

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/288546683>

Gas sensors 2. The markets and challenges

Article in *Nanotechnology Perceptions* · March 2009

DOI: 10.4024/N36HO08A.ntp.05.01

CITATIONS

3

READS

882

8 authors, including:



Jane Hodgkinson
Cranfield University

50 PUBLICATIONS 927 CITATIONS

[SEE PROFILE](#)



John Saffell
Alphasense Ltd.

33 PUBLICATIONS 626 CITATIONS

[SEE PROFILE](#)



Jeremy Ramsden
Collegium Basilea (Institute of Advanced Study), Basel, Switzerland

380 PUBLICATIONS 7,723 CITATIONS

[SEE PROFILE](#)

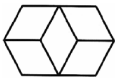
Some of the authors of this publication are also working on these related projects:



Improvement of biological mechanisms [View project](#)



Bioinformatics [View project](#)



Gas sensors 2. The markets and challenges

Jane Hodgkinson,^{1,*} John Saffell,² Jonathan Luff,^{3,4} John Shaw,⁵
Jeremy Ramsden,⁶ Carlos Huggins,⁷ Robert Bogue⁸ and Roger Carline⁹

¹ *Engineering Photonics Group, School of Engineering,
Cranfield University, Bedfordshire, MK43 0AL, UK*

² *Alphasense Ltd, Sensor Technology House, 300 Avenue West, Skyline 120,
Great Notley, Essex, CM77 7AA, UK*

³ *Sira Ltd, South Hill, Chislehurst, Kent, BR7 5EH, UK*

⁴ *National Physical Laboratory, Hampton Road, Teddington, Middlesex, TW11 0LW, UK*

⁵ *Tyco Safety Products, Security House, The Summit, Hanworth Road,
Sunbury-on-Thames, TW16 5DB, UK*

⁶ *Department of Materials, Cranfield University, Bedfordshire, MK43 0AL, UK*

⁷ *e2v Technologies Ltd, 106 Waterhouse Lane, Chelmsford, Essex, CMI 2QU, UK*

⁸ *Robert Bogue & Partners, Crockham Hill, Kent, UK*

⁹ *MNT Network, 2.43 Victoria Building, Brownlow Hill, Liverpool, L69 3BX, UK*

This paper looks at the market for gas and vapour sensors and its drivers, including legislative (regulatory) ones. The nature of the market is reviewed, considering market pull and technology push. The various market sectors, including medical and food, security, indoor and outdoor air quality (both domestic and industrial) and industrial process control are analysed in detail. Societal needs are assessed, and scientific and technological challenges for the future are discussed. The paper ends with a summary of priorities.

Introduction

Part 1 of this paper¹ dealt with technologies and applications. This companion paper deals with the markets and future challenges in the field, and draws widely on the conclusions of the UK's Micro and Nano Technology (MNT) roadmap for gas sensors.² As with any high technology,

* Author for correspondence. E-mail: j.hodgkinson@cranfield.ac.uk

¹ This issue, pp. 71–82.

² J. Hodgkinson, J. Saffell, J. Luff, J. Shaw, J. Ramsden, C. Huggins, R. Bogue and R. Carline, *MNT Gas Sensor Roadmap*. UK MNT Network, published at www.gas-sensor-roadmap.com (2006).

there is a seemingly eternal debate about whether developments are driven by “technology push” (meaning that engineers and scientists are inventing new devices, which the rest of the society then finds a use for), or “market pull” (meaning that society develops a desire for something, which engineers and scientists then invent, “to specification” as it were). A rather well known analysis of the introduction of the stirrup and its consequences in mediaeval times is instructive in this regard:³ in reality, it is probably artificial and inaccurate to try to separate these two influences. As R.V. Jones points out in his account of the development of aerial radar systems in World War II,⁴ sometimes the pilots did come to the scientists and ask whether they could develop something with particular characteristics, and at other times the scientists themselves developed devices that they thought would effectively combat a perceived threat, but sometimes along the way developed other devices with sophisticated technical properties but without any apparent use, whereupon they would ask the pilots whether they might have some use for such a thing—and sometimes indeed it turned out that they did. In other words, users and inventors are better connected than we suppose, and anyway reality can be messy, disorganised and difficult to yield to analysis! Furthermore, there are other drivers not encompassed in the above. Legislative demands are often significant, such as for domestic flammable gas detection in Asia, for indoor air quality in Canada and some northern European countries, and for automotive emissions in many countries nowadays. Legislation is, of course, strongly embedded in the life and culture of a country and is frequently influenced by events as well as irreducible factors such as human toxicity. It must also be recognized that only very rarely are upper allowable limits for exposure to a substance fixed without regard to the current detection technology; in many cases these limits are lowered *pari passu* with technical advances.

The structure of this paper is as follows: after a fairly brief consideration of the market, including further discussion on its pull and technology’s push, and the effects of legislation, there is an extensive analysis of the market broken down into sectors, followed by a discussion of technical challenges and priorities for new developments, focusing on those involving nanotechnology. The paper closes with a consideration of societal needs and how can they can to some extent be met by publicly funded research. The final section contains a succinct summary and some conclusions.

The size of the market

Whatever the exact nature of drivers for innovation, it should be possible to estimate the actual annual global sales of gas sensors. As it happens, estimates vary considerably.⁵ The market can be divided into: the actual *sensors* themselves, that is, the technology heart of the device; *components*, which include the sensors but also auxiliary subsystems such as power supplies and user interfaces; and the *complete detection instruments*. Naturally, the largest figures (in

³ L. White, *Medieval Technology and Social Change*. New York: Oxford University Press (1966).

⁴ R.V. Jones, *Most Secret War*. London: Hamish Hamilton (1978).

⁵ A number of sources have been consulted to obtain these figures. Published ones include P. McGeehin et al., *A Strategic Framework for 2015*. Report of the UK Foresight Sensors Task Force (2002); and *World Industrial Gas Sensors, Detectors and Analysers Markets*. Frost and Sullivan (2006). Manufacturers have also been consulted.

monetary value) refer to the complete instruments—estimates range from 1500 to 5000 million USD. The upper estimate of the components market itself is 2800 million USD, implying that considerable value is added to the components by the instrument makers. The actual sensor modules comprise a relatively small proportion of the components market, estimates ranging from 250 to 500 million USD. This figure does not include the so-called Lambda sensors for monitoring oxygen in motor-car exhausts.⁶ All new European cars are fitted with at least two Lambda sensors; the global market is estimated at 2400 million USD and growing at about 10% per annum. Putting these figures in context, it is worth noting that gas sensors only comprise a few percent of the total sensors market,⁷ which is dominated by motion sensors.

Market pull

Although presently a relatively small segment, gas sensors have excellent growth prospects. The importance of automotive sensors, especially those required for engine management, is already apparent from the remarks in the previous paragraph. In the fairly short term it is expected that growth of this market will be strongly driven by China and India (despite the global financial crisis). In the long term, of course the likely exhaustion of mineral oil deposits casts doubt on the future of the internal combustion engine, unless, for example, a viable hydrogen economy emerges, in which case hydrogen leak detectors may be needed. On the other hand, demand for vehicle cabin air quality monitoring is also growing strongly worldwide, and is largely independent of the type of motive power of the vehicle because of the need to monitor exhaled gases such as CO₂. Domestic carbon monoxide detection is another rapidly growing market (in Europe). Industrial safety, already well developed in Europe and North America, is now growing strongly in Asia, especially China. There is huge current expenditure on developing gas sensors for homeland security in the USA, but this may suffer fatigue in the course of time, or will likely be event-driven. Trends for urban air quality sensors are harder to predict, partly because there is often little tangible economic benefit arising from their installation, and also because the need for them may diminish if gas sensors for automotive engine management and industrial process control succeed in significantly diminishing noxious emissions. Nevertheless, at the level of the individual consumer interested in his or her well being, and carrying the belief that monitoring the immediate environment will contribute to that, return on investment is very hard to quantify. Personal gas sensors incorporated in wristwatches or in mobile phones may deliver some benefits to individual asthmatics or other with impaired lung function, but only if they are able to act on the readings.

