

2.5. Comparison of key variables for on-line monitoring techniques

The information in Table 2.5.1 compares the key variables related to the range of potential on-line monitoring techniques described within this chapter. Comparisons can be drawn between techniques to enable suitable method development, screening and the level of accuracy and monitoring required.

Table 2.5.1 Comparison of the key variables for on-line monitoring techniques

Technique	Cost	Accuracy	Time to obtain result	Sample volume required	Advantages	Disadvantages	References
Olfactory/sensory	Low	Subjective. Depends on level of calibration and training – to ppt levels	Immediate	Small	Once trained panels can be highly subjective	Requires manual operation. Accuracy dependant on compound.	Suffet <i>et al.</i> , 1998 Young <i>et al.</i> , 1996 Hrudey <i>et al.</i> , 1988
Gas and liquid chromatography	Medium-high	Very – GC to ppt levels LC to ppb levels	Variable ~30mins	Small	Automated, accurate, minimal supervision	Accuracy varies with compound and medium	Jeffery <i>et al.</i> , 1989 Liška and Slobodnik 1996 van Hout and Brinkman 1993
Infrared spectroscopy	Medium	Moderate – to $\mu\text{g/l}$ levels. Response time and sensitivity depend on partition coefficients of solution and membrane		Small	Continuous analysis	Limited applicability in complex matrices	Mizaikoff 2003 Kastner <i>et al.</i> , 1997
TOC	Medium	Generally ppm levels	Few mins per sample or continuous	Small	Non specific, can be measured continuously on-line	Instruments can be fragile	Thomas <i>et al.</i> , 1999
Biomonitoring	Low-medium	Subject to variability in age and population	Continuous – abnormality triggers an alarm	Large	Provides an excellent picture of overall river quality	Not able to screen for all or specific compounds	Kawamura <i>et al.</i> , 1995 Bode and Nursch, 1999
Parametric analysis (Std 6 + Nitrate)	Low	Dependent on individual test – ppm levels	10-15 minutes dependant on specific test	Small	Can be automated	Provide little information, manual operation required	Drage <i>et al.</i> , 1998

Low = <£5,000, Medium = £5,000 - £20,000, High = >£20,000

2.6. Existing monitoring programs - case studies

There are several monitoring programs already established, examples of which monitor the Ruhr Basin, Germany (Bode and Nusch 1999) the Rhine Basin, Germany (van Hout and Brinkman 1993) the Danube Basin, Hungary (Pintér 1999, Literáthy and László 1999) and the River Trent, United Kingdom (Drage *et al.*, 1998).

2.6.1. Case 1: Ruhr basin (Bode and Nursch 1999):

The River Ruhr is dual-use i.e. it acts as a supply for drinking water and receives treated industrial and municipal effluents. The aim of this monitoring program is to provide advanced water quality monitoring.

Two monitoring stations were set up, one at Hattingen and the other at Essen, Lake Baldeney. The Hattingen site samples from a section of the river to guarantee a homogeneous, and therefore representative, sample. The water quality parameters monitored at both were temperature, oxygen content, pH, conductivity, turbidity, spectral absorption coefficient, chlorophyll-fluorescence and ammonium. In addition the Hattingen site was monitored for chromium and flow. It also has two bio-monitors, a *Daphnia* monitoring device and a mussel test.

The Hattingen station was designed to provide state-of-the-art technology whilst doubling as an information centre and showpiece for visiting groups. Total investments in the site came to DM 1.24 Million, operating costs were reported at DM 152,800 per year. The Baldeney station was significantly cheaper to initiate, as there were no costs incurred for building purchases and it utilised existing equipment. Total investment was DM 136,500 whilst operating costs, which were expected to rise through upgrades, were DM 54,600.

During 1996 elevated ammonia concentrations nearly reached 3 mg/l, resulting in unionised ammonia-nitrogen concentrations as high as 100 µg/l, exceeding the NOEC-value (No Observed Effect Concentration) for chronic fish toxicity of 20 µg/l. These

levels resulted in increased fish mortality within the water near the Baldeney site and coincided with increased pH-values. Increased Chlorophyll, Oxygen and pH levels have also been reported during the summer months. The Mussel and Daphnia tests have proved to be very effective and reliable although no 'real alarm' has been reported in connection with biological pollution in the river. The monitors have been used to reassure public concerns during a spate of odour complaints that occurred in January 1998.

2.6.2. Case 2: Rhine basin (van Hout and Brinkman 1993):

The Rhine Basin program is an initiative which aims to improve the quality of surface waters by getting a better understanding of the rivers ecological function. One of the main program objectives is to develop a water monitoring system that transfers laboratory methods into routine methods for on-site, on-line and preferably unattended continuous monitoring. Several compound classes have been identified for monitoring; these were selected on the basis of the following criteria;

- They are produced or used in the Rhine Basin area in large quantities
- They are expected or known to be toxic
- Current analytical methodology is inadequate

Table 2.6.2.1 summates monitoring techniques applied and detection levels for pollutant compounds expected within the Rhine.

A SAMOS LC (System for the Automated Measurement of Organic micropollutants in Surface water) has been applied. Spiked samples of Rhine water show minimum detection levels between 0.1 and 3 ug/l. 100 ml of Rhine water was spiked with a mixture of 27 pesticides. This system has proved quite effective as the concentration limits, set by the EC, are 0.1 ug/l for a single pesticide and 0.5 ug/l for the sum of them. These results indicate that the techniques can be used for drinking water monitoring where it meets detection levels for single and multiple pesticides set by the EC.

This report is nearly ten years old, however upon publication it stated that it was the aim to install several LC units at key points along the Rhine in order to establish a geographical platform for comparative studies.

Table 2.6.2.1 Methods for, and detection levels of, the contaminants in the Rhine Basin Program (van Hout and Brinkman 1993).

Type of compound	Monitoring technique applied	Detection level(s)	Medium
Polar pesticides	On-line trace enrichment, separation by gradient liquid chromatography and diode array detection	~ 0.3 ug/l varies with compound and medium	Various water types including river water
	Mass spectrometer with a thermospray or particle beam interface as detector	5-20 ng/l	River water
Phthalate esters	GC with mass-selective detection	0.02-0.05 ug/l	North-Rhine Westphalian waters
	LC with fluorescence detection. For the aqueous phase solid-phase extraction is applied.	Recovery rates of ~90% at concentrations of 0.1-5 ug/l	Water
Fluorescent whitening agents	For the sludge's supercritical fluid extraction is applied.	Recovery rates > 95% at concentrations of 0.05-0.2 g per Kg of dry material	Sludges
	Solid-phase extraction on C-18 or polymer-loaded membrane disks, separation by GC and detection with either nitrogen-phosphorus or a mass-selective detector	10-30 ppt	2.5 ml samples of tap water. 2.5 ml samples of river water.
Organic sulphonic acids	Solid-phase extraction, using ion-pair reagents, in combination with ion-pair chromatography and fluorescence detection	50-100 ppt ~ 1 ppb	Unknown
	LC combined with UV photoconversion and post-column morin complexation followed by fluorescence detection	2-4 ug/l	For fenit, cyhexatin and fenbutatinoxide in soil.
Organotin compounds		0.2-1 ug/l	For fenit, cyhexatin and fenbutatinoxide in sediment.
		0.02-0.04 ug/l	For fenit, cyhexatin and fenbutatinoxide in surface water.

