

# ONLINE MONITORING TECHNOLOGIES FOR DRINKING WATER SYSTEMS SECURITY

ANDREA G. CAPODAGLIO\* AND ARIANNA CALLEGARI  
*Department of Hydraulic & Environmental Engineering  
University of Pavia, Via Ferrata 1, 27100 PAVIA, ITALY*

**Abstract.** More stringent constraints placed nowadays on water companies to provide high quality drinking water, increasing water resources scarcity in many areas of the planet, forcing water companies to work on marginal water bodies for supply, and the threat of hostile actions by political extremists and terrorist groups, that may willingly and deliberately cause contamination of an otherwise safe supply, are recent issues that have spurred demand for more efficient and comprehensive online water monitoring technologies. Traditionally, quality parameters associated with drinking water provision were monitored using routine grab samples followed by laboratory analysis. This approach only allowed to capture small data sets, mostly unrepresentative of the true variance at the source, and allowed potentially important events to occur undetected. This paper examines state-of-the-art technologies for online monitoring of water quality in supply water systems, and reports some recent application examples.

**Keywords:** online monitoring, drinking water, system security, water quality, inorganic pollutants, organic pollutants, biological pollutants

## 1. Introduction

A safe and reliable supply of drinking water is nowadays an issue that bears strategic significance worldwide. In many areas of the globe the demand for high quality freshwater far exceeds the available supply, already; it is estimated, for example (WHO, 2003) that over 2 million deaths each year are currently caused worldwide by pathogenic bacteria during the consumption of unsanitary water: it is easily foreseeable that in the future the issue of freshwater resource

---

\* To whom correspondence should be addressed. Andrea G. Capodaglio, Department of Hydraulic & Environmental Engineering University of Pavia, Via Ferrata 1, 27100 Pavia, e-mail: Italy capo@unipv.it

and drinking water supply scarcity will continue to escalate, driven by population growth and economic development pressure.

More stringent constraints placed nowadays on water companies to provide high quality drinking water, increasing water resources scarcity in many areas of the planet, forcing water companies to work on marginal water bodies for supply, and the threat of hostile actions by political extremists and terrorist groups, that may willingly and deliberately cause contamination of an otherwise safe supply, are recent issues that have spurred demand for more efficient and comprehensive online water monitoring technologies.

Micro-biological contamination of drinking water has an immediate effect on the emergence of infectious diseases. Availability of micro-biologically safe drinking water is probably the most effective and economical way to ensure public health. In addition to “traditional” microbiological contamination by human waste, contamination of drinking water sources with pesticides and herbicides as part of the major contaminating factors is a growing problem worldwide.

During the last 2 decades, several studies revealed the presence of hazardous contaminants in wastewater effluents, being discharged in rivers and streams due to “normal” anthropic activities, including pesticides (Öllers et al., 2001), natural and synthetic hormones (Kolpin et al., 2002), plasticizers, personal care products and pharmaceuticals compounds (Daughton and Ternes, 1999; Jones et al., 2002).

A recent study estimated that there are 1,415 human pathogens including 217 viruses and prions, 538 bacteria and rickettsiae, 307 fungi, 66 protozoa and 287 helminths; about 12% are considered to be emerging pathogens. Their number continues to grow, as evidenced by the relatively recent emergence of severe acute respiratory syndrome (SARS), caused by a novel coronavirus. In the past 30–40 years, on average at least one new pathogen has been identified each year, and many more have re-emerged after periods of inactivity or by appearing in areas where they were not previously reported (Cunliffe, 2008). Pathogens identified in recent years include a range of organisms that can be transmitted directly from water or by water-related vectors. While a high proportion of the substantial burden of water-borne disease is caused by classical by pathogens such as *Salmonella typhi* and *Vibrio cholerae*, the spectrum of challenges is expanding (Table 1).

There are many reasons why water-borne pathogens emerge. In some cases this can be due to advancements in disease diagnosis and detection of the causative organisms: for example, it is likely that *Cryptosporidium* caused diarrhoeal illness before it was diagnosed as a human pathogen in 1976. In other cases true emergence can be caused by factors such as new environments, new technologies and changes in human behaviour. Some pathogens have

emerged for a combination of reasons. *Legionella* was first detected in 1977 following the 1976 outbreak of Legionnaires' disease in Philadelphia. However, increased use of water-cooled air conditioning systems and spa pools has contributed to increased incidence of Legionnaires' disease.

TABLE 1. Possible water borne pathogenic agents

Agent	Disease
<b>Viruses</b>	
Astroviruses	Diarrhoea
Hepatitis E virus	Hepatitis
Influenza A (H5N1)	Influenza
Rotaviruses	Diarrhoea (most common cause of infant death)
SARS coronavirus	SARS
Small round structured viruses (include norovirus)	Diarrhoea (most common cause of viral gastroenteritis)
West Nile virus	Encephalitis
<b>Protozoa</b>	
Blastocystis hominis	Diarrhoea
Cryptosporidium parvum, Cryptosporidium hominis	Diarrhoea
Cyclospora	Diarrhoea
Microsporidia	Enteritis
<b>Bacteria</b>	
Burkholderia pseudomallei	Melioidosis (pneumonia, skin abscesses)
Campylobacter	Diarrhoea
Coxiella burnetii	Q fever
Enterohaemorrhagic Escherichia coli	Bloody diarrhoea, haemolytic uraemic syndrome
Helicobacter pylori	Gastric ulcers
Legionella pneumophila	Legionnaires' disease, Pontiac fever
Mycobacterium ulcerans	Skin and subcutaneous ulcers
'atypical' Mycobacteria	Hypersensitivity pneumonitis, pulmonary disease, cutaneous infection
Vibrio cholerae O139	Cholera
<b>Helminths</b>	
Schistosoma	Schistosomiasis

As far as deliberate human hostile actions on urban water supplies, although none has been reported to date, in January, 2002, the FBI circulated a reserved bulletin warning water industry managers that al-Qaida terrorists may have been studying American dams and water-supply systems in preparation for new attacks (IonLife, 2002).

Traditionally, quality parameters associated with drinking water provision were monitored using routine grab samples followed by laboratory analysis. This approach only allowed to capture small data sets, mostly unrepresentative of the true variance at the source, and allowed potentially important events to occur undetected. It is clear, that, in view of what just reported, this can no longer be considered a satisfactory procedure, and that online monitoring of water supplies, for a larger number of parameters than currently available, is quickly becoming an unavoidable choice.

Water utilities around the world are already using some form of online monitoring to warn of contamination of drinking water, in anticipation of yet-to-be specified regulations: in the United States, turbidity is currently the only quality indicator for which there is a regulatory requirement for continuous online monitoring; in Europe, the EU drinking water monitoring regulations (Council Directive 98/83/EC) do not specifically require online measurements (Awwa, 2002).

## **2. Definition and Rationale for Online Monitoring**

Online monitoring is usually defined as the unattended sampling, analysis and reporting of a parameter; it produces a sequence of data at much greater frequency than that permitted by manual (grab) sampling and it also allows real-time feedback for either process control, water quality characterization for operational or regulatory purposes, and alert/alarm purposes.

Online monitoring can be carried out at onsite as well as remote locations and will deliver measurements at intervals of seconds-to-minutes apart. Clearly, online instrumentation must be placed at representative locations in the water system and must be periodically maintained by qualified technical personnel.