Note that world sensor manufacturing is led, in volume, by the USA, followed by Japan, Germany and the UK—which happens to be the order of GDP.⁸ However, the 2002

⁶ The output of these sensors is used by automotive engine management systems to control the fuel-air mix in the intake. They were invented in 1976 by Robert Bosch GmbH, which is still today the market leader.

⁷ N. Yamazoe, Towards innovations of gas sensor technology. *Sensors Actuators B* 108 (2005) 2–14.

⁸ At the time of the study—it would be interesting to see how far this correlation continues; the GDP ranking continues with France, China, Italy and Spain. Since then, China's GDP has moved ahead of Germany's.

Sensor Foresight study⁹ has noted that the UK is particularly strong in gas sensing, within this larger market.

Technology push

Figure 1 illustrates graphically the trends (arrows) in different market volumes versus maturities of the technologies feeding the markets. This shows a clearly that the balance between market pull and technology push depends on both how much more the market can be expected to grow and the maturity of the technology. In this article we do not attempt to estimate the *ultimate* market size; even markets that are already large, such as gas sensor-based fire detection, may still grow substantially. On the other hand, the more mature the technology, the less technology push there can be, unless a new, disruptive technology is introduced.

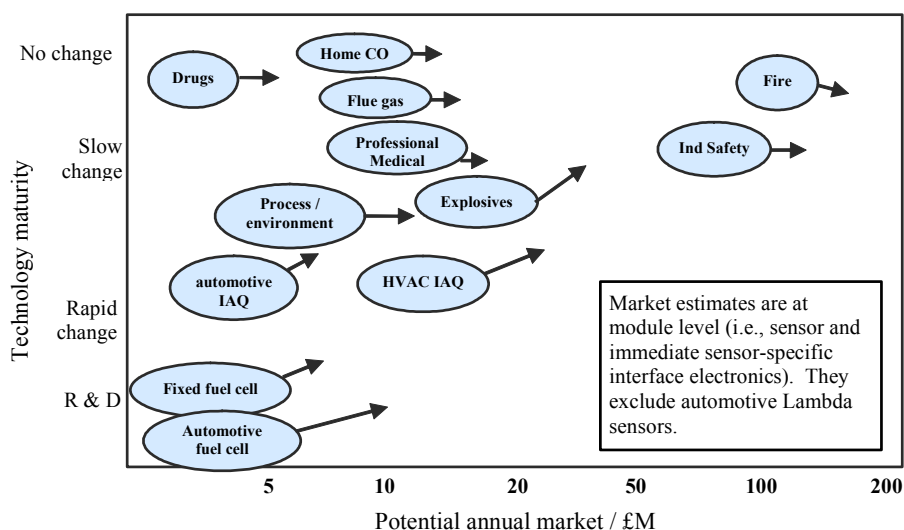


Figure 1. Diagram of the degree of maturity of different gas detection technologies versus market size, as collated by Huggins.² Arrows show anticipated future developments.

A more explicit attempt to formulate degrees of maturity has been made by Mankins.¹⁰ His original scheme comprised nine levels, the last being ultimate proof of maturity through successful space mission operations; for the humbler terrestrial environment eight levels probably suffice. Furthermore, Mankins placed proof of concept after the formulation of an application, whereas the actual experience of scientists and engineers suggests that proof of concept should directly follow basic principles. Our revised scheme of technology readiness therefore comprises the following levels: (1) Basic principles observed and reported; (2) proof of concept; (3) technology application formulated; (4) component validation in the laboratory

⁹ P. McGeehin et al., *A Strategic Framework for 2015*. Report of the UK Foresight Sensors Task Force (2002). Available at <http://www.foresight.gov.uk>.

¹⁰ J.C. Mankins, *Technology Readiness Levels*. NASA Advanced Concepts Office, 6 April 1995.

environment; (5) component validation in the real environment; (6) prototype system demonstration in the real environment; (7) commercial introduction; (8) commercial success.

Levels 1 and 2 are quite likely to take place in the laboratory of an individual researcher and are part of the general scientific activity taking place in a country. The researcher may proceed independently to level 3, but levels beyond 4 would take place in an industrial environment (level 4 itself might well be undertaken as a collaborative effort between industry and the researcher). Costs start rising rapidly at level 4 and beyond, which therefore will only proceed if there are strong grounds for anticipating an adequate return on investment.

The role of new technologies, not as yet included in Figure 1, and how some of the necessary research and development might be financed are dealt with in sections near the end of this article.

Legislation as driver

Legally binding regulatory requirements comprise a third factor. Although legislation is ostensibly neither market pull nor technology push, it is related to both. A booming market will generally attract more attention than a small one, and many maximum allowed exposure limits have moved with improvements in detection capability.

In industry, recent European Union (EU) Integrated Pollution Prevention and Control (IPPC) legislation now requires companies to show a continuous improvement in their emissions, not just stay within the defined limits. Acceptable levels of pollution are determined by industry best practice, thereby setting a flexible standard that is intended to move emission levels continuously downward, following the industry leaders. The drive is for self-validation, forcing companies to demonstrate the validity of their data, which may require periodic independent audits. In the UK, one step towards this European model has been taken by the MCERTS programme—the Environment Agency’s Monitoring Certification Scheme.

Automotive emissions are measured by government enforcement agencies through controlled sampling of the exhaust (e.g., in the UK this measurement forms part of the annual “MOT” test for roadworthiness that all cars are required to undergo; in Switzerland cars have a separate annual emissions test), but this cannot be expected to accurately reflect emissions under normal driving conditions. Therefore there is also increasing interest in monitoring emissions at the side of the road, in which case target species must be measured relative to the main gaseous exhaust product, CO₂; automotive emissions could be measured using remote optical detection as cars drive past. This is an example of legislation driving the uptake of technology. If a certain mode of sensing becomes an obligatory legal requirement, then a large market is presumably assured, which should make the necessary investment in research and development easy to procure. By the same token, the tendency for common legislation to be adopted in many countries simultaneously (e.g., in all the countries of the EU) enlarges the guaranteed market and should make the investment even more attractive.

Different countries have different management cultures; for example, US companies adopt prescriptive standards (e.g., some US utilities are required to survey their gas lines regularly for leaks, regardless of the location of the pipe and the consequences of a possible incident), whereas UK procedures are often based on risk analyses, offering more scope for flexibility in achieving a goal. In the past, larger companies have developed safety systems and robust internal standards that are more stringent than international standards, subsequently their

internal standards may be adopted as *de facto* good practice throughout the industry. However, these companies have now reduced their effort, preferring to test new developments when they are offered rather than taking a proactive approach, placing a greater degree of risk with the developer, which unfortunately looks as though it might stifle innovative product development in smaller companies.

The nature of the market

This section considers the market for gas and vapour sensors in more detail. We shall consider the following sectors in turn: (1) medical and food; (2) security (explosives and drugs); (3) air quality and fire, subdivided into (a) general outdoor, (b) commercial and domestic fire CO, (c) domestic, (d) industrial, and (e) vehicle cabin; (4) automotive (engine control); and (5) industrial process control.

At first sight it appears that applications can be divided into different basic categories:

- “safety”- Monitoring gases known to be dangerous or indicative of danger, in order to safeguard life or property. Categories 1–3 listed above would be of this type.
- “control”- Monitoring gases in order to optimize an industrial process to reduce costs or environmental emissions (categories 4 and 5 above).
- “legal”- In many categories there are examples of regulated processes, for which the driver is to maintain legal compliance.

In categories 4 and 5, the output of the sensor will be more or less directly fed into the process controller; the feedback loop could be as simple as that of an automatic choke in a motor-car, or it could involve extensive numerical processing in a chemical engineering plant. But equally in the first three categories, the sensor output is intended to evoke action: the physician may prescribe treatment, baggage may be searched, and residents be advised to stay indoors or to evacuate their property.