2.6.3. Case 3: Danube River Basin, (Pintér, 1999):

The Danube Accident Emergency Warning System (DAEWS), reported by Pintér (1999), was established in April 1997 as a result of the short term priority action of the Environmental Program for the Danube River Basin. This was put into operation after several accidental water pollution incidents occurred in the Danube River Basin, some of which had transboundary effects.

The system is operational in Austria, Bulgaria, Croatia, Czech Republic, Germany, Hungary, Romania Slovakia and Slovenia. The system provides immediate information on the characteristics of the water within the basin to assist the governing bodies and water users of the quality of the river water so that preventative measures can be taken in the event of a pollution incident. Each country has at least one Principal International Alert Centre (PIAC) which monitor for changes in water characteristics, including water levels for flood control, and inform the other PIAC's downstream in the event of any abnormalities occurring. The early warning system prevents possible damage and potential operational problems.

Since April 1997 only a few pollution incidents have been recorded. One incident, which occurred on the 26 May 1998, was quite serious and resulted in severe water quality problems downstream including significant fish kills. The Hungarian PIAC sent "warning-incident" alerts to the PIAC's downstream on the 28.05.1998 and "end of alert" messages on 29.05.1998. Later tests showed that the water entering one of the sites downstream was good and the pollutant content of the chemical was around its detection limit.

Literáthy and László (1999) indicate the need for screening techniques capable of detecting organic and inorganic micropollutants in the Danube that do not rely on expensive and complex machinery.

2.6.4. Case 4: River Trent (Drage *et al.*, 1998):

This case study addresses the application of an on-line monitoring station for determining the presence of micropollutants in the River Trent (UK) with the aim of using the monitoring station as an inlet protection facility for a drinking water treatment works. The purpose of the station being to provide plant operators with data regarding river quality allowing them to make informed decisions regarding abstraction parameter.

The River Trent receives treated sewage effluent from 8 million people, industry and diffuse drainage sources so the river quality has the potential to be highly variable. Once it had been decided to use the River Trent as a source of drinking water there was a need to identify and apply monitors capable informing operators when the river water quality has fallen below the standard fit for abstraction.

One lone monitor does not cover a wide enough range of potential contaminants to provide sufficient protection but several monitors allow a high degree of protection. Table 2.4.4.1 indicates the instrumentation used for automatic on-line analysis within the monitoring station and levels of detection reported.

Table 2.6.4.1 On-line instrumentation used on the River Trent
(Adapted from Drage *et al.*, 1998.)

Instrument/Test	What does it monitor?	Detection levels
Standard six and Nitrate	pH, ammonia, dissolved oxygen, conductivity, turbidity, temperature and nitrate levels	Not reported
Surface oil detector	IR reflectance change at the water surface. Positive results indicate the presence of oil, miscible oils and solvents	Not reported
SAMOS LC	A pre-selected group of risk compounds	< 1.0 ug/l (ppm)
Sentex Aquascan Monitor	Volatile organic compounds	Sub ug/l (ppm) levels
AMTOX Nitrification Inhibition Monitor	Toxicity	Not reported

There is also smell-bell apparatus, a Cryptosporidium/Giardia filter and an Autosampler, which all require manual operation.

The monitoring station was placed 2 km downstream of the water abstraction point. This means that there won't be any warning of a pollution incident because if has been detected then the polluted water will have already been abstracted. It will allow the operators to see when the pollution has cleared. In order to ensure a representative sample is achieved the station should be located on a well-mixed section of the river. Since system installation no serious problems have been reported. No target or unknown compounds have been detected at levels of concern since very early testing detected the presence of high levels of pesticides and phenols. Spiked samples have been analysed; these also serve as a means of calibration, which have triggered the alarms. This supports the confidence in the equipment to detect the presence of pollution within the river samples.

2.7. Conclusion 'Why is there the need for abstraction monitoring?'

With constant attention being paid to the quality and standards expected when producing water intended for human consumption an increasingly large onus is placed upon governing bodies and water companies to ensure that guidelines are adhered to and standards are met.

It may be thought that abstraction monitoring may only be required at certain periods during the year or only after periods of either heavy drought or precipitation yet this would be an incorrect assumption to make. It is important at all times. The frequency of the monitoring and sample size would need to be established independently at each inlet station, depending on the flows at each inlet, relative pollution risks and the ratio between sample size to plant operations, in order to ascertain what would provide the user with a representative sample.

The papers by Drage *et al.*, (1998), van Hout and Brinkman (1993), Bode and Nusch (1999), Pintér (1999) and Literáthy and László (1999) indicate that abstraction monitoring has proved to be of use. Albeit a multifaceted suite incurs high commissioning, operational and maintenance costs. These costs are difficult to justify without positive results and the detection of real events.

2.7.1. What makes a good monitoring system?

Existing gaps in the monitoring market call for ideal early warning monitoring system to be:

- Reproducible and verifiable
- Cost effective
- Effective/covers all potential costs
- Reliable – gives minimal false positives
- Non-time consuming
- Durable - robust
- Low maintenance (self operating, no need for manual input/training)
- On-line
- Provides warning in sufficient time to enable action
- Allows remote operation
- Functions all year round

A decision would need to be made as to whether it is important for the monitoring station to be able to provide a full range of monitoring or if target compounds will be suitable. The frequency of monitoring will depend upon the likelihood of the river becoming polluted and the impact factors in the event of a pollution incident.

Monitoring suits are costly (Drage *et al.*, 1998, Bode and Nursch, 1999) and technologies that support existing and proved appliances are being constantly assessed. More cost effective and rapid alternatives are sought.

2.7.1.1. Emerging monitoring technology

Electronic Noses provide an interesting alternative in the field of monitoring technology. Recent findings in the field of sensor arrays (Electronic Noses and Tongues) have shown that it may be possible to detect concentrations of a pollutant within a body of liquid by analysing the headspace gas above that sample (Gardner and Bartlett, 1999, Bourgeois *et al.*, 2002). This technique is proving to be much faster than existing analytical techniques and requires very little user in-put. The gas sensors within the array can hold many forms but basically work in the same way. The conductivity of the sensors change when subjected to different volatile chemicals within each sample (tastes and odours). In theory each taste or odour samples should have a characteristic 'fingerprint'. In practice this will be harder to ascertain as results may prove hard to duplicate. Climatic (ambient) changes from one day to the next could cause the sensors to confuse classes or concentrations of pollutant (Bourgeois *et al.*, 2002). It is also true that relative humidity (RH), sample temperature and sample constituency may change having a marked effect on the response observed by the sensors (Gardner and Bartlett, 1999).

Non-intrusive forms of monitoring are becoming more popular especially when dealing with a product or system where the material being monitored is costly and it could prove expensive to destroy samples in order to perform analysis on them. Sensor arrays have the ability to run 24 hours a day without human input (unless a problem occurs) cutting down on the need for highly trained human panels.