Monitoring requirements can be defined in relationship to:

- Source water quality: (a) variability, in space and time (very low for ground-water, low for lakes, high for rivers); (b) vulnerability (type and location of possible contaminating activity), time-of-travel of the contaminant to the intake, effectiveness of barriers, control options after an alarm
- Water treatment: process optimization options and response times, sampling frequency must allow adequate process control

- Distribution systems: minimization of deterioration of water quality over time and distance, early detection of cross-connections and water losses

In addition, it must be considered that online monitors could have different sensitivity and selectivity according to the matrix and range of concentrations analyzed.

TABLE 2. Online monitoring Objectives and Strategies in a multibarrier drinking water system (From Awwa, 2002)

Activity	Monitoring Strategy	Objectives
Contaminant source identification	Surrogate parameters (TOC, DOC, UV <sub>254</sub> , pH, conductivity) Specific parameters (related to known sources of contamination) Biotest and toxicity tests	Define potential contamination in relation to vulnerability of source water
Monitoring of discharges into the source water	Specific organic/inorganic contaminants	Identify water pollution accidents
BMPs/protection of water source	Hydrological parameters Environmental parameters (solar radiation, O <sub>2</sub> , Chl)	Prevent source deterioration Environmental Management
Drinking water quality protection	Specific organic/inorganic contaminants Treatment-related parameters (Q, turbidity, pH, TOC, DOC, etc.) Biotests/toxicity	Allow appropriate responses to contaminant presence (intake shut-up, additional treatment, treatment adjustment)
Emergency response	Specific organic/inorganic contaminants Biotests/toxicity	Drinking water pollution control Risk management Treatment modification

TABLE 3. Online monitoring parameters associated with source monitoring

Parameter
Ammonia, Biological/toxicity tests, Bromide, Chl, Conductivity, D.O., Flow, Nutrients (N,P), Metals, pH, Redox potential, Level (reservoir), Specific org. contaminants (e.g. pesticides, phenols, etc.) Temperature, TOC/DOC (or surrogates, e.g. UV <sub>254</sub> ), Turbidity

TABLE 4. Online monitoring parameters associated with water treatment

Parameter	Use
Alkalinity	Coagulation/corrosion control
Biological/toxicity tests	Treatment effectiveness
Flow	Chemical additives control, Disinfection control
Fluoride	Dosage control
Ozone	Disinfection/oxidation control
Particle count	Filtration control, Disinfection control
pH	Coagulation/corrosion control,
Redox potential	Disinfection/inactivation control
Residual disinfectant (free/comb. chlorine,	Disinfection/inactivation control
Ozone, chlorine dioxide)	Disinfection/oxidation control
TOC/DOC (or surrogates)	Coagulation control, Disinfection/oxidation control
Turbidity	Filtration optimization, disinfection control

A multibarrier approach to drinking water quality protection, such as those that are commonly used by facilities worldwide, is based on the concept that contaminants must be subject to as many points of control/treatment (barriers) as possible prior to the tap. The ideal location for control of contaminants is as close to the source as possible. A source water with low vulnerability is therefore characterized by few potential contaminant activities, transit time longer than that required for laboratory analysis, and the presence of multiple physical barriers between contaminating activities and point of intake. In a source water with moderate vulnerability, online monitoring of surrogate parameters (such as TOC, DOC, UV<sub>254</sub>, pH and conductivity) may be considered to keep track of potential pollution. In a high vulnerability water source, online monitoring of chemical–physical–biological parameters (turbidity, pH, conductivity, redox, fish toxicity) and surrogate parameters in addition to specific indicators (e.g. VOCs, phenols and specific toxicity tests) may be preferred. This is summarized in Table 2.

Some parameters commonly used to monitor in online mode a supply source are listed in Table 3. Parameters used to monitor online water treatment are listed in Table 4. Both tables list also parameters for which online monitoring technology may not be widely available, nor field proved at the moment, but that may be useful for the given purpose (Awwa, 2002).

The availability of real-time analytical information is one of the key benefits of online monitoring instrumentation: this information must however be conveyed to the appropriate user by means of a data collection and transmission system which is often referred to as SCADA, which consists of the individual online instruments, connected to Programmable Logic Controllers (PLCs) or

Remote Telemetry Units (RTUs), that convert instrument outputs to the desired units, compare them to criteria set by the user, and generate signals for alarm or control to other process equipment. A host computer, that can be used to visualize or store data, or to further utilize them for specific purposes, almost always complements these systems.

### 3. Online Monitoring Instrumentation Overview

Generally speaking, online monitoring instrumentation can be divided in:

- Physical monitors (Turbidity, particles, color, conductivity, TDS, hardness, alkalinity, acidity, streaming current, radioactivity, temperature, redox potential)
- Inorganic monitors (pH and DO, disinfectants, such as Chlorines and ozone, metals, fluoride, nutrients, cyanide)
- Organic monitors (Carbon and hydrocarbons, UV adsorption, VOCs, pesticides, disinfection by-products)
- Biological monitors (nonspecific, algae, protozoa, pathogens)
- Hydraulic monitors (flow, level and pressure)

This paper will focus on the four former classes, discussing for each basic operating principles, and evaluation of the technology for online applications in the water distributing system.

#### 3.1. PHYSICAL MONITORS

A wide array of technologies can be used for monitoring physical parameters, among them: light scattering/blocking (turbidity, particles, SS), light absorbance (color), electrochemical (conductivity, hardness, Redox), electrophoretic (streaming current), chemical titration (alkalinity, acidity, hardness) and other (radioactivity, temperature) (Table 5).

Turbidity refers to the clarity of a water sample, and can be defined as an optical property that causes light to be scattered and absorbed by suspended particulate matter (inorganic or organic) in the sample. It is one of the most commonly monitored parameters in the water industry, and the one that is most amenable to online monitoring. A turbidimeter consists of a light source, a sample cell and a photodetector; commercial instruments differ in the type of light source and the number and location of photodetectors.

Color is caused by the absorption of visible light by dissolved/colloidal substances or small suspended particles and can be an indication of pollution by disinfection by-products, industrial pollutants and/or metals, although it does

not, by itself, represent a health risk. Color is in fact regulated as an aesthetic parameter only and is seldom monitored online, except in cases where the water source is subject to industrial effluents and/or storm runoff inputs. Color is measured either visually or spectrophotometrically.

Dissolved organic/inorganic impurities (TDS) are compounds of different nature and sources, and constitute the solid residue after all the water evaporates. TDS must be determined gravimetrically in the laboratory, however, since these species tend to increase the electrical conductivity of the solution, conductivity is often used as a surrogate measure for TDS, especially when in online mode.

Hardness is defined as the sum of divalent cations in a water sample, and is relevant in drinking water systems for aesthetic reasons and for corrosion concerns. Alkalinity is defined as the acid-neutralizing capacity of a solution. Both can be determined by chemical titration (hardness with EDTA, alkalinity with an acid solution).

