lower is the price higher is the number of point could be surveyed for the same investment
- Number and importance of measured parameters: linked to the WHO suggestion and the variety of events which can be detected. We could also in addition of security issues address simultaneously safety issues to reinforce the interest of the solution

For each criterion, we have affected a score for each probe. Table 14 defines the importance of the parameter and the score associated. For each probe, the number of points associated to the selected parameters which can be measured is added. The maximum quotation is 18 points (100%). According to our criteria, the probe which has no one of the most important parameters (Chlorine, optic measurement) has a quotation equal to zero. The maximum score is 100% for the probe which has all the useful parameters (Intellitect). The two most important parameters are Chlorine concentration and turbidity. Some drinking water networks are treated with monochloramines especially in the USA and China markets, in these cases this parameter is as important as chlorine. Nevertheless, the number of this kind of network in the world is lower than the chlorinated ones.

Parameter	Importance
Temprature	1
Turbidity	3
Conductivity	2
pH	1
ORP	1
chlorine	4
Monochloramine	3
Oxygen	0
Color	1
Pressure	2
Nitrate	0
Chloride	0
Ammonium	0
Chlorophyl a	0
Rhodamine	0
Blue Green Algae	0

Table 14: Importance of the Parameters

PARAMETERS		
6 CENSE	12	67%
MANTA	0	0%
CS304	4	22%
PIPESONDE	10	56%
W-20XD	10	56%
MS 5	8	44%
QUANTA G	0	0%
TROLL 9500	10	56%
INTELLISONDE	18	100%
MESM 3000	9	50%
YSI 6920	12	67%

Table 15: Score of each probe due to available parameters

To take into account the price of a probe, we affected the score of 0% to the most expensive probe (Horiba). Thus, each score is complementary proportional to this highest price. Results are in table 16. – Prices are given in k€.

PRICE		
6 CENSE	9	55%
MANTA	3,5	83%
CS304	*15*	25%
PIPESONDE	9	55%
W-20XD	20	0%
MS 5	*10*	50%
QUANTA G	*10*	50%
TROLL 9500	4	80%
INTELLISONDE	6	70%
MESM 3000	1,5	93%
YSI 6920	6	70%

Table 16: Score of each probe due to the price (K€)

To affect a score to the criteria ‘insertion depth’, we need to classify the probe in 3 length of insertion: the score of 100% is affected to the probes which do not need to have an insertion depth (flush mounted probe). 67% is affected to the probe with less than 5 cm of insertion depth and 33% for probes with an insertion depth of more than 5 cm. The results are in table 17:

INSERTION DEPTH	
6 CENSE	100,00%
MANTA	33,33%
CS304	33,33%
PIPESONDE	33,33%
W-20XD	33,33%
MS 5	33,33%
QUANTA G	33,33%
TROLL 9500	33,33%
INTELLISONDE	66,67%
MESM 3000	100,00%
YSI 6920	33,33%

Table 17: Score of each probe due to insertion depth

The average of the score is in table 18. The 3 first probes have a very good score compared to the others. We will test them in the SecurEau project. Despite its low quotation, we wanted to test the probe from Hach because it was widely used in the U.S. project, it could be a reference. For the moment, the supplier was unable to sell it because it was not addressed to the European market. (in addition, the chlorine sensor is not ready yet on the probe). Finally, 4 probes will be tested. All the data we used to sort the probes were given by the suppliers' specifications. A testing phase is essential.

SILSENS	81%	1
INTELLITEC	79%	2
CENSAR	74%	3
YSI 6920	57%	4
IN-SITU INC.	56%	5
HACH LANGE	48%	6
HYDROLAB	43%	7
EUREKA	39%	8
HORIBA	30%	9
HYDROLAB	28%	10
GREENSPAN	27%	11

Table 18; Average score for each probe and ranking

For the 4 selected probes, table 19 lists the pros and cons for each:

	ADVANTAGE	INCONVENIENT
SILSENS	Built for a large production	No optic measurment
	Low cost & low maintenance (once a year)	
	High accuracy	
	No insertion depth	
INTELLITECT	High number of parameters	Low Accuracy
	Easy to install	5 cm of insertion depth
		Maintenance
CENSAR	Fitted with a large production (sensors on chip)	No optic measurment
	Insertion depth can be reduce	Maintenance
HACH	High number of parameters	14 cm of insertion depth
	Experience in EPA project	Maintenance
		Accuracy

Table 19: Summary of the pros and cons for the 4 selected probes

II. TEST PROTOCOL

This test protocol is inspired from the ISO Norm 15839. It has been developed and applied in another European project called AQUAFIT4USE. This protocol is divided into 2 main parts: the first is the "laboratory tests" on synthetic sample to evaluate the performances of sensors in a controlled and simple sample. In the second part the sensor behaviour is evaluated in real conditions. This second part allows us to study the long-term drift of the sensor in a real matrix. This chapter will sum up the main information concerning sensors evaluation's methodology that will be used in this project.

