Chapter Two - Literature Review

2.1. Introduction

The need to improve abstraction water quality monitoring has become necessary due to increasing pressure being placed upon water utilities to produce water that meets the increasingly stringent requirements set by the European Union as well as higher expectations of the consumer.

Water quality monitoring should ideally consist of an instantaneous and continuous method for identifying all compounds of interest; this however is not technically or economically possible. The selection of the most suitable detection techniques often depends upon the specific problem being tackled, the availability of laboratory equipment, the degree of sophistication, sensitivity, selectivity, cost and time requirements (Jeffery *et al.*, 1989, González-Toledo *et al.*, 2003).

The objective of this review is to compare the existing abstraction monitoring techniques used to measure changes in water quality. The application of these techniques for detecting taste and odour episodes will be discussed and their limitations to cost effective real-time monitoring highlighted. The potential application of using non-specific gas sensors as an online technique for monitoring changes in water quality will be introduced.

2.2. Water quality standards

Standards of water quality vary depending on national, regional and local guidelines. Regulatory bodies use guidelines as a basis for developing a certain standard, that if properly adhered to, will ensure the safety of drinking waters supplied (Council Directive 98/83/EC). European standards are set by the European Union (EU) directives with the Environment Agency of member countries acting as the environmental regulator of the water industry. For example the UK Environment Agency (EA) enforce standards in

England and Wales. In the majority of European countries there are absolute standards in place for chemical composition within rivers (EU Directive 75/440/EEC). The main aim of these standards is to protect the end user whether they are humans, animals or industry. The protection of public health and ecosystems are established through specific directives that define physical, chemical, organoleptic and microbial parameters.

2.2.1. Abstraction

Surface waters abstracted for drinking water treatment need to comply with the specific standards related to the quality of the water and the number of people to be supplied. Two EU directives are in place that relate to the quality of abstracted water. EU Directive 75/440/EEC (OJ L 194, 25.7.1975, p.26) concerns the quality required of surface water intended for the abstraction of drinking water, and EU Directive 79/869/EEC (OJ L 271, 29.10.1979, p.44) concerns the methods of measurement and frequencies of sampling and analysis of surface water intended for the abstraction of drinking waters.

It is intended that these will be repealed and replaced by Water Framework Directive COM(97)49, proposal for a Council Directive establishing a framework for community action in the field of water policy (Water Framework Directive (COM(97)49)).

2.2.2. Water intended for human consumption

The production of water from drinking treatment plants requires the product to meet EU Directive 80/778/EEC (OJ L 229, 30.8.1980, p.11) as amended by Council Directive 98/83/EC (OJ L 330, 5.12.1998, p.32) concerned with the quality of water intended for human consumption. These directives set standards for physical, chemical and microbial parameters along with maximum levels for contaminants and the water characteristics. The main objectives being;

- to protect human health from the adverse effects of any contamination of water intended for human consumption,
- to ensure that water intended for human consumption is wholesome and clean.

The introduction of the Water Framework Directive aims to restructure European water legislation with the following main objectives (Blöch 1999):

- expanding the scope of water protection to all waters, surface waters and groundwater,
- achieving "good status" for all waters by a certain deadline,
- water management based on river basins,
- "combined approach" of emission limit values and quality standards,
- getting the process right,
- getting the citizen involved more closely,
- streamlining legislation.

2.3. Taste and odour episodes

The problems related to taste and odour problems in drinking water can be improved with a better understanding of the chemical causes in drinking water supplies (Suffet *et al.*, 1999). Table 2.3.1 lists common culprit compounds that have been identified in water systems, the lowest levels at which a taste and odour were detected and the descriptors associated with the taste and odour (adapted from Young *et al.*, 1996). Suffet *et al.* (1999) introduced a revised drinking water taste and odour wheel to help develop a common language for taste and odour sensory panels and drinking water practitioners whilst presenting common organoleptic characteristics found in drinking water. The wheel, presented in Table 2.3.2, shows descriptors for both taste and odour causing compounds and provides typical mouth and nose feel descriptors. Raw and treated water drinking water wheels are similar to those used in the beer and wine industry as reference standards for flavour terminology (Mallevialle and Suffet 1987).

Table 2.3.1 Chemicals causing off-flavours and odours in drinking water (adapted from Young *et al.*, 1996).

