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UNIVERSITÉ LILLE 1

JARINGAN AIR CERDAS: INSTRUMEN UNTUK PEMANTAUAN KUALITAS KIMIA AIR MINUM SECARA *REAL-TIME* DAN *ON-LINE* DI DALAM JARINGAN DISTRIBUSI

TESIS

Diajukan sebagai salah satu syarat untuk memperoleh gelar Magister Teknik

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SMART WATER GRID: INSTRUMENTATIONS FOR REAL-TIME AND ON-LINE MONITORING OF CHEMICAL DRINKING WATER QUALITY IN DISTRIBUTION NETWORK

THESIS

Proposed as one of the requirement to obtain a Master degree

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Pemantauan kualitas air sangat penting untuk menjamin kesehatan masyarakat. Di samping itu, efisiensi pemantauan juga harus terus ditingkatkan untuk menyederhanakan proses operasional dan meminimalisasi biaya operational. Untuk menghadapi permasalahan ini, ada sebuah sistem baru yaitu Jaringan Air Cerdas (JAC) yang menyediakan pemantauan kualitas air secara real-time dan on*line*. Tujuan utama dari penelitian ini adalah untuk memahami sistem pemantauan kualitas air minum secara real-time dan on-line di dalam jaringan distribusi (SPKAM-RO) dan potensi aplikasinya. Studi literatur ini bertujuan untuk meningkatkan pemahaman seputar SPKAM-RO dalam jaringan distribusi, khususnya di lingkup instrument pengukuran atau sensor. Kemudian parameter yang diteliti fokus kepada parameter kimia dari kualitas air. Hasil studi menyimpulkan bahwa adanya kesenjangan antara teknologi sensor yang tersedia dengan peraturan yang berlaku di Prancis. Instrumen pengukuran atau sensor komersial terkini adalah IntellisondeTM. Di sisi lain, beberapa studi terbaru menunjukan bahwa Surface Acoustic Wave (SAW) sensor, Electronic Tongue/Nose dan sensor fiber optik sangat menjanjikan untuk SPKAM-RO, akan tetapi saat ini belum pada tingkat yang bisa diaplikasikan di lapangan.

Kata Kunci: Jaringan air cerdas, suplai air, pemantauan on-line, sensor



ABSTRACT

Name: R.M. Sandyanto AdityosulindroFormation: Civil Engineering, Specialty Environmental EngineeringTitle: Smart water grid: Instrumentations for real-time and on-line
monitoring of chemical drinking water quality in distribution
network

Monitoring of drinking water quality is critical to ensure public health security. Moreover the efficiency of monitoring should also continuously improve to simplify the operational process and minimize operational costs. To deal with these problems, there is a new system called smart water grid (SWG) systems which provide a real-time and on-line monitoring of drinking water quality. The main objective of this research is to better understanding the real-time and on-line drinking water quality monitoring system (RO-DWQMS) and their implementation. This literature research aimed to improve our understanding of RO-DWQMS for the purpose of replacing or supporting existing sampling and laboratory analysis methods in distribution network level, particularly in domain of measurement instruments or sensors. Then water quality parameters reviewed in this article are focused on chemical parameters. This study concluded that there is a gap between sensors technologies available and current regulations. State of the arts of commercial measurement instruments or sensors today is IntellisondeTM. In other hand, some recent study have been showed that in Surface Acoustic Wave (SAW) sensor, Electronic Tongue/Nose, and Fibre-optic are very promising for RO-DWQMS, but they are not at a stage where they can readily used in existing operations.

Key Words: Smart water grid, Water supply, On-line monitoring, Sensors

RÉSUMÉ

Nom Prénom: R.M. Sandyanto ADITYOSULINDROParcours: Génie Civil Spécialité Génie environnementaleTitre: Reseaux d'eau intelligent: Instrumentation pour le suivi de la
qualité chimique d'eau potable en temps réel et en ligne dans les
réseaux de distribution

Suivi de la qualité d'eau potable est essentiel pour assurer la sécurité de la santé publique De plus, l'efficacité de suivi devrait également améliorer continuellement pour simplifier le processus opérationnel et de minimiser les coûts opérationnels. Pour faire face à ces problèmes, il y a de système de Réseaux d'Eau Intelligent (REI) qui fournit de suivi en temps réel et en ligne de la qualité d'eau potable. L'objectif principal de cette recherche est de mieux comprendre le système de suivi de la qualité de l'eau potable en temps réel et en ligne (SSQEP-TL) dans les réseaux de distribution et leur application potentielle. Cette recherche théorique visant à améliorer notre compréhension sur le Système de Suivi de la Qualité de l'Eau Potable en Temps réel et en Ligne (SSQEP-TL) dans les réseaux de distribution, particulièrement dans le domaine des instruments de mesure ou des capteurs. Puis les paramètres de la qualité d'eau examinés dans cet article sont axées sur les paramètres chimiques. Cette étude a conclu qu'il existe un écart entre les technologies de capteurs disponibles et la réglementation actuelle. L'Etat des arts d'instruments de mesure ou des capteurs aujourd'hui est IntellisondeTM et certains études récentes sur Surface Acoustic Wave (SAW) sensor, Electronic Tongue/Nose, et capteur à fibre optique sont très prometteurs pour SSQEP-TL. Mais ils ne sont pas à un stade où ils peuvent facilement utilisés dans les opérations existantes.

Mots-clés:

Réseaux d'eau intelligente, Approvisionnement en eau, Suivi en ligne, Capteurs

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LIST OF ABBREVIATIONS

AAS-ATE	: Absorption Spectrometry coupled Electrothermal Atomization
AMI	: Advanced Metering Infrastructure
AMR	: Automated Meter Reading
BTEX	: Benzene, Toluene, Ethylbenzene, and Xylene
DO	: Dissolved Oxygen
DSS	: Distributed Sensing Systems
DWQI	: Drinking Water Quality Index
EDS	: Event Detection System
EPAL	: Empresa Portuguesa das Águas Livres
EPS	: Extended Period Simulation
ETAAS	: Electrothermal Atomic Absorption Spectrometry
F-AAS	: Flame Atomic Absorption Spectrometry
FIA	: Flow Injection Analysis
GC-FID	: Gas Chromatography-Flame Ionization Detector
GC-MS	: Gas Chromatography – Mass Spectrometry
GEO	: Geosmin
GPRS	: General Packet Radio Service
GPS	: Global Positioning System
HG-AFS	: Hydridegeneration - Atomic Fluorescence Spectrometry
IARC	: International Agency for Research on Cancer
ICP-MS	: Inductively Coupled Plasma Mass Spectrometry
ICTs	: Information and Communication Technologies
IEEE	: Institute of Electrical and Electronics Engineers
IUPAC	: International Union of Pure and Applied Chemistry
LEO	: Low Earth Orbit
LPGF	: Long Period Grating Fibre
MIB	: 2-Methylisoborneol
NADH	: Nicotinamide adenine dinucleotide reduced
ORP	: Oxidation Reduction Potential
РАН	: Polycyclic aromatic hydrocarbons
QCM	: Quartz Crystal Microbalance
RO-DWQMS	: Real-time and On-line Drinking Water Quality Monitoring Systems
SAW	: Surface Acoustic Wave
SCADA	: Supervisory Control and Data Acquisition
SWG	: Smart Water Grid
THM	: Trihalomethanes
TOC	: Total Organic Carbon
TTEP	: Technology Testing and Evaluation Program
USEPA	: United States Environmental Protection Agency.
VOC	: Volatile Organic Compound
WLAN	: Wireless Local Area Network

CHAPTER 1 INTRODUCTION

1.1 BACKGROUND

Population growth which is not proportional to the environmental carrying capacity is a fundamental problem in human welfare. Environmental carrying capacity is the maximum size of population that the environment can support indefinitely, given the food needs, housing, water and others that are available in the environment. The population is connected to national security as an indicator of challenge and opportunity, a multiplier of conflict and progress, and a resource for power and prosperity (Sciubba, J.D., 2012).



Figure 1.1 Percentages of urban population by region

(United Nations, 2012)

In the 20th century, the trend of population growth defines that there has been an increased of global population of 1.6 billion in 1900 to 6.1 billion in 2000, but the trend defining that the 21st century will be the transition to an urban population (*Sciubba, JD, 2012*). In 2008-2010, for the first time, more than half of the world population lived in urban areas (Sciubba, JD, 2012). In 1900, only 13% of the world population lived in cities. In 2050 this number will grow by 70%. This urbanization is both a symbol of our economic and social progress and challenges of urban infrastructure.



Figure 1.2 Proportion urban and rural in France (left) and proportion of urban area by major region (right) (United Nations, 2012)

Similarly, in France, the urbanization rate is always increased throughout the year and estimated to reach over 85% this year. Urban population growth in some regions of developing countries will be accompanied by the emergence of urban poverty. They were also implications for the environmental degradation by pollution (air, water and soil), the increased demand for resources, groundwater depletion and destruction of forest areas. Some evidence has shown that there are negative effects of urbanization on the quality of water resources and drinking water (Lee, 2000; Palamuleni, 2002; Kulaksiz and Bau, 2011; Rygaard et al. 2011).

In developed countries or regions, urban performance no longer depend only on physical capital but also on the availability and quality of communication and social infrastructure (Caragliu et al., 2009). This paradigm is based on emergent concept named smart city. Smart City is a strategic device to encompass modern urban production factors in a common framework and, in particular, to highlight the importance of Information and Communication Technologies (ICTs) (Caragliu et al., 2009). In the smart city concept, smart grid play the integral part to provide the communications and data distribution between suppliers and consumers in order to improve the efficiency, importance, reliability, economics, and sustainability.

In the domain of drinking water, there exists the concept "smart water metering" which is refers to a system that measures water consumption or abstraction and communicates that information in an automated mode for monitoring and billing purposes (without the need for manual readings) (UK Departement for Int. Dev., 2011). This concept is often referred to smart water grid or smart water management, which still only focus in the water efficiency (monitoring of water consumption and leakage) with Automated Meter Reading (AMR) and Advanced Metering Infrastructure (AMI).



Figure 1.3 Smart water metering system (UK Departement for Int. Dev., 2011)

1.2 PROBLEMS

Drinking water is a basic human needs and a very important role in supporting health and quality of the citizen's life, but it is very vulnerable to an intentional and accidental contamination, especially in distribution network (USEPA, 2009). In this case, the role of monitoring water quality in drinking water distribution networks is essential and must be continually developed to ensure the safety of drinking water and the effectiveness of monitoring method.

According to Storey et al. (2011) and Zhuiykov (2012), there is a need for online monitoring of existing water systems, because the laboratory methods are too slow to develop the operational response and not provide a high level of protection of the public health in real time. In addition, there is an obvious need to detect quickly towards instances accidental or deliberate contamination, because of the potentially severe consequences for human health.

With new technologies of information and communication technologies (ICTs), the current trend is to use the concept of smart grid as a base for data communications and data distribution between a numbers of water quality sensors deployed and monitoring centre. We can call those systems as "**Real-time and On-line Drinking Water Quality Monitoring Systems**" (**RO-DWQMS**). Furthermore, combining the smart water metering (quantitative aspect) with the RO-DWQMS (quality aspect) could lead us to the real "smart water grid systems" (SWG).

As the writer's knowledge, there is no scientific or academic definition for SWG systems, but based on the description of Shu Shihu (2011) in his publication and other point of view, the SWG can be defined comprehensively as an urban water supply system equipped with a smart monitoring system (flow and pressure meters, water quality sensors, water consumption meters and leakage sensors) and data transmission system in order to protect the users and provide better information about their water.

4



Figure 1.4 Conceptual framework of research

1.3 OBJECTIVES AND SCOPES OF RESEARCH

This study is submitted to complete the internship research of second year master program, with main objective is to better understanding the real-time and on-line monitoring drinking water quality monitoring system (RO-DWQMS) and their potential application. For that purpose, it will be divided in three sub-objectives as follows:

1. Identifying chemical parameters and chemical indicators of drinking water quality in distribution networks.

- 2. Describe the state of the art of measurement instruments for drinking water chemical quality monitoring
- 3. Describe implementation method in distribution network

To limiting scope of the study, this research focus on RO-DWQMS for the purpose of replacing or supporting existing grab and analysis methods in distribution network level. Then the parameters will be reviewed is the chemical parameters of water quality and for other parameters such as microbiological and radioactive are not discussed in this study.

1.4 RESEARCH PLANNING

Chapter 1. Introduction

This chapter describes the research background and problems and also the research framework that explain the relationship between the variables studied. Objective of the research is also described in this chapter

Chapter 2. Chemical Parameters and Indicators in RO-DWQMS

This chapter describes the chemical parameters of water quality required by the regulations and its signification for health. This chapter also describes the selection process of chemical indicators of drinking water quality to be monitored in the distribution system as well as brief profiles of each chemical indicator chosen.

Chapter 3. Measurement Methods and Instruments for RO-DWQMS

This chapter describes the available and developing methods and instruments for monitoring chemicals of the chemical parameters and indicators that were defined in the previous chapter. Specifically, the methods described are based on the purpose of real-time and on-line drinking water quality monitoring

Chapter 4. Implementation of RO-DWQMS in Distribution Network

This chapter describes implementation of the real-time and on-line drinking water quality monitoring and the role of smart grid in this system.

Conclusion

CHAPTER 2

CHEMICAL PARAMETERS AND INDICATORS IN RO-DWQMS

2.1 INTRODUCTION

Drinking water that has good quality and safe to be consumed is a basis of good health. Water provides the essential elements, but when it is polluted, it could become the source of undesirable substances that is harmful to human health. A number of cases of acute, chronic and endemic diseases were believed to be caused by poor drinking water quality.

The Centers for Disease Control and Prevention identified 30 occurrences of outbreaks of waterborne diseases associated with drinking water between 2002 and 2003 (Liang et al., 2006). Degradation in the distribution system is frequently cited as a major factor in infectious diseases associated with drinking water. A reported pathway of accidental contamination by pathogens in the distribution system is interconnections with non-potable water sources (K. Lahti and L. Hiisvirta, 1995). In 1993, Giardia and Cryptosporidium caused more than 400,000 people in the United States suffered from the gastrointestinal tract due to an outbreak in Milwaukee that related to the increased of turbidity in two drinking water plants serving the country (Mac Kenzie et al., 1994; Morris et al., 1996). In Italy, a study showed that consumption of drinking water with high trihalomethane concentration may increase the risk of melanoma and possibility of hormone-dependent tumors cancers such as prostate, breast and ovarian (Vinceti M. et al., 2004).

In other hand, threat of intentional contamination in drinking water distribution system is also of particular concern in United States since the terrorist attacks on September 11, 2001. For example, in 2003, Iraqi agents were arrested before they executed their plotted plan to poison a water tank in Khao, Jordan. The tank supplied water to American Troops (New York Times, 2003).

According to USEPA (2008), understanding the health effect related to drinking water contamination is an important issue in public health surveillance which involves the analysis of health-related data sources to identify disease events that may stem from drinking water contamination.

To ensure the high quality protection of drinking water, periodic monitoring is required for each parameter which required by the regulations. However, knowing how many potential substances that could contaminate the potable water system, the sensors of specific contaminants would be prohibitively expensive and logistically impractical (USEPA, 2005). Thus it is necessary to choose the most important parameters as indicators of water quality without losing important information of all parameters or use the multi-parameter sensors.

2.2 DEFINITION OF PARAMETER AND INDICATOR

2.2.1 Parameter

Parameter is a measurable quantity to present simpler and shorter main characteristics of a statistical ensemble or element which express the essential characteristics of a phenomenon (www.larousse.com). In French regulation of *l'arrêté du 11 Janvier 2007* "relative to the limits and references of raw water and water quality intended for human consumption", there are lists of chemicals that is designated as a parameter. So we could say that the chemical parameters describe the chemical quality of water.

2.2.2 Indicator

It is a device, instrument or term used to provide guidance, information on the value of a quantity (www.larousse.com). Another definition is given by *l'Institut International du Développement Durable*; an indicator that quantifies and simplifies phenomena and helps us understand complex realities.

Other definition says that the indicator is a substance, such as sunflower (for the pH indicator with color), indicating the presence or concentration of certain component (www.merriam-webster.com). In this case, we note that certain substances/chemical parameters can be an indicator of one or more other substances/chemical parameters.

2.3 PARAMETER OF DRINKING WATER QUALITY

2.3.1 Drinking Water

In France, drinking water is included in class of « water intended for human consumption ». This text is now included in the French regulation *Code de la santé publique (article L 1321)*. Water in public distribution must be pleasant to drink, clear, colorless, tasteless and odorless. It should not present a risk to the health of the consumer in the short term and long term. And then it must also be balanced and should not be aggressive (Rauzy, 2004).

2.3.2 Limits and References of Quality (Limites et Références de Qualité)

Looking on the *l'arrêté du 11 Janvier 2007* « relative to the limits and references of raw water and water quality intended for human consumption», there are limits and references of drinking water quality. The parameters for drinking water quality generally fall into three categories: chemical, microbiological and the radioactivity.



Figure 2.1 Parameters Classification

In theory, the limits of quality are mandatory to respect the values for parameters that directly affecting the health and references of quality are targets to control parameters for the operation of production facilities and distribution, but normally not directly affect to health (Rauzy, 2004).

2.3.3 Sampling Program

The French regulation of *arrêté du 11 janvier 2007* « Relative to the program of sampling and analysis of sanitary control for water supplied from a distribution network » was explained that the sampling is done at three levels:

- At the resource. This is the point of use of the raw water before treatment.
- At the production level, at the end point of water treatment process or downstream of the reservoir.
- In distribution. At the tap normally used by consumer. This sampling point for a unit of distribution water. There are the points in the consumer network where the water quality considered homogeneous. The sampling locations are determined in each department by a prefectural order.

In this regulation also stated words of routine and supplementary monitoring. Routine monitoring provides information on the organoleptic and microbiological quality of water and the efficiency of water purification treatments. In addition, supplementary monitoring intends to check whether all quality criteria are met (Rauzy, 2004). The frequency of routine and supplementary monitoring conducted on the basis of population served.

2.4 NEGATIVE EFFECT OF CHEMICAL PARAMETERS

2.4.1 Health Effect

Contaminant levels in drinking water are sometimes high enough to cause acute or immediate health effects. Examples of acute health effects are nausea, lung irritation, skin rash, vomiting, dizziness, and even death (Zaslow and Herman et al., 1996).

Drinking water contaminants are more likely to cause chronic health effects that occur long after repeated exposure of small amounts of a chemical. Examples of chronic health effects include damage cancer, liver and kidneys, nervous system disorders, immune system damage and birth defects (Zaslow and Herman et al., 1996). Table B.1 in Appendix B listed the chemical parameters of the limits of drinking water quality and its effects on health.

2.4.2 Organoleptic effects

The perception of taste and odor by consumers in drinking water is an important issue for water suppliers and a major cause of consumer complaints (Krasner et al., 1983). Therefore, the organoleptic effects are basically comfort criteria. This is the color, smell, taste, turbidity. The use of poor aesthetics of water quality may lead consumers to change its water source to another to look for the better water, but safety is not guaranteed.

2.4.3 Effects on the distribution networks

The adverse effects that most commonly encountered at the drinking water distribution network are corrosion and scaling. According to the IUPAC definition, corrosion is an irreversible reaction interfacial material (metal, ceramic and polymer) with the environment which results in the consumption of material or dissolution of material from a component of the environment (Heusler, 1990).

Several aspects of water chemistry, including alkalinity, pH and concentrations of organic matter, have great rates impact on corrosion, the solubility of lime deposits and the rate of lead and copper release (Ferguson et al., 1999; McNeill and Edwards, 2004; Taylor et al., 2006).

2.5 CHEMICAL PARAMETERS AND INDICATORS TO BE MONITORED

In an evaluation of the drinking water quality, decision making based on water quality data is a crucial issue, as many numbers of parameters compromises the quality (Ramesh et al., 2010). Currently, monitoring many different specific contaminants is not feasible concerning the high investment cost (USEPA, 2005) and the availability of instruments.

According to Helbling and VanBriesen (2008), a surrogate parameter of water quality can be an indicator of the broad range of pathogenic contaminants. On the other hand, some researchers have proposed water quality index (WQI) to simplify the analysis (Horton, 1965; Ott, 1978). WQI is a mathematical tool to integrate the complex water quality data into a numerical score that describes the overall water quality status (Ramesh et al., 2010). To create a drinking WQI

(DWQI), the selection of parameters as the indicator is needed for the index so that it can describe the overall quality of drinking water. According to Wu Shan et al. (2011), to select specific indicator of water quality through proper analysis, we will observe the principles of feasibility, the scientific, completeness and independence.