TABLE 5. Physical online monitors technology

Application	Most Appropriate Technology	Other Technologies
Turbidity		
Low turbidity raw water,	Single Beam (tungsten or LED) turbidimeter	Particle counters Particle monitors
Clarified water, Filter effluent	Modulated four-beam turbidimeter	
High turbidity raw water	Ratio turbidimeter Modulated four-beam turbidimeter	
Filter backwash	Transmittance turbidimeter Surface scatter Ratio turbidimeter Modulated four-beam turbidimeter	EMERGING TECHNOLOGIES Laser light source (660 nm) and improved optics turbidimeters
Color	Online colorimeter Spectrophotometer	
TDS	Two-electrode conductivity probe Electrodeless (toroidal) probes	
Hardness	EDTA titration online Ion-specific electrodes (ISE)	
Alkalinity	Online alkalinity titrator	



### 3.2. INORGANIC MONITORS

Inorganic monitors are used in online mode to detect influent and effluent water quality, and for treatment process control; the applicable technologies are listed in Table 6.

Online monitoring of inorganic constituents is still in the early phase for many elements of interest to drinking water concerns. For metals, available technology is an adaptation to automatic operation mode of complex colorimetric methods developed for laboratory applications, and therefore turns out to be expensive and/or complex to operate, nor still suitable for installation in remote or unmanned sites.

TABLE 6. Online inorganic monitor technology

Parameter	Currently applied technology	Other technology developments (not currently/commonly avail.)
D.O., pH Chlorine, nitrate, fluoride	Ion-selective electrodes (IESs) Membrane Electrode Sensors for DO (polarographic or galvanic)	Fiber-Optics Chemical Sensors (FOCSs or optodes) for pH, DO Iodometric DO measurements
Chlorine and compounds	Colorimetric (DPD), Iodometric, polarographic membranes and amperometric methods Absorbance (spectrometric) for ClO <sub>2</sub>	ClO <sub>2</sub> : Iodometry, Amperometric meth. I, DPD, amaranth, chlorophenol red, LGB dye, ion chromatography
Iron, manganese	x-ray fluorescence (complex), colorimetry	
Ammonia, nitrite, nitrate	Colorimetric, FOCS (ammonia) Ion Sensitive Gas Membrane electrodes	
Phosphorous, cyanide	Colorimetric, FOCS (cyanide)	

Also, for many metals of interest in drinking water systems (As, Cd, Pb, Hg, Se, Zn), online monitoring technologies do not exist at all. Some promise for future application comes from developments in optode technology, coupled with miniaturized spectrophotometry.

### 3.3. ORGANIC MONITORS

The technology for online monitoring of organic compounds includes TOC analyzers, UV absorption and differential spectroscopy; it is much more developed than that for inorganics, for this reason, although neither EU nor US regulations require online monitoring of these substances, many drinking water utilities routinely use online organics monitoring to some degree.

TOC methods measure the carbon content of dissolved and particulate organic matter in the water, without giving information about the nature of this organic substances. Table 7 shows the different fractions of carbon measured by an organic carbon analyzer.

TABLE 7. Carbon fractions measured by organic carbon analyzers

Carbon fraction		Definition
Total carbon	TC	Sum of organically and inorganically bound carbon (incl. elemental C) present in water
Total inorganic carbon	TIC	Sum of elemental carbon, CO <sub>2</sub> , CO, CN, CS, CCl <sub>4</sub> , etc.
Total organic carbon	TOC	Organic carbon bound to particles <100 μm (TOC = TC–TIC)
Dissolved organic carbon	DOC	Organic carbon in water bound to particles <45 μm
Nonpurgeable organic carbon	NPOC	Organic carbon present after scrubbing the sample to eliminate inorg. C and VOCs <sup>a</sup>
Volatile organic carbon	VOC	TOC fraction removed from the sample by gas stripping

<sup>a</sup>Most commercial TOC analyzers actually measure NPOC

TOC measurement is defined by well established methods and occurs generally according to a four-step process: sample treatment (filtration), inorg. C removal (acidification to pH < 2), oxidation (with UV, catalyzed UV, chemical oxidation, etc.) and CO<sub>2</sub> determination (NDIR detectors, colorimetry, or conductivity methods). Detection limits depend on the specific technique's operating temperature (usually >0.2 mg/l for low temp., >1 mg/l for high temp.).

Most organic compounds found in water absorb UV radiation: using a UV spectrometer it is therefore possible to estimate the concentration of these compounds. Originally, a UV light source with the single wave length of 254 nm was used for such measures, however, in recent years, instrumentation reading the entire UV–VIS spectrum (200–750 nm) has been developed and marketed (S-can, 2008). UV absorption is a well-defined and commonly used methodology; evidence shows strong correlation between these measurements and organic carbon concentration measured with standard methods such as

TOC or others (Figure 1). In addition, it has been shown that other parameters can be measured indirectly by correlating their concentration values to UV absorption in the full spectrum (Figure 2); several commonly sought organic compounds have typical absorption spectra that make their identification quite easy with appropriate instrumentation (Figure 3).

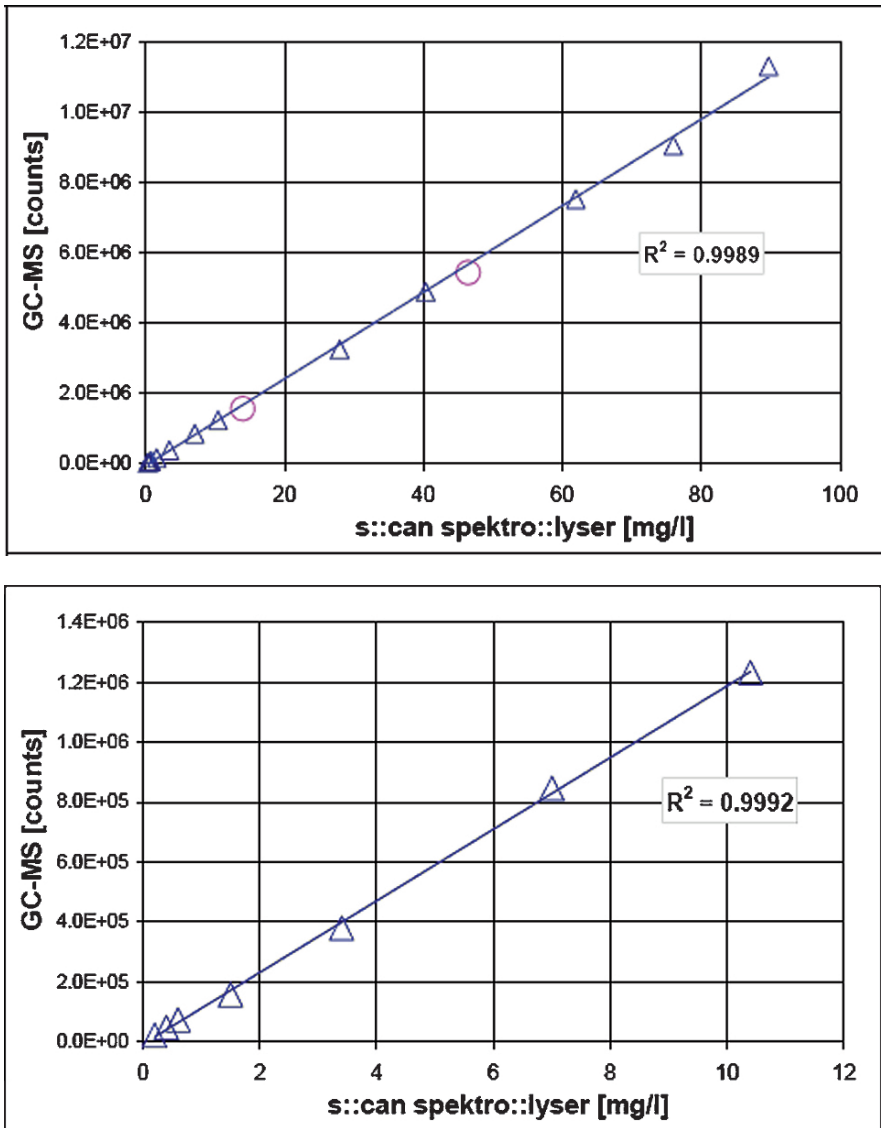


Figure 1. Calibration of an online UV-VIS spectrometer for benzene detection against GC-MS laboratory methods, in distilled water and groundwater (Courtesy S-can, 2008)