Gas sensor technology has been shown to be able to detect pollutants in raw and treated waters (Bourgeois and Stuetz 2000) and used as a non-invasive method for on-line monitoring of a cultivation during a bio-process (Liden H *et al.*, 1998). This technology could be applied as an on-line monitoring technique and would certainly compliment other existing monitoring techniques.

Sensor arrays will need the capability to reach levels of detection in the ppb range, with a high success rate, if they are to play a future part in the detection of pollutants or contaminants at low-levels.

2.8. Sensor arrays

Sensor arrays, so called ‘Electronic’ or ‘E’ nose are used primarily as an analytical tool to distinguish between different odours based on their chemical composition. They act as a means of artificial olfaction, designed not to replace existing olfactory techniques but to aid them. The system design, sensor types employed and analysis techniques applied vary from one array and manufacturer/user to the next.

2.8.1. The sensor array system

The sensor array system generally comprises of the three key features, sensor array, signal processor and analysis technique (Figure 2.8.1.1).

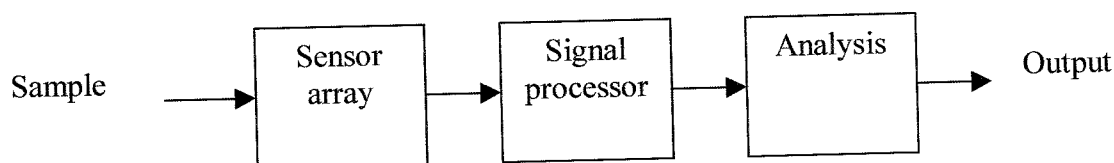


Figure 2.8.1.1 Key components of a sensor array (Stuetz and Nicholas, 2001).

2.8.2. Sensor types

The type of sensor(s) incorporated into different sensor array systems depends upon the function and purpose that the array is to serve. Gas sensors (Gardner and Bartlett 1999) and optical sensors (Walt *et al.*, 1998) are used in Electronic Noses where the component requiring measurement is within the gas phase. Multi-channel electrodes coated with lipid/polymer membranes (Toko 1998, Ju *et al.*, 2003) and ion sensitive electrodes (Di Natale *et al.*, 1997) can be used in the liquid phase for electronic tongues (Krantz-Rülckler *et al.*, 2000).

An electronic nose can comprise of either a single sensor (Kish *et al.*, 2000, Mielle and Marquis 2001) or an array of sensors. In general the sensors used should be responsive to

components within the gas phase and should be either specific or if the purpose of the array is to detect known pollutant or component such as either carbon monoxide (CO) or hydrogen sulphide (H₂S), or non-specific if the purpose of the array is to detect multi components within a gas phase. Whichever sensors are utilised to comprise an array they should be able to recognise significantly different odour profiles and generate discernable signal responses that reflect this. An array of varying sensor types could potentially be used to provide an odour fingerprint that subsequently could be used for identification, classification and quantification of gaseous samples (Doleman and Lewis 2001).

Of the several types of gas sensor, available for use within an electronic nose, the three most common are the conducting polymer (CP), metal oxide (MOS/MOX) and acoustic wave gas sensors (surface and bulk (SAWs and BAWs respectively)) (Figure 2.8.2.1). Other gas sensor types available for potential use within an electronic nose are:

- Field effect transistors (both MOS and Polymer) (Covington *et al.*, 2001)
- Biosensors (Ziegler *et al.*, 1998, Karube and Nomura 2000)
- Potentiometric sensors (Ion selective) (Jiménez-Morales *et al.*, 2002)
- Optical fibre/sensor (Walt *et al.*, 1998, Gardner and Bartlett 1999)
- Potassium iodide (KI) sensors (Doll *et al.*, 1996)

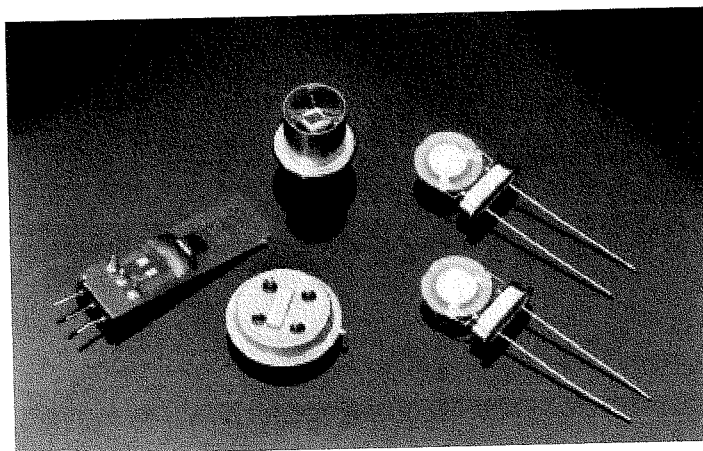


Figure 2.8.2.1 Photograph of the four most common sensors (metal oxide, conducting polymers, surface acoustic wave and quartz crystal microbalances (BAWs)) used in commercial sensor array systems. (Courtesy of Marconi Applied Technologies).

2.8.2.1. Conducting polymers (CP)

CP sensors (Figure 2.8.2.1.1) are produced (grown) by chemical or electrochemical polymerisation from a solution consisting of the chosen base monomer. The three most common of are Aniline (C_6H_7N), Pyrrole (C_4H_5N) and Thiophene (C_4H_5S) (Figure 2.8.2.1.2). Once polymerised the monomers form a conjugated system (Figure 2.8.2.1.3). When an electron enters the polymer chain (Figure 2.8.2.1.4) via the carbon atom (a) the adjacent double bond breaks, the resulting electron pair splits, one joins the free electron to form a new double bond whilst the other progresses through the structure (b). The process continues down the molecule (c) providing an electron path and therefore conduction. When the polymer is fully oxidised it ceases being a conducting material and adopts an insulating role (Gardner and Bartlett, 1999). Various fabrication methods have been reported for conducting polymers (Shurmer *et al.*, 1991, Amrani *et al.*, 1993, Doleman *et al.*, 1998a,b, Guardarrama *et al.*, 2001a,b); the choice of which varies depending on the type, size and properties the sensor requires. The design of the substrate is critical to ensure reproducible sensor characteristics (Hodgins, 1995).

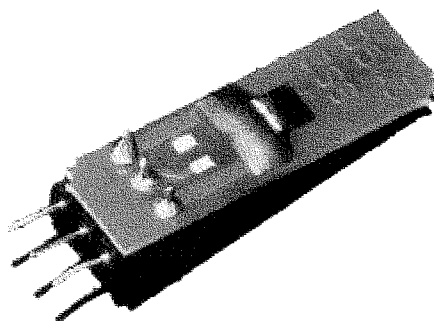


Figure 2.8.2.1.1 Photograph of a conducting polymer sensor
(Courtesy of Marconi Applied Technologies).

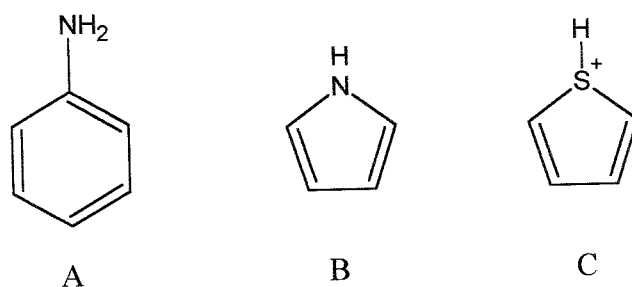


Figure 2.8.2.1.2 Single monomer units (A) Aniline, (B) Pyrrole and (C) Thiophene.