The concept of raw water quality assessment using (WQI) was broadly discussed and applied (Smith, 1990; Dojlido et al., 1994; Pesce & Wunderlin, 2000; Córdoba et al., 2010; Srebotnjak et al., 2012; Akkoyunlu et Akiner, 2012) while its use in drinking water is still limited (Ramesh et al., 2010; WU Shan et al., 2011).

It is important to select indicators by looking at the parameters used in the WQI to see what parameters are important as an indicator of chemical quality of drinking water. Basically, the choice of indicators is linked to local conditions, but some parameters such as temperature, salinity, conductivity, pH, dissolved oxygen (DO), turbidity, metals and coliform always used as important indicators for raw water (Scanes, 2007; Córdoba et al., 2010; Liu et al., 2012). Moreover, Ramesh et al. (2010) proposed 22 parameters to be analyzed in order to determine DWQI.

Group 1	Group 2	Group 3	Group 4	Group 5
pН	Total Alkalinity	Fluoride	Cadmium	Total Coliforms
Conductivity	Hardness	Nitrate	Chromium	Salmonella
Sodium	Calcium	Nitrite	Lead	
Chloride	Magnesium	Manganese	Copper	
Sulphate	Iron	Zinc	Nickel	

Table 2.1 Parameters proposed as indicators

Group 1 & 2 : Parameter related to potability ; Group 3, 4, 5 : Parameter related to health (Ramesh et al., 2010)

Moreover, several studies have been shown that many contaminants affect one or more parameters of water quality such as TOC, free chlorine, pH, conductivity, turbidity and ORP (Pintar and Slawson, 2003; USEPA, 2005; Hall J.

Class	Description	тос	CI2	ORP	COND	pН	TURB
1	Petroleum products	Ť		_	_	_	-
2	Pesticides (reactive)	î	\downarrow	\downarrow	-	-	-
3	Inorganic compounds	_	↓	↓	Ť	_	_
4	Metals	-	_	_	î	Ļ	_
5	Pesticides (non-reactive)	1	_	_	î	_	_
6	Chemical warfare agents	Ť	-		-	_	-
7	Radionuclides (metal-salt)	-		-	î	_	-
8	Bacterial toxins (with dechlor agent)	-	ų	4	î	-	-
9	Plant toxins	†	-	_	-	_	-
10	Pathogen (clean with dechlor agent)	-	x	4	1	T	-
11	Pathogen (dirty with growth media)	î	4	+	-		î
12	Persistent chlorinated organics	1	_	1		_	-

et al.,2007; Allgeier and Umberg, 2008; Xie and Giammar, 2011; Okeke et al., 2011).

Figure 2.2 Effect of contaminants on the water quality parameters (Allgeier and Umberg, 2008)

It is found that almost of mentioned parameters are included in the *l'arrêté du 11 Janvier 2007* "relative to the limits and references of raw water and water quality intended for human consumption" (see Table B.1 and B.2 in Annex B).

2.6 DISCUSSIONS

It seems difficult to choose and determine the chemical parameters of water quality to be monitored in the distribution network considering almost all the parameters have a negative effect on health. Even more if considering the potential for deliberate/intentional contamination by man (e.g. terrorist), the chemical parameters variation will larger and unpredictable. To deal with this problem, some researchers proposed the DWQI to reduce the number of parameters measured and try to still maintain their reliability. DWQI is generally based on the Delphi technique or aggregation and statistical technique. Until now, DWQI applications are still very limited due their vulnerability. For example if there is only one chemical parameter whose concentration exceeds the MCL, and not represented in DWQI, it could be very harmful to consumers.

Another alternative is using global water quality parameters as indicators and these indicators take an important role in monitoring process. Generally, this method generally keeps a check on all the important parameters, but the monitoring frequency will vary. From the writer's point of view, the most important is determine the objective of monitoring (e.g. to replace existing monitoring system, to support existing monitoring system or to prevent intentional contamination by terrorist), because if not previously determined, there are too many chemical parameters in water.

In application to replace existing monitoring system, we must choose chemical parameters to be monitored in Drinking Water Distribution Network (DWDN) with looking the current regulation. In France, concerning the *l'arrêté du 11 Janvier 2007* relative to the limits and references of raw water and water quality intended for human consumption, we see that there are 28 chemical parameters of quality limits and 19 chemical parameters of quality references of drinking water. Next, we consider the *l'arrêté du 11 Janvier 2007* relative to sampling program and analysis of sanitary control for the water provide by a drinking water distribution network. Obviously, at the level of drinking water distribution network, we must focus on the 16 chemical parameters of quality limits and 13 chemical parameters of quality references. Then, for other parameters that must be monitored at the point of production can be leave temporarily to control conventionally remembering that they are easier to be monitored due to its location where near the plant.

As described above, it will be difficult and inefficient to measure all the required parameters. So, in order to simplify the monitoring process, certain parameters will be selected as indicators for on-line monitoring. Considering previous studies (USEPA, 2005; Jeffrey Yang et al., 2009; Ramesh et al., 2010; Okeke et al., 2011) and the assumption that the reference parameters are easier to monitor and may reflect the presence of a number of chemical parameters of quality limits, so we take the 14 reference parameters of quality of drinking water as chemical indicators (priority indicators to be monitored online) and 16

chemical parameters of quality limits as other parameters to be controlled at the network of drinking water. The steps in the selection of parameters to be monitored as an indicator of the drinking water chemical quality are explained in the figure 2.3. Finally, in applications for real-time and on-line monitoring, the parameters or indicators selected must be adapted to available sensors in the market.

First Priority	Second Priority			
Indicators to be monitored:	Parameters to be monitored:			
1. Aluminum total	1. Acrylamide			
2. Ammonium	2. Antimony			
3. Free and total chlorine	3. Benzene			
4. Chlorite	4. Benzo[a]pyrene			
5. Conductivity	5. Cadmium			
6. Color	6. Vinyl chloride			
7. Copper	7. Chromium			
8. Iron total	8. Copper			
9. Odor	9. Epichlorohydrin			
10. pH	10. PAH			
11. Taste	11. Nickel			
12. Temperature	12. Nitrates			
13. Turbidity	13. Nitrites			
14. TOC	14. Lead			
	15. THM			
	16. Turbidity			

Table 2.2 Chemical substances to be monitored in real-time and on-line in distribution network



Note: * turbidity and copper appeared (required) within two (quality limits and quality references)

Figure 2.3 Selection processes of chemicals indicators to be monitored in the drinking water distribution network

Chemical/Biological	Indicators							
parameters	Al	NH4	Cl2	Colour	DO	O&T	Turbidity	TOC
Heavy Metal							1	
Ammonia								
Nitrite			\downarrow					
Nitrate			2					
Microbiology			\rightarrow	1			1	
Pesticides			\downarrow					
THM	-		\downarrow	7	1	1		\downarrow
НАА	1							
Copper			÷					
Iron			\rightarrow		\downarrow		1	
Cynobacteria						\checkmark		
Actinomycetes					1	\checkmark	~	
Organic Compounds				100		\checkmark	↑	
Inorganic Compounds								
Cryptosporidium		9	2	0		7		
Giardia L.		$\sum_{i=1}^{n}$		~		\sum		
Benzene								

 Table 2.3 Response of chemical indicators against the presence of several biological and chemical parameters

Note:

- $\sqrt{}$: Related (response specific has not been identified)
- ↑ : Concentration of indicator increased
- ↓ : Concentration of indicator decreased

Capabilities of chemical indicators to detect some chemical and other biological parameters make chemical indicators as a first priority for monitor realtime and on-line. Fig. 2.2 and table 2.3 show the relations between chemical indicators with chemical/biological parameters and also several contaminants important. Further information about table 2.3 can be found in Appendix A and Appendix B table B3.

CHAPTER 3

MEASUREMENTS METHODS AND INSTRUMENTS FOR RO-DWQMS

3.1 INTRODUCTION

Nowadays, there is a need for better monitoring existing water systems by on-line system, because the laboratory methods are too slow to develop the operational response and do not provide a high protection level of public health in time real. Furthermore, there is an obvious need to detect and respond quickly the accidental or deliberate contamination, because of potentially severe consequences for human health (Storey et al., 2011 ; Zhuiykov, 2012).

There are instrument for real time detection (quick response) that are inexpensive, compact and automated to identify an object. Computer technology developments open a wide area in the field of modern and intelligent remote sensing systems (Brignell, 1996). In a field of analytical chemistry, real time and online monitoring can be done by automated analysis. Automated analysis help to simplify the monitoring process by avoiding manual sample collection, sample preparation and batch analysis (Skoog, 2007). For real-time and on-line monitoring purpose, sensor would probably be the most preferable option (USEPA, 2005; Jeffrey Yang et al., 2009; Storey et al., 2011; Zhuiykov, 2012).

Real-time monitoring means rapid measurement process without waiting, immediate or short time. While online measurement means that the measuring instrument is connected and under the direct control of the system which it is associated.

This chapter describes the measurement methods and instruments for monitoring the chemical indicators and parameters defined in the previous chapter. Specifically, the methods described are based for the purpose in real-time and on-line monitoring of drinking water quality.

3.2 DEFINITION OF MEASUREMENT INSTRUMENT AND SENSOR

The measurement instrument is a set of chemical analysis device which is composed of transducers, display system and microprocessors to transform the information present in the physical and chemical properties of analyte to the form that can be recorded, handled and understood by humans (Skoog et al., 2003).

Transducer is a device that converts one energy form to another form of energy. It is an important element that switches non-electric domain information (the physical and chemical properties of the analyte) to electric field or inversely. According to Skoog et al. (2003), sensor is an analytical device or instrument which is capable to continuously monitoring certain chemical species. Another definition says that the sensor is a device that is capable to responding the presence of substances reversibly and continuously (Chamjangali et al., 2009).

Smart sensor can be defined as a device containing a main sensing element, an analyzer (a component for signal amplification and filtering system combined with software dedicated to data processing, compensation and acquisition) (Tanner and White, 1996) and a transmitter (a component for data transmission). The term smart is used to signify that the sensing element is intimately associated with a microprocessor, and specifically programmed with algorithms derived from artificial intelligence (Rumelhart et McClelland, 1992).

3.3 PERFORMANCE CRITERIA OF MEASUREMENT METHODS

The choice of measurement method is determined based on qualitative criteria such as rapidity (measurement time), ease, skill of experimenter, cost, stability (maintenance interval), equipment availability and cost per sample. Moreover, there are other numerical criteria (quantitative criteria) called coefficients of merit that are defined in the table 3.1.

Furthermore, according to Aisopou et al. (2012), the use of water quality sensors for general monitoring operational decision support and early contamination warning can only be beneficial if the sensors have good characteristic in resolution, repeatability, accuracy, ease of installation and operation and management (O & M) cost. Concerning to O & M cost, USEPA recommended to use the reagent-free sensor to minimize labour & reagents costs.

Criteria	Description	Coefficients of Merit
Precision	The reproducibility of the values obtained by	Absolute standard deviation,
	following the same procedure in different	relative standard deviation,
	locations by different people (a measure of	coefficient of variation,
	random error)	variance
Accuracy	The difference between the averages measured	Absolute systematic error, relative systematic error
	concentration of an analyte and the true	
	concentration (a measure of systematic error).	
Sensitivity (Resolution)	The ability to discriminate small differences in	Sensitivity, calibration and analysis
	analyte concentration. The sensitivity of	
	calibration which is equal to slope of	
	calibration curve of concentration studied (the	
	highest grade, most sensitive).	
Detection limit (DL)	The concentration or the lowest mass of analyte	Blank plus three times the standard deviation of blank
	that can be detected with a given level of	
	confidence. This limit depends on amplitude	
	ratio of the analytic signal to the statistical	
	fluctuations of blank signal	
Measurement range	The lowest concentration for which quantitative	Limit of Quantification and
	measurements can be carried out (Limit of	
	Quantification) to the concentration above	
	which the calibration curve ceases to be linear	Limit of Linearity
	(Limit of Linearity).	
Selectivity	The level at which other species contained in	
	the sample matrix do not interfere with the	Coefficient of selectivity
	analytical process.	

Table 3.1 Numerical criteria for selection of measurement method

(Skoog et al., 2003)

The sensors selection must also depend on ease of installation which is can be categorized in flow cell type or in-pipe probe type. In flow cell type, the sensor is inserted into the slit of cell and periodically the device suck an amount of sample to be analyzed in it. In practice, the installations of flow cell type instruments or sensors are factory assembled with all required flow cells, mounting fittings and pipework on a compact panel, so they will need a small building for the installation. Otherwise, the in-pipe probe type sensor is a probe inserted directly in pressurized distribution pipe.



Figure 3.1 Example of sensor implantation in flow cell type (left) or in-pipe probe type (right) (S::can, 2012; Intellitect Water, 2012)

3.4 STATE OF THE ARTS OF MEASUREMENTS METHODS AND INSTRUMENTS

Measurement instruments are the core of RO-DWQMS. The objective of this section is to describe the state of the arts of measurement instruments and sensors to fulfill the needs of real-time and on-line monitoring the chemical indicators and chemical parameters defined in the previous chapter, and then writer does not endorse or recommend any of the following technologies. There are also exists several measurement instruments/sensors designed to detect toxic substance (described elsewhere in USEPA, 2005c) which is important against intentional contamination, but it is not the focus in this research. To keep the validity of data, the summary information below was obtained from company website and scientific article.

3.4.1 Measurements Methods and Instruments for Chemical Indicators

1.) <u>Aluminum</u>

A low detection limit is necessary for aluminum analysis in drinking water. Atomic Absorption Spectrometry with Electrothermal Atomization (AAS-ATE), Flame Atomic Absorption Spectrometry (F-AAS), Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and Spectrometry UV-VIS provided by exchange resins are available measurement instruments (Garg et al., 1999).

All available instruments used especially for ICP-MS and F-AAS are expensive, but an Aluminium Acoustic Wave Sensor based on acoustic wave devices may be an alternative. This sensor is made of Piezoelectric Quartz Crystal which covered by sensitive aluminum membrane (Veríssimo et al., 2006). The principle is to measure differences in the frequency of crystal oscillation prior and after sample injection due to changes in the coated crystals mass because of the analytespecific adsorption process.



(A) pressure regulator, (B) Milli-Q water, (C) injection port, (D) crystal cell, (E) oscillator, (F) device counter / timer PXI 6608, (G) personal computer (H) waste, (I) nitrogen

Figure 3.2 Experimental setup for the quartz crystal methodology (Veríssimo et al., 2008)

The aluminium measurement instrument available in the markets is <u>Aztec 600</u> <u>aluminum analyzer</u> (fig. C1, Appendix C), <u>Stamolys CA71AL Analyser</u> (fig. C3, Appendix C) and <u>Aluminum EnviroLyser</u> (fig. C2, Appendix C). These commercial instruments based on colorimetric method and possessed the ability to real-time and on-line monitoring and self-cleaning.
2.) <u>Ammonium (NH4⁺)</u>

Various methods have been developed for estimating the ammonium concentration in water. For colorimetric method, phenolic reagent and its by-product of the reaction are highly toxic (Stich, 1991). Other method like spectrophotometric monitoring is always interfered by other photoactive substances or suspended particles in samples (Kwan et al., 2004). Moreover, chromatographic methods need expensive pre-column derivatization to treat the samples for fluorescent detection (Meseguer-Lloret et al., 2005).

Kwan et al. (2005) has proposed a quick determination of ammonium with bienzyme sensor by immobilizing glutamate dehydrogenase (GIDH, EC 1.4.1.2) and glutamate oxidase (GXD, EC 1.4.3.11) on an oxygen electrode of Clark type (GXD / GIDH Bienzyme Ammonium Biosensor). Briefly, the measuring principle is described as follows: 1.) GIDH consumes ammonium for specific amination of 2-oxoglutarate in the presence of NADH; 2.) GXD consumes dissolved oxygen (DO) for the oxidative deamination of glutamate produced by GIDH; 3.) DO acts as an essential material for the enzymatic activity of GXD and is consumed with a maximum rate that is proportional to the concentration of ammonium during the measurements; 4.) A detectable signal, measured as the first derivation of the current-time curve, was monitored at -600 mV versus Ag/AgCl by the Clark electrode.



Figure 3.3 Schematic diagram of a GXD/GlDH bienzyme ammonium biosensor

(Kwan et al., 2005)

As writer's knowledge, there are not many ammonium measurement instruments with an appropriate detection limit for drinking water sample. The measurement instrument available in markets are <u>On line water analyzer UV500</u> (Fig. C21 appendix C), <u>YSI-6920DW multi-probe</u> (Fig. C22 appendix C) and <u>Ammo::lyserTM eco</u> (Fig. C17 appendix C)

3.) Free and Total Chlorine

According to Murata et al. (2008), Voltametric detection with Highly Boron-Doped Diamond Electrodes showed high sensitivity and good stability without pretreatment. In addition, a detection limit of 8.3 ug/l was performed by using flow injection analysis (FIA) and this method can be applied for monitoring free chlorine in the drinking water.

Helbling and VanBriesen (2008) have been done the laboratory measurement scale of residual chlorine againts microbial intrusions. They used an EPA-approved colorimetric diethyl-p-phenylene diamine method, <u>Hach CL 17</u> (Fig. C4, appendix C). The measurement principle is free chlorine in the water sample oxidizes the DPD indicator reagent at a pH between 6.3 and 6.6 to form a magenta colored compound. The resulting color intensity is proportional to free chlorine concentration in sample. Another option, there are reagent-free sensor like <u>AZTEC® Chlorine Residual Analyzers Series CL1000B</u> (Fig. C5, appendix C), <u>CLF10sc/CLT10sc Reagentless Chlorine Analyzer</u> (Fig. C6, appendix C) and <u>AC20 Analyseur</u> (Fig. C7, appendix C) which based on measure the current between electrodes on the applied potential difference.

4.) <u>Chlorite (ClO₂⁻)</u>

The online measurement of chlorite in drinking water, however, is difficult because of low electrolytes concentrations in water disinfected. A recent study is used an automatic on-line amperometric sensor system for measurement of chlorite ion with sol–gel based electrochemical probe (Myers et al., 2012). As writer's knowledge, chlorite measurement instrument is very limited in market, <u>ProMinent® DULCOMETER® D1C Chlorite Package</u> (Fig. C8, appendix C) and

<u>Chlorite EnviroLyser</u> (Fig. C2, appendix C) are some available instrument. This commercial instrument based on the amperometric and colorimetric method and possessed of ability to real-time and on-line monitoring.

5.) Conductivity

The principle of the conductivity measurement is carried out by forcing a current through a sample of electrolyte and measure the resulting voltage drop. This is usually done with two or four electrodes exposed to electrolyte (Hyldgård et al., 2008). There are wide ranges products of conductivity sensors available in market. In general, the conductivity sensor is a part into a multi-parameter sensor e.g. <u>YSI-6920DW multi-probe</u> (Fig. C22, appendix C) and <u>IntellisondeTM</u> (Fig. C20, appendix C).

6.) <u>Colour</u>

Water colour can be measured quantitatively based on a colorimetric method. The principle is a light with a specific wavelength can be absorbed by the colour in solutions and changes in wavelength which are measured by sensor. Thus, the absorbance is proportional to concentration of substance in sample (Liu et al., 2009). The colour measurement instrument available in the markets is <u>Aztec</u> <u>Color analyzer 600</u> (Fig. C1, appendix C) and <u>On line water analyzer UV500</u> (Fig. C21, appendix C). These commercial instruments based on colorimetric method and needs reagents. But recently, <u>IntellisondeTM</u> (Fig. C20, appendix C), a multiparameter sensors can measure colour without reagents.

7.) Copper(Cu)

The spectrometry methods (Karaböcek, 2000; Mashhadizadeh et al, 2008) and Voltametry methods (Mohadesi et Taher, 2007) have been proposed to measure copper in water. These methods usually have a low enough limit of detection and specificity, but also disadvantages such as high costs for equipment and testing, time consuming and complicated operation (Chamjangali et al., 2009). Therefore, these methods are not suitable for online analysis in the field.

Currently in field of water quality measurement, there was a tendency for monitoring by fiber optic sensor is based on the principle of refraction rather than by electrochemical methods (Booksh and Gentleman, 2006; Goicoechea et al., 2008, Rahman et al., 2011). fiber optic sensors have been showed several advantages such as immunity to electromagnetic interference, the high sensitivity, a small sensor unit, security environments, ability to process signal at large distances from the sensor with little degradation, and have the ability to work under high temperature and high pressure conditions (Zhao et al., 2001).