There is considerable overlap between the different categories, as the following examples show. Nuisance odours from a landfill site may lead to clinical depression among nearby residents, therefore turning the problem into a medical one. Domestic indoor air quality is an important factor determining the likelihood of an asthmatic attack, which can also be considered as a medical problem. Emission controls can lead to economic, long-term health, and environmental benefits.

1. Medical and food

Clinical diagnostics. Capnography¹¹ may be said to be the ultimate noninvasive technique, and is especially useful in anaesthetics. The gas concentrations in a single exhaled breath are considered to give a direct indication of the partial pressure of those gases in the blood. Other applications in breath diagnostics include detection of *H. pylori* in the gut, a major risk factor for gastric ulcers. Although gas detection cannot give information about the nature of the bacterial colonies (for which endoscopy would be needed), it can be used for screening to give an indication that further (more expensive) tests are necessary. A long term goal is to provide

¹¹ The measurement of exhaled breath as a function of time.

general practitioners with noninvasive analysers that detect volatile disease markers. For certain prevalent conditions with a well defined aetiology, such as asthma, the goal is to provide the sufferer with a personal device (possibly incorporated into a mobile phone) that can be used to monitor his or her condition. At present, this field excites much interest but is held back by a lack of good quality clinical data on gaseous biomarkers in both sick and healthy populations.

Food. The food processing industry is characterized by the need for rapid development of “new” products in order to maintain sales to jaded consumers, hence tends to be product-led rather than process-led and there is a tendency to maintain existing practices rather than risk the introduction of new technologies that may not be readily applicable to genuinely new product lines. However, there are some generic needs in the industry that may be addressed through the application of new technologies; they would find ready acceptance if the sensors were reliable and inexpensive. Those relevant to gas sensors include:

- Freshness and other aspects of quality monitoring. Useful indicators for quality, e.g. in connexion with fish spoilage (volatile amines), fruit ripening (ethylene) and wine production (alcohols) are often gases or vapours. Gas sensors therefore provide technology for rapid quality assessment. However, successful application requires some knowledge of the complex mixture of the components likely to be present in the gas phase, and the acquisition of this knowledge still requires both academic and industrial research. The “electronic nose” approach has not been successful hitherto, due to the complexity of food aromas, typically engendering misleading sensor responses, as well as the expense and difficulty of calibrating these instruments. Some of the issues are currently being addressed through the application of microsystems and nanotechnology (MNT).
- Detection of micro-organisms if their metabolic activity results in the generation of a distinctive gas or mixture of gases; otherwise the DNA-based approach of modern bacteriology is likely to be used.
- Foreign body/contaminant detection, although mostly gases are not involved; sensors must be noninvasive to reduce risk of further contamination; we note that plastics and insects in particular are not readily detected using current techniques; and that tracing the origin of contaminants (e.g., lubricants) to a point in the production process is important.

Detection of allergens, which may be introduced by equipment used for multiple products; rapid allergen test kits are of interest to both retailer and consumer. Twelve allergens are considered as being of significant risk to consumers at present, but none are gases.

2. Security

In recent times, the level of attention paid to homeland security has risen rapidly, generating a rapid increase in R&D expenditure in industry and academia, and helping to establish the case for start-up companies. Translating this activity into real markets and sales remains however more uncertain, not least because homeland security is the most technically challenging of all gas detection markets; maybe specific niche markets will emerge.¹²

¹² Although it goes beyond the scope of this article, it is worth noting that the terrorism problem may be reduced by tackling the underlying causes and mechanisms (see, e.g., S. Galam, *The sociophysics of*

Explosives. The presently available detection technologies are few, given the difficult combination of generally fast-moving entities (humans and baggage), variable environments (e.g., airports, open fields), the low concentrations of the materials present in the ambient air or adsorbed on surfaces, and a highly complex and variable background matrix of other gases and vapours. To this end the analysis technologies used tend at present to be derived from high resolution (and expensive) laboratory techniques, for example ion mobility spectroscopy (IMS).

In the USA, the major homeland security spend immediately following the events of 9/11 was focused on explosives detection at airports. Few chemical sensor or bench-sized spectroscopy systems are well established in the field, all of which suffer from significant problems in throughput (IMS and similar technologies are limited by the need for manual sampling), specificity and detection level (chemical sensors) and, generally, environmental ruggedness.

Drugs. Drugs “of abuse” (e.g., heroin) pose major problems to countries whose citizens either produce or consume them (e.g., the encouragement of international crime, deterioration of consumer’s health leading to burdens on state healthcare systems, risk or injury to third parties through motoring accidents involving incapacitated drivers). The existing technology is essentially supported by IMS type systems with challenges as described above, but the user base has limited confidence in technology, perceiving other policing methods to be more reliable (questioning suspects, identifying behaviour patterns and the use of intelligence). There may therefore be more realistic opportunities for gas and vapour sensors to gain market entry for drug detection by assisting traditional policing methods and improving their efficiency, especially at the moment of investigating a suspected criminal or an item of baggage. A notable example is the “breathalyser” detector for alcohol in the breath.

There have been extensive R&D programmes in several countries to develop MNT devices. A nonexhaustive list of candidate technologies includes microcantilevers with functionalized absorption sites interrogated by changes in resonant frequency or Q-factor, Raman spectroscopy, optical waveguide lightmode spectroscopy (OWLS) and functionalized polymer chemical sensors interrogated by electrical resistance. Unfortunately, these candidate technologies may not overcome the mix of challenges discussed above.

Civil defence against chemical, biological or nuclear attack. Threat species have the properties of being both harmful and easily transported or ingested. Harmful gases or aerially dispersed agents of biological warfare such as viruses or bacterial spores come under the scope of this article. Given that normal air contains micro-organisms, captors specific to particular pathogenic viruses etc. will be required. Offering widespread coverage against all threats and in all vulnerable locations is not likely to be cost-effective. It is therefore often assumed that chemical detection is needed following an incident, to enable “first responders” (civil defence officers) to correctly identify, map and contain the threat species. To this end, there are major programmes to develop several MNT-based sensors networked together to give area coverage and fast feedback for the first responders.

It is likely that the core sensor capability for chemical analysis will involve a combination of microelectromechanical systems (MEMS)-based sensors, and the use of microfluidic

terrorism, in: J.J. Ramsden and P.J. Kervalishvili (eds), *Complexity and Security*, pp. 13–37. Amsterdam: IOS Press (2008).

techniques would seem a sensible extension. Recent thinking has extended the range of possible threat species, from those deliberately conceived to be highly toxic (which are difficult to handle) to lower toxicity but more widely available hazardous chemicals as might be found in the chemical process industry, such as a massive benzene spill. This thinking potentially extends the market for sensor technologies traditionally considered for use in industrial health and safety.

It should be noted that the only relatively common gaseous radioactive element is radon, the main source of which is granitic construction materials, but volatile compounds of other radionuclides could be synthesized. Detection of radioactive emissions applicable to matter in any phase is adequate for gases.

With all of these sensors, communication via a network is a key element, and so low-cost integrated radio frequency (RF) communications and lower cost scintillation counters will be the key to a successful system. These communications ideally need to be independent of infrastructures that are not under secure government control.

3. Air quality (including fire)

Much attention is focused on the BTEX (an acronym for benzene, toluene, ethylbenzene, xylene) family of carcinogenic aromatic hydrocarbons. The different compounds can be measured separately using laboratory analytical equipment, but it is difficult to separate them using on-line field methods, and unfortunately the individual carcinogenic impact for each hydrocarbon is very different. Benzene is considered to be the most dangerous, classed as carcinogenic at the 1 ppm level, while other aromatics are not considered to be dangerous until their concentration exceeds hundreds of ppm. The BTEX family is present in common situations such as petrol stations (which might be considered intermediate between outdoor and indoor) and fuel bunkers, where the benzene level frequently exceeds EU legislated limits. Detecting benzene without cross-response to the other BTEX compounds is a difficult challenge with disposable stain tubes as the only technology currently available and considered relatively crude. Three possible technologies can potentially separate benzene from other BTEX hydrocarbons: IMS (or, most likely, the more advanced DMS/ FAIMS), GC/MS, and IR or UV spectroscopy (not trivial: deconvolution of the combined spectra will be a challenge). Research is required to select the preferred technology and in parallel to determine whether the market volume and regulatory pull are adequate for the anticipated investment costs.