Chemical	**Odour descriptor**	**Odour Threshold (ug/l)**	**Taste descriptor**	**Taste threshold (ug/l)**
2,4,6-trichloroanisole	Dusty, musty, earthy rotten vegetable	0.00008	Musty, stale, antiseptic, earthy	0.025
2-chlorophenol	Musty, sweet, floral, chemical, TCP	0.088	Chemical, bitter, TCP, antiseptic	0.14
2-isobutyl-3-methoxypyrazine	Woody, stale, musty, coal dust, ash	0.00005	Creosote, stale, dusty, coal dust	0.004
2-isopropyl-3-methoxypyrazine	Sooty, dusty, cabbage, wet paper	0.00003	Musty, vegetable water, stale, peas, asparagus	0.0099
2-methylisoborneol	Musty, earthy, brazil nuts, peaty	0.0063	Earthy, musty, moldy, peaty	0.0025
4-chloroanisole	Musty, medicinal, perfume, musky, wet paper	2.0	Musty, stale, perfume, earthy, aniseed, sweet	6.2
geosmin	Musty, earthy, stagnant, grassy, beetroot, mould	0.0013	Musty, earthy, stale, beetroot, mould	0.0075
isopropyl benzene	Windolene, polish, paint pear drops	10	Stale, bicarbonate	60
MTBE	Estery, vanilla, sweet	15	Estery, bitter	40
phenol	Wet paper, wet newspaper, cardboard	9.5	Metallic, bitter	2

Table 2.3.2 Tabulated drinking water taste and odour wheel (Suffet *et al.*, 1999).

Classifications	Descriptors	Associated compounds
Taste	Sweet	Sugar
	Sour	Citric acid
	Salty	Sodium chloride
	Bitter	Caffeine, quinine hydrochloride
Odour	Earthy/musty/ moldy	Earthy = geosmin, earthy/potato bin = 2-isopropyl-3-methoxypyrazine, musty = 2-methylisoborneol musty/moldy = halogenated anisoles, muddy = unknown
	Chlorinous/ ozonous	Chlorinous/bleachy = free chlorine/monochloramine, swimming pool = dichloramine ozonous = ozone in solution
	Grassy/hay/straw/ woody	Grassy (fresh, sweet) = cis-3-hexenyl acetate, grassy (green, sharp) = cis-hexen-1-ol dried grass = unknown, hay/woody = B-cyclocitral, woody/pencil shavings = unknown sweet tobacco = B-cyclocitral
	Marshy/swampy/ septic/sulfurous	Decaying vegetation = dimethyl disulphide, septic = unknown, swampy = dimethyl trisulphide rubbery = unknown, rotten eggs = hydrogen sulphide, onion = isopropyl mercaptan, creeky = unknown
	Fragrant/vegetable/ fruity/flowery	Sweet = 4-nonyl phenol, fruity/orange like = decanal, geranium = diphenyl ether, cucumber = trans-2-cis-nonadienal
	Fishy/rancid	Rotten fish = trimethylamine, fresh fish = unknown, rancid fish = trans, trans-2,4-heptadienal, buttery = unknown, aquarium like/algae = unknown, rancid = octanal, rancid/sweaty socks = methyl butanal
	Medicinal/phenolic	Medicinal = Chlorophenols/Bromophenols/Iodomethanes.
	Chemical/hydrocarbon/ miscellaneous	Model glue = styrene, sweet solvent = MTBE, sweet organic chemical = m-xylene, cat urine = unknown, plastic = methyl methacylate, sweet medicinal = 2-ethyl-4-methyl-1,3-dioxolane, sweet (tutti fruity) = 2-ethyl-5,5-dimethyl-1,3-dioxane, shoe polish = cumene, petroleum = 1,3-pentadiene, varnish = indan, gasoline = BHT, paint/putty/solvent = alkyl benzenes
Mouth feel/nose feel	Pungent/oily/chalky/tingling/ Drying/astringent/cooling/ metallic	Astringent = aluminium sulphate, cooling = menthol

Taste and odour episodes can occur as a result of industrial spills in the abstraction source. This has been reported as the main cause of pollution within drinking water systems. Reported episodes include on the Ohio River, Pennsylvania, USA in 1989 and 1992 (Noblet *et al.,* 1999, Schweitzer *et al.,* 1999a, 1999b) and in river water, ground water and tap water in Barcelona, Spain (Ventura *et al.,* 1995, Romero et al., 1998). Taste and odour causing compounds can also impact upon water systems during periods of heavy drought, when water levels are low, the natural dilution rate of a body of water is reduced leading to potentially higher impact rates for smaller pollution events and after periods of heavy rainfall dilution rates will increase (Bourgeois *et al.,* 2002) however sewers can overflow into water courses or excess run-off from roads and land carrying fuels, fertilizers and pesticides into waters (Jian-Ying Hu *et al.,* 1999, Komai *et al.,* 2002). During the summer months algae blooms flourish in lakes or reservoirs, (Jones and Korth 1995, Kajino and Sakamoto 1995, Montiel *et al.,* 1999) metabolites of which can leave an earthy/musty taint in the water (Suffet *et al.,* 1999).

The standardised means of identifying these taste and odours utilises the human sense of smell (olfactometry) via a smell bell system. These systems provide a manual odour examination by smelling a sample of aspirated water at 60 °C.