A study by Chamjangali et al. (2009) has found a new fiber optic sensor by immobilizing a new chromogenic reagent 1-phenyl-1,2-propanedione-2-oximecarbazone thiosemi (PPDOT) on the membrane triacetylcellulose. This sensor showed good stability, lifetime and also low production cost. In the market, available measuring instrument are <u>Stamolys CA71CU</u> (Fig. C3, appendix C) and <u>EnviroLyzer® Copper</u> (Fig. C2, appendix C). Actually, a multi-heavy metalparameters are already exists, the <u>Heavy Metals Online Analyzer OVA5000</u> (Fig. C29, appendix C) can measure until 6 heavy metal parameters in drinking water and already equipped with EDS (explained in section 4.2). OVA5000 measurement principle based on stripping voltammetric detection, with this method, metal will be preconcentrated onto an electrode surface at negative potentials and then selective oxidation process (stripping process) will applied during an anodic potential sweep to gives off electrons which are measured as a current.

8.) <u>Total Iron</u>

A new quantitative electroanalysis measurement method for total iron determination was developed by Jezek et al. (2007). They proposed a single-use screen-printed sensor device covered by the immobilization of 10-phenanthroline, potassium hexacyanoferrate (III), potassium hydrogen sulphate, sodium acetate and potassium chloride. Compare to conventional laboratory methods like colorimetry and stripping voltammetry, this sensor is simple, inexpensive, quick measurement and requires no reagents The measurement instrument of iron

available in the markets is <u>Iron analyzer Aztec 600</u> (Fig. C1, appendix C) and <u>Stamolys CA71FE</u> (Fig. C3, appendix C).

9.) Odor 10.) Taste

Ji et al. (2000) have been developed the piezoelectric odor sensor with quartz crystal microbalance (QCM) under the molecularly imprinted formation as sensing element. These devices are able to directly detect MIB at concentrations above 10 ppb (10 ug/l). Normally, the quartz crystals are sandwiched between two electrodes, which are then coated with a substrate capable of adsorbing substances to be measured. Measurement is based on the decrease in resonant frequency of the crystal corresponds to mass increase. This method provides a simple and inexpensive method for a wide range of odorous compounds.

A more recent study by Braga et al. (2012) showed that the measure based on the combination of polymeric electronic tongue/nose sensor, impedance measurement and multivariate statistical analyzes can measure MIB and GEO as low as 25 ng/l. Electronic tongue/nose is an instrument consists of head space sampling, sensor array, and pattern recognition modules, to generate signal pattern that are used for characterizing odors/taste. In markets, <u>GEMINI electronic noses and ASTREE Electronic Tongue</u> (Fig. C4 & C25, appendix C) are the available instrument, but these instruments do not possess ability to real-time and on-line measurement.

11.) <u>pH</u>

A fiber optic pH sensor based on nanostructured layer by layer (LbL) coatings of neutral red (NR) and polyacrylic acid (PAA) were fabricated (Goicoechea et al., 2008). The detection mechanism is based on measurement of light modulation absorbance due to optical variation properties of LbL-NR/PAA detection which acts as an active coating. Generally, the pH sensor is available in a multiparameter sensor, e.g. <u>YSI-6920DW multi-probe</u> (Fig. C22, appendix C), <u>l'IntellisondeTM</u> (Fig. C20, appendix C) and <u>On-Line Water Analyzer UV500</u> (Fig. C21, appendix C).



Figure 3.4 Experimental device of pH detection with fibre optic pH sensor (Goicoechea et al., 2008).

12.) <u>Température (T)</u>

Valdivielso et al., (2003) have been proposed to use 2,4,5-triphenylimidazole (lophine) as a temperature sensor with optical fiber. The reflected optical power increases with temperature in accordance with expected behavior of lophine. Generally, the temperature sensor is available in a multiparameter sensor, e.g. <u>YSI-6920DW multi-probe</u> (Fig. C22, appendix C), <u>l'IntellisondeTM</u> (Fig. C20, appendix C) and <u>On-Line Water Analyzer UV500</u> (Fig. C21, appendix C).

13.) <u>Turbidity</u>

The turbidity sensor has been widely applied in monitoring of water quality (Martínez-Máñez et al., 2005; Liu et al., 2009). A recent laboratory study by Tai et al. (2012) has shown that a smart nephelometric turbidity sensor based on IEEE 1451 devoted to the distributed measurement system can be adapted to online water quality monitoring. IEEE 1451 is a set of smart transducer interface standards developed by the Institute of Electrical and Electronics Engineers (IEEE) Instrumentation and Measurement Society's Sensor Technology Technical Committee that describe a set of open, common, network-independent communication interfaces for connecting transducers (sensors or actuators) to microprocessors, instrumentation systems, and control/field networks (NIST, 2009). This standard intends to make easier for the sensor manufacturers to



develop smart devices by incorporating existing and emerging sensor- and networking technologies.

Figure 3.5 Exploded view of the transducer (left) and experimental (right) (Tai et al., 2012)

Generally, turbidity sensor is available in a multi-parameter sensor like <u>YSI-6920DW multi-probe</u> (Fig. C22, appendix C), <u>l'IntellisondeTM</u> (Fig. C20, appendix C) and <u>On-Line Water Analyzer UV500</u> (Fig. C21, appendix C).

14.) <u>TOC</u>

A TOC measurement requires the instrument essentially consists of two parts: the first must ensure the mineralization of organic matter in sample while the second must measure CO2 emissions (Visco et al., 2005). The analytical methods available for detecting carbon dioxide are non-dispersive infrared analysis (NDIR), conductivity detector, CO2 electrode detector, and flame ionization detector (FID) (Visco et al., 2005). Actually, there are wide range of TOC real-time & on-line monitoring instrument available on market <u>astroTOCTM UV</u> <u>Process Total Organic Carbon Analyzer</u> (Fig. C28, appendix C), <u>5310C On-Line</u> (Fig. C27, appendix C) and <u>On line water analysis UV500</u> (Fig. C21, appendix C).

3.4.2 Measurements Methods and Instruments for Chemical Parameters

1.) Acrylamide

Measurement methods and instrument for acrylamide monitoring in drinking water are very limited. Kleefisch et al. (2004) have been proposed the quartz microbalance sensor for the detection of acrylamide. The principle is measure the resonance frequency of the oscillating quartz chip which is lowered when its mass increases due to analyte binding. Compare to analytical methods such as GC-MS, this sensor is robust, low-cost, and also has a quite lower detection limit (10 μ g/l). To the best of writer's knowledge, there is no real-time and on-line measurement instrument or sensor for acrylamide detection in drinking water.

2.) Antimony (Sb)

Hydridegeneration combined to atomic fluorescence spectrometry (HG-AFS) is a powerful tool for the speciation of metalloids, such as Se, As and Sb, particularly in environmental samples at concentrations lower than μ g/1 (Deng et al., 2001). In order to measure very low concentration without an expensive chromatographic technique, a preconcentration stage is commonly used before used HG-AFS or Electrothermal Atomic Absorption Spectrometry (ETAAS) (Fang et al.,2009; López-García et al., 2011). To the best of writer's knowledge, there is no real-time and on-line measurement instrument or sensor for Antimony detection in drinking water.

3.) Benzene

Ultrasound-assisted emulsification microextraction coupled to gas chromatography with flame ionization detector (USAEME-GC-FID) has been successfully applied to the determination of Benzene, Toluene, Ethylbenzene, and Xylene (BTEX) compounds in water samples. The proposed method had many advantages including simple and fast extraction, minimum organic solvent consumption, good repeatability and reproducibility, low cost and high accuracy (Hashemi et al. 2012). As the writer's knowledge, the real-time and on-line commercial measurement instrument for benzene monitoring in water sample is very limited on market and <u>AF46 Dual Wavelength UV Absorption Sensor</u> (Fig. C9, appendix C) is one of them.

4.) **Benzo(a)pyrene**

Fernández-Sánchez et al. (2004) have been proposed a flow-trough optical sensor (optosensor) based on the immobilization of benzo[a]pyrene on a non-ionic resin (Amberlite XAD-4) solid support. The proposed method had many advantages including very low detection limit 3 ng/l, fast response time 40 s and simplicity. As writer's knowledge, there is not many measurement instrument available on market for measuring Benzo(a)pyrene and <u>Online Solid Phase Extraction (SPE)</u> coupled with High-performance liquid chromatography (HPLC) with UV detection (Fig. C21, appendix C) is one of them.

5.) Cadmium (Cd)

Atomic Absorption Spectroscopy (AAS) and Inductively Coupled Plasma (ICP) are adopted in finding the concentration of cadmium, but they have some drawback like non-linearity and difficulty of handling halogens (Raikar et al., 2012). So they proposed the long period grating fibre optic sensors (LPGF Optic Sensor) due to their small size, high sensitivity and possibility of distributed measurements. In other hand, one of the commercial measurement instruments is <u>Online Heavy Metals Analyzer OVA5000</u> (Fig. C29, appendix C).

6.) <u>Vinyl chloride (CH2=CHCl)</u>

To the best of writer's knowledge, there is no real-time and on-line measurement instrument or sensor for vinyl chloride detection in drinking water. In laboratory, the standard method for measuring the vinyl chloride is gas chromatography couple with mass spectrometry (GC-MS).

7.) Chromium (Cr)

Sánchez-Moreno et al. (2010) have been developed the Chromium (VI) Potentiometric Sensors based on graphite-epoxy (GE). This sensor showed good quantitative criteria and exhibit optimal potentiometric characteristics such as wide dynamic response ranges (measurement range), high selectivity responses, low detection limits, rapid response times, simple, robust and could be used for on-line monitoring of hexavalent chromium concentration. As the writer's knowledge, <u>Online Heavy Metals Analyzer OVA5000</u> (Fig. C29, appendix C) and <u>In-Field Hexavalent Chromium Water Analysis</u> (Fig. C10, appendix C) are commercial measurement instrument available today.

8.) <u>Copper (Cu)</u>

Measurement methods and instrument for copper monitoring was already explained in section 3.4.1

9.) Epichlorhydrine

As writer's knowledge, there is no real-time and on-line measurement instrument or sensor for Epichlorhydrine detection in drinking water. Laboratory measurement methods and instrument also very limited. In laboratory, the standard method for measuring the Epichlorhydrine was Gas Chromatography couple with Flame Ionization Detector (GC-FID) (Cai and Zou, 2010).

10.) Polycyclic aromatic hydrocarbons (PAH)

There are several real-time and on-line measurement for PAH monitoring in drinking water i.e. <u>The HydroCTM PAH</u> (Fig. C11, appendix C), <u>EnviroFlu-HC</u> (Fig. C12, appendix C), <u>On line water analyser UV500</u> (Fig. C22, appendix C). Furthermore, HydroCTM PAH and EnviroFlu-HC are easier to install in the pipeline while on line water analyser UV500 is less flexible but capable to measuring various parameters.

11.) <u>Nickel</u>

Normally, several complicated, time consuming and expensive preconcentration – separation techniques are needed before measuring Nickel (Sun et al., 2006; Yunes et al., 2003). In other hand, Aksuner et al. (2012) have been proposed a precise, low cost, sensitive and highly selective optical sensor (optode) for determination of Ni(II), based on the fluorescent thiazolo-triazol derivative

entrapped in PVC matrix. In other hand, <u>Online Heavy Metals Analyzer</u> <u>OVA5000</u> (Fig. C29, appendix C) is one of real-time and on-line monitoring instrument available in market.

12.) Nitrate and 13.) Nitrite

Many commercial real-time and on-line probe sensor and flow-cell analyzer have been recently proposed for nitrate and nitrite monitoring in drinking water i.e. <u>TONI® On-line TN analyzer</u> (Fig. C26, appendix C), <u>AV450 UV nitrate monitor</u> (Fig. C14, appendix C), <u>NITRATAX clear sc</u> (Fig. C15, appendix C) and <u>ISEmax</u> <u>CAS40/CAM40</u> (Fig. C16, appendix C). Some of nitrite sensors are exist in multiparameter sensors i.e. <u>TONI® On-line TN analyzer</u> (Fig. C26, appendix C), <u>YSI-6920DW multi-probe</u> (Fig. C22, appendix C) and <u>On line water analyser UV500</u> (Fig. C21, appendix C).

14.) <u>Lead (Pb)</u>

Nowdays, sophisticated analytical techniques like atomic absorption, atomic emission, inductively coupled plasma spectroscopy and voltammetry (Espada-Bellido et al., 2009; Faye et al., 2012) are currently used for lead detection in water, but there is still disadvantage due to its cost, complexity and chemical used. Recent studies about lead detection by fluorescent sensor have been done by Guo et al. (2008) and Faye et al. (2012). The detection mechanism uses a flash to excite electrons of substances and causes the Calix-DANS3-OH to emit light which detected by spectrometer. This proposed method promises a free-reagent, low cost, quick measurement, simple and small instrument, despite it still face detection limit and selectivity problems.

As writer's knowledge, <u>Online Heavy Metals Analyzer OVA5000</u> (Fig. C29, appendix C) is one of the real-time and on-line commercial that available in market.



Figure 3.6 Schematic diagram of the microreactor (Faye et al., 2012)

15.) Total trihalomethanes (THM)

Nowadays, mostly THM analysis is performed by chromatography or atomic absorption spectroscopy, which is expensive and not portable for in situ measurements (James et al., 2005). Recently, electronic noses technologies have been developed by scientists worldwide that are useful for VOCs & Chloroform monitoring (Goschnick et al., 2005; Wilson et al., 2012), but they are still not applicable in drinking water analysis due to their detection limit. Electronic noses consist of a group of chemical sensors that have chemical-selective layers, i.e., materials with the function of interacting chemically or physically with the analytes, which produce a signal used to qualify and/or quantify the analytes (Gonçalves and Balogh, 2012). For field measurement, there is <u>Triton field portable THM sensor</u> (Fig. C18, appendix C) which is provide real-time Total THM measurement and <u>MS2000 THM Monitor</u> (Fig. C19, appendix C) which is capable to real-time and on-line monitoring Total THM in drinking water.

16.) <u>Turbidity</u>

Measurement methods and instrument for turbidity monitoring was already explained in section 3.4.1

17.) Multi-parameter measurement instrument

There is no universal monitoring instrument for water quality monitoring and contaminant detection (Storey et al., 2011). However, individual parameter instrument are limited and not economic for practical applications. In recent years, development of solid-state multi-parameter sensor for drinking water quality monitoring is limited on classical parameters such as turbidity, pH, temperature, conductivity, free chlorine, etc (e.g. IntellisondeTM, Hach pipe sonde and <u>YSI-6920DW multi-probe</u>) (see fig. C20, C22, C30 in appendix C). In the other hand some multi-parameters for heavy metals and nitrogen monitoring have been present, but usually still require reagents and has and large complicated instruments (<u>OVA 5000 On-line heavy metal monitor</u> and <u>On line water analyser UV500</u>) (see fig. C21, C29 in appendix C).

As writer's knowledge, <u>IntellisondeTM</u> is the only commercially available in-pipe type sensor that able to real-time and on-line monitoring without separated analyzer or transmitter. An <u>IntellisondeTM</u> detection system consists of several electrochemical – optical sensors (see the figure below) and already integrated with data logging and communication technology (i.e. Ethernet, GPS, GPRS, Modbus RTU RS232). Despite of the advantages, this sensor showed several drawbacks due to fouling problems (see case study section 4.5.2).



Figure 3.7 Detail view the sensing elements of IntellisondeTM (Aisopou et al., 2012)

3.5 DISCUSSIONS

Sensors are suitable alternative for measurement instrument in RO-DWQMS. There are also qualitative and quantitative criteria that can be used as the basis of sensors selection. USEPA itself has TTEP, a rigorously test technologies against a wide range of performance characteristics (USEPA, 2005c). However, these tests are very technical and specific, for the initial selection process, Delphi method (Landeta et al., 2011) may be considered for selecting multiple sensors before being tested through TTEP.

Based on the measurement methods and sensors availability on the market, it appears that there is a gap between sensors technologies available and current regulations, where the commercial sensors for RO-DWQMS not yet available for all chemical parameters required by French regulation. Some parameters such as Odor, Taste, Acrylamide, Antimony, Vinyl Chloride and Epichlorhydrine, there are no available real-time and on-line sensors on the market. The availability of reliable sensor is still limited to global or classic water quality parameters like Free chlorine, Conductivity, pH, Temperature and Turbidity. Several available sensors for measuring metals such as Total iron, Aluminium and Copper which are exists in reference quality of French regulation still use a chemical reagent in the analysis process. The impact of using sensors that require chemical reagents may be not felt so significant if we used in water treatment plants due to the limited number of sensors deployed, but if we used in distribution network, especially for real-time and on-line monitoring, it could be problems in term of maintenance and amount of waste generated as well. In addition, the costs allocation for replacement reagents also cause this tool may be uneconomical.

There are also no vendors or companies which can provide all sensors required by French regulation. With these conditions, real-time and on-line monitoring for the parameters required by French regulation must combine different sensors from multiple vendors. This has become one of major obstacles in application if RO-DWQMS in order to get the maximum security level. In addition, several factors such as high capital cost and sensors compatibility are also constraints. State of the arts of measurement instruments or sensors today is IntellisondeTM. This is only commercial in-pipe type sensor that able to real-time and on-line monitoring up to 12 physical-chemical parameters including flow meter with appropriate detection limits. Furthermore this sensor is also integrated with a data transmitter, so that the data transmission process can be performed without other tools such as separate analyzer or transmitter which is generally installed around the sensor. Besides the various advantages, IntellisondeTM still has shortcomings i.e. vulnerable to fouling, even though this sensor was already equipped with anti-fouling technology.

Recent study in Surface Acoustic Wave (SAW) Sensor, Electronic Tongue/Nose and Fibre-optic sensor promises simple and low cost sensors with low detection limit and also possibility for real-time and on-line monitoring. In addition, fibre optic sensors have been showed several advantages such as immunity to electromagnetic interference, high sensitivity, a small sensor unit, security environments, ability to process signal at large distances from the sensor with little degradation, and have the ability to work under high temperature and high pressure conditions (Zhao et al., 2001).



Figure 3.8 Principle process of DSS (Tanimola and Hill, 2009)

Furthermore, fibre optic sensors can be used in distributed measurement/sensing systems (DSS). DSS is a system utilises sensing cables that are based on standard fibre optic cables and intend to obtain a measurement profile along the entire length of pipe by sensing cable at flexible intervals (detail process described elsewhere in Tanimola and Hill, 2009). Fortunately, this kind of

sensors can be easily integrated into SCADA systems. If we can merge with sensing element that has been described previously (in Chamjangali et al., 2009; Goicoechea et al., 2008; Valdivielso et al., 2003), in the future there are big opportunity to have a multi-parameter sensors for water quality monitoring along the pipeline.



CHAPTER 4

IMPLEMENTATION OF RO-DWQMS IN DISTRIBUTION NETWORK

4.1 INTRODUCTION

In order to achieve the high security level and efficient drinking water distribution network, the implementation of RO-DWQMS in distribution network is an important issue.



Figure 4.1 Implementation process flowchart (USEPA, 2009 with changes)

This goal can be achieved by establishing precisely the main objective of real-time & on-line monitoring system, selecting the appropriate parameters or indicators to be monitored, choosing the appropriate instruments/sensors and determining the event detection system to be used. Ideally, when a contamination event is detected and a specific contaminant is identified by the RO-DWQMS, the water quality model can immediately run scenarios to determine extent, location and concentration of contaminants throughout the distribution system at various times. This information will support the operator in monitoring center to more quickly conduct initial response actions.

Despite of their benefits, there are some constraints in implementation of RO-DWQMS i.e. availability instrument (see section 3.4), high capitals costs and sensor integration (USEPA, 2009). There are also some reason why selecting the appropriate water quality indicators is important to reduce number of sensors which will be deployed in network. Besides that, the number of sensor required and data transmission is also a crucial part in implementation of RO-DWQMS in distribution network.

4.2 EVENT DETECTION SYSTEM

The software that analyzes data from on-line water quality monitoring instruments/sensors is referred to an Event Detection System (EDS). The function of the EDS is to identify and alarm when changes in water quality indicate a potential contamination event (USEPA, 2009).

Rather than just relying on monitoring process based on threshold limit, EDS can provide more detailed information, including anomaly changes. In other words, some contamination incidents might not cause water quality parameters to move outside of threshold limit, but still cause significant changes in water quality and it can be detected by an EDS (USEPA, 2010).