3(a). Outdoor air quality

Customers for outdoor and urban air quality and emissions monitoring include government environmental and enforcement agencies as well as industries that are major potential emitters of pollutants, most commonly from a stack (chimney).

Industrial emissions. Dilution from emissions sources is typically rapid, hence measurement of the emission is technically easiest at the source, with cross-stack instruments designed to detect particular substances in a well-known (hence reasonably estimatable) background matrix. Determining the total emission volume is more difficult since this requires knowledge of both the concentration and the flow rate profile in the stack. Monitoring emissions from combustion processes is achieved by measuring the ratio of the target gas to the

CO₂ produced during combustion; the total flow rate for the latter is inferred by metering the process on a “what goes in must come out” basis.

Emission standards for toxic substances are based on their concentrations at a fixed distance from the source, the measuring position being selected by where they could cause harm to factory staff or residents (who may also be factory employees).

There are two approaches:

- (i) To monitor background levels at the point of potential harm: this can be difficult since the target area can be wide and concentrations can be at the sub-ppm level (below 1 part in 10⁶);
- (ii) To make cross-stack measurements and combine them with weather monitors and dispersion modelling software.

Certain substances still present major challenges for monitoring. Volatilized heavy metals require improvements in sampling as they can be present in many phases, notably within airborne particles or as vapour (e.g., mercury, lead). Organic molecules such as dioxins present sampling challenges because they need detection at minute levels (e.g., less than 10⁻⁹) and yet are very “sticky” (i.e., adsorb promiscuously). The Stack Testing Association (STA) leads the UK by training operators in stack monitoring, and by writing standards and establishing best practice.

Bioreactors, including landfill sites. Malodorous emissions from sites such as landfill and waste water treatment works (WWT) can be a great nuisance for residents. As with outdoor industrial emissions, problems arise with point detection of the offending gases and with mapping of the gas plume; computer models of the site may be used to predict gas distributions using local wind and precipitation measurements as well as the output from a network of point sensors.

Site operators are driven by a need to

- (i) defend compensation claims from residents, requiring a zero trace and/or quantified level of odour at a particular time in the past and at a particular location;
- (ii) demonstrate that overall levels of odour around their sites are consistent with their original planning applications and to gain support from nearby residents;
- (iii) understand and manage the sources of odour within the site in order to reduce the problem.

Gas emissions from such sites often comprise an odourless carrier gas in large quantity together with smaller levels of offensively odorous molecules. It can be difficult to predict which odour species will be present and to measure them once the gas has left the site. Therefore, some operators have taken the view that their needs could be met by characterizing the composition of the odour (e.g., by measuring mercaptans) close to its source, measuring the concentration of the higher concentrations of odourless carrier gas (e.g., methane for old landfill matter and wastewater treatment works, H₂ for recently dumped landfill matter) at the site perimeter, and then modelling the gas dispersion with the help of wind monitors. Useful software models require a good understanding of the topology of the site, which can be costly to acquire and may only have been achieved to date for particularly problematical sites. Developing high-throughput site models (possibly based on newly available digital elevation

maps from satellites) could provide an improvement in applications knowledge that could significantly drive the market for gas sensors.

3(b). Fire

Fire detection primarily uses nongaseous indicators (smoke, heat), but gaseous emissions are also recognized as possible though not well characterized targets. Carbon monoxide is a recognized product of many (but not all) nuisance fires and fire detectors incorporating CO sensors are being increasingly deployed. Characterization of other gas or vapour targets for detection of early stage fires and false alarm scenarios is an active area of research. Broadly expected and therefore useful targets may be small organic molecules including:

- (i) methane, ethane, ethylene and acetylene
- (ii) partially oxidized derivatives (including formaldehyde, formic acid, acetaldehyde and acetic acid)
- (iii) possibly some aromatics and inorganic species such as NO_x, SO_x, HCl and Cl₂. In fact, the sensor types required for fire detection will expand as relevant targets continue to be identified.

The main drivers in the fire detection area are to gain competitive advantage by cost saving and/or enabling higher specification products (detectors and systems), especially addressing false alarm problems. There are significant price constraints arising from the competitive market and the “grudge” (i.e., legislation-driven) nature of the purchase. Sensors are constrained by the need for low power (less than 2 mW), reliability for up to 10 years without significant maintenance, and the need to comply with understandably conservative detector standards and validation processes.

The market barriers are:

- (i) identification of targets
- (ii) availability of useful sensors
- (iii) restrictive validation specifications
- (iv) system and building codes (where fire protection uses existing detection technologies)
- (v) conservatism of the industry and of the customer.

Sensing just CO is not accepted for fire detection in standards such as UL standard 268,¹³ so CO detection is generally used in combination with other sensors (optical scattering and heat) with algorithms adjusting gain or alarm thresholds. This limits the uptake of CO sensing for fire detection but probably does not affect technical requirements for the devices (low power, long life, and stable response (~ 0–200 ppm, discrimination better than 5 ppm). These criteria are met by commercially available electrochemical devices, although their finite lifetimes and lifetime guarantees remain problematic. While electrochemical sensor prices have decreased, they are still rather high compared with the optical and heat sensing elements. Lower unit costs and, to a lesser extent, device size reduction are desirable, and this may provide opportunities for nonelectrochemical devices.

¹³ Underwriters Laboratories. *Standard for Smoke Detectors for Fire Alarm Signaling Systems*. Standard 268 Edition 4, Underwriters Laboratories Inc., Northbrook, Illinois (1996).

In the US and to a lesser extent elsewhere there is an additional stimulus for CO sensor deployment for domestic and possibly also vehicular toxic gas detection (which could be piggy-backed onto fire detection). There is increasing (US) state legislation requiring CO detector deployment in residential and other occupied buildings, and the activity of advocacy groups may make this effectively mandatory for these sites and for vehicles, especially given the litigious nature of US markets. Legislation and codes may be slower to develop outside the USA, but market and legislative forces will probably show similar trends. Specifications for the more power-rich vehicular environment may be more relaxed than for fire/toxic gas protection of residential and commercial properties. In some cases where detection of a hazard is required, there may be no need for selective determination of CO versus flammable vapours. While standards such as UL 2034¹⁴ can clarify the specification, they can also be technically limiting by specifying the sensor technology rather than the performance requirement.

The market for toxic and flammable sensors other than CO is restricted in Europe and North America due to commercial safety and health and safety requirements. However, it is a common building requirement in Asian countries such as Korea and in specific industries such as leisure craft building (including boats).

The world market for fire detectors was estimated to be around £2000M in 2003,¹⁵ of which the US represented 38% and the 7 largest EU countries represented 28%. The market for ionization detectors was around 7% and is falling, whereas devices based on optical scatter showed the strongest sales with 40–70% of the market. Fire detectors that also incorporate CO detectors, either individually or in combination with optical and/or heat detectors represented less than 3% of the market, except in UK where they may have reached 12%.

3(c). Domestic and commercial indoor air quality

Asthmatics and other at-risk people have become aware of the possibility that their indoor air quality environment may be the source of long term health problems. Dangerous gases include ozone from photocopiers, nitrogen oxides from heating sources, diurnal release of cleaning solvents and formaldehyde from new buildings, furniture and carpets.

Building control systems now use carbon dioxide monitoring to optimise ventilation control, but this ignores volatile cleaning fluids. Monitoring ozone and nitrogen oxides will need either improved selectivity semiconductors or improved sensitivity electrochemical sensors. Specific VOC detection is unlikely to emerge in the short term. Research into the detection of classes of organic molecules such as aldehydes or alcohols through NIR spectroscopy is needed to show whether it may be possible to detect some classes of VOCs at sub-ppm levels (down to 10^{-9}) at reasonable cost.