Figure 2.3.1 Photograph of a smell bell
(Courtesy of Severn Trent Water Ltd.)

2.3.1. Olfactometry

The simplest form of detection for off-tastes or odours is to either taste or smell the products as they are produced. Human senses are a sensitive tool for the detection and quantification of tastes and odours that have been used or many years (Wnorowski 1992, Schulz *et al.*, 1996). The biological sense of smell in humans in particular is extremely intricate and can distinguish many compounds at very low concentrations (Leffingwell 2002). A taste or odour is the characteristic property of a substance that makes it perceptible to the sense of taste or smell. With years of training a master blender can distinguish malt whiskies by flavour just as a perfumer can classify fine fragrances and its components by smell. These properties enable the consumer to make an instant assessment upon the products quality and also allow panels of highly trained individuals to assess organoleptic properties with ranging descriptors (Hrudey *et al.*, 1988, Young *et al.*, 1996). There can be large variations in sensitivity between individuals and within individuals from day to day which should be considered when interpreting thresholds (Hrudey *et al.*, 1988, Young *et al.*, 1996).

2.3.1.1. Flavour profile analysis (FPA)

Originally introduced for use within the food and drink market FPA has been applied to the drinking water sector (Krasner *et al.*, 1995). FPA panels are trained to identify odours in raw and treated drinking water, using familiar descriptors such as musty, medicinal or floral (Bartels *et al.*, 1986, Mallevialle and Suffet 1987, Young *et al.*, 1996). Selecting the panel is a rigorous as several criteria should be met to enable a standardised procedure (Bartels *et al.*, 1987, Obermeyer and Thies 1992). Panels can vary in size depending on the purpose of the test, the skill of the panel and type of result the assessors require. Expert panels can consist of three to ten people where consumer panels may have more than eighty members (De Greef *et al.*, 1983). Once each individual has made an independent assessment of the sample the panel meets to determine a consensus of the assessment (Suffet *et al.*, 1988). Burlingame (1999) addresses the lack of standardisation for odour profiling of environmental odours and contrasts the findings to both

instrumentation and laboratory techniques. He concludes that the odour profiling method should be refined using a varied set of conditions. There is a need for odour standards, particularly for the calibration and training of odour intensity.

Krasner (1988) reports the use of a seven-point scale for the classification of flavour profile intensity. The scale ranges from zero to three and every half point refers to a descriptor from very slight (1/2) to strong (3) with zero being odour free. Rashash *et al.* (1997) and Mallevialle and Suffet (1987) state that the water industry utilises a standard eight point scale rated from zero (odour free) to twelve (strong). Crozes *et al.* (1999) uses a five-point intensity scale from threshold (1) to strong (12). In each case the result is expressed as a 'mark' where zero refers to the reference water/sample (Rigal 1995). Suffet *et al.* (1988) present the importance of limiting fatigue and the effect nasal tiredness can have upon perceived aroma intensity. If no rest is permitted between sample evaluation an individuals odour perception can diminish. The results published indicate that by the time the tenth sample had been evaluated the perceived intensity was reduced by 67% of the true intensity, but allowing as little as two minutes rest between sample analysis this value was reduced to 17% (Suffet *et al.*, 1988).

FPA is appropriate for planning, monitoring and evaluating water treatment processes (Suffet et al., 1995). Applications of FPA include the evaluation of flavour compounds in Camembert cheese (Kubícková and Grosch 1998). The assessment of adsorptive processes (activated carbon dosing) for taste and odour control within a drinking water treatment plant (Crozes *et al.*, 1999) and the analysis of the orally perceived attributes of Chardonnay wine (Zamora and Guirao 2002). Precision and accuracy have not been determined for FPA and the variation in panelists' responses should be expected to exceed that of analytical techniques (Suffet *et al.*, 1988) although greater human precision can be gained if the panelists are properly trained (Wnorowski 1992).

2.3.1.2. Threshold odour number (TON)

The TON method determines the degree of dilution required necessary to produce a sample of barely perceptible odour (Rashash *et al.*, 1997). TON is best applied for threshold determination or for determining whether dilution will produce a better flavour (Suffet *et al.*, 1995). Rashash *et al.* (1997) indicates several drawbacks are associated with the TON method.

- The TON scale is open-ended so the number assigned may be influenced by an individual ability to detect a certain odour.
- Composite odours are not subdivided into individual odours.
- Dilution can change the characteristics of the perceived odour.

TON requires dilution were FPA does not so it is not possible to directly compare results as dilution affects the nature of the sample (Mallevialle and Suffet 1987). The Threshold odour number also referred to as the 'flavour threshold test' (Suffet *et al.*, 1995) is defined as A + B/A. Where A = Volume of the water sample and B = Volume of reference water (Rigal 1995). The threshold flavour number (TFN) is deduced in the same manner (Rigal 1995). Young *et al.* (1996) have determined the taste and odour thresholds for 59 potential drinking water contaminants. The results of which indicated that although many chemicals such as chlorophenols and microbial metabolites can produce taste and odours within drinking water they are often at concentrations much lower than any health based limits, although pesticide organoleptic thresholds were above prescribed limits.