For example, in RO-DWQMS with free chlorine as indicator, as described previously (see Appendix A page A1), chlorine is one of the most sensitive chemical parameters so we can use as an indicator and its concentration relate with other chemical parameter like E. Coli, Nitrite and THM. In RO-DWQMS, if an anomaly is detected, warning alarm will active and the response must be given by operator (e.g. block off suspected pipe segment), then verification could be done by field measurement using portable measuring instrument. Portable instrument is important to measure quickly rather than take the sample and analyze in laboratory. EDS use algorithms to analyze the data generated by sensors to filter out variations in water quality that typically occur and identify contamination events.



Figure 4.2 Example: Role of EDS in RO-DWQMS with free chlorine as indicator

There are quantitative criteria to select an appropriate EDS, several quantitative and qualitative criteria are already mentioned in section 3.3. Others criteria like false response rate, ease of calibration, calibration and maintenance frequency and compatibility with sensors are also considered in EDS selection.

Currently, there are some commercially available EDS developed for drinking water applications. Hach Event Monitor, S::can Water Quality Monitoring Station and YSI EcoWatch Software are part of package systems containing both on-line monitoring equipment and EDS software. Guardian Blue's Event Detection System integrates five Hach water quality sensors (i.e. Hach CL17 chlorine analyzer, pH, temperature and conductivity electrode, Hach 1720D turbiditimeter, astroTOC UV analyzer) or Hach PipeSonde (Fig. C30 appendix C) with Hach Event Monitor software to provide RO-DWQMS. Every 60 seconds the system analyzes sensor data and calculates the trigger signal, which indicates a deviation from the water quality baseline. The system alarms if a trigger signal exceeds a user-set threshold, indicating an "event", then the event fingerprint is compared to fingerprints stored in agent library (contaminant database) to classify the threat contaminant suspected. This system also equipped by Automatic Sampler to capture a real-time water sample at designated monitoring locations and allows water utilities to conduct additional analysis.



In other hand, Sandia National Laboratories, in conjunction with the U.S. Environmental Protection Agency (USEPA), developed the CANARY: Event Detection Software, a free, open source software solution for water utilities. CANARY reads in time series data to identify anomalous water quality events. CANARY can read data from any sensor manufacturer for any type of water measurements and any number of sensors (USEPA, 2010). In addition to anomalous conditions or potential contamination events, CANARY can detect unexpected normal events such as a sensor malfunction or a pipe break (Storey et al., 2011).

4.3 SENSOR PLACEMENT

Determining the number of sensors and their locations in the distribution system is a critical process in meeting the main objective of an on-line water quality system and maximizing cost effectiveness (USEPA, 2009). There are some optimization software for locating and determining the number of sensors like optiMQ-S, TEVA-SPOT and PipelineNet (Ostfeld and Salomons, 2005; USEPA, 2009). All of optimization software requires distribution system hydraulic model for extended period of time (e.g. hours or days). This type of hydraulic model is also called an Extended Period Simulation (EPS) model which can be constructed with water distribution system modeling software like EPANET and WaterCAD. Further consideration should be performed to the locations identified by the software if it does not comply with operator access, site security, environmental conditions, and existing infrastructure (USEPA, 2009).

4.4 ROLE OF SMART GRID: SCADA SYSTEM

As described previously, The smart grid is a terms in electricity distribution network that uses computer technology to provide the communications and data distribution between suppliers and consumers in order to improve the efficiency, importance, reliability, economics, and sustainability. One of the smart grid applications in industry and infrastructure is SCADA system. Generally, the SCADA (Supervisory Control and Data Acquisition) system is an operational twin composition of a large and strong software package and a networking infrastructure into a global supervision system (Kang et al., 2011). Like AMR and AMI for water flow metering, SCADA systems can provide the communication and data acquisition infrastructure necessary to manage the data produced from sensors (USEPA, 2009). The general configuration of the SCADA network composed of three parts: master station, communication links, and remote substation. The SCADA data transmission can be done with radio, fiber optics wire, GPRS, WLAN or Low Earth Orbit (LEO) Satellites (Vaccano and Villacci, 2005; Avlonitis et al., 2007; USEPA, 2009; Dehua et al., 2012). The issues that required attention in SCADA systems included reliability, overall security and data transmission speed (Sanchez J., 2006).

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Figure 4.4 Example of SCADA configuration network (http://en.wikipedia.org/wiki/DNP3)

4.5 CASE STUDIES

Some cases studies have been done for the sake of verify the measurement instruments or sensors in domain of real-time and on-line water quality monitoring. The following table summarizes the case studies results of utilization the Intellisonde and Hach Guardian Blue which are carried out in the laboratory or field and the short explication are given after that.

Sensor	Advantages	Drawbacks	References
Intellisonde™	Reliable, simple and easy to implement sensor; Can be integrated into existing network monitoring software; Sensor has a good dynamic response, repeatability and accuracy	Sensor has a low accuracy, poor stability and fouling problems.	Intellitect water, 2012; Aisopou et al., 2012
Hach Guardian Blue	Can detect the wide range contaminants; Sensor has a little maintenance; Troubleshoot can be done remotely; Can be programmed to recognize future occurrences of the same event and notify operations	Sometimes created many false alarm; The results of agent library for contaminant identification are erroneous; Astro TOC [™] UV Analyzer had many maintenance problems	Hohman, 2007

Table 4.1 Summary of some cases studies results

4.5.1 Water Quality Monitoring Pilot Project Using Intellisonde[™] in Lisbon

In January 2010, EPAL (a water supply company in Portugal) commenced a pilot project to monitor water quality in Lisbon's distribution network using Intellisonde. The objective is to evaluate the water quality data and test the sensor capability to integrate with existing network management system.



Figure 4.5 Implantation of Intellisonde[™] in Lisbon water supply (Intellitect water, 2012)

In this trial, 4 sensors was inserted into distribution network pressurized pipes and connected to existing EPAL's network monitoring software. Sensor needs maintenance routines every 6 month for replacement the Chlorine Sensors and Reference Electrodes, which had reached the end of their useful life. The result showed that the sensors were very reliable, simple and easy to implement. The water quality data was also successfully integrated into existing network monitoring software, downloaded and combined to understanding flows and water quality through distribution network

4.5.2 Laboratory and Field Study of IntellisondeTM

Laboratory and field trial study has been done by Aisopou et al. (2012) using IntellisondeTM in water transmission main and also in three district meter areas of water distribution system. This sensor has a good dynamic response and

repeatability for capturing trends and sudden changes. The performance of this instrument was also consistent to the laboratory analysis, even though that there were several drawbacks due to low accuracy, poor stability and fouling problems.



Figure 4.6 Deterioration of the water quality sensors: a) bio-fouling; b) lime scale builtup; c) free and total chlorine data corresponding to the deteriorating performance (Aisopou et al., 2012)

4.5.3 Pilot Field Study of Hach Guardian Blue's Event Detection System

Guardian Blue's Event Detection System is in of the most complete monitoring instrument which intended to drinking water quality monitoring. One of the advantages is this instrument equipped with an Agent Library which is able to tentatively identify contaminants based on the chemical fingerprint produced by an 'unknown' substance.



Figure 4.7 Hach Guardian Blue's Event Detection System configuration: A) Event Monitor; B) astroTOC UV analyzer; C) Hach CL17 chlorine analyzer, pH, temperature and conductivity electrode and Hach 1720D turbiditimeter (Horman, 2007)

In reality, a field study by Horman (2007) showed that this instrument can detect the wide range of contaminant even though the free chlorine sensor is too sensitive and created several false alarms. The results for the Agent identification system are also erroneous. Some of the results could be possible but others are not even close. The TOC analyzer produced the majority of the problem. This sensor malfunctioned often and required a great deal of maintenance.

4.6 DISCUSSIONS

Implementation of RO-DWQMS in the existing distribution network is a crucial issue today. In this section the implementation process has been described briefly and systematically and also discussed the important elements. A fundamental thing that must be owned by utilities to implement the RO-DWQMS is distribution system hydraulic model. Hydraulic model is digital information about flow, elevation, pipe length and other physical information as a base for water quality simulations in EPS mode. Hydraulic models can be created using software EPANET and WaterCAD.



Figure 4.8 Example of implications several objectives to parameters monitored and sensors used

Before going to the next phase, the utilities needs to define precisely the purpose of implementation, as this will affect the parameters to be monitored. Then these parameters are closely related to type of sensor used.

Generally, recent sensors are equipped with EDS. EDS is very important for anomaly detection, because some contamination incidents might not cause water quality parameters to move outside of threshold limit, but still cause significant changes in water quality. Sensor compatibility issues are still an obstacle because not many stand alone EDS like CANARY which can be connected to any type of sensors. To obtain such a techno-economic monitoring system, determination of number and location of sensors also becomes crucial issues in RO-DWQMS. Determination of number and location of sensor can be done with software like optiMQ-S, TEVA-SPOT and PipelineNet, where this software requires the distribution network hydraulic model developed by EPANET. After sensors and EDS determined, data transmission can be done with radio, fiber optics wire, GPRS, WLAN or LEO Satellites in frame of SCADA system. Some cases studies have been done for the sake of verify sensors and utilization of IntellisondeTM in Lisbon in 2010 was one of the most successful.

CONCLUSIONS

Urbanization is a worldwide problem and it has shown negative effects to water resources and drinking water quality. Drinking water is a basic human needs and a very important role in supporting health and quality of the citizen's life, but it is very vulnerable to an intentional and accidental contamination, especially in distribution network. In this case, the role of monitoring water quality in drinking water distribution networks is essential and must be continually developed to ensure the safety of drinking water and the effectiveness of monitoring method. To deal with these problems, there are smart water grid systems which provide a real-time and on-line monitoring of drinking water quality. This literature research aimed to improve our understanding of real-time and on-line drinking water quality monitoring system (RO-DWQMS) in distribution network, particularly in domain of measurement instruments or sensors. This paper generally divides in 3 main parts, first part concern about chemical parameters to be monitored by considering the France regulation, second part describe state of the arts in measurement instruments and sensors and last part showed the implementation of RO-DWQMS in distribution network. The results of resume and data analysis from diverse scientific journal, research paper and website led to the following conclusions:

- Determining the implementation purpose of RO-DWQMS in distribution network is a fundamental step and that will affect the type of parameters to be monitored and sensors to be used.
- In this study an example of chemical indicators / parameters selection is given in order to completely replace the existing grab & analysis methods with the RO-DWQMS in distribution network level. The selection is based on current regulations and related research. The result 14 chemical indicators and 16 chemical parameters were selected. From various study we know that the 14 selected chemical indicators have an important role in monitoring process due to its signification to health, to distribution systems and relation with other parameters.

- There is a gap between sensors technologies available and current regulations, where the commercial sensors for RO-DWQMS not yet available for all chemical parameters required by French regulation. In addition, several factors such as high capital cost and sensors compatibility are the current constraints.
- State of the arts of measurement instruments or sensors today is IntellisondeTM. This is only commercial in-pipe type sensor that able to real-time and on-line monitoring up to 12 physical-chemical parameters including flow meter with appropriate detection limits. This sensor is simple, compact, easy to install, and already integrated with transmitter data. Despite of that, fouling problems is still a constraint in sensor performance.

Recent study in Surface Acoustic Wave (SAW) sensor, Electronic Tongue/Nose and Fibre-optic sensor promises simple and low cost sensors with low detection limit for real-time and on-line monitoring. But they are not at a stage where they can readily used in existing operations.

- Implementation steps of RO-DWQMS are as follows: 1.) Create a distribution system hydraulic model 2.) Define precisely the main objective, 3.) Selecting the appropriate parameters or indicators to be monitored, 4.) Choosing the appropriate instruments / sensors and determining the event detection system to be used, 5.) Choosing data transmission system and 6.) Determine their number and location in distribution network.
- EDS has an important role in RO-DWQMS. EDS can detect not only if water quality parameters move outside of threshold limit, but also anomaly detection. State of the arts of EDS is Hach Event Monitor which integrated with Agent Library (contaminant database). Using five chemical indicators, this software is capable to detect anomaly changes and predict wide ranges contaminants based on algorithms analysis. However, depend on the case study, this EDS still need to develop to improve TOC sensors performance, reduce false alarms and false contaminant identification.

RECOMMENDATIONS FOR FURTHER RESEARCH

RO-DWQMS is a new emerging concept due to development of sensor technology and communications, so further studies are needed to improve this system so it will be ready for field application. These are several recommendations for further research related to the RO-DWQMS

- There are needs of laboratory research to determine more relationship between the global water quality parameters / indicators (see table 2.1) with other chemical / microbiological parameters to be used as the basis for algorithms analysis so it can develop contaminant prediction in EDS.
- There are needs of sensor which can detect Odor, Taste, Acrylamide, Antimony, Vinyl Chloride and Epichlorhydrine.
- Concerning the high capital cost of available commercial sensors. Studies about sensor selection method are urgently needed. With same reason, a comparative study of various sensors placement methods is necessary.



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Appendix A

(Profiles of indicators and parameters to be monitored)

CONTENTS

A.1 Profiles of chemical indicator to be monitored in drinking	
water distribution network	. A1
A.2 Profiles of chemical parameter to be monitored in drinking	
water distribution network	 . A7

A.1 Profiles of chemical indicator to be monitored in drinking water distribution network

1.) Aluminum Total

The total aluminum is the sum of forms in suspension, colloidal and monomer (Verissimo and Gomes, 2008). Aluminum is the most abundant metal on earth and constitutes about 8% of the earth crust. In the water treatment process, aluminum is used as a coagulant $Al_2(SO_4)_3, 18H_2O$ (Verissimo et Gomes, 2008). There is no doubt that aluminum is a neurotoxin. An epidemiological study showed that a low dose of long-term exposure can cause Alzheimer's disease (Flaten, T.P., 2001). Aluminum sulphate (the coagulant) is known as one of the sources of taste and odor in drinking water (Young et al, 1996). In the lead pipeline, the solubility of lead corrosion generally corresponds to aluminum concentration (Kim et al., 2011).

2.) Ammonium (NH_4^+)

Ammonium is an essential parameter in assessing the drinking water quality and industrial processes (Kwan R.C.H et al., 2005). The ammonium is present in many cleaning products and disinfectants. Ammonium ions are a waste product of metabolism of men and animals. So this is an excellent indicator of water pollution by organic waste from agricultural, domestic or industrial. The physico-chemical water treatment is very effective in removing suspended solids, phosphorus, oil and heavy metals, but is unable to remove the soluble ammonium (Peavy et al., 1985). Ammonium can transform into nitrate, which is very toxic to humans (Kurama et al., 2002). In addition, ammonium and other organic compounds can react with chlorine and reduce the disinfection capacity (Rusell S., 1994).

3.) Free and Total Chlorine

They were the most sensitive indicators of the wide range contaminants (USEPA, 2005). Chlorine is one of the most widely used disinfectants. It is easily applicable and very effective against the pathogenic microorganisms. When chlorine is added to water for disinfection, it reacts first with dissolved organic and inorganic compounds in water (e.g. to form chloramines). The total amount of chlorine is employed during this process is referred to as "chlorine demand of water". Free chlorine is the concentration of hypochlorous acid (HOCI) and hypochlorite ion (CIO-) in water that does not react with organic matter. While chlorine is the total concentration of free chlorine, but you must have the free chlorine 0.1 mg / 1 in the distribution to ensure protection against contamination. Chlorine gives no harmful effect on health but it can cause the unpleasant odor or flavor. As the indicator, the decrease in the concentration of free chlorine is associated with microbiological activity (Dukam et al., 1996; Hall et al., 2007; Helbling and VanBriesen, 2008), corrosion of pipe iron (Frateur et al., 1999), nitrite concentration (Pintar and Slawson, 2003), pesticide (USEPA, 2009) and THM (Chowdhury et al., 2008).



Figure A.1 Response of free chlorine versus controlled injections of E. coli (Helbling and VanBriesen, 2008)

4.) <u>Chlorites (ClO₂)</u>

It is used for disinfection in a few plants of municipal water treatment in the form of chlorine dioxide (ClO₂). An advantage in this application, compared to more commonly used chlorine, is that trihalomethanes are not produced from organic contaminants. However, chlorine dioxide is reduced to chlorite by iron, manganese, and organic matter in water (Werdehoff et Singer., 1987). When ClO₂ is used under typical conditions for disinfection of water, about 50-70% is converted to chlorite ion (ClO₂⁻) and 30% to chlorate ion (ClO₃⁻) based on following reaction (USEPA, 2000) ;

$$2\text{ClO}_2 + 2\text{OH}^- \iff \text{ClO}_2^- + \text{ClO}_3^- + \text{H}_2\text{O}$$

Chlorite can cause hemolytic anemia in a low exposure level while higher levels of exposure can lead to increased methemoglobin (WHO, 1996). This substance is potentially mutagenic (USEPA, 2000; WHO, 2005; Richardson et al., 2007) and genotoxic (Feretti et al., 2008).

5.) Conductivity

The conductivity of water is often used as a general indicator of drinking water quality (Ramesh et al, 2010; Onabolu et al, 2012). The electrical conductivity of a substance is defined as the ability or power to conduct or transmit electricity. Conductivity in water is affected by the presence of dissolved inorganic solids such as chloride, nitrate, sulfate, phosphate anions, sodium, magnesium, calcium, iron, and aluminum cations (USEPA, 2012). Conductivity is also affected by temperature, warmer the water, more the conductivity (AWRI, 2011). Because the electric current is carried by ions of the solution, the conductivity increases when the concentration of ions increases and the concentration also proportional to the water hardness. No significant effects of conductivity on health, but in high concentrations, it can give a laxative effect and salty water. At the distribution network, a low mineral water (conductivity <200 S / cm) can be corrosive to pipes and can cause dissolution

of toxic metals such as lead. Excessive mineralization (conductivity> 1100 S / cm) can be the source of deposits (Syndicat Eaux de la Faye, 2012).

6.) <u>Color</u>

The color is a property of natural water and treated water that is perceptible to most people without any kind of instrumentation (Hongve and Åkesson, 1996). The colored water is not



preferred by consumers (Hurlimann, A. and McKay J., 2007).

Figure A.2 Correlation of color and MPN E. coli in river water in winter (♦), in spring (▲), summer (●) and autumn (■) (Okeke et al., 2011).

The color of water due to the absorption of certain wavelengths of radiation normal white light by substances dissolved or dispersed in the colloidal state. The color measured water containing in suspended solids is called "apparent color" and that measured on water samples after remove the suspended

particles is the "true color". Water can be colored for several reasons such as the presence of colored organic matter from decaying of natural vegetation like soil leaching or the presence of industrial waste colorful like waste from pulp and paper and textiles industry. In the pipe, the presence of metals from corrosion (rust) can colorize water (AWWA, 1971; MassDEP, 2012). Recently, a study by Okeke et al (2011) showed that the seasonal variation of E. coli in rivers strongly correlated with color.

7.) <u>Copper (Cu)</u>

Copper occurs in nature as the metal and form of minerals, especially cuprite (Cu_2O) and malachite ($Cu_2CO_3(OH)_2$). Copper is widely used in the metal and electrical industry. Drinking water contains very small amounts of copper (usually released by the inner pipe). Exposure of copper in the long term may cause kidneys and livers damage and Wilson disease (USEPA, 2012). Copper also has the organoleptic effect. It can give off flavors, stain laundry and plumbing fixtures. In the pipeline, the increased flow can immediately increase the concentration of bacteria and copper due to detachment (Lehtola et al., 2007). The corrosion rate of copper line is influenced by the alkalinity, pH and concentrations of organic matter (McNeill and Edwards et al., 2004). A recent study showed that Cu and its corrosion products may decrease the concentration of chlorine in higher pH and accelerated the formation of haloacetic acid (HAA) (Zhang and Susan, 2012).



Figure A.3 Chlorine decay (left) and the formation of HAAs (right) in the presence of different concentrations of Cu (II); [HOCl] initial 10 mg / L; triplicate; pH 8.3 (Zhang et Susan, 2012).

8.) <u>Total Iron</u>

Iron is found mainly in waters deprived of oxygen. Its origins are diverse. But in general, the iron in water comes primarily from natural sources by dissolution of minerals in the case of ground water or sediment. Sometimes it can come from industrial discharges or corrosion of metal pipes. the use of iron salts as coagulants for drinking water production can also bring iron (e.g. FeCl₃) (Shi et al., 2004). Iron is an essential element for humans. However, in the distribution system, corrosion of pipe can cause several drawbacks such as the organoleptic effect from the crust of corrosion, the reduction of chlorine, dissolved oxygen (Sarin et al., 2004), biofilm growth (Siyuan et al., 2005), and the adsorption of substances such as arsenic (Raven et al., 1998) and radium (Field et al., 1995).