For polymer chains to grow electrochemically a layer of conducting polymer must be deposited between two electrodes. The two electrodes are then connected together, making the polymer one of the electrodes in the electrochemical cell. A potential is applied to the cell and further layers of conducting polymer are grown on the electrode (the originally deposited material). The sensor characteristics and growth rate can be controlled through choice of the applied current or voltage (Gardner and Bartlett 1999). The length of the polymer chain determines the resistance of the sensor, the longer the chain the greater the resistance (Hodgins 1995). Different gaseous samples will exhibit slightly different gaseous/polymer interactions at the polymer surface (Amrani *et al.*, 1993).

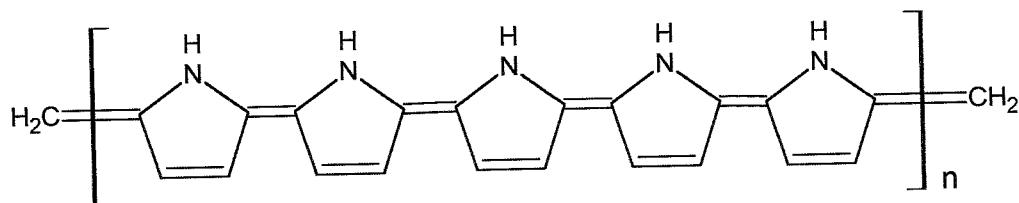


Figure 2.8.2.1.3 Polymerised pyrrole structure

There are a variety of possible polymer/gaseous interactions that can occur, all of which create physical changes in the polymers structure (Gardner and Bartlett 1999). The polymer is either reversibly oxidised or reduced in the presence of gaseous samples. As the resistance of the film changes from its baseline value the corresponding change in conductance can be recorded and represented (Figure 2.8.2.1.5). If several different responses from differing sensors were collated for an odour a fingerprint odour profile could be generated. Once exposure has been carried out the sensors are purged by exposing them to a reference gas for a predetermined period, this results in the resistance value decreasing back to the baseline levels therefore readying the polymer chain for the next exposure. The sensor response characteristics observed would depend greatly on the type of odour they are exposed to (Shurmer and Gardner 1992, Doleman *et al.*, 1998, Severin *et al.*, 2000).

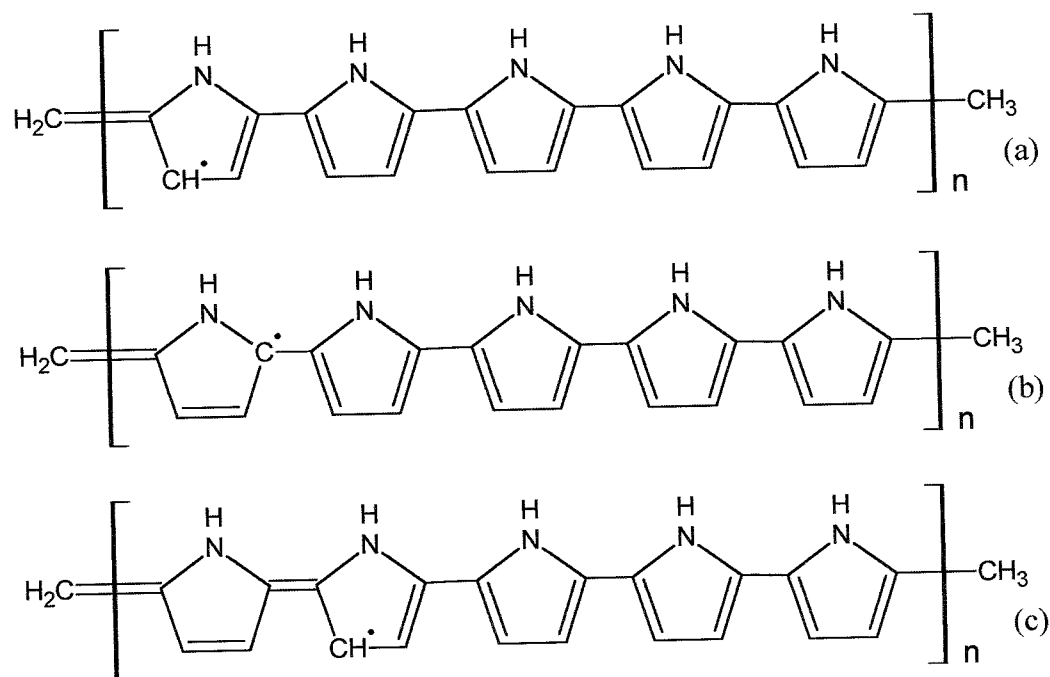


Figure 2.8.2.1.4 Representation of bond breakage and formation caused by electron passage through the compound during conduction.

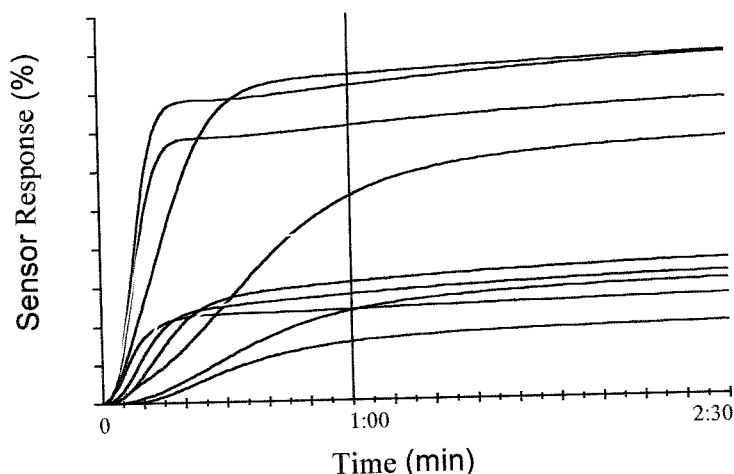


Figure 2.8.2.1.5 Response profile from an array of conducting polymer sensors.

The acquisition period show last for 2min 30 seconds, a time slice can be taken at any time e.g 1 min (as shown).

Table 2.8.2.1.1 summarises some of the reported strengths and weaknesses for conducting polymer sensors. The ability to respond rapidly, reversibly with an excellent level of reproducibility to a broad range of gaseous samples at temperatures surrounding ambient make CP one of the most common sensor types. Although they are an order of magnitude lower in sensitivity than the MOS they can still detect samples within the ppm ppb range. Observed responses can be extremely sensitive to RH (Bourgeois *et al.*, 2002) and effected by the presence of solvents (Stuetz, 2001). Slight changes in the RH could therefore indicate a physical anomaly in sample character that the primary function of the sensor may be unable to detect. CP sensors can be manufactured from a variety of materials suggesting that variations in fabrication could enable a ranging spectrum of sensors with the capability of detecting the majority of gas phase constituents (Gardner and Bartlett 1999). Drift effects, caused by sensor aging, is a problem if the user wants to compare data from a non-sequential data collection set, especially if long periods of time have elapsed between collections (Bourgeois *et al.*, 2002). Cross comparison should be suitable if the data is collected and compared sequentially over a short time frame where aging is insignificant (Bourgeois *et al.*, 2002).