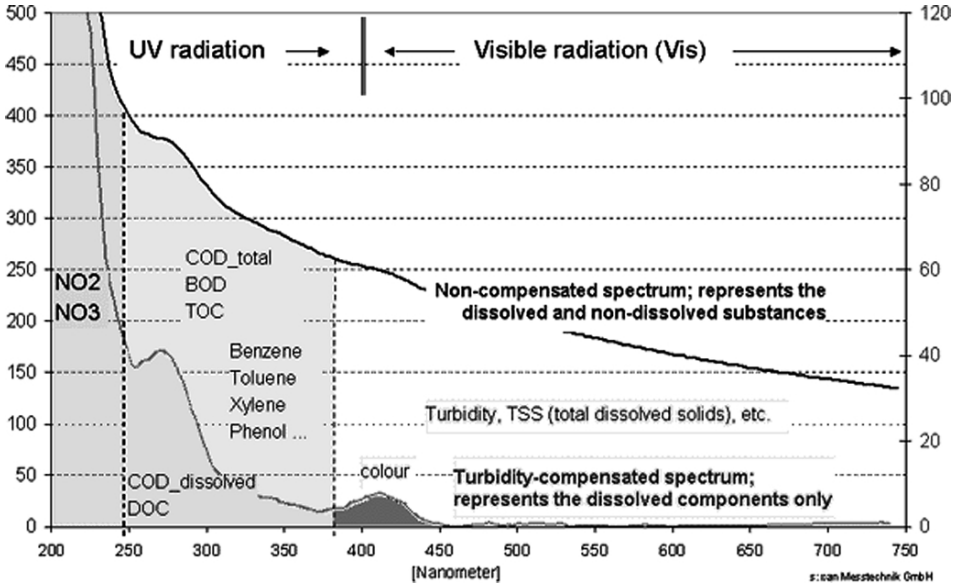


Figure 2. Correspondence between spectral absorption areas and quality parameters (Courtesy S-can, 2008)

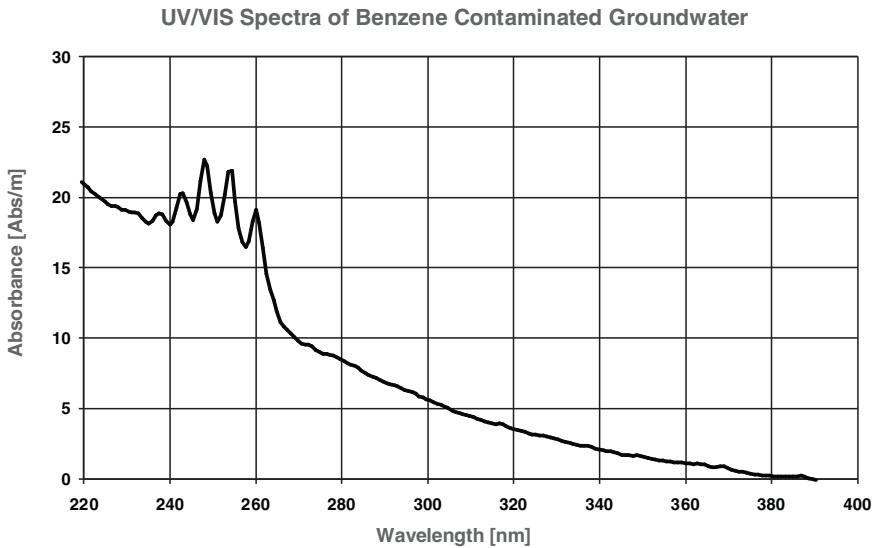


Figure 3. Typical spectral absorption image of benzene in water (Courtesy S-can, 2008)

Hydrocarbons in general are probably the main class of water pollutants found in surface and ground water (i.e., source water for drinking water systems). Methods for online hydrocarbon detection include: fluorometry, reflectivity, light scattering and turbidity measurement, ultrasonic methods, electrical conductivity, spectroscopy, gas-phase detection (after volatilization), resistance-based sensors; some of these methods, however, give just an indication of the presence/absence of oil on the water surface.

Volatile Organic Compounds (VOCs), including, among the others, aromatic compounds, halogenates and trihalometanes, are compounds that evaporate when exposed to air and can be of health concern when found in drinking water systems (trihalometanes are disinfection by-products – DBPs – that can be precursors to the formation of carcinogens). Their presence in drinking water can be a symptom of accidental pollution in the source water, of treatment failure/deficiency, or of incorrect disinfection procedures.

Current online monitoring technologies for VOCs include purge-and-trap gaschromatography with flame ionization (FID), electron capture (ECD) or photoionization detectors or mass spectrometry (MS). Detection limits for different substances vary according to the detector method.

Pesticides, including insecticides, fungicides and herbicides comprise triazines and phenylurea compounds; they are monitored in drinking water systems in order to: detect accidental pollution in source waters, and check the effectiveness of treatment specifically designed to remove such substances. Online monitoring of pesticides can be carried out using composite techniques, such as:

- High pressure liquid chromatography (HPLC)/diode array (DA) detection, consists of extraction and enrichment, chromatographic separation and DA detection.
- Gas chromatography (GC), consists of extraction and enrichment, GC separation and mass spectrometer (MS) detection.
- Liquid chromatography/mass spectrometry, consists in extraction and enrichment, LC separation and MS, thermospray, electrospray or particle beam detection.

Each technique is capable to optimally detect a group of compounds, for example, HPLC/DA can be used to analyse; atrazine, chlortoluron, cyanazine, desethylkatrazine, diuron, hexazinone, isoproruton, linuron, metazachlor, methabenzthiazuron, metobrorumon, metolachlor, metoxuron, monolinuron, sebutylazine, simazine and terbutylazine.

In theory, any analytical laboratory method can be adapted for use as online measurement, provided that the requirements for consumables and manual intervention can be minimized: current online systems are often a “robotized” adaptation of known offline laboratory procedures, however, not always this solution is the most efficient one. A series of novel technologies, such as optochemical sensors, biosensors, and microbiological sensors are being tested for organics and hydrocarbon analysis. Advances already in use include differential UV spectroscopy for DBPs detection and microphase solid-phase extraction (SPE) for the analysis of semivolatiles organics (Yongtao et al., 2000).