9.) Odor and 10.) Taste

There are several main sources of odor and taste in drinking water such as the chemical and microbial content of the natural water, chemicals used during treatment and contamination or reactions that occur during distribution and storage (Dietrich, 2006). There was no direct effect of odor to health (Dionigi et al., 1993) but for most consumers, taste and odor are the only way to determine the safety of tap water (McGuire, 1995) and associated with the safety of drinking water (Srinivasan and Sorial, 2011).



Cyanob acteria

Figure A.4 Diagram of the formation of MIB and Geosmin (Srinivasan and Sorial, 2011).



Figure A.5 Cyanobacteria appear to have been primarily responsible for unpleasant taste and odor problems and increased treatment costs in the water supply system in Saginaw-Midland (Saginaw Bay, Lake Huron, United States) during 1974-1980. Changes of the peak biomass of cyanobacteria in Saginaw Bay have been accompanied by strong changes the maximum concentration of the odor (A), and the number of days the smell of drinking water exceeded the threshold (threshold = 3) (B) (Bierman et al., 1984).

Geosmin (trans-1 0,10-dimethyl-trans-9-decalol $C_{12}H_{22}O$) et le MIB (2methyl-isoborneol $C_{11}H_{20}O$ were identified as major causes of taste and odor compounds in drinking water from surface water (Pirbazari et al., 1993; Jüttner et Watson, 2007) which is mainly lead by the metabolism and biodegradation of certain types of bacteria such as cyanobacteria, filamentous bacteria and actinomycetes (Watson et al., 2008). The detection

limits of man for these compounds are extremely low, for the MIB from 10 ng / 1 (Korth et al., 1992) to 0,1 μ g/l (Borjesson et al., 1993) and for Geosmin 4 ng/l to 0.2 μ g/l (Polak and Provasi, 1992).

11.) <u>pH</u>

The pH is a measure of the activity of hydrogen ions (H +) contained in the water. The pH scale ranges from 0 to 14, a high acidity (pH = 0) and a base (pH = 14). There are no studies yet that show a direct relationship between pH and health. A pH <7 promotes the formation of an unpleasant odor, corrosion and dissolution of metals such as lead and cadmium in the pipeline (Xie et al., 2011). The water has a pH greater than 8.5 may promote the intensity of the color and the appearance of scale in the pipe (Morris J.C., 1971; Government of Nova Scotia, 2012). A recent study presented in the stagnant flow condition, the formation and dissolution of corrosion products of lead are very high at pH 7 and decreases rapidly at pH> 7 (Kim, E.J. et al., 2011).



Figure A.6 The total concentration of lead observed in the test pipe loop at different pH values and water flows (Kim, EJ et al., 2011).

12.) Temperature

Temperature is important in chemical reactions. A drop in temperature usually leads to slow chemical reactions. In the copper pipeline, the temperature gradients and pipe orientation are important factors in understanding the corrosion process (Jason and Edwards, 2004). The temperature also plays a role in consumer acceptance. At T> 25 $^{\circ}$ C, it can cause the palatability of drinking water, development of odors and the proliferation of unwanted organisms (Silvey et al., 1972). The concentration of odor also increases with temperature (Whelton and Dietrich, 2004).

13.) <u>Turbidity</u>

Turbidity is considered to reduce the transparency of a liquid due to the presence of undissolved materials. The turbidity of the water comes from the presence of various suspended solids and colloidal materials such as silt, clay, organic and inorganic matter, plankton and other microorganisms (Sadar, M.J., 1996). Turbidity is a general indicator of the water contamination by microorganisms of the solid particles, organic substances and metals (USEPA, 1999). Turbidity also a factor in consumer acceptance because it is associated with unpleasant tastes, odors (LeChevallier, M.W., 1981) and gastrointestinal tract disease (Mac Kenzie et al., 1994; Morris et al., 1996).

For a long time, the turbidity was known as a parameter associated with outbreaks of cryptosporidium and other waterborne disease (Juranek and MacKenzie, 1998). A recent study showed that the turbidity variation related with pesticides (Hall et al., 2007) and turbidity (Okeke et al., 2011).



Figure A.7 Correlation of turbidity and MPN E. coli in river water in winter (\blacklozenge), in spring (\blacktriangle), summer (\bullet) and autumn (\blacksquare) (Okeke et al., 2011).

14.) Total Organic Carbon (TOC)

TOC is the gross amount of organic matter which is not removed by the step of removing inorganic carbon. TOC in the raw water is mainly due to humic substances and matters partially degraded plant and animal. Humic acid, fulvic acid, amines, and urea are the types of natural TOC. Detergents, pesticides, fertilizers, herbicides, industrial chemicals, and chlorinated organic compounds are examples of synthetic sources (Visco et al., 2005). TOC may be nutrients essential for survival and multiplication of bacteria in the drinking water distribution network (Polanska M. et al., 2005). In addition, the abnormal changes of TOC related to the formation of disinfection by-products (THM) (Abd El-Shafy and Grunwald, 2000), odor and taste (Davies et al., 2004), pesticides (Hall et al., 2007), benzene (Visco et al., 2007).

All chemical indicators of the drinking water quality and its significations are summarized in the table B.3 in Appendix B.

A.2 Profiles of chemical parameter to be monitored in drinking water distribution network

1.) Acrylamide (C₃H₅NO)

Acrylamide is an organic solid white, odorless, like crystal. Acrylamide is a chemical intermediate in the synthesis of polyacrylamides, primarily synthetic polymers used as additives for water treatment. During production of acrylamide based polymer coagulant aids, a small amount of residual acrylamide may remain as an impurity. When these coagulant aids are used in water treatment, there is potential for residual acrylamide to be introduced into the water. Acrylamide is classified as probably carcinogenic (2A) by International Agency for Research on Cancer (IARC, 2012).

2.) Antimony (Sb)

Antimony is a silvery, lustrous gray metal present in the crust at a concentration of about 0.2-0.5 mg/kg. It is rarely present in the environment in its purest form, but is often found as sulphides and chlorides of trivalent (Sb III) and pentavalent (Sb V). It is used in alloys to increase hardness, and in the chemical industry as catalyst. It is also used to manufacture semiconductors, glass and fireworks. Antimony is regulated as a contaminant in drinking water, because it can cause health effects such as nausea, vomiting and diarrhea, when exposure exceeds the threshold for relatively short periods. Long term exposure can lead to increased blood cholesterol and lowers blood sugar (Westerhoff et al., 2008). Antimony trioxide (Sb₂O₃) is classified as possibly carcinogenic to humans (Groupe 2B) and antimony trisulfide (Sb₂S₃) not classifiable as to its carcinogenicity to humans (Groupe 3) by International Agency for Research on Cancer (IARC, 2012).

3.) Benzene (C6H6)

The presence of benzene in water is due to the discharge of the chemical industry (eg manufacture of styrene, phenol). It is a liquid organic solvent insoluble in water. It is also a cyclic hydrocarbon from oil, it is added to gasoline to increase octane value. Contamination of drinking water distribution network by benzene is also possible by soil contamination and permeation through plastic piping materials. Long term exposure can lead to anemia, decreased blood platelets and increased risk of cancer (IARC 2012; USEPA, 2012) and also potentially genotoxic (ATSDR, 2007).

4.) Benzo[a]pyrene

Benzo[a]pyrene is a polycyclic aromatic hydrocarbon (PAH) with the formula $C_{20}H_{12}$. Benzo[a]pyrene is not produced, and has no industrial use. It is a ubiquitously in the environment because it is formed during the combustion of organic matter. The principal source of benzo[a]pyrene present in surface waters is atmospheric. Leaching linings of storage tanks of water and water distribution could also contribute to the presence of benzo [a] pyrene in drinking water (USEPA, 2012). The effects of this substance on health are reproductive problems and increased risk of cancer (IARC, 2012; USEPA, 2012).

5.) Cadmium (Cd)

Cadmium occurs naturally in trace amounts in many geological formations. It is mainly used in various industries such as coatings industry, the manufacture of alloys, painting and the production of phosphate fertilizers. It can also move through the environment from sewage and chemical fertilizers and resulting risk of diffuse pollution. Drinking water can be contaminated by corrosion of galvanized pipes (USEPA, 2012).). It was found chronic ingestion of cadmium with Itai-itai disease, observed in Japan during 1910-1945. This disease is accompanied by symptoms of kidney and chronic renal failure (Friberg and Vahter, 1983 ; USEPA, 2012). Cadmium is also classified as carcinogenic for human (Group 1) by International Agency for Research on Cancer (IARC, 2012).

6.) Vinyl Chloride (CH2=CHCl)

The presence of these substances in water is of human origin. Vinyl chloride is a colorless organic with a sweet odor, and is used to make polyvinyl chloride plastic (PVC), material often used for pipe networks and treatment plants. Its presence may be due to a release of poor quality PVC. Vinyl chloride is a carcinogen (Group 1) (IARC, 2012).

7.) <u>Chromium</u>

The presence of chromium in water is not common. It is most often related to discharges of industrial wastewater. It can occur naturally in soil in very small quantities. In groundwater, the predominant form of chromium is oxidized like hexavalent chromium (Cr (VI)), présente sous forme de chromate ($\text{CrO}_4^{2^-}$) and dichromate ($\text{Cr}_2\text{O}_7^{2^-}$). Cr (VI) is toxic and mobile (Group 1 ; CIRC, 2012), while the trivalent chromium [Cr (III)] is less toxic and less mobile (Group 3 ; IARC, 2012) because it precipitates out of solution at pH 5 and above. In chlorinated drinking water, chromium is usually present in the hexavalent state (Santé Canada., 1986). The effects of this substance on health are allergic dermatitis and cancer risk (IARC, 2012; USEPA, 2012).

8.) Copper

Copper was already explained in section A.1 in this Appendix.

9.) Epichlorhydrine

Epichlorohydrin is an organochlorine compound, colorless liquid with a pungent, garlic-odor, sparingly soluble in water. It is a raw material used in the production of epoxy resins, glycerol, synthetic elastomers, and it is also applied in the pharmaceutical and paper industries (C. Sarzanini et al., 2000). In addition, it is widely used in the production of drinking water pipes as well as in the synthesis of cationic polyelectrolytes (flocculants), which are used in the purification process of surface water and wastewater (L. Lucentini et al., 2005). Exposure to epichlorohydrin at levels above the MCL for relatively short periods of time can damage the skin, liver, kidneys and central nervous system. Lifetime exposure can also cause chromosomal aberrations and probably carcinogenic (Group 2A) (CIRC, 2012; Sarzanini et al., 2000).

10.) Hydrocarbures aromatiques polycycliques (HAP)

They are a group of organic compounds whose structure has two or more benzene rings. HAP released into the environment primarily as a result of incomplete combustion of various fuels, including in the composition of petroleum and its products drifts (Neff, 1979). In the *l'arrêté de 11 Janvier 2007*, PAHs are the sum of benzo [b] fluoranthene, benzo [k] fluoranthene, benzo [ghi] perylene, indenol [1,2,3-cd] pyrene. Benzo [a] pyrene is one of the most toxic PAHs of this family of molecules. PAHs are carcinogenic substances (USEPA, 2012) and can disrupt the endocrine system (Brun et al., 2004).

11.) <u>Nickel</u>

This metal is released into the aquatic environment of the dissolution of rocks and soils, atmospheric deposition and biological cycles. In addition, the high consumption of nickel in industrial activities and wastewater leads to pollution of the environment (Aouarram et al., 2007). It is a moderately toxic (Group 2B), while the nickel compounds are carcinogenic (Groupe 1) (IARC, 2012). It can also cause allergic reactions and a disorder known as nickel-eczema (Mckenzie and Smythe, 1998).

12.) <u>Nitrate</u> et 13.) <u>Nitrite</u>

Nitrate and nitrite ions are present naturally in the environment. They are the nitrification result of the ammonium ion (NH4⁺) present in water and soil, which is oxidized to nitrite by Nitrosomonas bacteria and to nitrate by Nitrobacter bacteria. The presence of nitrates and nitrites in water is an indicator of pollution from agriculture (fertilizer) to urban (malfunction of sewage) or industrial. Nitrate can be reduced to nitrite, which can react with secondary or tertiary amines present in the human body and causes the formation of nitrosamines. They are known to be carcinogenic and at high concentrations in the blood can react with iron (II) of hemoglobin to form methemoglobin, which lacks the ability to carry oxygen. This condition is known as methemoglobinemia (Fung et al., 2008).

14.) <u>Lead (Pb)</u>

A recent study showed that 50-75% of total lead in tap water can be attributed to the release of lead from pipes and lead service pipes (Sandvig and Kirmeyer, 2008). Lead can cause delays in physical or mental development of children and also kidney problems and high blood pressure in adults (EPA, 2012). There is a possibly carcinogenic (Groupe 2B) while the inorganic compounds of nickel are probably carcinogenic (Groupe 2A) (IARC, 2012).

15.) <u>Total Trihalomethanes (THM)</u>

THMs are the result of reactions between chlorine used in water treatment and organic compounds. They are chemical compounds of the family which includes chloroform (CHCl₃), bromoform (CHBr₃), dibromochloromethane (CHBrCl₂), et bromodichloromethane (CHBr₂Cl). They have been known to cause cancer, liver problems, kidney and central nervous system (Mosteo et al., 2009; USEPA, 2012).

16.) <u>Turbidité</u>

Turbidity was already explained in section A.1 in this Appendix.

Appendix **B**

(Summary tables)

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No	Chemical Parameters	MCL*	Unit	Potential Health Effects	Sampling Location	Reference
1	Acrylamide (C ₃ H ₅ NO)	0.1	µg/l	Disturbance of the nervous system or blood problems; Increased risk of cancer	A & B	Cavalli et al., 2004; USEPA, 2012
2	Antimony	5	µg/l	Increase of blood cholesterol	В	Westerhoff et al., 2007; IARC 2012
3	Arsenic	10	µg/l	Increased risk of cancer	А	Thirunavukkarasua, 2001
4	Barium	0.7	mg/l	Increase in blood pressure	А	USEPA, 2012
5	Benzene (C ₆ H ₆)	1	μg/l	Anemia; Reduction in blood platelets; Increased risk of cancer potentially genotoxic	В	ATSDR, 2007; IARC 2012; USEPA, 2012
6	Benzo[a]pyrene	0.01	µg/l	Reproductive problems, increased cancer risk	В	USEPA, 2012
7	Boron	1	mg/l	A reduction in sexual function; A gastrointestinal disorders	А	USEPA, 2012
8	Bromates (BrO ₃ ⁻)	10	_μg/1	Increased risk of cancer	А	USEPA, 2012
9	Cadmium (Cd)	5	µg/l	Itai-itai disease, Increased risk of cancer	В	USEPA, 2012; IARC, 2012
10	Vynil Chloride (CH2=CHCl)	0.5	μg/l	Increased risk of cancer	A & B	IARC, 2012
11	Chromium (Cr)	50	µg/l	Allergic dermatitis and cancer risk	В	USEPA, 2012; IARC, 2012
12	Copper (Cu)	2	mg/l	Injury to the kidneys and livers, Wilson disease	В	USEPA, 2012
13	total cyanide	50	µg/l	Nerve damage or thyroid problems	А	USEPA, 2012
14	1,2 - dichloroethane $(C_2H_4C_{12})$	3	µg/l	Increased risk of cancer	А	USEPA, 2012
15	Epichlorhydrine	0.1	µg/l	Damage the skin, liver, kidneys, central nervous system and chromosomal aberrations, probably carcinogenic	A & B	Sarzanini, 2000; IARC, 2012
16	Fluorides (F)	1.5	mg/l	Dental fluorosis and skeletal fluorosis, bone disease	А	USEPA, 2012
17	Polycyclic aromatic hydrocarbons (PAHs)	0.1	µg/l	Increased risk of cancer, disrupt the activities of the endocrine system	В	USEPA, 2012
18	Mercury (Hg)	1	µg/l	Kidney damage	А	USEPA, 2012

Table B.1 Chemical parameters of drinking water quality limits and its health effects

No	Chemical Parameters	MCL	Unit	Potential Health Effects	Sampling Location	Reference
20	Nickel 20 µg/l Increased risk of cancer, allergy dermatitis		Increased risk of cancer, allergy dermatitis	В	Aouarram et al., 2007; IARC, 2012	
21	Nitrates (NO ₃ ⁻)	Nitrates (NO3 ⁻) $50[a]$ mg/lMethemoglobinemia (blue baby disease)		A & B	Fung et al., 2008	
22	Nitrites (NO_2^-)	0.1 et 0.5[b]	mg/l	Methemoglobinemia (blue baby disease)	A & B	Fung et al., 2008
23	Pesticides (substance) and Total pesticides	0.1[c] et 0.5[d]	µg/l	Liver damage, Increased cancer risk; Anemia, Reproductive problems	А	Sanches et al., 2010
24	Lead (Pb)	25 et 10[e]	µg/l	Kidney problems, hypertension, irreversible intellectual impairment in children	В	USEPA, 2012; IARC, 2012
25	Selenium	10	µg/l	The loss of hair or fingernail, numbness in the fingers and toes, circulatory problems	А	USEPA, 2012
26	Tetrachlorethylene and trichlorethylene	10	μg/l	Increased risk of cancer and liver problems	A	USEPA, 2012
27	Total trihalomethanes (THM)	100	µg/l	Problem of central nervous system, increased risk of cancer; liver lesion	A & B	Mosteo et al., 2009; USEPA, 2012
28	Turbidity	1	NFU	Associated with outbreaks of Cryptosporidium and other waterborne disease	A & B	Mac Kenzie et al., 1994; Morris et al., 1996; USEPA, 2012

[a] The sum of the nitrate concentration divided by 50 and nitrite divided by 3 must remain below 1; [b] At the exit of treatment plants (production point); [c] For each pesticide except aldrin, dieldrin, heptachlor, heptachlor epoxide = 0.03; [d] at the production plants; [e] start from 2013; *According to French Regulation of *l'arrêté du 11/01/2007*; A : at production level; B : at distribution network level

MCL: Maximum Contaminant Level

No	Parameters	MCL*	Units	Sampling Location
1	Total Aluminum	200	μg/l	A & B
2	Ammonium (NH ₄ ⁺)	0.1	mg/l	A & B
3	Total Organic Carbon (TOC)	2	mg/l	А
4	Free and total chlorine	Acceptable to consumers and no abnormal change		A & B
5	Chlorite (ClO2)	0.2	mg/l	В
6	Chlorides (Cl-)	250	mg/l	А
7	Conductivity	\geq 200 and \leq 1100	μS cm1 at 25 °C	A & B
8	Colour	15	mg/l Pt	A & B
9	Copper		mg/l	В
10	Balance calcocarbonic	waters must be in chemically balance	- A	А
11	Total Iron	200	μg/l	A & B
12	Manganese	50	µg/l	А
13	Odor	Acceptable to consumers		A & B
14	рН	6,5 – 9		A & B
15	Taste	Acceptable to consumers		A & B
16	Sodium	200	mg/l	A & B
17	Sulfate	250	mg/l	А
18	Temperature	25	⁰ C	A & B
19	Turbidity	0.5 and 2 [a]	NFU	A & B

Table B.2 Chemical parameters of drinking water quality reference

[a] 0.5 NFU at point of production and 2 NFU at consumers tap; *According to French Regulation of *l'arrêté du* 11/01/2007; A : at production level; B : at distribution network level

MCL: Maximum Contaminant Level

					Sign			
No.	Indicators	MCL	Units*	Related to health	Related to distribution network	Related to consumers acceptance (Organoleptic effect)	Relation with other parameters	Reference
1	Total Aluminum	200	μg/l	A low dose in long- term exposure can cause Alzheimer's disease	Related to the solubility of lead corrosion	Aluminum sulphate (coagulant) is known as one of the sources of taste, odor and color in drinking water	Indicator of heavy metals in water	Young et al., 1996; Flaten, T.P., 2001; Kim, E.J. et al., 2011; Verissimo et Gomes, 2008
2	Ammonium (NH4+)	0.1	mg/l	None	Decrease the effectiveness of disinfection	(-)	Indicator the existence of NH3, NO2-, NO3-	Rusell S., 1994; Kurama et al., 2002; Kwan R.C.H et al., 2005
3	Free Chlorine (HOCl, ClO-) and Total Chlorine (HOCl, ClO- , Chloramines)	Acceptable to consumers and no abnormal change	None	None	Indicator of corrosion in distribution network	Can cause odor and unpleasant taste	The decrease of free chlorine concentration associated with Microbiological activity, Nitrite (NO2-) , Pesticides and THM	Dukam et al., 1996; Frateur, I. et al., 1999; Pintar et Slawson, 2003; Hall et al., 2007 ; Helbling and VanBriesen, 2008; Chowdhury et al., 2008; USEPA, 2009

Table B.3 Chemical indicators of drinking water quality at distribution network level