Rigal (1995) presented the so-called 'state of the art' for flavour and odour evaluation in European countries and the next European standard for these parameters. The standard is based upon the dilution method and produces a TON and a TFN of a water sample. Assessments of taste and odour thresholds are performed separately. Trials were successful and enabled Rigal to obtain a good knowledge of the sensitivity of the panels involved in the laboratory testing. The odour threshold concentration (OTC) is reached

when the sample is at the lowest concentration where an odour can be perceived (Rashash *et al.*, 1997).

Table 2.3.1.2.1 lists the two most commonly reported compounds found to cause taste and odours in the aquatic environment, the descriptor attached to them, their OTC value, the ranges in which each have been reported and the method of detection used to determine their OTC. The OTC number can be subject to water temperature and chlorine concentration within the water sample (Ito *et al.*, 1998) and can be expected to vary from day to day based on an individual ability, with a differing factor of 100 not uncommon (Young *et al.*, 1996).

The descriptor has been reported to change with the concentration detected, e.g. MIB has a earthy/musty odour at lower concentrations yet more camphorous at higher concentrations (Krasner *et al.*, 1983).

2.3.1.2.1. Olfactometry assessment

Olfactory and organoleptic assessments can be discriminated in different ways (Davis *et al.*, 1992, Rigal 1995). Tests such as the 'paired test' or 'triangle test' enable slight differences to be established between samples or between samples and a reference sample.

Table 2.3.1.2.1 Comparison between OTC values for the two most commonly reported off tastes/odours in drinking water

Compound	Descriptor*	OTC	Range of concentrations detected/tested	Method of analysis/determination	Reference
Geosmin	Earthy, musty	2 ng/l	Not reported	CLSA-GC/MS	Krasner *et al.*, 1983
	Earthy, musty	2 ng/l	Not reported	CLSA-GC/MS	McGuire *et al.*, 1981
	Earthy, musty	4 ng/l	Not reported	FPA	Mallevialle and Suffet, 1987
	Earthy, corn, musty	6-10 ng/l	6-100 ng/l	FPA/Weber-Fechner plot	Rashash *et al.*, 1997
	Earthy	16 ng/l	Not reported	Simultaneous distillation extraction, FPA/Sensory GC	Young *et al.*, 1999
	Earthy	18 ng/l	Not reported	CLSA, FPA/Sensory GC	Young *et al.*, 1999
	Musty	30 ng/l	22-164 ng/l	Panel TON test verified by stripping GC/MS	Ito *et al.*, 1988
	Musty, earthy, stagnant, grassy, beetroot, mould	3.8 ng/l	1.3-3.8 ng/l	FPA	Young *et al.*, 1996
	Earthy	20 ng/l (in water)	20-30 ng/l	GC-MS	Zoeteman *et al.*, 1980
2-MIB	Earthy, musty	2 ng/l	Not reported	CLSA-GC/MS	Krasner *et al.*, 1983
	Earthy, musty	2 ng/l	Not reported	CLSA-GC/MS	McGuire *et al.*, 1981
	Earthy, musty	6-10 ng/l	6-100 ng/l	FPA/Weber-Fechner plot	Rashash *et al.*, 1997
	Earthy, musty, camphorous	9 ng/l	Not reported	FPA	Mallevialle and Suffet, 1987
	Musty	10 ng/l	4-14 ng/l	Panel TON test verified by stripping GC/MS	Ito *et al.*, 1988
	Musty, earthy, brazil nuts, peaty	15 ng/l	6.3-1.5 ng/l	FPA	Young *et al.*, 1996
	Earthy	20 ng/l (in water)	20-30 ng/l	GC-MS	Zoeteman *et al.*, 1980

2.4. Techniques applied for water monitoring

In comparing analytical techniques it is important to note that no two applications are identical. For example in gas chromatography analysis, although a comparable result is obtained different experimental procedures and equipment are often used. Variations can occur from sample preparation, oven temperatures, retention times, carrier gas/elutant type, column height and packing material and detection options applied. These variations also extend to the manufacturer of each component. Such variation makes intricate comparison difficult therefore this review will focus upon comparing the end result or value in each case rather than discerning system differences.