### 3.4. BIOLOGICAL MONITORS

There are two basic types of biological monitors currently in use: those that use biological species as indicators of the presence of contaminants of concern (e.g. toxic chemicals), and those that screen for the presence of biological species of concern (e.g. nuisance algae, pathogens). In common US terminology, the term *biomonitor* usually indicates the former, and is in fact used as synonymous with *toxicity monitor*. In EU terminology, biomonitor refers generally to all types of biologically-based systems.

At the present time, many existing biological monitors are quite new and can be considered experimental/unique applications. Table 8 shows an overview of the most common types of online biological monitors. Sensitivity of test organism to individual compounds must be determined initially.

Online biological monitors are a very active area of R&D due to increasing regulatory and public demand pressures. While bacterial-based systems show great sensitivity and ease of operation, and development in this area will likely derive from improved fingerprinting of organisms and maintenance cost reduction, most advances can be expected from protozoan monitor technology, with techniques in UV absorption/scattering analysis that may soon allow automated detection of *Cryptosporidium* and *Giardia*. Also, molecular techniques initially applied to the recognition of the genomic sequence of specific organisms in clinical applications (Bej, 2003), have also shown great potential for use in the detection of pathogens in water, and are producing extremely interesting results that could lead to widespread online use in the very next future (see also Section 5).

TABLE 8. Online biological monitors

Technology	Measurement	Comments
Fish tests	Swimming pattern	Low sensitivity
	Ventilation rate	Sophisticated requirements
	Bioelectric field	Requires exotic “electric fish” species
	Avoidance patterns	Interpretation complex
Daphnid tests	Swimming activity	Good performance, no determination of causes
	Behaviour	
Mussel tests	Shell positions/opening	
Algae tests	Fluorescence (photosynthesis)	Commercial monitors available
Bacteria tests	Luminescence	Commercially available, toxicity data for over 1,000 compounds
	Respiration of nitrifiers	
Chlorophyll-a	Fluorometry	Interference w/pigments, diss. organics, sensitive to environmental variables
Chlorophyll-a and algal absorption	Reflectance radiometry	Commercial systems available
Protozoan Monitors	Concentration	By filtration on membrane cartridge
	Centrifugation	With modified blood cell separators, minimal operation time
	Laser scanning cytometry	Analysis possible within 3 min, particles must be confirmed by trained operator
	Particle characterization	Measure particle size/distribution, high number of false positive and negative results
	UV spectroscopy	Online system, unlabeled parasites, differentiation problems
	Multiangle light scattering	Successfully tested in lab
	Nucleic acid molecules and magnetized microbeads	Oocysts detected within 20 min, not fully automated

### 3.5. INDIRECT MONITORING: “FINGERPRINTING”

Chemical fingerprinting describes the use of a unique chemical signature, isotopic ratio, mineral species, or pattern analysis to identify different chemicals. Optical fingerprinting by UV, VIS, and NIR absorption spectroscopy can be effectively achieved by low-cost and compact spectrometric devices, that can also be linked to an online diagnostic system, to directly identify some compounds (e.g. benzene) present in the water or to give an indication of the possibility of the presence of related compounds.

In optical fingerprinting, a wide portion of the UV, VIS and NIR spectrum can be monitored simultaneously at high measurement frequency (minutes or fractions thereof); Figure 4 shows the spectral fingerprint of a typical municipal wastewater, in the range 230–630 nm, together with three other spectral readings from the same source that were recorded within 18 min from the first. These show clearly different features, indicating a pronounced change in water quality. Although this alone will not, in general, indicate the compound or compounds responsible for the change (they will need to be further investigated, if a definite answer is desired), but that can nevertheless trigger an alert to the system's operator, indicating deviation from routine conditions.

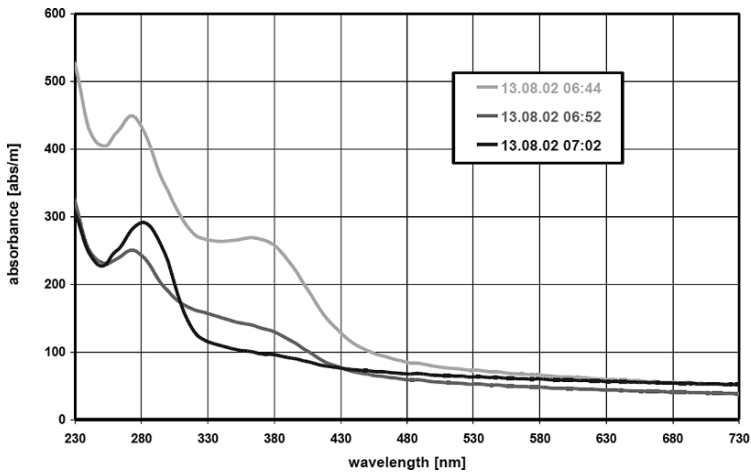


Figure 4. Optical fingerprinting of source water indicating rapid quality changes (Courtesy S-can GmbH)

#### 4. State-of-the-art Application Examples

Some relevant applications taken from recent literature, are illustrated in the following sections, as examples of the current state-of-the-art in online monitoring technology.

##### 4.1. RIVER TRENT (UK): ONLINE MONITORING OF MICROPOLLUTANTS

The River Trent drains the large, mainly urban, catchment of Midlands, with 4 million residents, in the UK; although traditionally it has been considered too polluted to serve as a drinking water supply source, the river has undergone marked improvements in quality until, in 1996, it was targeted as such. Water is currently withdrawn from the river into bankside storage lakes, from where is



taken to a purification plant. At this point, it became necessary to identify a suitable online monitoring strategy in order to protect this planned development (Kirmeyer et al., 2002).

TABLE 9. Online and laboratory parameters measured in the River Trent system

Parameter	Monitoring frequency	Method	
		Online	Laboratory
<i>Cryptosporidium</i> and <i>Giardia</i>	3/week		X
VOCs	Hourly	X	
Anions	Hourly	X	
Herbicides and phenols	Every 2 h	X	X
pH	Continuous	X	
Ammonia	Continuous	X	X
D.O.	Continuous	X	
Conductivity	Continuous	X	
Turbidity	Continuous	X	
Temperature	Continuous	X	
Nitrate	Continuous	X	X
Oil on water	Continuous	X	
TOC	Continuous		
Ammonia toxicity	Continuous		
Heavy metals			X
Antimony			X

In order to protect water quality and provide operational data to the treatment plant operators, a list of parameters subject to online/laboratory monitoring has been established (Table 9). Online monitors provide an alarm when a preset warning limit is exceeded, prompting immediate additional investigation. When a second, “action” preset limit is exceeded, water extraction into storage is automatically terminated.

Online monitors include traditional inorganic, organic and oil monitors, as well as an automated liquid chromatography (HPLC) system for monitoring organics, originally developed for analysis of triazine and phenylurea in the Rhine River, and uniquely adapted to detect other acid herbicides and phenolic compounds known to be frequently present in the Trent, at levels < 1.0 µg/l. VOCs are detected by means of a purge-and-trap GC analyzer. Maintenance requirements are relatively high (each unit requires 2–3 h of onsite attendance twice a week, in addition to the time required to review data, prepare buffers and standards, etc.).

Overall, in about 10 years of operation, the system has recorded several incidents of parameter abnormality in the River Trent, including ammonia

toxicity events and contamination by various herbicides. It has been confirmed that online monitoring gives a far better definition of each recorded event than otherwise available, while spot samples analyzed at the laboratory in parallel have always been in good agreement with the online results.