No.	Indicators	MCL	Units*	Related to health	Related to distribution network	Related to consumers acceptance (Organoleptic effect)	Relation with other parameters	Reference
4	Chlorite (ClO2–)	0.2	mg/l	Hemolytic anemia, methemoglobin, potentially mutagenic and genotoxic	Ĵ	(-)	(-)	WHO, 1996; USEPA, 2000; WHO, 2005; Richardson et al., 2007; Feretti et al., 2008
5	Conductivity	≥200 et ≤1100	μS/cm at 25 °C	None	Conductivity <200 µS/cm can be corrosive and lead to dissolution of toxic metals. conductivity> 1100 µS/cm can lead to scaling deposits	In high concentrations, giving an unacceptable taste and odor	Sensitive to wide range contaminants. Indicator of the presence of dissolved inorganic solids such as Cl-, NO3-, SO42-, PO43-and or Na, Mg, Ca, Fe, Al and proportional to the water hardness	USEPA, 2012; Syndicat Eaux de la Faye, 2012

No.	Indicators	MCL	Units*	Related to health	Related to distribution network Related to consumers acceptance (Organoleptic effect)		Relation with other parameters	Reference
6	Color	15	mg/l Pt	None	An indicator of problems in the distribution network	Important factors affecting consumer acceptance. The colored water is not preferred by consumers	Number of E. Coli correlated with the color	AWWA, 1971; Hurlimann, A. and McKay, J., 2007; Okeke. et al, 2011; MassDEP, 2012
7	Copper (Cu)	1	mg/l	Livers damage and Wilson disease	There is possibility of release of Cu and its compounds from copper pipes	Can give unpleasant flavors to the water, stain laundry and sanitary equipment	Cu and its corrosion products may decrease the concentration of chlorine in higher pH and accelerated the formation of haloacetic acid (HAA)	USEPA, 2012; Zhang and Susan, 2012
8	Total Iron	200	µg/l	None	1.) Indicator of pipeline corrosion. 2.) Cause biofilm growth on the pipeline	Can give a reddish brown color in water	1.) Reduce the concentration of chlorine and dissolved oxygen ; 2.) can adsorb some substances such as arsenic and radium	Field et al., 1995; Raven et al., 1998; Sarin, P. et al, 2004; Siyuan, C. et al., 2005

No.	Indicators	MCL	Units*	Related to health	Related to distribution network	Related to consumers acceptance (Organoleptic effect)	Relation with other parameters	Reference
9 and 10	Odor and Taste	Acceptable to consumers and no abnormal change	None	None	An indicator of problems in the distribution network	Important factors affecting consumer acceptance. Water with an unpleasant odor and taste is not preferred by consumers	Indicator the presence of cyanobacteria , actinomycetes , organic and inorganic compounds	Dionigi et al., 1993; McGuire, 1995; Watson et al., 2008
11	рН	6.5 – 9	None	(-)	A pH <7 promotes the corrosion and dissolution of metals such as lead and cadmium in the pipeline	A pH <7 promotes the formation of an unpleasant odor	Affected by wide range contaminants	Morris J.C., 1971; Xie et al., 2011; Kim, E.J. et al., 2011; Government of Nova Scotia, 2012
12	Temperature (T)	25	0C	None	Temperature gradients is the important factor of copper corrosion process in indoor plumbing	At T> 25 ° C, it can cause the palatability of drinking water, development of odors	At T> 25 ° C, it can cause odors development and proliferation of microorganisms	Silvey et al., 1972; Jason and Edwards, 2004; Whelton and Dietrich, 2004

No.	Indicators	MCL	Units*	Related to health	Related to distribution network	Related to consumers acceptance (Organoleptic effect)	Relation with other parameters	Reference
13	Turbidity	0.5 and 2 [a]	NFU	An indicator associated with cryptosporidium outbreaks and other waterborne disease	None	Important factors affecting consumer acceptance and also associated with unpleasant tastes and odors	Indicator of general contamination by microorganism, solid particles, organic substances (pesticides) and metals	LeChevallier, M.W., 1981; Mac Kenzie et al., 1994; Morris et al., 1996; USEPA, 1999 ; Hall et al., 2007
14	Total Organic Carbon (TOC)	2 and no abnormal change	mg/l	(-)	6)	(-)	Indicator the existence of Cryptosporidium and Giardia L., THMs , and Benzene. TOC concentration also related to Odor and Taste	Shafy et Grunwald, 2000; Davies et al., 2004 ; Polanska M. et al., 2005; Visco et al., 2005 ; Hohman, 2007

*According to French Regulation of *l'arrêté du 11/01/2007*

[a] 0.5 NFU at production and 2 NFU at consumers tap

(-) Data not found / not available

	1.) Parameter	.) Parameter: Aluminum									
	Instrument	Maasuramant	Measurement	instrument	Softwara		Performance	e criteria			
No	name	principle	Sensing elements	Analyzer	used	MCL	DL[MR]	Others	Advantage	Drawback	Reference
Con	nmercial Instru	uments				1					
1	Aztec 600 Aluminum Analyzer	<u>Colorimetric</u> <u>detection:</u> light absorbance through colored sample is proportional to analyte concentration	Photodiode in photometer	(-)	(-)	200 µg/l	(-) [0 - 300 µg/l]	Precision: 5%, Accuracy: 5%, MT: 5 min, Sensibility: 1 μg/l	Auto- validation, calibration & cleaning; RO- M capability; Measurement up to 3 streams	Need chemical reagents; Flow cell type instrument; Large size instrument	ABB, 2011
2	Stamolys CA71AL Analyzer	<u>Colorimetric</u> <u>detection</u>	Photodiode in photometer	(-)	(-)	200 μg/l	(-) [10 - 1000 μg/l]	Precision: 10 µg/l, MT: 5 - 10 min, Stability 6 month	Auto- validation, calibration & cleaning; RO- M capability	Need chemical reagents, flow cell type instrument, large size instrument	Endress + Hauser, 2008
Dev	eloping Instru	ments		1	2	~~~					
3	Aluminum Acoustic Wave Sensor	<u>Piezoelectric</u> <u>microbalance</u> <u>detection</u> : decrease in crystal resonant frequency due to mass increase corresponds to analyte concentration	Piezoelectric quartz crystal coated with aluminum ionophore and complex polymer	Counter device PXI 6608, National Instruments	LabView	200 µg/l	70 µg/l [(-)]	MT: 2 min	Adjustable sensitivity, already tested in field, good correlation with laboratory method	Sample must be pre- concentrated separately	Veríssimo et Gomes, 2008

Table B.4 Recapitulation of measurement instrument for monitoring of drinking water quality reference

MCL : Maximum Contaminant Level; DL : Detection Limit; MR : Measurement Range; (-): Data not available; RT: Response Time; MT: Measurement time; RO-M: Real-Time & On-line Monitoring

	2.) Parameter: An	mmonium									
	Instrument	Measurement	Measurement i	nstrument		I	Performanc	e criteria			
No	name	principle	Sensing elements	Analyzer	Software used	MCL	DL[MR]	Others	Advantage	Drawback	Reference
Con	nmercial Instrume	ents		200							
1	YSI-6920DW multi-probe (Multi-parameter sensor)	(-)	See table B.6 page B34	See table B.6 page B34	See table B.6 page B34	0.1 mg/l	(-) [0 - 200 mg/l]	Sensitivity 0.001-1 mg/l; Accuracy 10%; RT: 3 min, Stability: 6 month	See table B.6 page B34	(-)	YSI Inc. (2006)
2	On line water analyzer UV500 (Multi-parameter sensor)	<u>UV-Vis spectroscopic</u> <u>detection</u>	(-)	(-)	(-)	0.1 mg/l	(-) [0 - 100 mg/l]	RT: 3 min	See table B.6 page B34	See table B.6 page B34	Tethys Instruments, 2010
3	Ammo∷lyser [™] eco (Multi- parameter sensor)	Voltametric detection	See table B.6 page B35	See table B.6 page B35	See table B.6 page B35	0.1 mg/l	(-) [0.1 - 2 mg/l]	Sensitivity: 0.02 mg/l, Stability: 6 month	See table B.6 page B35	(-)	S::can, 2012
Dev	eloping Instrumer	nts			0 7 0	a y					
4	Bienzyme sulfonate hydrogel-based biosensor	Measuring O2 reduction consumed by GXD using a Clark electrode	Clark electrode coated with GIDH & GXD	(-)	Biosensortrend version 2.1.1	0.1 mg/l	0.037 mg/l [0.179 - 5.388 mg/l]	RT: 2 s, MT: 4 min, Stability: 7 days	Rapid measurement, Good precision et selectivity	Poor stability, need expensive reagents	Kwan et al., 2005
L	MCL : Maximum Co	ontaminant Level DI	L : Detection Limit	MR : M	easurement Range (-): Data n	ot available	RT: Response	Time MT: 1	Measurement tin	ne
				0.000							

3.) Parameter: Free and Total Chlorine Measurement instrument Performance criteria											
Performance criteria	Per	Software	t instrument	Measuremen	Measurement	Instrument					
MCL DL[MR] Others Advantage Drawback Reference	MCL	used	Analyzer	Sensing elements	principle	name	No				
			and the second second		nents	mmercial Instrun	Con				
Acceptable nd no bnormal hange 0.035 mg/1] MT: 2.5 min, Precision and Accuracy: 5% RO-M capability; Flow cell type with compact device Need chemical reagents Hach, 2011; Helbling and VanBriesen, 2008	Acceptable and no abnormal change	Advanced Data Logger, AGG software	(-)	Photodiode in photometer	<u>Colorimetric</u> detection	Hach CL 17, Chlorine Analyzer	1				
Acceptable nd no bnormal hange (-) mg/l [0 - 10 mg/l] (-) mg/l [0 - 10 mg/l] (-) mg/l (-) Hach Lange, 20% (-) Hach Lange, 2010	Acceptable and no abnormal change	(-)	(-)	Three-electrode system	Amperometric detection	CLF10sc and CLT10sc Reagentless Chlorine Analyzer	2				
acceptable nd noPrecision: 0.05 mg/l,See table B.6 page(-)YSI Ins., 2006hange[0 - 3 mg/l]Sensitivity: 0.01 mg/l; RT: 3 min,B.4(-)YSI Ins., 2006	Acceptable and no abnormal change	See table B.6 page B34	See table B.6 page B34	See table B.6 page B34	(-)	YSI-6920DW multi-probe (Multi- parameter sensor)	3				
Acceptable nd no bnormal hange(-) [0 - 5 mg/l]RT: 20 s, MT: 5 min:See table B.6 page B34See table B.6 page B34Intellitect Water Limited, 2012	Acceptable and no abnormal change	(-)	(-)	See table B.6 page B34	(-)	Intellisonde TM (Multi- parameter sensor)	4				
	1			I	ents	veloping Instrum	Dev				
Acceptable nd no bnormal hange0.0083 mg/l [20 - 100 mg/l]MT: 10 min, Stability 3 month,Low DL; Good sensitivity and selectivityMurata et al., 2008	Acceptable and no abnormal change	EZ Chrom Elite, Scientific Software, Inc.	Bioanalytical Systems LC-4C Amperometric Detector	Boron-Doped Diamond (BDD) electrodes	Voltammetric detection	Cyclic voltammetry (CV) - Boron- Doped Diamond (BDD) electrodes	5				
acceptable nd no bnormal hange(-) mg/l mg/lPrecision: 0.05 mg/l, Sensitivity: 0.01 mg/l; RT: 3 min,See table B.6 page B34(-)Acceptable nd no bnormal hange(-) [0 - 5 mg/l]RT: 20 s, MT: 5 min:See table B.6 page B34See table B.6 page B34Acceptable nd no bnormal hange(-) [0 - 5 mg/l]RT: 20 s, MT: 5 min:See table B.6 page B34See table B.6 page B34Acceptable nd no bnormal hange(-) [0 - 5 mg/l]RT: 10 min, Stability 3 month,Low DL; Good sensitivity and selectivityAcceptable nd no bnormal hange0.0083 mg/l [20 - 100 mg/l]MT: 10 min, Stability 3 month,Low DL; Good sensitivity and selectivitye (-): Data not availableRT: Response TimeMT: Measurement t	Acceptable and no abnormal change Acceptable and no abnormal change Acceptable and no abnormal change	See table B.6 page B34 (-) EZ Chrom Elite, Scientific Software, Inc. Measurement Ra	See table B.6 page B34 (-) Bioanalytical Systems LC-4C Amperometric Detector Limit MR : 1	See table B.6 page B34 See table B.6 page B34 Boron-Doped Diamond (BDD) electrodes DL : Detection	(-) (-) ents <u>Voltammetric</u> <u>detection</u>	YSI-6920DW multi-probe (Multi- parameter sensor) Intellisonde [™] (Multi- parameter sensor) veloping Instrume Cyclic voltammetry (CV) - Boron- Doped Diamond (BDD) electrodes MCL : Maximum Cor	3 4 Dev 5				

	4.) Parameter: Chlo	orite									
	_	Measurement	Measureme	ent instrument	Software	P	erformance	e criteria			
No	Instrument name	principle	Sensing elements	Analyzer	used	MCL	DL[MR]	Others	Advantage	Drawback	Reference
Con	nmercial Instrument	S									
1	ProMinent® DULCOMETER® D1C Chlorite Package	Amperometric detection: Measure the current between electrodes on the applied potential difference	DULCOTEST® CLT 1 sensor: Clark type membrane covered sensor consists of a 2- electrode system	DULCOMETER® D1C controller	(-)	0.2 mg/l	(-) [0.02 - 0.5]	RT: 1 min, Sensitivity: 0.01 mg/l	Free reagents, Real-time & on-line monitoring capability; Not sensitive to temperature fluctuations	(-)	(ProMinent, 2006)
2	EnviroLyzer® Chlorite	<u>Colorimetric</u> <u>detection</u> (ASTM 4500- Cl G)	Photodiode in photometer	(-)		0.2 mg/l	(-) [0 - 2.5 mg/I]	MT: 10 min	Auto- validation, calibration, cleaning; Real-time & on-line monitoring capability	Need chemical reagents; Flow cell type instrument, Large size instrument	Applitek, 2010
Dev	eloping Instruments					2.1		ð			
3	Sol–gel based electrochemical probe, EC	<u>Amperometric</u> <u>detection</u>	Three-electrode electrochemical sensor-based sol-gel	Model 650C electrochemical workstation (CH Instruments)	GRAMS/32AI software (version 6.0)	0.2 mg/1	0.08 mg/l [(-)]	RT: 3 s, Stability: 3 weeks	Free reagents; Good selectivity and accuracy	Poor stability	Myers et al., 2012
	MCL : Maximum Cont	aminant Level	DL : Detection L	imit MR : Measur	ement Range (-): D	ata not av	ailable	RT: Response Tim	e MT: M	leasurement time	e

	5.) Parameter: C	onductivity											
	Instrumont	Magguramant	Measurement i	nstrument	Softwara	Р	erformance	e criteria					
No	name	principle	Sensing elements	Analyzer	used	MCL	DL[MR]	Others	Advantage	Drawback	Reference		
Con	nmercial Instrum	ents		8									
$\frac{1}{1} \begin{bmatrix} \text{Intellisonde}^{TM} \\ (Multi- \\ parameter \\ sensor) \end{bmatrix} (-) \begin{bmatrix} \text{See table B.6} \\ page B34 \end{bmatrix} (-) \begin{bmatrix} \text{(-)} \\ \text{(-)} \end{bmatrix} (-) \begin{bmatrix} \text{(-)} \\ 1000 \\ \mu\text{S/cm} \end{bmatrix} \begin{bmatrix} \text{RT: 20 s,} \\ \text{MT: 5 min:} \end{bmatrix} \begin{bmatrix} \text{See table B.6} \\ page B34 \end{bmatrix} \begin{bmatrix} \text{See table B.6} \\ B.6 \\ page B34 \end{bmatrix} \begin{bmatrix} \text{See table B.6} \\ B.34 \end{bmatrix} \begin{bmatrix} \text{See table B.6} \\ D \\ D \\ D \end{bmatrix} \begin{bmatrix} \text{RT: 20 s,} \\ D \\ $													
2	YSI-6920DW multi-probe (Multi- parameter sensor)	(-)	See table B.6 page B34	See table B.6 page B34	See table B.6 page B34	200 - 1000 μS/cm	(-) [0 - 100000 μS/cm]	Sensitivity 1- 100 uS/cm, Accuracy 0.5%	See table B.6 page B34	(-)	Jeffrey Yang et al., 2009; YSI Inc., 2011		
3	Sensor) Sensor) Weight of the sensor) Sensor)												
Dev	Developing Instruments												
As t	he writer's knowled	lge, there is no in	strument available	e. Standard 1	nethod for me	asuring (Conductivity	in water sampl	e is Probe method	I NF EN 27888	8 (T 90-031)		

MCL : Maximum Contaminant Level

DL : Detection Limit MR : Measurement Range (-): Data not available

RT: Response Time MT: Measurement time



	6.) Parameter: C	olour									
	Instrument	Magguramant	Measurement	instrument	Software	P	erformance	e criteria			
No	name	principle	Sensing elements	Analyzer	used	MCL	DL[MR]	Others	Advantage	Drawback	Reference
Con	nmercial Instrum	ents									
1	Aztec 600 color analyzer	Colorimetric detection	Photodiode in photometer	(-)	(-)	15 mg/l Pt-Co	[0 - 500 mg/l Pt- Co]	Accuracy 0.5 mg/l (2%), Precision 1%, Sensitivity 0.1 mg/l Pt- Co, Stability 12 month	See table B.4 page B9	See table B.4 page B9	ABB, 2011
2	Intellisonde™ (Multi- parameter sensor)	(-)	See table B.6 page B34	(-)	(-)	15 mg/l Pt-Co	[0 - 50 mg/l Pt- Co]	RT: 20 s, MT: 5 min:	See table B.6 page B34	See table B.6 page B34	Intellitect Water Limited, 2012
3	On line water analyzer UV500 (Multi- parameter sensor)	<u>UV-Vis</u> spectroscopic detection	(-)	(-)	6(-)	15 mg/l Pt-Co	[0 - 100 mg/l Pt- Co]	Response time: 10 s	See table B.6 page B34	See table B.6 page B34	Tethys Instruments, 2010
Dev	Developing Instruments										
As the writer's knowledge, there is no instrument available. Standard method for measuring Colour in water sample is Comparative Visual NF EN ISO 7887 (T90-034).											
MCI	L : Maximum Contam	inant Level	DL : Detection Lim	it MR :	Measurement	Range (-)): Data not ava	ailable RT: R	esponse Time	MT: Measurem	ent time
					26	刃					

	7.) Parameter: Copper											
	Instrument	Measurement	Measureme	nt instrument	Software	P	erformance	criteria				
No	name	principle	Sensing elements	Analyzer	used	MCL	DL[MR]	Others	Advantage	Drawback	Reference	
Con	nmercial Instru	nents										
1	Stamolys CA71CU	Colorimetric detection	Photodiode in photometer	(-)	(-)	1 mg/l	(-) [0.1 - 2 mg/l]	Precision 10 µg/l, MT: 5 - 10 min, Stability 6 month	See table B.4 page B9	See table B.4 page B9	Endress + Hauser, 2008	
2	OVA 5000 On-line heavy metal monitor (Multi-metal parameter sensor)	<u>Stripping</u> <u>voltammetric</u> <u>detection</u> :	Three- electrode system (Au-Pt- Ag/AgCl)	(-)	Labview OVA 5000 software	1 mg/l	1 μg/l [(-)]	(-)	See table B.6 page 35	See table B.6 page 35	Cogent Envronmental Ltd., 2012	
3	EnviroLyzer® Copper	<u>Colorimetric</u> <u>detection</u> (ASTM 3500-Cu C)	Photodiode in photometer	(-)	€.×	1 mg/l	(-) [0 - 5 mg/l]	MT: 10 min	Auto- calibration, validation & cleaning, RO-M capability	Need chemical reagents; Flow cell type large size instrument;	Applitek, 2010	
Dev	eloping Instrume	ents										
4	PPDOT Fibre- optic sensor	Spectroscopic- Fluorescent detection: Measure the absorbance reflected by the membrane PPDOT	PPDOT Fibre-optic sensor	Spectrometer		1 mg/l	0.052 mg/l [0.48 - 12.9 mg/l]	MT: 13 min, Stability: 20 days, Precision 5%	Simple, compact, regenerable & low cost sensor, requires no reagents	Poor rapidity and stability	Chamjangali et al., 2009	
MCI	: Maximum Conta	minant Level D	L : Detection Li	mit MR : M	leasurement R	lange (-):	Data not avail	able RT: Re	sponse Time	MT: Measure	ment time	