Table 2.8.2.1.1 Advantages and disadvantages of using conducting polymer sensors.

Conducting Polymer Sensors	
Operational overview – Partial oxidation during exposure to a gaseous sample leads to a change in the polymer resistance. The resulting change in the corresponding voltage can be observed and recorded before the sensors are desorbed and the cycle is repeated.	
Advantages	Disadvantages
<ul style="list-style-type: none"> • Respond to a broad range of gaseous samples¹⁺² • A wide range of polymers available for synthesis^{2,3+6} • Ease of preparation³ • Operate within a wide range of conditions around room/ambient temperatures^{2,3, 4,5+6} • Rapid (reversible) response and recovery times^{3,5+6} • Excellent reproducibility² • High sensitivity (ppm to ppb levels)² • Full recovery to baselines² • Low power² • Functional groups that interact with different classes of odourant molecules can be incorporated into active materials, providing high sensitivities⁴ • Organic materials tend to be easier to use than oxides and may be easier to modify than inorganic materials to react with specific gaseous species⁴ • Small⁶ • Lack of specificity can be an advantage if sensors are incorporated into an array⁶ 	<ul style="list-style-type: none"> • Sensitive to water⁴ • Usually thermally unstable⁴ • Organic materials can be poor conductors making conductivity measurements difficult⁴ • Subject to long-term drift effects³ • Sensitivities are generally an order of magnitude lower than oxide films³ • Lack of specificity⁶

1) Hodgins 1995

2) Stuetz 2001

3) Gardner and Bartlett 1999

4) Di Natale 1999

5) Hatfield *et al.*, 19946) Bartlett *et al.*, 1989

2.8.2.2. Metal oxide sensors (MOS)

The MOS/MOX sensor usually occur in the form of Tin oxide (SnO₂) yet variants have been know where the metal oxide can be Indium (In₂O₃), Zinc (ZnO), Titanium (TiO₂) and Tungsten (WO₃) (Meixner and Lampe 1996, Gardner and Bartlett 1999, Di Natale *et al.*, 2001). Slight variations in construction lead to different sensing properties (Gardner

and Bartlett 1999). MOS sensors (Figure 2.8.2.2.1) can be classified as ‘thick’ or ‘thin’ film devices and are typically fabricated under the same general conditions. Manufacturing approaches are documented by Gardner *et al.* (1995), Meixner and Lampe (1996), Papadopoulos *et al.* (1996), Gardner and Bartlett (1999) and Siciliano (2000). The subject area of metal oxide sensors has been previously reported with respect to current status and future prospects for SnO₂ sensors (Gopel *et al.*, 1995) and basic construction, mechanisms and operation (Gardner and Bartlett 1999). The sol-gel technique, formally known as chemical solution deposition, is the preferred fabrication method for thin-film sensors (Capone *et al.*, 2000). The sol can be formed by dissolving a salt in an oxygen-free carbonate buffered solution. After adding further components to be incorporated in the final product the mixture is oxidised by sparging it with compressed air. The gel is formed once the sol is oxidised and precipitates from the liquid. The precipitate is allowed to settle before being removed from the supernatant liquid and dried in a vacuum, forming the gel (Capone *et al.*, 2000). Sol-gel films are deposited using spin-on techniques and have been applied by Gardner *et al.* (1995) and Capone *et al.* (2000, 2001).

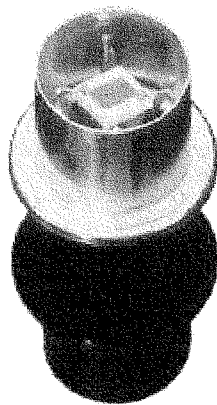


Figure 2.8.2.2.1 Photograph of a metal oxide sensor
(Courtesy of Marconi Applied Technologies).

Different dopants of catalytic materials, such as Pt, Pd, Os and Fe can be added, in small amounts to enhance sensor selectivity and sensitivity (Di Natale *et al.*, 2001, Distante *et al.*, 2000). By selecting the dopant used and the operating conditions these sensors have

been developed for a range of applications (Gopel *et al.*, 1995, Meixner and Lampe 1996). Papadopoulos *et al.* (1996) found that the addition of noble metals to either the sensing film or the filter showed an enhanced sensor response to hydrocarbons, especially butane and propane. Similarly Gardner and Bartlett (1999) showed how the sensor responses for a range of gases are affected when three different metals (Pt, Pd and Ag) are doped on a SnO₂ sensor (Figure 2.8.2.2.2) and thus enabling the choice of dopant to tailor the sensing characteristics to match desired environments.

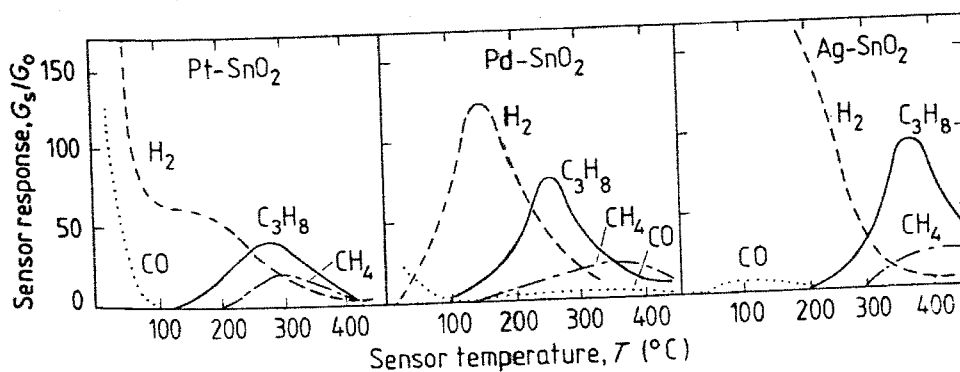


Figure 2.8.2.2.2 Dopant effects on metal oxide sensor response characteristics (Gardner and Bartlett, 1999)

Table 2.8.2.2.1 summarises the advantages and disadvantages of using MOS. MOS are more suited than CP sensors for the measurement of gas phase samples at elevated temperatures as they operate in the region of 300 – 500°C, which enables a fast reaction at the oxide surface whilst preventing a layer of water forming on the sensor surface (Gardner and Bartlett 1999). Stuetz (2001) states that a low response to RH is a positive attribute of these sensors whilst Di Natale (1999) suggests that a high sensitivity to RH, along with EtOH and CO₂, are negative effects. Depending on the substance being monitored and manner in which the sampling is being applied a low sensitivity to RH, as mentioned by Stuetz (2001) may not necessarily be considered either a positive or negative feature for metal oxide sensors. Delpha *et al.* (2001a) investigated SnO₂ gas sensor responses with two greenhouse gasses, forane 134a and CO₂ where high values of RH were seen to mask forane 134a at concentrations between 200-400 ppm but had little impact with respect to CO₂.