Asthma and rhinitis are human responses to pollutants in the air. Most at-risk people respond to either inorganic gases (specifically ozone and nitrogen oxides) or biological particulates. Inorganic gases are detectable at the required 10^{-9} level, but lower cost, hence more prevalent sensors are required. Detection of airborne bioparticulates may remain a technical

¹⁴ Underwriters Laboratories. *Standard for Single and Multiple Station Carbon Monoxide Alarms*. Standard 2034 Edition 2, Underwriters Laboratories Inc., Northbrook, Illinois (1996).

¹⁵ *Fire Detection Systems, the European Market 2003–2008. Intelligent Controls in Buildings*. i&i Ltd-Proplan, Watford (2004).

challenge for years to come; real time monitoring might be able to use:

- molecularly imprinted polymers (MIPs) for simple allergens and specific proteins;
- toxic particulate broadband detection by monitoring respiration in a model biological system (living cell or tissue);
- electrochemical or optical detection using synthetic enzymes coupled to electrodes or waveguides.

3(d). *Industrial air quality*

Gas sensor systems are designed to alert personnel to possible health and safety hazards to both themselves and to their workplace. The chemical process and energy industries, handling large quantities of both toxic and explosive materials including gases and vapours, are particularly safety conscious. In general, requirements are characterized by a good understanding of the target species in a relatively controlled environment, but matrix interferences are less well understood. Sensor systems must be considered as elements of a safety management process that is ultimately aimed at accident prevention, with accident alerting as a last resort—remembering that false alarms are expensive.

In most cases safety gas sensors will be rarely energized, so regular validation procedures are important, either through self-validation or by routine calibration tests, which are labour intensive. A related consideration is the fail-safe ability to “zero trace”, in other words to be able to rely on a zero indication to signify that all is well. Here lies a difference between sensors that *can* detect hazardous gases, and those that *always* detect them if they are present at a predetermined level. *The need for a fail-safe sensor technology is paramount.*

Flammable leak detection. Most flammables are alkanes, subsequently burnt to provide power. Methane is an important target because of its high concentration in natural gas. Flammable gases are typically quantified with respect to their lower explosive limit (LEL) on a scale created for this purpose: the %LEL scale (such that at 100% LEL the gas is at the lowest explosive concentration in air). The LEL is different for each flammable gas, for example the Institute of Gas Engineers and Managers state levels of 4.9% v/v in air for methane, compared with only 2.8% v/v in air for ethane.¹⁶ Definitions of individual LELs vary but the IGEM figures are often accepted as the industry standard. Further away from a leak source, an indication is given either by measurement of the low concentration of the dispersed gas (typically on the ppm scale) or by acoustic detectors that measure the ultrasonic “whoosh” of gas as it escapes from a small orifice. Permanently installed monitors must be sited carefully to maximize their chances of detecting a leak, as discussed above, and therefore access might be difficult for calibration. Portable gas detectors must be more robust, lightweight and battery-operated. They can be carried to calibration points, but the trend in gas distribution is towards autonomous operators who rarely need to visit a central depot. Both types need to satisfy the requirements of intrinsic safety; for portable instruments this can make battery management difficult and limit the available power. Very low power catalytic sensors or optical detection of hydrocarbon is at the top of the wish list for many gas detector manufacturers.

¹⁶ *Dealing With Reported Gas Escapes*. Publication SR/20, the Institution of Gas Engineers and Managers (1998).

Leaks from gas distribution systems are managed by adding an odorant at low ppm concentrations such that members of the public are able to notice a characteristic smell before the gas concentration becomes explosive. Managing this important safety measure requires a regime of sampling to ensure that the odorant reaches all parts of the distribution system with the required concentration. At present, panels of people with trained noses assess the level of odour in gas samples, and there is the potential to replace such subjective panels, at least in part, with objective instruments that can measure the odorant concentration and also discriminate the odour itself in a manner representative of a human nose. Development of a reliable mercaptan detector capable of sensing one part in 10^9 is apparently underway, but overall more concentrated research is needed to achieve market requirements in a reasonable period.

Toxic gases. The aim of toxic gas detectors is to limit the occupational exposure of personnel, and to demonstrate that this has been achieved to avoid subsequent litigation. Market drivers are occupational exposure levels determined by a country's regulatory authority; in the UK the HSE publishes its prescribed limits in EH40 as Workplace Exposure Limits (WELs).¹⁷ Drivers in different countries are different, but are linked by a global understanding of toxicity levels with slow convergence of permitted exposure levels.

Historically workers were only protected from short-term exposure dangers to toxic gases. But this is changing: long term exposure is now considered in EH40 and other exposure limit documents, with the result that VOCs, rarely a short term danger, are now considered to be damaging in the long term. This change has led to a rapid growth of VOC detectors such as PIDs and lowered safety levels for asthma-inducing inorganic gases such as SO_2 and NO_x .

Users would like sensors to be specific because otherwise they might be forced to implement expensive measures aimed at reducing the concentration of a less hazardous gas. This is particularly important for the measurement of the BTEX compounds, which have very different toxicities but often similar levels of sensor response.

Asphyxiants and oxygen. Oxygen is the most important gas for humans; our bodies need oxygen levels between 19% and 23%; the oxygen concentration in dry air is normally 20.9%. The continual danger of low oxygen levels in confined spaces means that worldwide almost all confined-space workers wear gas detectors that monitor oxygen concentration. While toxic and explosive sensors read zero concentration or near zero for most of the time, oxygen sensors must continuously measure the actual oxygen concentration with good accuracy from -30 to 50 °C, in applications with frequent rapid changes in temperature, pressure and humidity—a significant challenge to oxygen sensor manufacturers.

High concentrations of CO_2 , N_2 or He (used in nuclear power plants) can lead to oxygen dilution, a serious health concern. New standards are being written to enforce the need to monitor CO_2 , especially where boilers are used, both in homes and in industry. A draft British standard for portable CO_2 measurement in ambient and mechanically ventilated sites is being fast-tracked at the request of HSE. Spillage from poorly ventilated flues can lead to CO poisoning, but it is now recognized that even if the CO levels are not life-threatening, CO_2 spillage can lead to fatigue and ill health, and if the CO_2 levels exceed a few percent, then the

¹⁷ HSE. *Workplace Exposure Limits*: Containing the list of workplace exposure limits for use with the Control of Substances Hazardous to Health Regulations 2002 (as amended). HSE Books (2005).

oxygen concentration can be dangerously low. CO₂ is toxic at high concentrations (as iconically demonstrated and documented in the Apollo 13 moon mission).

3(e). *Automotive and aircraft cabin air quality*

Increased driving comfort and safety can be a major marketing feature as concerns grow about the health affects of exposure to pollutants whilst driving and especially when stationary in traffic jams. Automatic activation of the heating ventilation and air conditioning (HVAC) air recirculation system now uses an air quality sensor located in the main air inlet duct of the system. When the threshold for the target gases (at present CO) is reached, the sensor signals the HVAC system to switch to recirculation mode thereby preventing further ingress of pollutant. In the future this system will be extended to monitoring NO_x and VOC nuisance odours.

4. Industrial process control

The process industries are generally defined as those that employ continuous or batch processes to convert raw materials into products such as chemicals, petrochemicals, pharmaceuticals, plastics, rubber, paper, food, cement and glass. The utilities (i.e., power generation, gas and water supply) are often also included in this category, as they mostly employ combustion processes. A fast developing sector is that of biotechnology using bioreactors (fermenters); and there is a trend to manage landfill waste disposal sites as giant gas-producing bioreactors.

These industries are major users of sensor and control instrumentation that fulfils tasks such as process monitoring and control, product quality assurance, plant safety, protecting the workforce and monitoring emissions to the environment. They contribute significantly to the national economy but are not exempt from mounting financial, legislative and other pressures that include: an increasingly competitive business environment leading to the need to reduce operating costs, increase productivity and reduce waste; carbon taxes and credit trading schemes; rising fuel and energy prices; reduction in skilled manpower (particularly instrument and process engineers leading to unmanned control systems); growing public concern over safety, the environment and business ethics and ever more stringent environmental and health and safety legislation.