#### 4.2. THE LLOBREGAT RIVER AUTOMATIC MONITORING NETWORK

The Llobregat River, near Barcelona (Spain) is characterized by a highly variable flowrate; to ensure sufficient supply during drought periods, dams have been built along its course. In addition, a continuous, automatic system with ten stations along its course has been put in place to monitor critical water quality parameters; these may vary depending on the monitoring location, in order to account for different needs and conditions. There are three types of stations: basic (1, upstream), complete (2, midstream) and special (7, mid-to-downstream); these are described in Table 10.

TABLE 10. Llobregat River online monitoring stations characteristics

Station Type	Parameters monitored	Purpose
Basic	Temperature, pH, D.O., conductivity, turbidity, redox, TOC	Upstream impact of towns/industries Impact of tributary and drainage system
Complete	Basic station parameters PLUS ammonia and phosphates	Impact of tributary confluence
Special	Complete station parameters PLUS UV adsorption, cyanides, total Cr, hydrocarbons, organic micropollutants	Impact of potash mines on salinity Discharges from industries/farms

The objectives of the monitoring network are:

- To provide warning of pollution incidents, ensuring safety of the water produced by the purification plants
- To control instream water quality by monitoring changes in pollution indicators
- To provide information for the operators of the water systems and planners through data access with a specifically created SCADA user interface

In the course of several years of operation the Automatic Water Quality Monitoring Network has recorded various incidents of pollution, including:

- Repeated occurrences of salinity discharges from potash mines, caused by accidental breakage of collectors or leaching due to rainfall
- An event of chromium pollution in a tributary stream, due to industrial source discharges
- Multiple overflows of drainage and sewer systems causing variations of turbidity, TOC, ammonia, UV adsorption and DO
- Highly significant variations of physical and chemical parameters (mainly DO, pH) due to photosynthetic activity

#### 4.3. ON-LINE MONITORING NETWORKS FOR DRINKING WATER SECURITY OF KARST WATER

Springs in geological karstic formations are the main source for drinking water supply for about 60% of the Austrian population. Water quality from these springs shows rapid, occasional instabilities for some parameters, caused by natural events, such as heavy rainfalls. Rapid fluctuations of raw water quality, especially concerning turbidity, but also elevated concentrations of dissolved organic substances, and increased bacteria counts can occur in an unpredictable way during storm weather. Furthermore, anthropogenic events like accidents and spills in proximity of the springs might also affect the quality of the raw water.

The raw water quality is obviously one of the most important factors determining the final quality of the drinking water, in addition, rapid changes of source quality can limit the efficient usage of treatment procedures during drinking water production. As it is impossible to predict the impact of such events, it is vital to enhance drinking water security by monitoring the composition of the raw water continuously.

Main springs and important locations in the trunk mains had been monitored online since the late 1990s. Buildings equipped with power supply, pipe installations and special foundations had to be built for housing cabinet analysers, for monitoring spectral absorption coefficient ( $UV_{254}$ ), TOC, turbidity, electrical conductivity and pH. In year 2000, a novel submersible UV-VIS-spectrometer, introduced by Scan Messtechnik GmbH, capable of measuring light absorbance in the spectral range of 200 nm to 750 nm, and thus turbidity, organic carbons (e.g. TOC, DOC) and Nitrate without any sample preparation were adopted. This new monitoring equipment provided new opportunities to the Waterworks by allowing to monitor the totality of springs, even those without power supply, and by eliminating pumps, filters, membranes and reagents that were used by the old instrumentation, lowering substantially the overall cost of monitoring operations (Weingartner and Hosftaeder, 2006).

At present, Vienna Waterworks operates a SCADA-based monitoring systems in order to monitor turbidity, SAC254, Nitrate, TOC, DOC, temperature and electric conductivity at 22 locations, since monitoring just one parameter would not meet the needs of efficient and safe drinking water supply, as different types of events cause different changes in the composition of the spring water. The results of these monitoring systems are transferred in real time to an early warning system that can be accessed from four central stations. This early warning system manages the raw water sources 24 h a day. Whenever current readings exceed limits that are specific to each parameter, the water of the spring of concern will not be used for drinking water production but drained away.

#### 4.4. USE OF ONLINE UV-VIS SPECTROMETRY FOR DRINKING WATER TREATMENT CONTROL

Oxidation of organic materials for drinking water disinfection is a commonly applied treatment step. During oxidation of natural organic substances in the source water, for example using ozone, large molecules, such as humic and fulvic acids, are cracked into smaller ones. A side-effect of this procedure is the increased availability of microbiologically assimilable organic carbon (AOC): whereas the original large molecules are not readily accessible to microorganisms, the smaller oxidation products can be digested and thus can stimulate bacterial regrowth in the distribution network. AOC is an important parameter especially in drinking water networks where no residual disinfectant is present in the water; its measurement is performed using cell cultures, which is a lengthy procedure.

Online UV/VIS spectroscopy has proven itself as a tool that allows the collection of specific information on the removal efficiency for and subsequent concentrations of (organic) substances in water.

The use of two on-line spectrometer instruments, placed before and after a treatment step, and the calculation of the differential spectrum between these two sites could open up a further area in water quality monitoring and process control as it allows calculation and prediction of water quality parameters previously unavailable (van der Broeke et al., 2007).

Two on-line spectrometer probes were installed in the pilot plant of Amsterdam waterworks, Weesperkarspel. In this pilot plant, the full treatment train of the waterworks is represented. The source, an artificial lake with high concentrations of natural organic matter, is sequentially treated in an ozone reactor (four bubble columns), pellet softening reactor, biological activated carbon (BAC) filtration reactor and finally a slow sand filter. A parallel BAC reactor was fed with water from the full scale treatment plant, which uses

identical raw water, to be able to verify the effects of the changes in the ozone settings on water quality.

The AOC calibration obtained in this way is a surrogate parameter, in the sense that the AOC concentrations in the water are far below the concentrations that can be distinguished using a UV/VIS spectrophotometer without sample pre-concentration.

The developed calibration, in combination with the on-line spectrometer probe, allows for on-line, in-situ measurement of dissolved ozone concentrations. The use of two instruments simultaneously, required to perform on-line differential measurements, allowed the prediction of the changes in AOC levels in individual treatment steps in real-time.

#### 4.5. FULLY AUTOMATED WATER QUALITY ALARM STATION

The software *ana::alarm*, for use with online UV spectrometers in a specially-designed configuration (Figure 5), has been developed specifically for contaminant alarm systems based on thousands of spectra, and is successfully used in several applications in Europe.