Table 2.8.2.2.1 Advantages and disadvantages of metal oxide sensors.

Metal Oxide Sensors	
Operational overview – The chemically sensitive coating which forms the semiconducting film interacts with the gaseous sample at elevated temperatures (~300-500°C). Resulting changes in conductance caused by redox reactions at the sensor surface can be monitored. These sensors are operated under the Wheatstone bridge principle.	
Advantages	Disadvantages
<ul style="list-style-type: none"> • High sensitivity (down into ppb levels)¹⁺² • Low response to RH¹ • Respond to a wide range of gaseous compounds¹⁺³ • Capable of measuring samples at elevated temperatures¹ • High availability due to commercial production²⁺³ • Variety of types with range of sensitivities. Selectivity and sensitivity can be achieved by doping the MOS with different metal ions (ideal for constructing an array)³ • Relatively fast response (<10 seconds)³ • Used in arrays for odour measurement more than any other sensor type² • Responsive to a large number of combustible gases²⁺⁴ 	<ul style="list-style-type: none"> • Less sensitive than other sensor types^{1,2+3} • Subject to poisoning¹ • Response can be affected by the presence of some solvents¹ • High power consumption due to operation at high temperatures² • Can be discrimination difficulties due to similar combustion mechanisms of chemical structures on the sensor² • High sensitivity to compounds such as EtOH, CO₂ or humidity³

1) Stuetz 2001

2) Gardner and Bartlett 1999

3) Di Natale 1999

4) Simon *et al.*, 2001

Stuetz (2001) and Di Natale (1999) also indicate that MOS sensors are in general less sensitive than other sensor types whilst Gardner and Bartlett (1999) mention that sensitivity for MOS sensors is an order of magnitude higher than CP sensors. This difference may be attributed to observational differences of the chosen sensor type, structure and operating conditions employed by each researcher.

2.8.2.3. Acoustic wave sensors

Acoustic wave gas sensors are piezoelectric devices, examples of which include bulk acoustic wave (BAWs) (also known as quartz crystal microbalances) and surface acoustic wave (SAWs). Both sensors work by detecting the effects of sorbed molecules on the

propagation of acoustic waves (Gardner and Bartlett 1999). BAWs (Figure 2.8.2.3.1) record the change in oscillation frequency as gaseous molecules are adsorbed onto the quartz crystal, as the mass absorbed upon the crystal increases the oscillation frequency of the crystal decreases; The corresponding change varies depending on sensor coatings and the sample gas consistency (Gardner and Bartlett 1999). SAWs are very similar to BAWs only they operate at a higher oscillation frequency (Stuetz 2001). Table 2.8.2.3.1 summarises the advantages and disadvantages of using acoustic wave sensors. These sensors are highly selective and are able to measure both polar and non-polar samples and with manipulation of the sensor surface are able to differentiate between isomers and enantiomers (Gardner and Bartlett, 1999). This could prove to be of great significance applied to organic synthesis analysis where chiral compounds are produced. The positive features make the application of acoustic wave devices attractive, however the major drawback is that the coating process is not reproducible. These sensors are temperature sensitive which can mask the effects of the gaseous samples (Cheeke and Wang, 1999) this may (without further development) make their commercial application unviable but by enhancing coating sensitivity the sensors should be suitable for environmental control (Arn *et al.*, 1991).

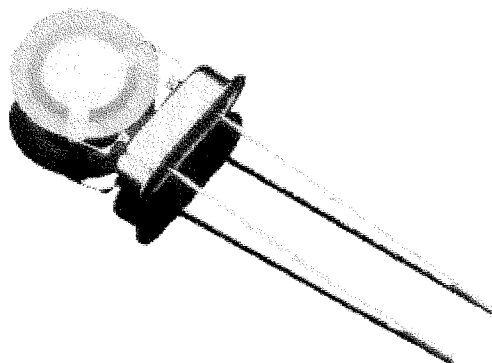


Figure 2.8.2.3.1 Photograph of a BAW sensor
(Courtesy of Marconi Applied Technologies)

Table 2.8.2.3.1 Advantages and disadvantages of acoustic wave gas sensors

Acoustic Wave Gas Sensors	
Operational overview – The oscillation frequency is reduced as gaseous samples are absorbed upon the sensor surface, the corresponding frequency change is recorded.	
Positives	Negatives
<ul style="list-style-type: none"> • High selectivity¹⁺³ (can distinguish between isomers and enantiomers although selectivity is dependant on crystal surface coating³) • High sensitivity^{1,3+5} • Versatile and able to measure both polar and non-polar species¹⁺³ • Stable over a wide temperature range¹ • Full recoveries to baseline¹ • Low power requirements (few mW)¹ • Low sensitivity to RH¹ • High stability¹ • Good reproducibility¹ • Well characterised coating chemistry¹⁺³ • Different sorbent coatings provide devices responsive to different gasses and vapours⁴ • Rapid response times⁵ • Respond to virtually all gases⁶ • Small⁶ • Inexpensive⁶ 	<ul style="list-style-type: none"> • Sensitivity dependant on temperature, humidity and flow of carrier gas³⁺⁴ • The coating processes for QCMs are not totally reproducible therefore no commercially viable³ • The SAW sensor is generally five to ten times more sensitive than the BAW⁴ • Polymer coated SAW devices are temperature sensitive⁴ (As the temperature increases the polymer expands reducing its viscoelastic modulus, this effect can mask any frequency changes caused by adsorbtion) • Selectivity of the BAW is dependant on the coating of the crystal⁴

1) www.marconitech.com

2) Stuetz 2001

3) Di Natale 1999

4) Gardner and Bartlett 1999

5) Arn *et al.*, 1991

6) Cheeke and Wang, 1999

2.8.2.4. Overviews of less common gas sensors

The field effect transistor (FET) works on the principle that the metal gate, in the metal-insulator-semiconductor structure, acts as a catalyst for gas sensing (Lundström *et al.*, 1992. Lundström *et al.* (1975) reported that these sensors contain gates made from catalytic materials, which show a great sensitivity to hydrogen and hydrogen containing compounds. More recently Covington *et al.* (2001) has reported the fabrication of a polymer gate FET. The polymer proved to be an attractive alternative to the catalytic

metals due to its ease of deposition, variety in polymer combinations and ability to operate at room temperature, as opposed to the standard operating temperature of 150 to 200°C (Gardner and Bartlett 1999). The effects of gas concentration, humidity and temperature have been documented for the FET (Covington *et al.*, 2001), all three polymer gate FETs tested exhibited a linear response when exposed to a fixed RH and temperature. The effects of RH will vary depending on the hydrophobic/hydrophilic tendencies of the polymer gate. The effects of temperature have been shown to follow an exponential function. These sensors have a high sensitivity, are small in size and have low cost requirements. However, the reproducibility and sensibility of the sensor are currently not sufficient to enable use in a real measuring system, particularly if it is intended to be used as a means for monitoring a multi-component gas mixture (Di Natale 1999).