2.4.1. Technical analysis

2.4.1.1. Chromatography

Chromatography is a separation technique that relies on the abilities of surfaces to adsorb substances. Chromatography is widely used for the identification of the components of mixtures (Jeffery *et al.*, 1989). Types of chromatography include size exclusion chromatography, in which molecules are separated based on their size by passage through a porous structure stationary phase. Ion exchange and ion chromatography, ions are separated based on their charge whereas in gas chromatography (GC), gaseous substances are separated based on their adsorption on or solubility in the stationary phase. Liquid chromatography (LC) is based upon the above principles but uses micrometer sized particles for the stationary phase so that equilibrium is achieved rapidly and separations are performed swiftly. For fundamentals on gas chromatography, including gas-liquid, gas-solid and pyrolysis gas chromatography, column and detector types and liquid chromatography, including liquid-liquid, liquid-solid, bonded phase, gel permeation, high performance along with apparatus and equipment refer to Jeffery *et al.* (1989). These methods, with additional detectors, detect a limited number of selected compounds but are costly and time consuming (Literáthy and László, 1999). GC and LC have many applications in the detection of pollutants within water systems, a few of many are presented (Tables 2.4.1.1.1 and 2.4.1.1.2).

2.4.1.1.1. Sample preparation

Solid phase extraction (SPE), solid phase micro extraction (SPME), liquid-liquid extraction (LLE) and closed loop stripping analysis (CLSA) are examples of sampling preparatory/isolation techniques (Lloyd *et al.*, 1998, Fernandez-Alba *et al.*, 1998). SPME/SPE are equilibrium techniques requiring careful control to enable quantitative analysis (Lloyd *et al.*, 1998). The technique avoids the use of large amounts of organic wastes, is inexpensive and allows easy automation (Fernandez-Alba *et al.*, 1998). SPME is applied but to a lesser extent compared to SPE (Fernandez-Alba *et al.*, 1998). In CLSA target compounds are stripped from the water by a recirculating stream of air. The trap retains the volatile and semi-volatile organic compounds allowing the purge gas through (Hassett and Rohwer, 1999). LLE can sometimes produce results not attainable using CLSA (Ventura *et al.*, 1995). CLSA is also referred to as purge and trap (Lloyd *et al.*, 1998) and is widely used for the analysis of ppt to ppb levels of non-polar organic compounds of intermediate molecular weight (Mallevialle and Suffet 1987). CLSA is as sensitive as or more sensitive than the human nose and qualitatively more reliable (McGuire *et al.*, 1981).

2.4.1.1.2. Sample detection

Detectors available include thermal conductivity detectors (TCD), flame ionisation detectors (FID), thermionic ionisation detector (TID), photo-ionisation detector (PID) diode array detection (DAD) and electron capture detector (ECD) (Fernandez-Alba *et al.*, 1998, Jeffery *et al.*, 1989). Specific molecular identification is achieved by interfacing the GC/LC with spectroscopic instruments, namely mass spectrometry (MS), Fourier transform infrared spectrometry (FTIR) and optical emission spectrometry (OES) (Jeffery *et al.*, 1989).

Special attention is given to MS because it is the most intensively developed detection technique in environmental analysis (Liška and Slobodník 1996). MS produces, separates and detects ions within the gas phase. To enable vapourisation gases, liquids

and volatile solids are injected into the instrument just before the ionisation chamber. In the ionisation chamber atoms of the elements are bombarded with a stream of high-energy electrons causing ionisation. The positive ions formed are pass through an electric field that accelerates the ions towards the magnetic field. As the ions pas through the magnetic field they are deflected according to their mass and charge. Providing the accelerating and magnetic fields stay constant ions of only one particular mass/charge ratio will be detected. Ions of smaller mass/charge ratio will be deflected too much. Ions of greater mass/charge ratio will be deflected too little. The ion detector is linked through an amplifier to a recorder. As the strength of the magnetic field increases ions of increasing mass will be detected and the recorder will produce a mass spectrum. The area under the peaks traced give the relative abundance of the different ions present. (Jeffery *et al.*, 1989). MS is expensive with a high cost of purchase and maintenance (González-Toledo *et al.*, 2003).

Tables 2.4.1.1.1 Applications of GC for water monitoring.

Application	Sampling method	Detector	Results (Pollutant compounds detected)	Time required to obtain result	Cost	Comments	Author(s)
Analysis of odorous compounds in potable water	CLSA	GC-MS	MIB and geosmin down to 4 ng/l	Not reported	Not reported	Linearity in data above 4 ng/l	Hasset and Rohwer, 1999
Rapid analysis of Geosmin and MIB in water	SPME	GC-FID	Geosmin – 0.1 ug/l MIB – 0.3 ug/l	15+ mins	Not reported	Data shows trade off between sensitivity and time required to obtain result	Lloyd *et al.*, 1998
	Purge and trap	GC-MS	Geosmin – 0.1 ug/l MIB – 0.1 ug/l				
		GC-FID	Geosmin – 0.1 ug/l MIB - 0.3 ug/l				
Evaluation of taste and odour events in drinking water	CLSA	GC-FID	12 taste and odour causing compounds detection ranging from 0.005 – 2 ng/l. (geosmin and MIB – 0.05 ng/l)	Not reported	Not reported	Sensory GC is highly sensitive for determining individual compounds in water	Khiari *et al.*, 1992
Determination of geosmin and MIB in water	CLS	GC-MS	Geosmin – 2 ng/l MIB – 2 ng/l	30+ mins	Not reported	Shipment of samples to laboratory then subsequent analysis takes 48 hours.	Palmentier *et al.*, 1998

Tables 2.4.1.1.2 Applications of LC for water monitoring.