Several of these factors will impact directly on future sensing, monitoring and control practices and can be seen as the key drivers behind the development of novel gas sensors:

- **High fuel and energy costs**, plus carbon trading will stimulate the development of more efficient combustion control techniques;
- **Environmental legislation** and emission trading schemes will necessitate improved stack emission monitoring technologies;
- **Public concerns and legislation** will require improved odour monitoring and control;
- **Health and safety** considerations will result in sensors for real-time monitoring of toxic organics in the workplace;
- Continual drive **to improve productivity**, combined with rising raw material costs will drive the development of improved techniques for characterising feedstock materials;
- The need to **reduce operating costs**, combined with the loss of skilled instrument engineers in many industries within this sector means that future generations of gas

sensors will need to exhibit very low ownership/life costs. Thus, high reliability, reduced calibration and maintenance requirements, and long field lifetime are critical. A further consequence of this trend is the desire for fully autonomous, fixed-point gas sensors that would operate unattended for at least two years. These would be battery-powered, require no hard wiring and communicate by short-range radio, yielding significant reductions in installation and operating costs.

Overall, these industries need to improve rapidly and so offer significant opportunities for improved gas sensors.

Ammonia for refrigerants and intensive farming. Refrigerant detection is becoming important because ammonia is replacing CFCs as a more environmentally acceptable refrigerant. However, ammonia is a difficult gas to measure. Low cost sensors currently do not survive the difficult temperature environment, while optical methods are too expensive for typical applications. Detection of ammonia is made at two points in the system:

- (i) Detection of refrigerant leakage at the compressor room. This brings the problem of monitoring constantly low level (1–5 ppm) background ammonia whilst being always ready to detect a breakthrough of 10 to 20 ppm. The task is not easy for electrochemical sensors that respond selectively to ammonia.
- (ii) Contamination of food stored in warehouses by ammonia causes food poisoning and is therefore dreaded by warehouses operators. The cost of dumping foodstuffs that have potentially suffered damage in an ammonia-poisoned warehouse is unpalatable, but detection of low ppm levels of ammonia at $-40\text{ }^{\circ}\text{C}$ is a technology challenge not yet met. We could be years away from an electrochemical solution. Heated metal oxides or heated amperometric sensors may be the answer. Optical detection may find a role if sensor costs can be reduced. New technologies based on bionanotechnology are also being researched.¹⁸

Intensive farming, specifically intensive poultry breeding generates very high levels of ammonia, which can damage livestock health. This is a cost-sensitive business, and low-cost ammonia sensors capable of withstanding continuously high ammonia levels at higher temperatures have been tried and failed; ppm level baseline stability is the main challenge. Industry must find an electrochemical or optical spot sensor that meets the performance and cost demands.

Bioreactors. Gas monitoring is important for two quite different kinds of bioreactors:

- (a) vessels in which micro-organisms are grown to secrete useful products such as pharmaceuticals;
- (b) landfills containing solid waste in which biological activity accelerates degradation.

We refer here to the type of control: open loop or closed loop, which we term “open” or “closed” bioreactors, respectively.

Closed bioreactors. This is a very important growth market. Current demands for bioreactor products, which include ever more sophisticated pharmaceuticals, are far in excess of

¹⁸ J.P. Sharkany, S.O. Korposh, Z.I. Batori-Tarci, I.I. Trikur and J.J. Ramsden. Bacteriorhodopsin-based biochromic films for chemical sensors. *Sensors and Actuators B* 107 (2005) 77–81.

production capacity. Demand for cultured organs and tissues such as skin is also pushing the development of unconventional bioreactors. Most bioreactions are batch processes taking place in vessels of the order of ten litres in size, but this figure may vary enormously depending on whether the process is still under development or is being scaled up. The process may typically run for several weeks, hence losing a batch is potentially very costly, and quasicontinuous monitoring is vital to ensure batch success.

At present the usual measured gaseous analytes are oxygen, ammonia and carbon dioxide. However, it is recognised that these analytes do not give a complete picture of cell metabolism in the reaction vessel, hence there is definite potential for developing sensors able to measure the gaseous signatures of cell metabolism. Other volatile analytes of interest include methane and hydrogen; some important ions such as acetate will also be in equilibrium with their volatile nonionized forms. Near infrared spectroscopy and semiconductor gas sensors are currently popular.

Open bioreactors. Pressures on available landfill volume in many countries have led to a strong increase in interest in the possibility of accelerating the degradation of municipal solid waste and biosolids. Hence some landfills have been transformed into gigantic bioreactors in which there is an active population of micro-organisms engaged in transforming waste into other products. Monitoring the gases emitted by this metabolic activity ensures that process targets are kept on track. Monitoring the gas profile of methane, hydrogen, heavier alkanes and VOCs allows one to age the landfill, which is important for determining the stage of the landfill. Fixed spectroscopy installations are being developed because this technology can monitor a range of compounds simultaneously.

5. Automotive

Electronics (including physical and chemical sensors) is now approaching 30% of total vehicle cost. Sensors are used in every part of the vehicle, from powertrain to steering, from safety to vehicle diagnostics and monitoring. There are nowadays 30–40 sensors of all types in a typical economy car, and around 120 in luxury models, a figure set to grow further. An increasing number of these sensors will use MNT in some form, but only where it provides the lowest-cost solution to a problem. The automotive sector is characterised by a relentless downward pressure on costs—OEMs do not want to pay more than €1–€2 for a sensor, no matter how complex. However, manufacturing volumes are large enough to take advantage of micro- and nanoproducting economies of scale.

Engine and exhaust management. Chemical sensors sensitive to one or several components of the exhaust gas are used to support combustion efficiency. For a sensor to be commercially viable for automotive applications it must be easy to use, rugged, reliable, vibration resistant, with fast response and low cost. Engine operating conditions impose further demands, such as high operating temperature, corrosive atmosphere, low concentration limits of the detected gas and a complex background matrix. Relevant gases to combustion control include HC, O₂, CO, CO₂ and NO_x.

Particles from diesel vehicles classed as PM10 and PM 2.5 (referring to 10 and 2.5 μm particle sizes) affect human health. Diesel particulate emissions are a complex mixture of solid and liquid components of soot and various adhered hydrocarbons. Diesel particulate filters are an effective means of reducing the emission of these materials, but during operation the filter

becomes clogged. Filter regeneration involves raising the exhaust temperature up to the soot ignition temperature, which uses additional fuel. Exhaust gas particulate sensors can help to find the optimal period between regeneration events, offering an opportunity for the development of microfabricated sensors.

Hydrogen. Future generations of motor cars may well be powered by hydrogen, probably used to generate electricity rather than to fuel internal combustion engines. Although the technology is still in its infancy, there is considerable activity directed towards developing hydrogen fuel cells for energy storage, and this is a strong driver for the development of better and cheaper hydrogen gas sensors. The route towards widespread use of fuel cells for energy storage includes using fuel cells as efficient batteries in portable equipment, energy for cars instead of fossil fuels, and ultimately to enable more efficient use of renewable energy sources, which are often only sporadically available or not in the needed location. Some roadmaps leading towards a hydrogen-based economy include a stage in which hydrogen is formed from fossil fuels or biomaterials. Alternatively, hydrogen and oxygen are formed from water using an electrolyser. Reversing this process, H₂ is used to generate electricity in a fuel cell or by enzymatic biological systems—the latter can be anticipated to remain purely a research topic for many years to come.

Gas sensors will be required:

- (i) For **safety**, to detect hydrogen leaks and quantify H₂ concentration with respect to its lower explosive limit (LEL) in air (4 % v/v¹⁶).
- (ii) For **process control**, to check the purity of hydrogen as it is formed. Assessment of the level of H₂ formed by electrolysis may be conveniently assessed by monitoring the internal pressure.
- (iii) To **measure contaminant gases** that arise in the production of H₂ from natural gas: examples are carbon monoxide (CO)¹⁹ and hydrogen sulphide (H₂S) in the presence of high concentrations of H₂. Bringing H₂S levels down to 1 part in 10⁹ would extend the lifetime of proton exchange membrane fuel cells.²⁰
- (iv) To **monitor leakage** in future hydrogen cars. The high gas pressure and high diffusion rates of the small molecules mean that leaks of hydrogen present a greater hazard in the confined space of an automobile.