II.1. DYNAMIC CHARACTERISTICS

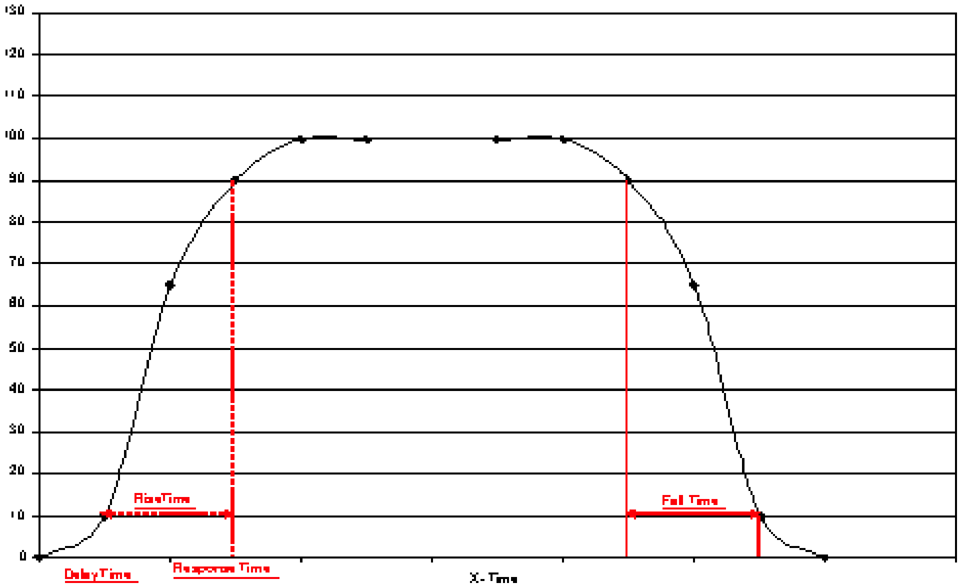

Figure 25: Dynamic response of the measuring line

Response time: T0 is the moment when the sensor is being exposed to a sudden value modification in the characteristic that has to be determined. Tr is the moment when the reading passes by the limits of a band structure which would be contained between 90 and 110% of the difference between the initial value and the end value of this sudden modification and this reading remains within this band. Response time is the difference between Tr and T0.

Delay time: Time interval between the moment when the instrument is exposed to an abrupt change of value of the characteristic to determine and the moment when the reading indicates continuously a value that is higher or equal to 10% of the difference between the initial value and the end value of the abrupt change.

Rise time: Difference between the Response time and the Delay time when the abrupt change of value of the characteristic to be determined is positive.

Fall Time: Difference between the response time and the latency time when the abrupt change of value of the characteristic to be determined is negative.

Figure 25 summarizes those several definitions. X axis represents time and Y axis the ratio between the value of the characteristic on the sample and the reading value on the instrument.

II.2. LINEARITY

The linearity of a sensor is evaluated by the value of the correlation coefficient. Its definition is given below:

$$R^2 = \frac{\left(\sum_{1}^{n}(xi - xm)(yi - ym)\right)^2}{\sum_{1}^{n}(xi - xm)^2 \sum_{1}^{n}(yi - ym)^2}$$

Where xm and ym are respectively the average of xi and yi.

The main concept is that the sensor's response is a linear function of the concentration of the characteristic to be measured and we can identify coefficients A and B of the linear expression Y=AX + B where A and B are:

$$A = \frac{\sum_{1}^{n} (xi - xm)(yi - ym)}{\sum_{1}^{n} (xi - xm)^2} \quad \text{and} \quad B = ym - A.xm$$

If we do this linear regression after a calibration (automatic or manual), A and B are significant indicators of the efficiency of this calibration. A must be close to 1 and B must be close to 0.
A and B can be interpreted as an expression of the trueness – linked to the calibration.

The interpretation of R² is not trivial, the perfect value is 1, and the difference between R² and 1 can be due to the non linearity of the measurement and/or to the dispersion of points. The coefficient R² is much influenced by the presence of aberrant points. The practice is to eliminate 10% of the most aberrant points – but not those at the extremity of the series. Of course, the choice of these points is subjective.

II.3. ACCURACY

Accuracy may be split into trueness and precision, where trueness accounts for the closeness of agreement between the mean value and the true value, while precision accounts for the closeness of agreement between the individual values among themselves. The figure 26 is a concrete and famous illustration of the difference between precision and trueness. It shows concretely what situations can occur.