Application	Sampling method	Detector	Results (Pollutant compounds detected)	Time required to obtain result	Cost	Comments	Author(s)
Analysis of pesticides in water	SPE	LC-MS	31 pesticides detected at concentrations ranging from 10 – 250 ug/l.	50+ Mins	Not reported	The coupling of LC-MS with SPA offers an effective method for implementing water quality	Jian-Ying Hu *et al.*, 1999
Taste and odour events in Barcelona's water supply	LLE	LC-OES and FID	Detection of 5 cyclic acetyls, concentration range 0.38 – 7.85 ug/l. 3 others not detected.	Not reported	Not reported	LLE-HPLC showed the presence of poly aromatic hydrocarbons where CLSA-GC did not.	Ventura *et al.*, 1995
Monitoring of pesticides and metabolites in ground waters	SPE	LC-DAD	Detection of 20 insecticides and pesticides, concentration range 0.01 - 0.2 ug/l.	Not reported	Not reported	LC-DAD requires higher preconcentration methods than GC-MS	Fernandez-Alba *et al.*, 1998
Detection of fluorescent whitening agents and organotin in the Rhine basin	SPE	LC-OES	Detection of fluorescent whitening agents at 0.1 – 5 ug/l and fentin, cyhexatin and fenbutatinoxide at 0.02 – 0.04 ug/l in surface water	Not reported	Not reported	Detection levels are in accordance with EC legislation for single and multiple occurrences of pesticides.	Van Hout and Brinkman

An interesting modification of the GC technique has been developed which combines instrumental and sensory analysis, known as chromatographic sniffing (Wnorowski 1992, Khiari *et al.*, 1992, Brownlee *et al.*, 1995). Sensory GC was found to be a valuable tool in identifying compounds of very low odour thresholds, which were present at or below the detection limits of the GC-MS (Cotsaris *et al.*, 1995). It should be noted that an OTC reported by sensory GC is usually lower than the concentration reported from olfactory analysis (Section 2.3.5), since in sensory GC samples are evaluated as an individual compound eluting from the GC column (Young and Suffet 1999). Samples not detected by techniques such as GC-FID can be detected by sensory GC (Khiari *et al.*, 1992).

Drage *et al.* (1998) reports the use of a Sentex Aquascan Monitor specifically for the detection of volatile organic compounds in a source of drinking water. The Aquascan purge and trap gas chromatograph (Sentex Systems) utilises an argon ionisation detector to determine the concentration of VOCs. Trichloroethylene has been detected twice in real river samples (River Trent, UK) at concentrations of 0.4 µg/l and 0.1 µg/l, both below levels of concern.

2.4.1.2. Infrared Spectroscopy

Infrared spectroscopic techniques study the properties of a molecule by means of its interactions with infra-red radiation. The radiation is dispersed into a spectrum after it has passed though the material being analysed (Jeffery *et al.*, 1989). Kastner et al. (1997) investigated the use of a hybrid infrared technique for the on-line in-situ analysis of hydrocarbons in water and although successful did not report levels of detection. Mizaikoff (2003) presents a paper on the use of infrared optical sensors for water quality monitoring where continuous analysis of environmentally relevant (volatile organic compounds) compounds in the aqueous phase. Qualitative and quantitative determination of a variety of organic analytes were achieved in the mg/l to µg/l range.

2.4.1.3. Total Organic Carbon (TOC)

TOC is the most relevant parameter for global determination of organic pollution of water and wastewater (Thomas *et al.*, 1999). This is a non-specific method for determining the amount of carbon-containing compounds within a water sample. Analysis requires the oxidation of the carbon compounds in the water, resulting carbon dioxide concentration is measured, variations upon this basic method exist but tend to produce more fragile instruments (Thomas *et al.*, 1999).