The strong hydrogen response of semiconductor sensors is often considered a problem for the detection of other gases. H₂ is a small, agile molecule, able to diffuse further and faster into sensor microstructures, and this offers opportunities for its discrimination on the basis of different temperature profiles, temperature modulation (fast heating and cooling) or thickness, sometimes with selective overlayers.²¹ These developments are reducing but not eliminating a fundamental issue with such broad spectrum detectors. Gas detectors used for both H₂ leak

¹⁹ C.T. Holt, P.K. Dutta, A.-M. Azad, S.L. Swartz and R.R. Rao. Carbon monoxide sensor for PEM fuel cell systems. *Sensors and Actuators B* 87 (2002) 414–420.

²⁰ I.J. Mathiak, W. Benz, I.K. van der Saar and I.M. van Doeselaar. Hydrogen desulfurization extends fuel cell life. *Hydrocarbon Processing* 86 (2006) 107–110.

²¹ T. Weh, M. Fleischer and H. Meixner. Optimization of physical filtering for selective high temperature H₂ sensors. *Sensors and Actuators B* 68 (2000) 146–150.

detection and measuring contaminants in an H₂ stream need better discrimination before benefits can be realised of the improved sensitivity when using nanostructured materials.

An important sensing mechanism that is relatively specific to hydrogen results from hydrogen absorption into palladium (Pd) and its alloys. H₂ is taken up by interstices in the lattice, which changes the work function or interface state (detectable in FET or Schottky diode devices), causes a physical expansion (detectable in microstructured cantilevers,²² in the manner of a bimetallic strip) or reduces the refractive index (detectable via optical interrogation). Response times are slow but can be improved by operating at elevated temperatures. Known problems include temperature-induced expansion of Pd, drift resulting from aging of Pd,²³ and humidity effects. Alloying with nickel improves some elements of performance, and doping CNT with Pd is a popular research theme.

Finally, hydrogen will also generate a response from other sensors based on the following:

- (i) *Combustion of gases*, in sensors such as pellistors and microhotplates, with cross-responsivity to other flammable species;
- (ii) *Thermal conductivity*;
- (iii) *Pt catalytic amperometric electrochemical* cells, but since they also respond to CO, this may cause problems in some applications such as fuel cells where CO is a poison to the cell.

Priorities for new technologies; overcoming technical challenges

Nanostructured metal oxides for Taguchi sensors. The gas sensing properties of conventional metal oxide semiconductor based sensors are mainly dependent on their surface chemistry. The sensor response relies on oxidation or reduction reactions of gases that diffuse onto the surface and into the subsurface of the oxide material. This causes a change in the depth of the electronic depletion layer at the material's surface, detected as a change in both bulk and surface resistivity of material. Therefore by increasing the surface to bulk ratio the use of nanoparticulate materials gives improvements in responsivity (utility) and enables lower operational temperatures (but unfortunately provides no improvement in selectivity).

Various problems are considered to limit standard metal oxide sensors at present, which are not addressed by changes in particle (crystallite) size for many materials. They are:

- Lack of selectivity to target gas species
- Sensitivity to humidity
- Dosimeter-type response (or very slow recovery) at low temperatures or operating powers.

The advantages of nanostructured materials may be best realized by enabling novel compounds such as perovskites to be conveniently fabricated. Nanosized forms of some photochemically active materials, e.g. titanium oxides, may also open up new sensing capabilities.

²² S. Okuyama, Y. Mitobe, K. Okuyama and K. Matsushita, Hydrogen gas sensing using a Pd-coated cantilever. *Japanese Journal of Applied Physics* 39 (2000) 3584–3590.

²³ A. Chtanov and M. Gal, Differential optical detection of hydrogen gas in the atmosphere. *Sensors and Actuators B* 79 (2001) 196–199.

Carbon nanotubes (CNTs). Both single-walled and multi-walled carbon nanotubes (SWCNT and MWCNT respectively) have potential applications in gaseous, chemical and biological sensing in sectors including process, automotive and extraction industries as well as environmental monitoring and health and safety. The nature of electrical conduction in high-quality semiconductor nanotubes means that even the adsorption of a single molecule can produce significant changes resulting in potentially high sensitivity and fast response compared to conventional solid-state sensors. Selectivity may be achieved through use of polymer layers permeable to specific gases or through chemical modification (doping) of the surface.

It should be noted that the potential of carbon nanotubes and indeed of other nanomaterials will not be realized until synthesis and post-processing methods have been developed which generate materials with selected electronic and structural properties. Sensors require well-defined metallic or semiconducting properties rather than the present mixture inherent in present nanotubes. Control of the growth kinetics and nanotube morphology are being actively studied worldwide in order to develop more tailored, all semiconductor CNT structures that can lead to reproducible, useful gas sensing layers with the required selectivity.

Once morphology is under greater control, a link between the required nanostructure and gas sensing properties needs to be better established, possibly through the use of high throughput, automated evaluation techniques. Outside academia, companies such as Nanomix are advancing CNT gas sensor technology. At present, CNTs are being studied in almost every university in the UK (for example, Cambridge alone has three separate groups dedicated to CNT technology), but gas sensing is not the primary CNT research focus; rather, gas sensing is often bolted on to other studies such as morphology and growth, semiconductor behaviour, mechanical properties and methods of analysis of this unusual nanomaterial.

Quantum dots (QD) and quantum wires (Q-wires) have been developed using different geometries with a wide variety of materials. Looking for routes for exploitation, universities and industry have been trying to find outlets for this new technology although with limited success: QDs are popular in biotechnology as photonic tags but the use of QDs as gas sensing elements needs more fundamental research.

QDs and Q-wires currently use III–V or II–VI materials. They typically show a problem of agglomeration of the primary particles, which thereby lose their advantage as nanoparticles. The preferred transduction method for these particles is photonic. Alternative detection methods using semiconductor or electrochemical transduction require basic research, and this whole area of QD sensor technology needs more research before it can be considered for gas sensing layers.

Chemiluminescence has been used for years to analyse NO_x concentrations and new developments are leading to new challenges in gas detection. Examples are QDs and their strong fluorescent properties: attaching a QD to chemically reactive matrices can lead to strong emissions at specific wavelengths at low gas concentrations. QD use is more relevant to liquid sensing and biosensors.

Microelectromechanical systems (MEMS). Silicon is the most common material used for the fabrication of MEMS devices due to the tremendous amount of knowledge, expertise and equipment available from the microelectronics industry. However, other materials may be more suited to individual applications. For example, silicon may not be sufficiently inert for use in some chemical or biochemical devices and glass would be preferred, or the application may require the use of an insulating (i.e., glass or polymer) substrate. The use of polymers in

particular may be advantageous due to possibly lower fabrication costs associated with moulding rather than etching. Further, some waveguide-based devices may require visible light transmission—this makes silicon unsuitable as it is opaque at wavelengths below 1.1 μm . High temperature applications ($> 400\text{ }^\circ\text{C}$) may favour the use of alternative materials such as SiC, particularly if integration of electronics with the sensor element is being considered.

Processing of nonsilicon materials often involves the introduction of lithographic, deposition and etch techniques that differ significantly from those used for silicon. There is currently a lack of capability in the UK for processing nonsilicon materials.

Materials used for specific sensing applications that are applied to a substrate through various deposition techniques include polymer composites, CNT, intrinsically conducting polymers, III–V materials and metal oxides. Deposition of sensing layer materials on MEMS devices requires more research, especially where high surface area layers are required.

While MEMS are, by definition, micro rather than nano, parts of the field are evolving into nanoelectromechanical systems (NEMS).