8	8.) Parameter: 7	Total Iron									
	Instrument	Massuramont	Measuremen	t instrument		Р	erformance	e criteria			
No	name	principle	Sensing elements	Analyzer	Software used	MCL	DL[MR]	Others	Advantage	Drawback	Reference
Con	mercial Instrum	nents				2					
1	Aztec 600 Iron Analyzer	<u>Colorimetric</u> <u>detection</u>	Photodiode in photometer	(-)	(-)	200 μg/l	(-) [0 - 1000 μg/l]	Precision & Accuracy 5 µg/l (5%), Sensitivity 1 µg/l, Stability 12 month	See table B.4 page B9	See table B.4 page B9	ABB, 2011
2	Stamolys CA71FE	<u>Colorimetric</u> <u>detection</u>	Photodiode in photometer	(-)	(-)	200 μg/l	(-) [10 - 500 μg/l]	Precision 5 μg/l, MT: 5 - 10 min, Stability 6 month	See table B.4 page B9	See table B.4 page B9	Endress + Hauser, 2008
Deve	eloping Instrume	ents			N						
3	Single-use screen-printed sensor devices	<u>Voltammetric</u> <u>detection</u>	Single-use screen- printed device covered by the immobilization of 10- phenanthroline, potassium hexacyanoferrate (III), potassium hydrogen sulphate, sodium acetate and potassium chloride	Electrochemical workstation (AutoLab, EcoChimie BV)	GPES	200 µg/l	10 μg/l [(-)]	RT: 5 min	Simple, inexpensive device, quick measurement and requires no reagents	(-)	Jezek et al., 2007
	MCL : Maximum	Contaminant Level	DL : Detection L	imit MR : Meas	urement Range (-):	Data not a	vailable	RT: Response Tir	ne MT: M	easurement time	

9.) 8	& 10.) Parameter: Odor et Taste											
	Instrument	Magsuramant	Measurement	instrument	Software	Per	formance c	riteria				
No	name	principle	Sensing elements	Analyzer	used	MCL	DL[MR]	Others	Advantage	Drawback	Reference	
Con	nmercial Instru	iments										
1	GEMINI Electronic Noses	(-)	Gas sensor array technology with headspace injection.	(-)	AlphaSoft	Acceptable no abnormal change	(-)	Precision: 5%	Can analyze up to 200 samples/day	Required manually pretreatment, not suitable for field monitoring	Alpha MOS, 2012	
2	ASTREE Electronic Tongue	<u>Electrochimic</u> Detection	Astree Electrochemical Sensor Array	(-)	AlphaSoft	Acceptable no abnormal change	(-)	Measurement time: 200s, Precision: 3%	(-)	Required manually pretreatment, not suitable for field monitoring	Alpha MOS, 2012	
Dev	eloping Instrur	nents										
3	Piezoelectric odour sensor with quartz crystal microbalance	Piezoelectric microbalance detection:	Quartz crystals coated by the substrate adsorbent	Quartz Chemical analyzer	6	Acceptable no abnormal change	10 μg/l MIB [(-)]	(-)	A simple and inexpensive sensor for a wide range of odorous compounds	(-)	Ji et al., 2000	
4	Electronic Tongue	Electrical impedance detection: measure the opposition of an electric circuit against passing current when a voltage is applied.	Gold interdigitated microelectrodes coated with ultra-thin polymeric films	Impendace analyzer Solartron SI 1260 et Multiplexer	LabView	Acceptable no abnormal change	25 ng/l MIB and GEO [(-)]	(-)	Very low detection limit	(-)	Braga et al., 2012	
MC	L : Maximum Con	taminant Level	DL : Detection I	Limit MR	: Measuremen	t Range (-): Da	ta not availabl	e RT: Respo	nse Time	MT: Measuremen	nt time	

11.)	Parameter: pH										
	Instrument	Maggunant	Measurement	instrument	Software	P	erformanc	e criteria			
No	name	principle	Sensing elements	Analyzer	used	MCL	DL[MR]	Others	Advantage	Drawback	Reference
Con	nmercial Instrum	ents									
1	Intellisonde™ (Multi- parameter sensor)	(-)	See table B.6 page B34	(-)	(-)	6.5 – 9	2 – 12	RT: 20 s, MT: 5 min; Sensitivity 0.2	See table B.6 page B34	See table B.6 page B34	Intellitect Water Limited, 2012
2	On line water analyzer UV500 (Multi- parameter sensor)	(-)	(-)	(-)	(-)	6.5 - 9	1 – 14	Response time: 10 s	See table B.6 page B34	See table B.6 page B34	Tethys Instruments, 2010
3	YSI-6920DW multi-probe (Multiparameter sensor)	(-)	(-)	See table B.6 page B34	See table B.6 page B34	6.5 – 9	1-14	Accuracy: 0.2, Sensitivity: 0.01	See table B.6 page B34	(-)	Jeffrey Yang et al., 2009; YSI Inc., 2011
Dev	eloping Instrume	nts				× 11					
4	NR / PAA pH sensor fiber optic	Spectroscopic- fluorescent detection: measurement the optical absorbance of the light modulation due to the optical variation of CpC-NR/PAA	NR / PAA pH sensor fiber optic	Spectometer Ocean Optics Inc. USB4000 CCD		6.5 - 9	3-9	Response time: 1 s, Sensitivity 0.03	Rapid measurement, good stability	(-)	Goicoechea et al., 2008
N	ICL : Maximum Cont	taminant Level	DL : Detection	Limit MR	Measurement F	Range (-):	Data not avai	ilable RT: Re	esponse Time M	T: Measurement	time

12.)	12.) Parameter: Temperature Measurement instrument Performance criteria											
	Instrument	Magsurament	Measurement	instrument	Software	Р	erformance	e criteria				
No	name	principle	Sensing elements	Analyzer	used	MCL	DL[MR]	Others	Advantage	Drawback	Reference	
Con	nmercial Instrum	ents										
1	Intellisonde [™] (Multi- parameter sensor)	(-)	See table B.6 page B34	(-)	(-)	25 C	(-) [-5 - 50 °C]	See table B.6 page B34	See table B.6 page B34	See table B.6 page B34	Intellitect Water Limited, 2012	
2	On line water analyzer UV500 (Multi- parameter sensor)	(-)	(-)	(-)	(-)	25 C	(-) [0 - 80°C]	MT: 3 min	See table B.6 page B34	See table B.6 page B34	Tethys Instruments, 2010	
3	YSI-6920DW multi-probe (Multi- parameter sensor)	(-)	(-)	See table B.6 page B34	See table B.6 page B34	25 C	(-) [-5 - 50°C]	RT: 3 min, Sensitivity 0.01°C	See table B.6 page B34	(-)	YSI Inc., 2006	
Dev	eloping Instrume	nts		110	1 IN	-						
4	Optical fiber sensor	Spectroscopic- fluorescent detection	lophine sensor	HP 34970A	7(-)	25 °C	5 – 45°C	MT: 10 min, Stability 2 month	Low cost and good immunity to humidity variation	(-)	Valdivielso et al., 2003	
MCI	L : Maximum Contam	inant Level	DL : Detection Lim	it MR-:]	Measurement Ra	ange (-): I	Data not availa	ible RT: Res	ponse Time	MT: Measurem	ent time	

13.)	3.) Parameter: Turbidity Measurement instrument Performance criteria											
	Instrument	Maggungenant	Measurement	instrument	Coftware	Pe	rformance	criteria				
No	name	principle	Sensing elements	Analyzer	used	MCL	DL[MR]	Others	Advantage	Drawback	Reference	
Con	nmercial Instrum	ents						÷				
1	Intellisonde TM (Multi- parameter sensor)	(-)	See table B.6 page B34	(-)	(-)	0.5 and 2 [a] and 1 NFU [b]	(-) [0 - 50 NFU]	See table B.6 page B34	See table B.6 page B34	See table B.6 page B34	Intellitect Water, 2012	
2	On line water analyzer UV500 (Multi- parameter sensor)	(-)	(-)	(-)	(-)	0.5 and 2 [a] and 1 NFU [b]	0 – 100 NFU	MT: 3 min	See table B.6 page B34	See table B.6 page B34	Tethys Instruments, 2010	
3	YSI-6920DW multi-probe (Multi- parameter sensor)	(-)	(-)	See table B.6 page B34	See table B.6 page B34	0.5 and 2 [a] and 1 NFU [b]	0 - 1000 NTU	Sensitivity: 0.1 NFU	See table B.6 page B34	(-)	YSI Inc., 2006	
Dev	eloping Instrume	nts				A comment						
4	Smart turbidity transducer IEEE 1451	<u>Nephelometric</u> <u>detection</u> : the intensity of scattered light is directly proportional to the turbidity	(-)	HP 34970A	(-)	0.5 and 2 [a] and 1 NFU [b]	0 – 100 NFU	RT: 5 s, Precision 5%, Accuracy 2%, Sensibility 0.03 NFU	Auto- calibration, real-time & on-line monitoring capability	(-)	Tai et al., 2012	
MCI	L : Maximum Contam	inant Level	DL : Detection Lin	nit MR :	Measurement F	Range (-): Dat	ta not availab	le RT: Respo	nse Time	MT: Measurem	ent time	

14.)	Parameter: TOC										
No	Instrument	Measurement	Measu instr	urement rument	Software	Р	erformance	e criteria	Adventego	Drowbook	Doforonco
INU	name	principle	Sensing elements	Analyzer	used	MCL	DL[MR]	Others	Auvantage	DIAWDACK	Kererence
Con	nmercial Instrum	ents									
1	AstroTOC [™] UV Process Total Organic Carbon Analyzer	NDIR detection: TIC removal and elimination by mineralization, Oxidation TOC to CO2 by UV reactor and CO2 detection by NDIR. CO2 measurement is proportional TOC concentration	(-)	(-)	(-)	2 mg/l	0.015 mg/l [0.015 - 5 mg/l]	RT: 8 min, Precision and Accuracy 2 - 4%	Auto- validation, calibration & cleaning; Real- time & on-line monitoring capability	Need chemical reagents; Flow cell type instrument; Large size instrument	Hach lange, 2009
2	5310 C On-Line	Combination of UV/persulfate oxidation with the <u>Conductometric</u> <u>Detection</u> (SM 5310 C and USEPA Method 415.3.)	(-)	(-)	6)	2 mg/1	(-) [4 µg/1 - 50 mg/1]	MT: 4 min, Precision 1%; Accuracy 2%, Stability 12 month	Auto- validation, calibration & cleaning; Real- time & on-line monitoring capability	Need chemical reagents; Flow cell type instrument; Large size instrument	GE Analytical Instruments, 2008
3	On line water analyzer UV500 (Multi- parameter sensor)	(-)	(-)	(-)	(-)	2 mg/l	(-)	MT: 3 min	See table B.6 page B35	See table B.6 page B35	Tethys Instruments, 2010
Dev	eloping Instrume	nts				- 14-					
As t	he writer's knowle	dge, there is no instru	ment availab	ole. Standard r	nethod for n	neasuring	TOC in wa	ter sample is Ch	romic Acid Oxida	ation NF ISO 14	235.
MCI	L : Maximum Contam	inant Level DL	: Detection L	imit MR	: Measuremen	t Range (-): Data not av	ailable RT: F	Response Time	MT: Measurem	ent time

1	.) Parameter:	Acrylamide (C3H5NO)									
	Instrument	Maagunamant	Measurement i	nstrument	Software	Per	formance cr	iteria			
No	name	principle	Sensing elements	Analyzer	used	MCL	DL[MR]	Others	Advantage	Drawback	Reference
Com	mercial Instru	nents		1000	1 1						
		As the writer's knowledg	ge, there is instrume	ent available							
Deve	loping Instrum	ents	1.1					222			
1	Quartz microbalance acrylamide sensor	Detecting piezoelectric microbalance: measure the decrease in resonant frequency of the crystal corresponds to the mass increasing of sensing element	Hunter/Vögtle- type tetralactam macrocycles	(-)	(-)	0.1 μg/l	10 µg/l	(-)	Robust and low-cost sensor	Cross- selectivity problems	Kleefisch et al., 2004
						10					

Table B.	5 Reca	pitulation	of measu	rement	instrumen	t for	monitoring	g of	drin	king	water	quality	limi	ts
10010 20		010001001011	01 11100000					- ×-				e creen c		•••

2.) Parameter: Antimony (Sb)											
No	Instrument name	Measurement principle	Measurement instrument		Software	Performance criteria					
			Sensing elements	Analyzer	used	MCL	DL[MR]	Others	Advantage	Drawback	Reference
Commercial Instruments											
As the writer's knowledge, there is instrument available $5 \mu g/l$											
Deve	Developing Instruments										
1	ETAAS with carbon nanotubes solid- phase extraction	(-)	(-)	(-)	(-)	5 μg/l	0.05 μg/l [(-)]	(-)	Very low detection limit and good sensitivity	Laboratory instrument; Not suitable for field analysis	López-García et al., 2011
MCL : Maximum Contaminant Level DL : Detection Limit MR : Measurement Range (-): Data not available RT: Response Time MT: Measurement time							ne				
3	8.) Parameter: Bei	nzene (C6H6)									
------	--	---	--------------------------------	-----------------------------------	-------------------	------------	------------------	--------	--	--	------------------------
	Instrument	Measurement	Measureme	nt instrument	Software	Per	formance cr	iteria			
No	name	principle	Sensing element	Analyzer	used	MCL	DL[MR]	Others	Advantage	Drawback	Reference
Com	mercial Instrumer	nts									
1	AF46 Dual Wavelength UV Absorption Sensor	Spectroscopic detection: The attenuation of light intensity, caused by substances absorption or scattering is detected by photodiodes.	Photodiode in photometer	C4000 Photometric converter	C4000 software	1 μg/l	(-) [(-)]	(-)	Good precision and sensitivity, requires no reagents, real- time & on-line monitoring capability		Optek, 2012
Deve	eloping Instrument	ts	1000			110					
2	Ultrasound- assisted emulsification microextraction coupled to gas chromatography with flame ionization detector	Sample extraction by ultrasound- assisted emulsification, separation by gas chromatography and detection by flame ionization detector	(-)			1 μg/l	2 μg/l [(-)]	(-)	Good repeatability, reproducibility, cost and high accuracy	Detection limit higher than MCL; Not suitable for on-line measurement	Hashemi et al. 2012
MC	L : Maximum Contami	nant Level DI	: Detection Lin	nit MR : Me	easurement Rar	nge (-): D	ata not availab	le RT:	Response Time	MT: Measureme	ent time

4	1.) Parameter:	Benzo[a]pyrene (C	20H12)								
	Instrument	Measurement	Measureme	ent instrument	Software	P	erformance crit	eria			
No	name	principle	Sensing elements	Analyzer	used	MCL	DL[MR]	Others	Advantage	Drawback	Reference
Con	mercial Instrum	nents									•
1	Online SPE coupled with HPLC with UV detection	Spectroscopic detection: Sample extraction by SPE, separation by HPLC and detection by UV detection	Θ	(-)	Online SPE PromoChr om software	0.01 μg/ł	0.025 μg/l [(-)]	MT: 10 min; Precisio n 0.86%	Provide automated real-time & on-line measurement	The measurement instruments are quite complex and large	PromoChrom Technologies Ltd., 2012
Dev	eloping Instrum	ents							/		
2	Optosensor- Amberlite XAD-4	Spectroscopic- fluorescent detection: A flash excites electrons in the molecules of substances and causes them to emit light detected by Spectrometer	Optosenso r covered by non- ionic resin (Amberlit e XAD-4)	Aminco Bowman Series 2 Iuminescence spectrometer	(-)	0.01 µg/1	0.003 μg/l [0.003-0.25 μg/l)	RT: 40 s	Low detection limit, simple and requires no preconcentrati on step		Fernández- Sánchez et al., 2004
M	CL : Maximum Con	taminant Level	DL : Detection	on Limit MR	: Measurement	Range (-)	: Data not available	e RT: R	esponse Time	MT: Measureme	nt time
					46	1					

5	5.) Parameter:	Cadmium (Cd)									
	Instrumont	Magguramont	Measurement i	nstrument	Software	Pe	erformance crite	eria			
No	name	principle	Sensing elements	Analyzer	used	MCL	DL[MR]	Others	Advantage	Drawback	Reference
Com	mercial Instru	ments			1						
1	OVA 5000 On-line heavy metal monitor (Measure 6 heavy metal parameters)	<u>Stripping</u> <u>voltammetric</u> <u>detection</u>	Three- electrode system (Au-Pt- Ag/AgCl)	(-)	Labview OVA 5000 software	5 μg/l	(-) [(-)]	(-)	See table B.6 page B35	See table B.6 page B35	Cogent Envronmental Ltd., 2012
Deve	loping Instrum	ients		_			_				
2	LPGF Optic Sensor	The resonances wavelengths correspond to concentrations of cadmium were in contact with the grating.	The singlemode Ge–B photosensitive fiber	(-)	(-)	5 µg/l	2 μg/1 [(-)]	(-)	small size and high sensitivity	(-)	Raikar et al., 2012
			1.00								

6	.) Parameter:	Vinyl chloride (C	H2=CHCl)									
	Instrument	Measurement	Measurement	t instrument	Software	Per	formance cr	iteria				
No	name	principle	Sensing elements	Analyzer	used	MCL	DL[MR]	Others	Advantage	Drawback	Reference	
Com	ommercial Instruments											
	As the writer's knowledge, there is instrument available 0.5 µg/l											
Deve	loping Instrum	ents										
	As the writer's knowledge, there is no instrument available 0.5 µg/l											
Note	standard metho	d for measuring th	ne vinyl chloride	is gas chroma	tography coup	ple with ma	ss spectromet	try (GC-MS)				
MCL	ACL : Maximum Contaminant Level DL : Detection Limit MR : Measurement Range (-): Data not available RT: Response Time MT: Measurement time											

	7.) Parameter: C	hromium (Cr)									
No	Instrument	Measurement	Measur instrui	ement ment	Software	I	Performance ci	riteria	Adventege	Drowbook	Doforonco
INU	name	principle	Sensing elements	Analyzer	used	MCL	DL[MR]	Others	Auvantage	Drawback	Kelerence
Com	mercial Instrum	ents	•					•	•		
1	OVA 5000 On- line heavy metal monitor (Measure 6 heavy metal parameters)	<u>Stripping</u> <u>voltammetric</u> <u>detection</u> :	Three- electrode system (Au- Pt-Ag/AgCl)	(-)	Labview OVA 5000 software	50 μg/l	(-)	(-)	See table B.6 page B35	See table B.6 page B35	Cogent Envronmental Ltd., 2012
2	In-Field Hexavalent Chromium Water Analysis	Voltammetric detection	(-)	(-)	LabVIEW	50 μg/l	(-) [10 - 1000 μg/l]	(-)	Portable instrument	(-)	Eltron Research & Development, 2009
3	EnviroLyzer® Chromium	<u>Colorimetric</u> <u>detection</u> (ASTM 3500- Cr B)	Photodiode in photometer	(-)	(-)	50 μg/l	(-) [0 - 500 μg/l]	MT: 10 min	See table B.4 page B12	See table B.4 page B12	Applitek, 2010
Deve	eloping Instrumer	nts	-	110	and the			<u></u>	•		
4	Chromium (VI) Potentiometric Sensors	Potentiometric detection	Graphite- epoxy (GE)	(-)	None	50 μg/l	33 μg/l [(52- 520000 μg/l)]	RT: 18 s; Stability 18 month	Simple, robust and could be used for on- line monitoring	(-)	Sánchez- Moreno et al., 2010
MCL :	Maximum Contamir	ant Level D	DL : Detection Lir	nit MR :	Measurement R	ange (-):	Data not available	RT: Resp	onse Time	MT: Measurem	ent time

8	3.) Parameter	: Copper (Cu)										
No	Instrument	Measurement	Measu instru	rement Iment	Software	Per	formance c	riteria	Adventage	Drowbook	Doforonco	
INU	name	principle	Sensing elements	Analyzer	used	MCL	DL[MR]	Others	Auvantage	DIAWDACK	Kererence	
Com	mercial Instru	iments		// R				100	1			
Have been described above (Table B.4 no. 7) 2 mg/l												
Deve	eloping Instru	ments				1.1			10			
	Have bee	n described above	e (Table B.4 no	. 7)		2 mg/l						