2.4.2. Parametric analysis

Individual parametric monitors are available and are used in accordance with Standard Methods. Nitrate, pH and ammonia are measured using Ion Selective electrodes, which involves measuring the flow of ions across a membrane. The flow of ions is proportional to the concentration of ions in the liquid being analysed. Conductivity is a measure of dissolved components in the water sample with the number of ions in solution altering the ability to conduct electricity. Turbidity is a measure of the light-transmitting properties of water. The turbidity measurement, nephelometric turbidity units (NTU), compares the light scattered by a sample to the light scatter of a reference suspension under identical conditions. (Gregory, 1998). Turbidimeters (Figure 2.4.2.1) can be used for the detection of cryptosporidium although they do not have the sensitivity required to enable detection of the small oocysts (Gregory, 1998). Particle counters are starting to emerge as an alternative for turbidity meters, they provide detailed information on the number and size of particles and are highly sensitive for particles larger then 1 micrometer. (Gregory, 1998). Amrane and Prigent (1998) applied turbidimetric device for the on-line monitoring of growth of filamentous microorganisms, their results showed that a turbidimetric device was able to effectively monitor the growth kinetics.

Drage *et al.* (1998) refers to the 'standard six and nitrate' multi-parameter monitor which measures turbidity, conductivity, pH, temperature, dissolved oxygen, ammonia and nitrate. This instrument is capable of indicating gross changes in water quality.

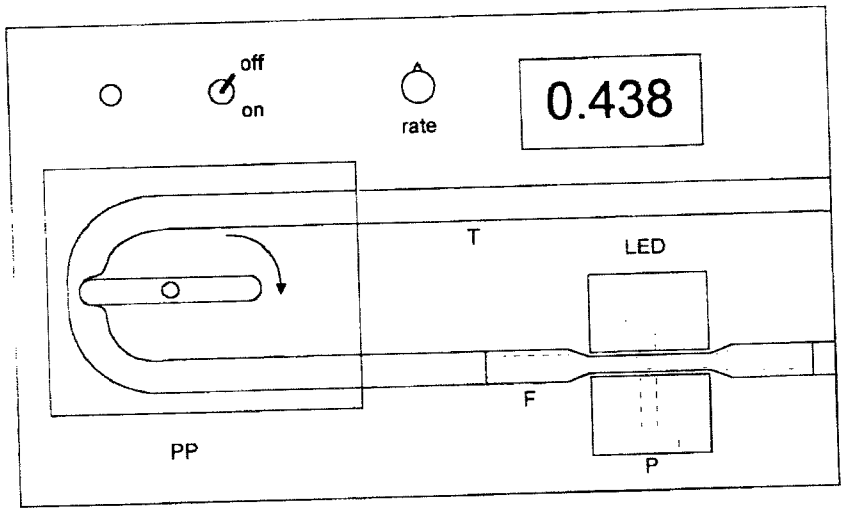

Figure 2.4.2.1. A turbidimetric device. F = flow-cell; LED = light emitting diode; P = photocell; PP = peristaltic pump; T = steam sterilisable silicone tube. (Amrane and Prigent, 1998)

2.4.3. Biomonitoring

Whist it is possible to monitor sources of water supplies it is not possible to monitor for all compounds. The number of parameters that require monitoring and the apparent inability to do so has led to the use of biomonitors that can be utilised online and maintained continuously. Biomonitors on rivers involve living organisms. The stresses placed upon them by the presence of toxic materials is measured. Organisms that have been used as biomonitors include mussels (Bode and Nursch, 1999), fish (Kawamura *et al.*, 1995), daphnia (Bode and Nursch, 1999) algae (Twist *et al.*, 1997) and bacteria (Strotmann et al., 1995).

2.4.3.1. Mussels

The mussel test relies on a lack of activity of the creatures to trigger an alarm (Bode and Nursch, 1999). In the mussel test the mobility and valve movements of the mussel are observed and registered. Tiny magnets are fixed to the mussel shells and as the mussel breaths and grazes during normal activity the shells will open and close allowing the magnets to trigger adjoining reed switches fixed beside the mussel (Bode and Nursch,

1999). The behavior of several mussels should be monitored to ensure reliability (Figure 2.4.3.1.1).

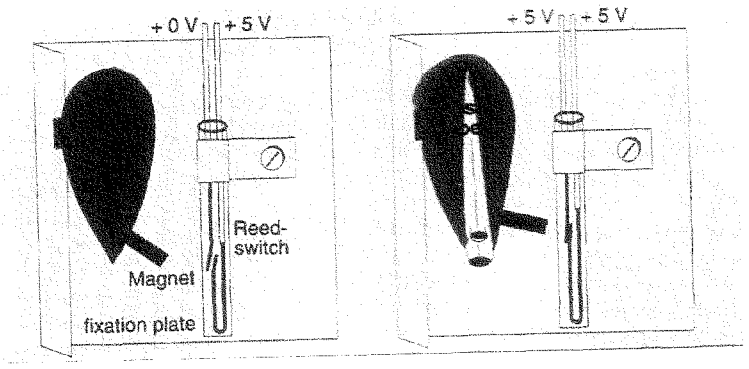

Figure 2.4.3.1.1 Illustration of the mussel test. (Bode and Nursch, 1999).