Operational overviews of other sensor technologies are summarised:

- Ion sensitive sensors (for example a pH electrode) utilise potentiometry to produce a potential that is proportional to the concentration of an analyte.
- Pellistors are catalytic gas sensors used for the detection of combustible gasses. They have been available for many years, are non-specific and can detect to ~500 ppm. However, can be poisoned by silicon, phosphorous and lead (Gardner and Bartlett 1999).
- Fibre optic sensors operate by recording changes in the optical properties of the fibre including optical path length (including swelling or refractive index), luminescence, absorption, fluorescence and reflectance, from up to several kilometers away using video technology. The fibres are not subject to electrical interference. Reproducibility and stability issues still exist although levels of detection are thought to be in the region of 1000+ ppm (Gardner and Bartlett 1999).
- The sensing electrode in the electrochemical sensor is coated with a layer of a catalytic precious metal. Electrochemical redox reactions of the analyte gas at the catalytic electrode are observed. The concentration of the gaseous sample can be deduced by measuring the current flowing between the catalytic, reference and counter electrodes in the sensor. These sensors are reliable and reasonable selective

and can be used to detect a range of toxic gasses (Gardner and Bartlett 1999). They have also been incorporated into the array of an electronic nose (Stretter 1992).

- Biosensors measure the formation products from enzyme based reactions by biological and physical means (Nistor and Emnués, 1999; Karube and Nomura, 2000). These electrochemical sensors operate under the ‘lock and key’ hypothesis and can be sensitive to many types of physical parameter. Biosensors have been suggested to have promising use for the future monitoring and screening of environmental pollution (Nistor and Emnués, 1999).

2.8.3. Instrumentation

The choice of sensors will depend upon the required functionality of the sensor array. A wide range of sensor types and sensitivities may be required if the sensor array is to have a non-specific application, however the function of the array can be more specific if known target contaminants are expected. The choice of sensors will depend upon the desired functionality of the array and the preferred selection of the sensor array manufacturer. Sensor array manufactures and available models have been listed in Table 2.8.3.1.1. In each case the sensor array system should consist of, in its simplest form, a sampling system, a sensor array module and data analysis capability (Figure 2.8.3.1).

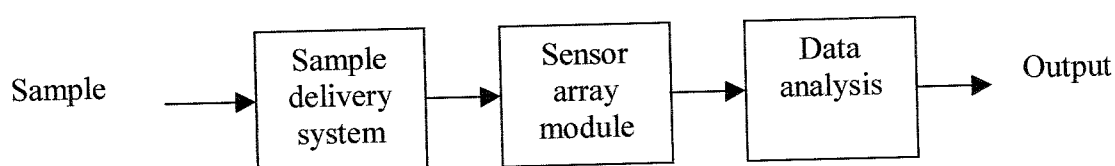


Figure 2.8.3.1 Principal components of a sensor array system (Stuetz 2001)

The marrying of these three stages into one instrumental set-up provides an alternative monitoring suite that can be used to complement existing analytical instrumentation and techniques. Sensor arrays can provide a simple non-invasive technique for monitoring changes in product and process quality.

Commercial sensor array systems are evolving that suit particular environments. Figures 2.8.3.2 – 2.8.3.5 show photographs of instruments produced by Bloodhound Sensors Ltd, UK, Marconi Applied Technologies, UK and Cyrano Sciences, USA. The Bloodhound BH114 (Figure 2.8.3.2) and eNOSE 5000 (Figure 2.8.3.3) require a personal computer (PC) to control the sensor array, sampling systems and to enable data processing. This limits the functionality of the instruments and limits their application to a laboratory-based environment (Gardner and Bartlett, 1999). The ProSAT (Figure 2.8.3.4) has an on board PC with data storage facilities whilst the Cyranose 320 portable sensor array (Figure 2.8.3.5) offers the flexibility to enable observations to be made at or near the medium being monitored.

Table 2.8.3.1 Sensor array manufactures and available models (Gibson *et al.* 2000).

Company and location	Models
Alpha MOS, France (www.alpha-mos.com)	Fox 2000, 3000, 4000, 5000, AlphaKronos, AlphaPrometheus, AlphaCent
Bloodhound Sensors, UK (www.bloodhound.co.uk/bloodhound)	Bloodhound BH114
Cyrano Sciences, USA (www.cyranosciences.com)	Cyranose 320
Etherdata, Iceland (www.etherdata.is)	FreshSense
HKR Sensorsysteme, Germany (www.home.t-online.de)	QMB6/HS40XL
Hewlett Packard, USA (www.hp.com)	HP4440A
Lennartz Electronic, Germany (www.lennartz-electronic.de)	MOSES II
Marconi Applied Technologies, UK (www.marconitech.com)	ENOSE 5000, ProSAT
MoTech Sensoric, Germany (www.motech.de)	VOCmeter, VOCcheck
Nordic Sensor Technologies, Sweden (www.nordicsensor.se)	NST 3210, NST 3220, NST 3220A
Osmetech, UK (www.osmetech.co.uk)	MultiSampler-SP
RST Rostock, Germany (www.rst-rostock.de)	Sam
Smart Nose, Switzerland (www.smartnose.com)	Smart NOSE-300
WMA Aircsense, Germany (www.aircsense.com)	PEN

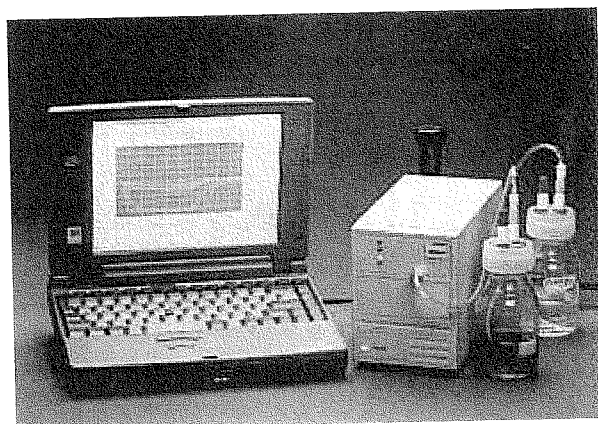


Figure 2.8.3.2 Photograph of BH114 sensor array system
(Courtesy of Bloodhound Sensors Ltd, UK).

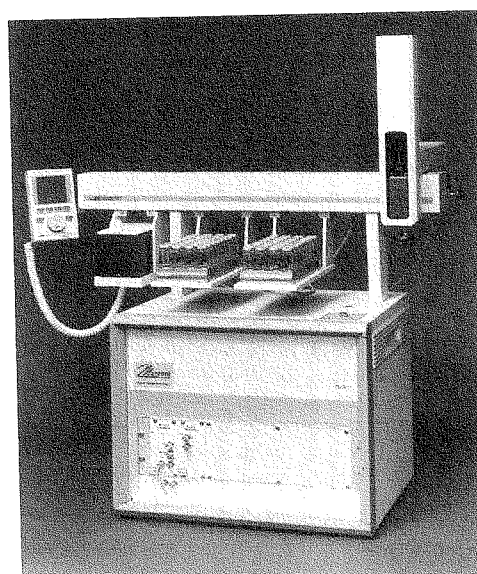


Figure 2.8.3.3 Photograph of eNOSE 5000 instrument with autosampler
(Courtesy of Marconi Applied Technologies, UK).