9	.) Parameter:	: Epichlorhydrin	e		1				1		
No	Instrument	Measurement	Measu instru	rement ument	Software	Pe	erformance	criteria		Drawhash	Defenerac
INO	name	principle	Sensing elements	Analyzer	used	MCL	DL[MR]	Others	Auvantage	Drawback	Kelerence
Com	mercial Instru	iments	and the second								
1	Argilent 7890A GC System equipped with flame ionization detector	(-)	(-)	Ð	(-)	0.1 μg/1	0.07 μg/l	Precision 2.21%; MT: <u>+</u> 15 min	(-)	Laboratory method; Not provide RO-M	Cai and Zou, 2010; Agilent Tech. Inc., 2010
Deve	loping Instru	nents				hered .					
	As the writer's chromatograp	s knowledge, ther hy standard EN 1	e is no instrur 4207.	nent available.	The standar	d method	for measuri	ng Epichlorhyo	drine in water sa	mple is Gas	
MCL :	Maximum Conta	minant Level	DL : Detecti	on Limit N	AR : Measure	ment Range	e (-): Data not	t available I	RT: Response Time	MT: Me	asurement time

1	0.)Parameter: Pol	lycyclic aromatic hydr	ocarbons (P.	AH)							
NT	Instrument	Measurement	Measur instru	ement ment	Software	Per	formance cr	iteria			Df
NO	name	principle	Sensing elements	Analyzer	used	MCL	DL[MR]	Others	Advantage	Drawback	Kelerence
Com	mercial Instrume	nts									
1	The HydroC™ PAH	Spectroscopic- fluorescent detection: A flash excites electrons of substances and causes them to emit light which detected by UV photodiode	(-)	(-)	Windows® Software DETECT™	0.1 μg/l	(-) [0 - 50 μg/l]	RT: 10 s, Sensitivit y: 0.1 µg/l	Free reagents; RO- M capability; Anti-fouling device	(-)	CONTROS Systems & Solutions GmbH, 2011
2	EnviroFlu-HC	Spectroscopic- fluorescent detection	(-)	(-)	(-)	0.1 µg/l	0.1 [0 - 50 µg/l]	(-)	Free reagents; RO- M capability; Anti-fouling device	(-)	TriOS Optical Sensors, 2009
3	On line water analyzer UV500 (Multi- parameter sensor)	<u>UV-Vis</u> <u>spectroscopic</u> <u>detection</u> :	(-)	(-)		0.1 μg/l	(-) [0 - 1000 μg/l]	RT: 3 min	See table B.6 page B35	See table B.6 page B35	Tethys Instruments, 2010
Deve	loping Instrument	ts									
	As the writer's kno Chromatography c	owledge, there is no inst coupled to a Fluorescen	trument availa ce Detector T	able. The sta 90-115.	indard method	for measur	ring PAH in v	water sample	e is High Perfor	mance Liquid	
MCL : I	Maximum Contamina	int Level DL : De	tection Limit	MR : Me	asurement Range	e (-): Data n	ot available	RT: Respo	nse Time	MT: Measureme	nt time

NoInstrument nameMeasurement principleMeasurement instrum Sensing elementsCommercial Instruments	ent er Software used M L	Performance criteriaICDL[MR]Others	Advantage	Drawback	Reference
No Instrument name Measurement principle Sensing elements Analyz Commercial Instruments Sensing Analyz	er used M L	IC DL[MR] Others	Advantage	Drawback	Reference
Commercial Instruments					
OVA 5000 On-line heavy metalsStripping voltammetric detection:Three- electrode system1Multi-metal parameter sensor)Multi-metal detection:Three- electrode system	Labview OVA 20 5000 µg software	20 g/1 (-) [(-)] (-)	Early warning system integrated	Need chemical reagents; Flow cell type instrument; Large size instrument	Cogent Envronmenta 1 Ltd., 2012
Developing Instruments					
2 Nickel optic sensor Nickel optic sensor Nickel optic sensor Nickel optic sensor Nickel optic substances and causes the fluorescent thiazolo-triazol to emit light which detected by spectrofluorimeter	PC er non C-) 20 µg	$\begin{array}{c} 0.05 \ \mu g/l \\ 10.05 \ \mu g/l \\ g/l \ 4400) \\ \mu g/l \\ \end{array}$ RT: 2 min min $\mu g/l \\ $	Good precision and accuracy	Measurement is quite dependent on pH	Aksuner et al., 2012

	12.)Parameter: N	itrate (NO3-) and 13.)	Nitrite (NO2-)							
	Instrument	Maggunomont	Measuremen	nt instrument	Software	Pe	rformance	criteria			
No	name	principle	Sensing elements	Analyzer	used	MCL	DL[MR]	Others	Advantage	Drawback	Reference
Cor	nmercial Instrum	ents						<u>8</u>	•	-	
1	TONI® On-line TN analyzer (multi- parameter sensor)	Wet oxidation and colorimetric detection	(-)	(-)	(-)	Nitrate : 10 mg/l ; Nitrite : 0.5 mg/l	(-)		RO-M capability; Can measure nitrate, nitrite, nitrogen kjeldahl and total-N	Need chemical reagents; Flow cell type instrument; Large size instrument	AppliTek, 2010
2	Nitrate EnviroLyzer®	<u>Voltametric</u> <u>detection</u> : Measure the current between electrodes on the applied potential difference	Ion selective electrode (ISE)	(-)	(-)	Nitrate : 10 mg/l	Nitrate: (-) [0 - 10 mg/1]	Measurement time 10 min	Auto-validation, calibration & cleaning; Real- time & on-line monitoring capability	(-)	AppliTek, 2010
3	AV450 UV nitrate monitor	Spectroscopic detection: The attenuation of UV light intensity caused by absorption/diffusion of nitrates is detected photometrically	(-)	AV400 Transmitter	(-)	Nitrate : 10 mg/l	Nitrate: (-) [0 - 100 mg/l]	Response time: 3 min, Precision & Accuracy: 2%,	Free reagents, auto-cleaning, turbidity measurement included, RO-M capability	(-)	ABB, 2011
4	NITRATAX clear sc	<u>Spectroscopic</u> <u>detection</u>	Sonde NITRATAX clear sc	transmetteur SC 1000	(-)	Nitrate : 10 mg/l	Nitrate: (-) [0.5 - 20 mg/l]	Sensitivity 0.1 mg/l, RT: 5 min, MT: 10 min	Free reagents, auto-cleaning, simple in-pipe probe sensor, RO-M capability		Hach Lange, 2010

No	Instrument name	Measurement principle	Sensing elements	Analyzer	Software used	MCL	DL[MR]	Others	Advantage	Drawback	Reference
5	ISEmax CAS40/CAM40	<u>Voltametric</u> <u>detection</u>	Ion selective electrode (ISE)			Nitrate : 10 mg/l	Nitrate: (-) [0 - 1000 mg/l]	Precision: 0.2 mg/l; Sensitivity: 0.1 mg/l; RT: 3 min; Stability: 6 month	Free reagents; Small in-pipe probe sensor; RO-M capability	Potentially interfered by high concentrations of chlorides	Endress + Hauser, 2008
6	YSI-6920DW multi-probe (Multi- parameter sensor)	(-)	(-)	YSI 6500 Process Monitor	YSI EcoWatch, YSI EcoNet Monitoring & Control Platform	Nitrate : 10 mg/l	Nitrate: (-) [0 - 200 mg/l]	RT: 3 min, Stability: 6 month, 10% bias, Accuracy 10%	Adjustable sensitivity; Free reagents; RO-M capability	(-)	Jeffrey Yang et al., 2009; YSI Inc., 2011
7	On line water analyzer UV500 (Multi- parameter sensor)	(-)	(-)	(-)		Nitrate : 10 mg/1 ; Nitrite : 0.5 mg/1	Nitrate or Nitrite: (-) [0 - 100 mg/l]	Response time: 3 min	Auto-validation, calibration & cleaning; Real- time & on-line monitoring capability; Anti- Fouling; Measurement capacity up to 6 streams	Need chemical reagents; Flow cell type instrument; Large size instrument	Tethys Instruments, 2010
Dev	eloping Instrume	nts			10 8			•		•	•
As t	As the writer's knowledge, there is no instrument available. The standard method for measuring Nitrite and nitrate in water sample is Spectrométrie T 90 – 012 or NF EN ISO										
1339	95.				-			-			
	MCL : Maximum	Contaminant Level	DL : Detection	n Limit MR	: Measurement H	Range (-): Da	ta not availab	le RT: Respo	onse Time MT:	Measurement time	

1	4.) Parameter: 1	Lead (Pb)									
	Instrumont	Magguramant	Measuremen	t instrument	Softwara	Per	formance cr	iteria			
No	name	principle	Sensing elements	Analyzer	used	MCL	DL[MR]	Others	Advantage	Drawback	Reference
Com	mercial Instrun	nents									
1	OVA 5000 On-line heavy metal monitor (Measure 6 heavy metal parameters)	<u>Stripping</u> <u>voltammetric</u> <u>detection</u>	Three- electrode system (Au- Pt-Ag/AgCl)	(-)	Labview OVA 5000 software	25 et 10 μg/l*	(-)	(-)	See table B.6 page B35	See table B.6 page B35	Cogent Envronmental Ltd., 2012
Deve	loping Instrum	ents				S.					
2	Fluorescent sensor	<u>Spectroscopic-</u> <u>Fluorescent</u> <u>detection</u> :	PDMS microfluidic device grafted by Calix- DANS3-OH	JEOL JNM ECS 400 MHz spectrometer	(-)	25 and 10 μg/l	42 μg/l [(-)]		Free reagents, low cost, quick measurement, simple and small instrument	Detection limit is not fit to the standard	Faye et al., 2012
				A							

1	5.) Parameter: '	Total trihalometh	anes (THM)			CI 🖉					
No	Instrument	ment Measurement Measurement Software Performance criteria		criteria	Advantage		Deferrer				
	name	principle	Sensing elements	Analyzer	used	MCL	DL[MR]	Others	Advantage	Drawback	Kelerence
Com	mercial Instrun	nents					100.00				
1	MS2000 THM Monitor	(-)	(-)	(-)	(-)	100 µg/l	(-) [1 - 1000 μg/l]	Precision: 2%, Accuracy: 5%, MT: 5 - 15 min, Stability 6 month	Free reagents; Real-time & on- line monitoring capability	(-)	Multisensor systems, 2011
2	Triton field portable THM sensor	(-)	(-)	(-)	(-)	100 μg/l	80 μg/l [(-)]		Provide rapid measurement	A portable instrument & not provide on-line monitoring	Triton Systems Inc., 2011
Deve	loping Instrum	ents						•	·	·	
As th	ne writer's knowl	ledge, there is no i	nstrument av	ailable. The sta	ndard method	d for measu	uring PAH is	Gas chromatogr	aphy (NF EN ISO	10301/T90-125	j).

16.) Parameter: Turbidity											
	Tre structure and	M	Measurement instrument		Software	Performance criteria					
No	name	principle	Sensing elements	Analyzer	used	MCL	DL[MR]	Others	Advantage	Drawback	Reference
Com	Commercial Instruments										
		Have bee	en described abo	ove							
Deve	loping Instrum	ents		1							
		Have bee	en described abo	ove							
						100 C					

MCL : Maximum Contaminant Level	DL : Detection Limit	MR : Measurement Range (-): Data not available	RT: Response Time	MT: Measurement time
			<i></i>	
			and the second	
			2460	
	000			

N	Instrument	rument Measurement Parameters Measurement Software J		Performan		Durantaala	Deferrer			
No	Name	principle	measured	Sensing elements	Analyzer	used	ce criteria	Advantage	Drawback	Reference
Comr	nercial Instrum	ents								
1	Intellisonde TM (measure 12 parameters):	(-)	Flow, Temperature, Free/Total Chlorine, DO, pH, ORP, Conductivity, Colour, Turbidity, Pressure, Ion activity	Integration of several electrochemic al & optical sensors	(-)	(-)	RT: 20 s; MT: 5 min: Stability: 3 weeks to 3 month	Free reagents; RO- M capability; Adjustable probe length; Insensitive to pressure and flow, in-pipe type sensor; Data transmitter integrated; Flexibility to integrated with any system	Low accuracy; Poor stability; Fouling problems	Intellitect Water Limited, 2012; Aisopou et al., 2012
2	YSI-6920DW multi-probe (measure 10 parameters)	(-)	Free Chlorine, Temperature, Conductivity, Ph, Redox, Nitrate/Chloride/Amm onium, Salinity, Conductivity, TDS, Turbidity	(-)	YSI 6500 Process Monitor	YSI EcoWatch, YSI EcoNet Monitoring & Control Platform	RT: 3 min, Stability: 6 month	Adjustable sensitivity; Free reagents; RO-M capability	(-)	YSI Inc., 2006
3	Hach pipe sonde (measure 7 parameters)	Combination of Electrode-based detection Amperometric, Nephelometric detection, glass sensor and thermistor, pressure transducer	Conductivity, ORP, Chlorine, Turbidity, pH, Temperature and Pressure	Integration of several electrodes, and nephelometer	Hach's Event Monitor™ Trigger System	Hach's Event Monitor™ Trigger System		Free reagents; RO- M capability; Can troubleshoot remotely; In-pipe type sensor; Equipped with Hach EDS software	Even in- pipe line type sensors, not integrated with transmitter	Hach, 2006

Table B.6 Recapitulation of multi-parameter measurement instrument for monitoring of drinking water quality

4UV-Vis spectroscopic (Measure 13 parameters)TOC, Nitrite/Nitrate, Ammonium, Sulfate, Phosphate, Hydrocarbons, Chlorophyll A, Color, the analyteAuto-validation, calibration & chemical reagents; Color Chlorophyll A, Color, the analyteNeed chemical reagents; Color, Chlorophyll A, Color, temperatureTOC, Nitrite/Nitrate, Ammonium, Sulfate, Phosphate, Hydrocarbons, Color, Chlorophyll A, Color, the analyteAuto-validation, chemical reagents; Color, Chlorophyll A, Color, Turbidity, pH, temperatureNeed chemical cleaning; RO-M capability; Anti- fouling; Measurement capacity up to 6 streamsNeed chemical reagents; Tethys Instrum 2010	No	Instrument Name	Measurement principle	Parameters measured	Sensing elements	Analyzer	Software used	Performan ce criteria	Advantage	Drawback	Reference
	4	On line water analyzer UV500 (Measure 13 parameters)	<u>UV-Vis</u> <u>spectroscopic</u> <u>detection</u> : Measure the color absorbance/refle ctance excite by the analyte	TOC, Nitrite/Nitrate, Ammonium, Sulfate, Phosphate, Hydrocarbons, Chlorophyll A, Color, Turbidity, pH, Conductivity, DO, temperature	(-)	(-)	(-)	RT: 3 min	Auto-validation, calibration & cleaning; RO-M capability; Anti- fouling; Measurement capacity up to 6 streams	Need chemical reagents; Flow cell type instrument; Large size instrument	Tethys Instruments, 2010
5 OVA 5000 On-line heavy metal monitor (Measure 6 heavy metal parameters) 5 <u>Stripping</u> <u>voltammetric</u> (Measure 6 heavy metal parameters) 5 <u>Stripping</u> voltammetric (Lead, Chromium, Mercury, Selenium. 5 <u>Cadmium, Nickel, Lead, Chromium, Mercury, Selenium.</u> 5 <u>Cadmium, Nickel, Lead, Chromium, Mercury, Selenium.</u> 5 <u>Cadmium, Nickel, Lead, Chromium, Mercury, Selenium.</u> 5 <u>Cadmium, Nickel, Lead, Chromium, Mercury, Selenium.</u> 5 <u>Cogent</u> System integrated 5 <u>Cogent</u> System integrated 5 <u>Cogent</u> System integrated 5 <u>Cogent</u> System integrated 5 <u>Cogent</u> Sinstrument; Large size instrument	5	OVA 5000 On-line heavy metal monitor (Measure 6 heavy metal parameters)	<u>Stripping</u> voltammetric detection	Cadmium, Nickel, Lead, Chromium, Mercury, Selenium.	Three- electrode system (Au- Pt-Ag/AgCl)	(-)	Labview OVA 5000 software		Early warning system integrated	Need chemical reagents; Flow cell type instrument; Large size instrument	Cogent Envronment al Ltd., 2012
6Ammo::lyser TM eco (Measure 3 parameters)Voltametric detection: Measure the current between electrodes on the applied potential differenceAmmonium, Nitrate, TemperatureIon selective electrode (ISE)S::can terminalsSensitivity: 0.02 mg/l, Stability: 6 monthFree reagents; Flexible to install (in-line or on wall); RO-M capability	6	Ammo::lyser TM eco (Measure 3 parameters)	Voltametric detection: Measure the current between electrodes on the applied potential difference	Ammonium, Nitrate, Temperature	Ion selective electrode (ISE)	S::can terminals	S::can software	Sensitivity: 0.02 mg/l, Stability: 6 month	Free reagents; Flexible to install (in-line or on wall); RO-M capability	(-)	S::can, 2012
Developing Instruments As the writer's knowledge, there is no instrument available.	Devel As the	oping Instrumer	nts dge, there is no ins	strument available.				<u>.</u>			

MCL : Maximum Contaminant Level

DL : Detection Limit

MR : Measurement Range (-): Data not available

RT: Response Time

MT: Measurement time

(Figures of measurement instruments and sensors)





Fig. C1. Colorimetric Analyzer Aztec 600

Mono-parameter measured: Aluminium, Colour, Total Iron

(ABB, 2011)

Fig. C2. EnviroLyzer®

Mono-parameter measured: Aluminum, Chlorine, Chlorite, Chromium, Copper, Iron, Nitrate, Nitrite,

Fig. C3. Stamolys Analyzer

Mono-parameter measured: Aluminum, Free/Total Chlorine, Chromium, Copper, Iron, Nitrate

Fig. C4. Hach CL 17, **Chlorine Analyser** Parameter measured: Free and **Total Chlorine**



(Cifec, 2001)

Residual Analyzers CL1000B



(Severn Trent Services, 2004)



(Hach Lange, 2010)

Fig C8. DULCOMETER® D1C Chlorite Package

Parameter measured: Chlorite

Fig C9. AF46 Dual Wavelength UV Absorption Sensor Parameter measured: Benzene Fig C10. In-Field Hexavalent Chromium Water Analysis Parameter measured: Chromium







(Prominent, 2006)

(Optek, 2012)

(Eltron R&D., 2009)

<u>Fig C11. The HydroC™ PAH</u>

Parameter measured: Polycyclic aromatic hydrocarbons (PAH)

Fig C12. EnviroFlu-<u>HCCL1000B</u> Parameter measured: Polycyclic

aromatic hydrocarbons (PAH)

Fig C13. Online SPE coupled with HPLC with UV detection

Parameter measured: Benzo[a]pyrene



(CONTROS Systems & Solutions GmbH, 2011)



(TriOS Optical Sensors, 2009)



(PromoChrom Tech. Ltd., 2012)

Fig C14. AV450 UV

nitrate monitor Parameter measured: Nitrate and Turbidity



Parameter measured: Nitrate

Fig C16. ISEmax CAS40/CAM40

Parameter measured: Nitrate and Ammonium



(ABB, 2011)

(Hach Lange, 2010)

(Endress + Hauser, 2008)

Fig C17. Ammo::lyserTM eco

Parameter measured: Ammonium, Nitrate and Temperature Fig C18. Triton field portable THM sensor Parameter measured: Total trihalomethanes (THM)

Fig C19. MS2000 THM Monitor

Parameter measured: Total trihalomethanes (THM)





(S::can, 2012)

(Triton Systems Inc., 2011)



(Multisensor systems, 2011)

Fig C20. IntellisondeTM

Multiparameter measured: 12 parameters (Flow, Temperature, Free/Total Chlorine, DO, pH, ORP, Conductivity, Colour, Turbidity)

Fig C21. On line water analyser UV500

Multiparameter measured: 13 parameters (TOC, Nitrite/Nitrate, Ammonium, Sulfate, Phosphate, Hydrocarbons, Chlorophyll A, Color, Turbidity, pH,

Fig C22. YSI-6920DW multi-probe

Multiparameter measured: 10 parameters (Free Chlorine, Temperature, Conductivity, Ph, Redox, Nitrate/Chloride/Ammonium, Salinity, Conductivity, TDS and Turbidity)



(Intellitect Water Limited, 2012)

(Tethys Instruments, 2010)

(YSI Inc., 2006)

Fig C23 Argilent 7890A GC System equipped with FID

Parameter measured: Epichlorhydrine

Fig C24. GEMINI Electronic Noses

Parameter measured: Odour

Fig C25. ASTREE Electronic Tongue

Parameter measured: Taste



(Agilent Tech. Inc., 2010)

(Alpha MOS, 2012)

(Alpha MOS, 2012)



B4, B5 and B6 in Appendix B