2.4.3.2. Fish tests

Fish tests can be used to continuously monitor for toxicity in water, (Kawamura *et al.*, 1995). Observations of the fish's behaviour give an indication to the water quality. These tests enable swimming patterns, ventilation rates and avoidance patterns to be observed. Figure 2.4.3.2.1 shows the application of such a test, the fish's movements are recorded using a video camera.

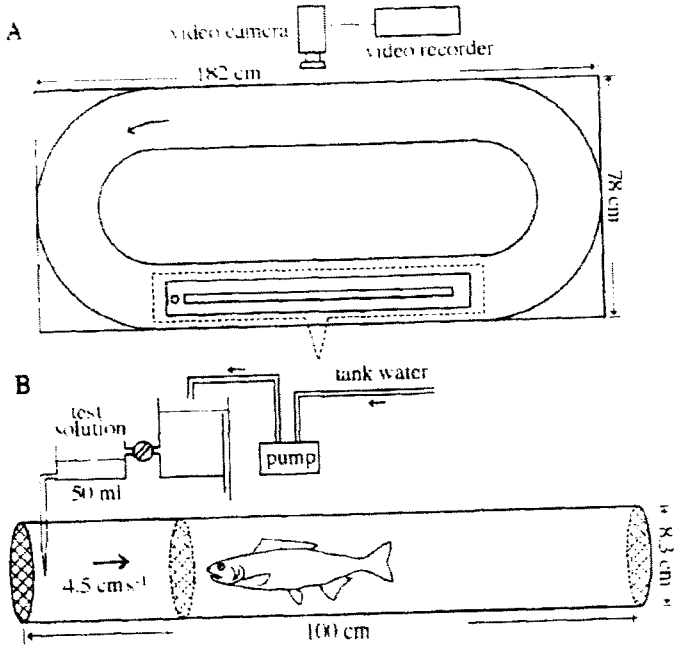

Figure 2.4.3.2.1 Application of a fish test, their behavior is monitored as they are subjected to known concentrations of pollutants (Kawamura *et al.*, 1995).

2.4.3.3. Daphnia tests

The dynamic daphnia test monitors the swimming activity of microcrustacea by means of infrared sensors (Figure 2.4.3.3.1). As the daphnia move within the system they occasionally break beams of infrared light between light emitter and detector, this break of signal registers a pulse. A deviation from normal pulse activity indicates an abnormality in the water affecting the organisms (Bode and Nursch, 1999).

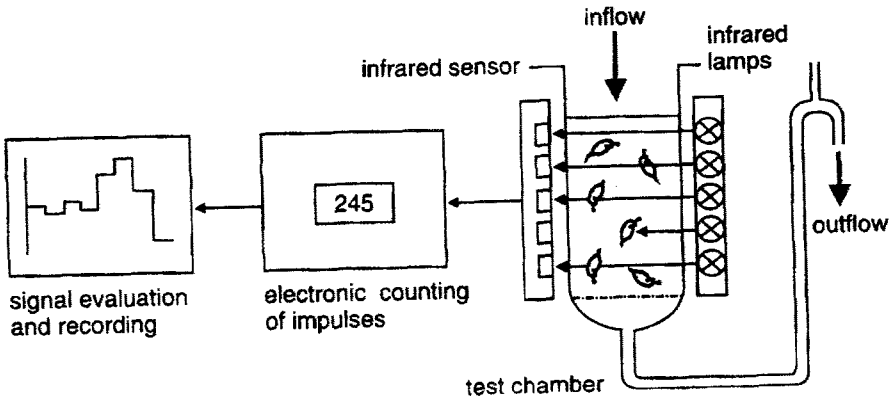

Figure 2.4.3.3.1 Dynamic daphnia test (Bode and Nursch, 1999).

2.4.3.4. Algae tests

Immobilised algae have been applied for the assessment of eutrophication in flowing surface waters (Twist *et al.*, 1997). The algal growth is monitored as the flow rate, hence nutrient supply, of the waters is altered. Baun *et al.* (1998) found algae growth inhibition tests to be more sensitive for monitoring toxicity than daphnia tests on samples collected from an agricultural area on Phuket Island (Thailand).

2.4.3.5. Bacteria tests

Strotmann *et al.* (1995) applied a nitrifying bacteria test to monitor the biological activity of activated sludge and a luminescent bacteria test to screen the effluent of a wastewater treatment plant. The nitrification test determines the oxygen consumption attributed to nitrification whilst the luminescent test determines the inhibition of luminescent bacteria during shock loading of pollutants, an increase in inhibition is revealed during the loading phase.

The use of organisms in controlled environments and the effects that pollution can have upon them, can be advantageous and provide information above that produced from technological sampling alone. They do not provide information on pollution type yet serve as an early warning for the occurrence of negative changes in water quality.