The training of the alarm parameters can be done by the instrument automatically, or is done manually guided by the PC software. It allows for a very simple half- or fully automatic setup and configuration of up to eight spectral alarm parameters within a few minutes. It will react on any type of

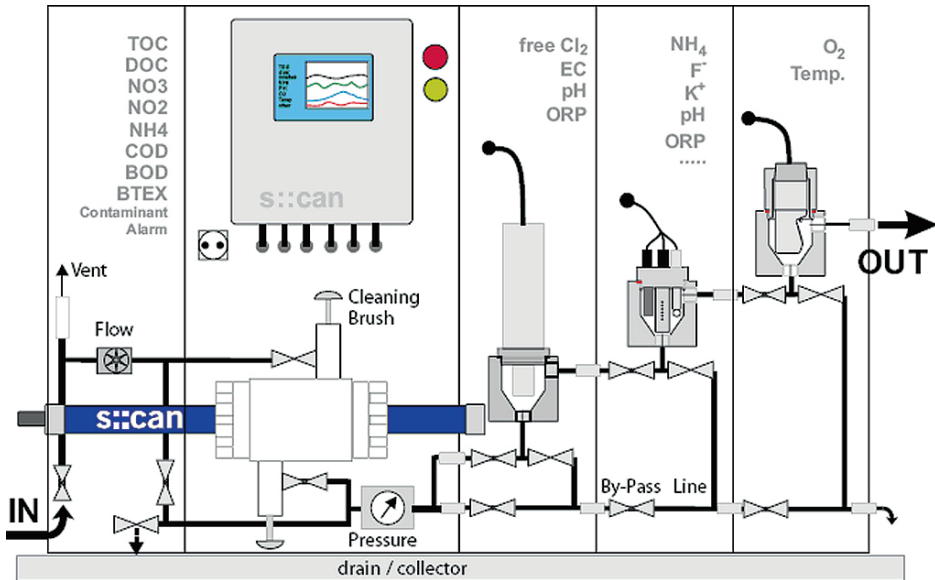


Figure 5. Configuration of online monitoring station for use with the software *ana::alarm*

organic contamination that provides an absorption signal in the UV range. The alarm sensitivity for many organic contaminants is between 1 and 500 ppb. At the same time it is most insensitive to any fluctuation of the matrix within the natural “normal” range, and thus keeps false alarms to an unmatched minimum. The approach and methods used are absolutely new and unique, and open a completely new perspective for water monitoring beyond the trending of “classical” concentration parameters (S-can, 2008b).

## **5. Recently Announced Technological Developments**

### **5.1. INTEGRATED CONTAMINANT WARNING SYSTEM**

A contaminant warning system (CWS) as an integrated tool that employs in-situ sensors, supervisory control and data acquisition (SCADA) systems, and water quality event detection systems (EDS) to continuously monitor network conditions and warn operations personnel of any potential contamination events, has been studied by the US Environmental Protection Agency (EPA) and Sandia National Laboratories (Hasan, et al., 2004; Grayman, et al., 2001). The sensor component can be comprised of various water quality sensing platforms, including contaminant-specific sensors, or existing water quality sensors (e.g., pH, Cl, electrical conductivity, etc.) as currently installed in many municipal water distribution systems to provide “surrogate” data to the CWS’s. It has in fact been proved by experiments conducted in laboratory and pipe test loop systems, that a majority of potential contaminants will change values of at least a surrogate parameter away from normal background levels (Byer and Carlson, 2005; Cook et al., 2005; Hall et al., 2007). Monitoring of surrogate parameters can therefore provide information on the presence of contaminants within a distribution system and this information can be transmitted to a central processing location through the SCADA system. The challenge is to analyze the surrogate parameter signals to accurately identify changes in water quality that are significantly beyond the range of the ambient variability of the background water quality. The recently developed the CANARY EDS software (Hart et al., 2007) is an open-source software platform that gathers water quality signal inputs from SCADA systems and processes the data using one or more event detection algorithms, using a number of statistical models to determine the probability of an anomalous water quality event occurring for a given time step and monitoring location within the distribution network (McKenna and Hart, 2008).

The CANARY system has not been used in real applications, yet, and offline case studies, based on real historical data, have evidenced some problems in correctly pinpointing alarm causes, as changes in the network

hydraulics (such as opening and closing valves, draining/filling of storage tanks and pump operations) can cause significant changes in water quality as waters of different ages and from different sources mix within the network.

## 5.2. EARLY DETECTION OF CONTAMINANTS

The existence of *Escherichia coli* (*E.coli*) in drinking water is an important indicator of faecal pathogens and potential micro biological contamination. Currently available detection methods for its presence in drinking water distribution networks are inadequate, for multiple reasons: first of all, current methods are very time consuming meaning that contamination will already have reached end-users before laboratory results are available; secondly, current sampling and analysis procedures lead to detection success rates of only 5% to maximum 25% (with optimized sample taking). Research by scientists from the Dutch KIWA shows that by using a network of on-line sensors, the success rate can be increased to 80% (Koerkamp and van Wijlen, 2008).

The core of this LabOnline system is based on a combination of a concentrator unit and a sensor system using disposable chips, which prevent the sensor system itself from cross-contaminations and guarantee reliable and high quality measurements in time. Initially designed for *E.coli*, the system is theoretically capable of detecting a broad group of microbiological contaminants like bacteria and viruses. Industrial production is scheduled for late 2009.

The same research group developed a sensor technology for pesticides based on a combination of an integrated optic chip, a biochemical transduction layer (micro)-fluidics, electronics and data acquisition and system control software, called Optiqua MobileLab. The Optiqua MobileLab sensor for the detection of pesticides will have the following characteristics: low cost per analysis, easy to use, detection of five pesticides (Simazine, Atrazine, Glyphosat, AMPA, BAM (2,6-dichlorbenzamide), detection of additional pesticides (available in later stages), on site detection, prompt analysis results (minutes), high resolution (e.g. detection limits 0.05 µg/L with a dynamic range of 0.05 – 10 µg/L), robust, low maintenance system.

## 5.3. MICRO ANALYSIS SYSTEM FOR WATER PATHOGEN MONITORING

Knowledge of the sequence of microbial genomes has led to the development of molecular methods for detection of microbial pathogens in clinical specimens as well as water and other environmental samples. A wide array of molecular techniques has therefore been applied to the study of microbiological water quality issues. The application of molecular techniques, such as PCR (Polymerase Chain Reaction) has generated a great deal of valuable information on the



occurrence, diversity, and biology of pathogens in water (Loge et al., 2002). In addition, molecular methods demonstrate rapid detection and enhanced specificity compared to other analytical methods.

A micro analysis system for water pathogen monitoring consists of a micro polymerase chain reaction (PCR) chip integrated with a continuous-flow microarray that is able to reduce the analysis time from about 24 h to within several hours as compared with the existing EPA approved methods was presented by Yong (2008).

Pathogen samples were successfully detected by the micro analysis system through DNA amplification by the micro PCR chip followed by direct transfer of the amplicons to the microarray for detection. In addition to one species monitoring, the system shows potential in direct monitoring of a range of pathogens at the same time through PCR and different probes immobilized on microarrays.

#### 5.4. TWO-DIMENSIONAL GAS CHROMATOGRAPHY SCREENING FOR NEW CONTAMINANTS

Comprehensive two-dimensional gas chromatography also referred to as GCxGC, is an analytical technique in which all the eluted compounds from a first column are successively submitted to a new separation in a second column with different selectivity. Contrary to gas chromatography (GC) which employs only one chromatographic column, GCxGC uses two chromatographic columns, coupled in series, with a modulator at their junction.