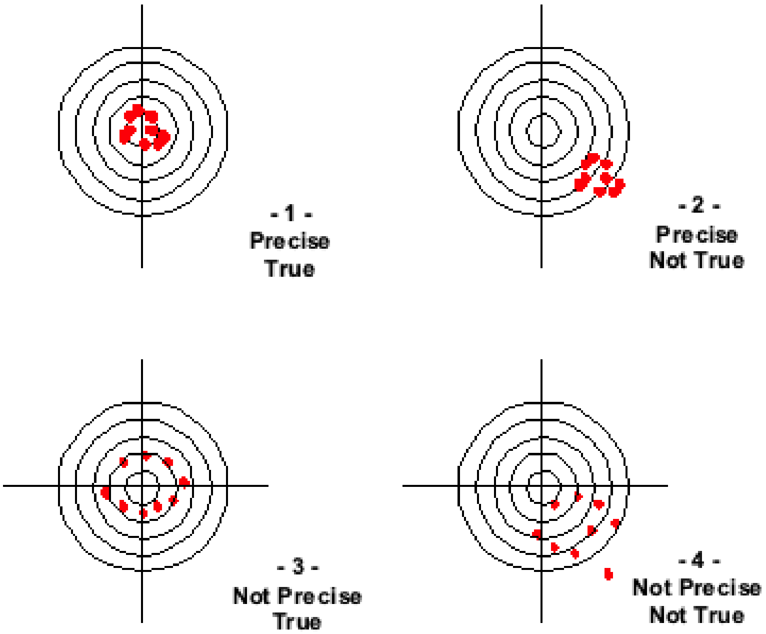

Figure 26: Trueness & precision - schematic representation

For example, for our application, precision can be considered as more important than trueness because what we want to detect when designing an early warning system is a change in water quality. Two simple mathematical tools are used to study the accuracy: the standard deviation and the average of the series.

The **standard deviation (s)** is the root of the average of the squared variations:

$$s^2 = \frac{1}{n} \sum_{1}^{n} (xi - xm)^2$$

Where xm is the average of xi

The norm already met other performance requirements – based on the standard deviation:

Limit of detection (LOD) : The smallest value of the characteristic that has to be determined and can be detected and is significantly higher than 0. We calculate the detection limit this way: we multiply the standard deviation by 3, Y1,i, for i =1 to 6. This factor 3 corresponds to 0,13% of risk to conclude that the substance is there, even though it isn't.

$$\mathbf{LOD = 3.S_{5\%}}$$

Smaller Detectable Change (SDC) : Smallest difference that is measurable significantly between two measurements. To determine the smallest detectable change as well for the high values of the characteristic to determine as for the low values and to record in the form of two different results (index 20 and index 80 respectively) calculated while multiplying by three the standard deviation of $y_{2,j}$ measurements, for J = 1 to 6 and of $y_{3,j}$ measurements, for J = 1 to 6.

$$\mathbf{SDC_{20\%} = 3.S_{20\%}}$$
$$\mathbf{SDC_{80\%} = 3.S_{20\%}}$$

Bias : Regular variation of the value measured compared to the reference value. Bias has to be determined for the high values (80%) and for the low values (20%) of the measuring range.

$$\mathbf{B_{20\%} = M_{20\%} - X_{20\%}}$$
$$\mathbf{B_{80\%} = M_{80\%} - X_{80\%}}$$

Where M is the average of the measurement and X the reference measurement.

The method that has been used to get all these results is mostly based on a repeated measurement with an average of results. For example, in the case of the dynamic characteristics, we implement an abrupt change between 20% and 80% of the measuring range 6 times. We calculate response time and other dynamic characteristics for each change and form an average. We use the same method to get the standard deviation at 5% and put the probe alternatively in a solution with a concentration of 5% of the measuring range and in a blank. We repeat the operation 6 times and then calculate the standard deviation of the 6 results.

CONCLUSION

The first part of this report deals with the environment of the Early Warning System, especially the constraints (including the sanitary conformity agreement) to integrate this system into a full-scale implementation. Specifications and measuring ranges of the different parameters have also been defined. In the second part, after the elaboration of a list of multi-parameter probes (with associated specifications). four of them have been selected. According to the manufacturer data sheets the chosen systems are as closed as possible to our specifications. The last part describes an evaluation protocol applied on sensors. Thanks to this normalized test protocol strong and objective data about the sensors' performances have been obtained which allows the manufacturer to improve its apparatus.

The EPA project, which began in 2003, has given solutions developed for the large bay sensor system market, So we have taken benefit of the major technological advances during these last 6 years. Moreover, micro-technologies are more mature since micro-electronic manufacturers (originally specialised in car manufacturing and aeronautic) develop more innovative sensors in particular in physio-chemical field. Environment and health are the most expanding domains to enlarge their market. To sum up, manufacturers are now able to produce ‘low cost’ and ‘low maintenance’ sensors for the environment.

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