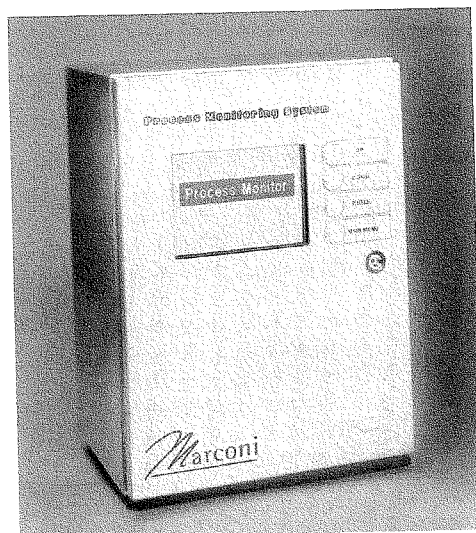


Figure 2.8.3.4 Photograph of ProSAT on-line process monitoring system
(Courtesy of Marconi Applied Technologies, UK).



Figure 2.8.3.5 Photograph of Cyranose 320 portable sensor array monitor
(Courtesy of Cyrano Sciences, USA).

2.8.3.1. Applications

The industrial and research market surrounding sensor array is constantly changing. The application of electronic nose devices is wide ranging as arrays of sensors have had several applications, all with different degrees of success. Table 2.8.3.1.1 lists some of the wider applications whilst Table 2.8.3.1.2 provides a more detailed look at environmental and consumer related applications. A comparative report documented by Doleman and Lewis (2001) between mammalian olfaction (human and monkey) and an

electronic nose, consisting of a conducting polymer composite array, concentrated on evaluating odour detection thresholds and discriminabilities for structurally similar pairs of odourants. Similar trends in odour detection thresholds were noted between the electronic nose and humans. Humans, monkeys and the electronic nose were all able to discriminate the samples as they became increasingly structurally dissimilar. Overall the electronic nose was significantly better, than both humans and monkeys, at discriminating the odourant pairs. This is not entirely surprising as many gaseous samples may not be discernable with the human nose yet can be chemically sensed by the array, e.g. CO.

Table 2.8.3.1.1 Applications of sensor array systems

Application	Reference
Measuring odour concentration following application of cattle slurry to grassland	Misslebrook <i>et al.</i> , 1997
Assessment of odours from livestock wastes	Hobbs <i>et al.</i> , 1995
Analysis of sugar aroma profiles	Kaipainen <i>et al.</i> , 1997
Monitoring the flavor of beer	Pearce <i>et al.</i> , 1993
Discrimination of pear odours	Oshita <i>et al.</i> , 2000
Quality control of olive oil aroma	Guadarrama <i>et al.</i> , 2001
Freshness evaluation of cod-fish fillets	Di Natale <i>et al.</i> , 2001
Analysis of medication off-odours	Schiffman <i>et al.</i> , 1997
Odour separation between groups of coffee, textile materials, whisky, tobacco and olive oils.	Ulmer <i>et al.</i> , 1997

Table 2.8.3.1.2 Environmental/consumer related applications of sensor arrays

Application	Array configuration	Observations and detection levels	Analysis technique	Reference
Monitoring changes in water and wastewater quality (on-line)	12 conducting polymer sensors (eNose 5000, Marconi Applied Technologies)	2-chlorophenol at 5 ppm in a mixed water	Principal component analysis	Bourgeois <i>et al.</i> , 2002
Monitoring fruit ripeness	12 commercially available MOS sensors (Source unknown)	Successfully tracked peach and pear ripeness (although patchy results for apples)	Principal component analysis and non-linear neural networks	Brezmes <i>et al.</i> , 2000
Monitoring an ethanol batch cultivation	2 sets of 5 metal oxide semiconducting field effect transistors sensors (MOSFET), 4 semiconducting tin oxide chemoresistors and an optical carbon dioxide detector	Selective sensor response and PCA data selection enabled ANN training to predict ethanol concentration in the cultivation	Principal component analysis and artificial neural networks	Lidén <i>et al.</i> , 1998
Discrimination of coffees	12 commercially available tin oxide sensors with partial overlapping sensitivities	Successfully classified three different coffee blends and classified a coffee at six different stages of a roasting process.	Multivariate analysis and discriminant function analysis	Gardner <i>et al.</i> , 1992
Detection of tainting compounds in raw and treated potable water	12 polypyrrole conducting polymer sensors (eNose 4000 Neotronics Scientific Ltd)	Geosmin – 10 pg/l 2-methylisoborneol – 1 pg/l 2-chlorophenol – 1 ug/l phenol – 1 mg/l diesel – 1 ug/l 2-chloro-6-methylphenol – 10 pg/l	Multiple discriminant analysis	Stuetz <i>et al.</i> , 1998
Measuring wastewater quality	12 conducting polymer sensors (eNose 5000, Marconi Applied Technologies)	Data analysis shows clear separation of RO water, final effluent and raw sewage	Principal component analysis and multiple discriminant analysis	Bourgeois and Stuetz 2000
Odour discrimination	A twelve element tin oxide array	The system separated 4 tobacco brands, 5 alcohol types and classified a set of three beers.	Principle component analysis	Shurmer and Gardner 1992
Discrimination of wine aroma	12 conducting polymer sensors	Clear separation of 3 white and 2 red wines respectively	Principle component analysis	Guadarrama <i>et al.</i> , 2001

Two different electronic noses, with differing arrays were compared and integrated to evaluate the freshness of cod-fish fillets (Di Natale *et al.*, 2001a). The two noses compared were LibraNose and FreshSense. The LibraNose contained 8 thickness shear mode resonators coated with varying metalloporphyrins. The FreshSense module contained 5 electrochemical sensors, each one having a preferred gas sensing orientation, being CO, H₂S, NO, SO₂ and NH₃. Both sensors exhibited sensitivities to changes in the headspace profiles of the fish samples. However the LibraNose was better suited to tracking the fish freshness in the early stages of spoilage while the FreshSense was more suited at the end of sampling. When the two arrays were virtually combined classification performance was significantly increased. Di Natale (2001b) also published findings on a similar subject comparing an array of quartz resonators to metal oxide chemoresistors for the quality evaluation of olive oil. Both arrays provided similar images but were differently interpreted by the two arrays. Again the combination of the two arrays enabled clearer separation between samples. This bolsters the requirement, costs permitting, for sensor arrays that contain a multitude of sensors with varying capabilities and sensitivities in order to operate an effective screening device.

Headspace samples of the volatile compounds arising from different types of sugar crystals were analysed by both GC-MS and an electronic nose Kaipainen *et al.* (1997). The GC-MS chromatographs were different for each sugar type and the headspace aroma profiles of sugar beet crystals were compared and found to include varying organic compounds. These were quantified to enable the comparison of concentration levels in each sample. The sensor array, containing 12 metal oxide sensors, was able to discriminate between acceptable and unacceptable sugar by its odour. Kaipainen's process was set so that each sugar crystal took 50 + minutes to analyse, suggesting that the electronic nose could not be used as fast on-line instrument. Although the sensor array was able to detect differing sugars it was unable to quantify component concentrations.