Developed in 1991, due to its principle, GCxGC offers a much better capacity of separation and a better sensitivity than conventional gas chromatography. Thanks to the sensitivity of GCxGC (three- to fivefold higher than GC) some compounds can be detected at the ng/L level. Semard et al. (2008) applied this technique to the screening of wastewater and effluents samples. A large range of drugs (antidepressors, antibiotics, anticoagulants...), personal care products (sunscreens, antiseptics, cosmetics...) and carcinogen compounds were found in the raw waste water samples. In addition to the above mentioned micropollutants, a wide variety of nitrogen aliphatic and aromatic structures that could act as DBP (disinfection by-products) precursors, were also uncovered. This technology does not yet have the potential for direct online application.

#### 5.5. MOLECULAR ONLINE DETECTION OF WATERBORNE PATHOGENS

Courtois et al. (2008) also propose a molecular technique, based on polymerase chain reactions to detect pathogens. To improve PCR diagnostics for routine analysis purposes, they focus on the processing of the sample, which is crucial



for the robustness and the overall performance of the method. Their objectives in sample preparation are to increase the concentration of the target organisms to the practical operating range of a given PCR assay; and to produce a purified DNA extract that would be representative of the initial water sample and would be free of PCR-inhibitory substances. This can be achieved by means of a two-step UltraFiltration (UF) procedure by using prototype hollow fiber UF cartridge, and a commercial UF centrifugal concentrator.

## 6. Discussion and Conclusions

This paper has overviewed existing instrumentation applicable to water supply online monitoring, and examined a few state-of-the-art application examples. It is clear that technological development in this field is very rapid, and that astonishing advances are anticipated in several areas (fingerprinting, opto-chemical sensors, biosensors, molecular techniques). Software applications, together with new generation sensors, are also contributing to the identification of otherwise difficultly monitored parameters.

In spite of the high technology being developed, monitoring costs are bound to become a lesser and lesser part of a water utility budget due to the fact that automation and technological simplification will abate the human cost factor (maintenance and other labour forms) and reduce significantly the complexity of procedures (with those, of reagent requirements, etc.).

Proper interpretation and use of the growing mass of water quality data that will become available through new technologies will allow better management of water resources, and water treatment and distribution facilities.

## References

- AWWA RF (2002) Online Monitoring for Drinking Water Utilities. Cooperative Research Report. (E. Hargesheimer, O. Conio and J. Popovicova, Eds.) AWWA Research Foundation, Denver, CO.
- Bej, A.K. (2003) Molecular based methods for the detection of microbial pathogens in the environment. *J Microbiol Methods*, **53**, 139–40.
- Byer, D. and K.H. Carlson, 2005, Real-Time Detection of Intentional Chemical Contamination in the Distribution System. *Am Water Works Assoc J* 97(7), 12.
- Cook, J. E., Roehl, R., Daamen, K. 2005, Decision Support System for Water Distribution System Monitoring for Homeland Security, Proceedings of the AWWA Water Security Conference, Oklahoma City, OK.
- Courtois, S., K. Sebti and Z. Do-Quang (2008) Universal concentration for large volumes of water samples before molecular detection of waterborne pathogens. Proceedings, Singapore International Water Week Conference, June, Singapore.

- Cunliffe, D.A. (2008) Emerging Enteric and Potentially Waterborne Pathogens in the Region. Proceedings, Singapore International Water Week Conference, June, Singapore.
- Daughton, C.G. and T.A. Ternes (1999) Pharmaceuticals and personal care products in the environment: agents of subtle change? *Environ. Health Perspect*, 107(6), 907.
- Grayman, W.M., R.A. Deininger, and R.M. Males (2001). Design of early warning and predictive source water monitoring systems, AWWA Research Foundation, Denver, 297 pp.
- Hall, J., A.D. Zaffiro, R.B. Marx, P.C. Kefauver, E.R. Krishnan, R.C. Haught and J.C. Herrmann (2007). On-line water quality parameters as indicators of distribution system contamination. *Am Water Works Assoc J* 99(1), 66.
- Hart, D.B., S.A. McKenna, K.A. Klise, V. Cruz and M. Wilson (2007). CANARY: A Water Quality Event Detection Algorithm Development Tool, in proceedings of: ASCE World Environmental and Water Resources Congress, Tampa, FL, May 15–19.
- Hasan, J., S. States, and R. Deininger (2004). Safeguarding the Security of public water supplies using early warning systems: A brief review. *J Contemp Water Res Educ*, 129, 27–33.
- Kirmeyer, G., N. Bazzurro and W. Grayman (2002). Case studies of online monitoring systems. In: Online monitoring for Drinking Water Utilities, AWWA Research Foundation, Denver, CO.
- Koerkamp M.K., M. van Wijlen (2008) Next generation sensors for detection of pesticides and E.coli in water. Proceedings, Singapore International Water Week Conference, June, Singapore.
- Kolpin, D.W., Furlong, E.T., Meyer, M.T., Thurman, E.M., Zaugg, S.D., Barber, L.B. and Buxton H. (2002) Pharmaceuticals, hormones, and other organic wastewater contaminants in U.S. streams, 1999–2000: A national reconnaissance. *Environ Sci Technol* 36, 1202.
- IonLife (2002) IonLife website (ionlife.org). “How safe is our water? The threat of terrorism” Jan. 31, 2002.
- Jones, O.A.H., Voulvoulis, N. and Lester, J.N. (2002) Human pharmaceuticals in the aquatic environment. *Environ Technol* 22(12), 1383.
- Loge, F.J., Thompson, D.E., & Call, D.R. (2002) PCR detection of specific pathogens in water: a risk-based analysis. *Environ Sci Technol* 36, 2754–9.
- McKenna, S.A., D. Hart (2008) On-Line Identification of Adverse Water Quality Events from Monitoring of Surrogate Data: CANARY Software. Proceedings, Singapore International Water Week Conference, June, Singapore.
- Öllers, S., Singer, H.P., Fässler, P. and Müller, S.R. (2001) Simultaneous quantification of neutral and acidic pharmaceuticals and pesticides at the low-ng/l level in surface waters. *J Chromatogr A* 911(2), 225.
- S-can (2008) S-can company website <http://www.s-can.at>. S-can GmbH, Vienna, Austria.
- Semard, G., Z. Do-Quang, A. Bruchet (2008) Screening of emerging contaminants in wastewaters using advanced GCxGC-TOFMS. Proceedings, Singapore International Water Week Conference, June, Singapore.
- van den Broeke, J., P.S. Ross, A.W.C. van der Helm, E.T. Baars, L.C. Rietveld (2007) Use of on-line UV/Vis-spectrometry in the measurement of dissolved ozone and AOC concentrations in drinking water treatment, Proceedings, IWA Automonet 2007.
- Weingartner, A. and F. Hofstaeder (2006) On-line monitoring networks for drinking water security of Karst water. All About Karst and Water, Vienna.
- WHO (2003) Emerging issues in water and infectious disease. World Health Organization, Geneva.

- Yong, C.K., I.K. Lao, R. Murthy, H.M. Ji, C.Y. Teo, Christophe Lay, H.H. Feng, W.T. Liu (2008) micro analysis system for water pathogen monitoring. Proceedings, Singapore International Water Week Conference, June, Singapore.
- Yongtao, Li, E.J. George, E.M. Hansen, J.J. Toma, M. Werner and P.D. Smith (2000) SPE Twin-PAL. Online in situ monitoring of semivolatile organic compounds in water. Proc. AWWA Water Quality Technology Conference, Salt Lake City, UT.