Explosives and drugs detection. It is very difficult to predict which technology mix will emerge in this field, and in fact the specific user demands are particularly difficult to determine. Nevertheless it seems likely that MEMS processes (for volume production capability) with an optical absorption sensor or micro mass spectrometer (for specificity and standoff²⁴ capability), perhaps combined with another technique to increase the sensitivity could lead to a positive change in generic capability.

Both the explosives and drugs detection markets would therefore benefit from the following:

- (i) *Improvements in sampling technology*, to bring the gaseous measurand to benchtop-type gas detectors without dilution. Developments in standoff detection would also solve this problem.
- (ii) *Improvements in discrimination ability* since highly sensitive, broadband gas detectors may be swamped by the higher levels of uninteresting species in the background matrix.

There has been substantial interest in the development of terahertz (THz) spectroscopy for standoff detection of many types of explosive whose nitrogen or peroxy bonds give a characteristic spectral response. Although drugs have also been identified using THz spectroscopy,²⁵ the lack of information content in the broad spectral bands means that specific drug identification against a complex background matrix is unlikely to be successful. THz detectors are more likely to concentrate on identification of the problem in solid form, with imaging providing an additional level of discrimination in a form similar to an x-ray security system. THz imaging offers a great opportunity for MNT, but in this case is not gas detection.

Aerial pollution detection. There are opportunities for MNT to deliver low power, low cost gas detectors which can be integrated with small weather monitoring stations, reporting the wind speed, direction and turbulence using three-dimensional anemometry at the point of emission or at 10 m height (the standard height for dispersion models).

²⁴ I.e., detection at some distance from the target.

²⁵ K. Kawase, Y. Ogawa and Y. Watanabe. Non-destructive terahertz imaging of illicit drugs using spectral fingerprints. *Optics Express* 11 (2003) 2549–2554.

Government monitoring requires low level (ppb) detection of a range of indicative substances, usually with a single instrument for each target species. Networks of monitoring stations are being established, usually in urban locations. Enforcement drivers are:

- (i) increased measurement capabilities and/or decreased overall capital cost for a class of gases, by developing multiple gas detection at sub ppm levels;
- (ii) lower capital cost to afford wider geographical coverage with a larger network of monitoring stations (sensorization).

Societal needs

Francis Bacon was perhaps the first to explicitly exhort scientists to consider the “relief of man’s estate” as well as the question intellectual environment as a motivation for their work.²⁶ Ever since, this idea has been hovering in the background, and nowadays when applying for funds from public sources, such as the European Union or the various research councils in the UK, the applicant is specifically asked to make a statement on how the proposed research would benefit society at large. Clearly this is pregnant with ethical implications. The scientist may have a clear personal vision of how society should develop, one may observe past trends and project them into the future, or a government may seek to impose a certain course of development on the people under its administration. Gas sensing is not immune from these considerations. In this article, and in the Roadmap, we have taken a fairly neutral view based on extrapolating visible trends, linking external drivers and anticipating associated future needs. Revolutions, however, frequently “buck the trend”, and here we point out that gas sensing fits in very well with the sensorization of the world that is part of the anticipated Nano Revolution.

The role of publicly funded research

The Roadmap has a dual role, on the one hand alerting industry to possibly neglected opportunities in new markets or technologies and on the other hand indicating to governments where a coordinated effort to increase research activity may yield valuable economic payback. Nevertheless, we fully recognize that the public funding of science for ultimately commercial ends is a highly contentious area with a very wide spectrum of current opinion ranging from the assertion that no scientific and technical research should be publicly funded to the assertion that all should be, with all the results of such research made freely available to the public.²⁷ The rationale for the former opinion is that research to develop existing technologies and invent new ones should be in the direct interest of the firms engaged in those technologies and in a position to exploit the new ones, and therefore “market forces” should suffice to ensure that an appropriate level of research is maintained. Curiously, in many developed countries nowadays market forces do not seem to be very effective in maintaining this state of affairs, for a number of possible reasons, (i) the returns are medium to long-term, and higher short-term returns can be obtained through other means, (ii) individual companies and their application market sectors

²⁶ F. Bacon, *The Advancement of Learning*. London (1605).

²⁷ See also J. Pethica, T. Kealey, P. Moriarty and J.J. Ramsden, Is public science a public good? *Nanotechnol. Perceptions* 4 (2008) 93–112.

are too small to justify large-scale development, especially when the results of that development are often more widely spread. The rationale for public support is partly an acknowledgment of this failure of the market forces, and partly a belief in the value of unfettered, curiosity-driven research as a means of human advancement.

In most countries nowadays the actual situation lies somewhere between these two extremes, and very few, if any, real attempts to analyse costs and benefits seem to have been made. In the UK, the Engineering and Physical Sciences Research Council (EPSRC) spends about £0.75 million pounds per annum on academic gas sensor research.²⁸ The British government is now strongly trying to promote “value for money” for publicly funded research, which means a reasonable commercial rate of return.²⁹ One consequence of this is that private companies are encouraged to participate in the research projects, and allowed to acquire rights over their outputs. A mixed funding strategy emerges, the industrial proportion generally rising with higher technology readiness levels.

The 2002 UK Sensors Foresight study⁹ reported that, for the entire sensor industry:

- Exports accounted for 60% of total sales, giving a positive trade balance of 10–20% of sales.
- A conservative analysis of (i) R&D investment made by the EPSRC, and (ii) the return to the treasury from identified spin-out companies, gave a real-terms rate of return of 15% per annum; this did not include smaller companies or benefits to sales in existing companies, so can be regarded as an underestimate.

This article is not the place to launch into an extensive discussion of this issue, but at least we feel it is important to suggest that an assessment of the commercial leverage arising from research council-funded research is considered, if such leverage is going to become the main criterion for maintaining the system.

To increase the efficacy of limited public and private funding, we seek to encourage better quality engagement between industry and academia, including technology providers and users, and those researching both sensor applications and technological solutions. Industrial users often know best what they need to achieve, but may not be aware of new potential solutions, whereas technology providers know best the opportunities and limitations of new approaches, but may not be aware of the potential for applying them. It was with this in mind that we brought together a group of users, sensor manufacturers, instrumentation specialists and researchers in the UK’s Micro and Nanotechnology (MNT) Gas Sensor Forum, to write the first roadmap in this area.² But that is not enough; it is our aim to engage more widely and to update that document as a focus for our discussions, therefore we encourage further debate and comments on it.

Summary and conclusions

Technology Priorities. High impact technologies include separation science, electronic components, optical light sources, nanomaterials, low cost/integrated optics, microelectro-

²⁸ This figure does not include work on basic technologies, e.g. semiconductor oxides, not explicitly aimed at developing gas sensors, but which are clearly of use for such development.

²⁹ Participation in large international experimental collaborations in fundamental particle physics appeared to be exempt from this stricture.

mechanical systems (MEMS), MEMS/CMOS integration and electrochemical cells. Specific MNT priorities are:

Nanomaterials

- Functionalized materials for gas filtration and separation.
- Reproducible manufacture of carbon nanotubes, quantum dots and nanostructured metal oxides for improved gas sensitivity and selectivity.

Microfabrication

- High temperature amplifiers and logic for extreme environments.
- Si MEMS integrated optics as a generic platform to address several niche markets, migrating telecoms manufacturing to small-run gas sensors.
- Broad spectrum MEMS to discriminate compounds: micro mass spectrometry, ion mobility spectrometry and gas chromatography.
- Establish credible production of new mid-IR light sources.

Grand research challenges. The following high risk areas of research are considered to offer significant, cross-niche benefits if they can be solved:

- VOC characterization against complex backgrounds (e.g., BTEX, landfill, indoor and cabin air quality).
- Identification of normal and abnormal variations in gaseous markers of disease in breath and gut gases.
- Improved selectivity and stability for semiconductor and other nanomaterial-based gas sensors.
- Combinatorial methodology for optimizing sensing materials.
- Integrated MEMS using combinatorial sensing arrays with widespread applicability.
- Room temperature mid-IR and far-UV low-cost, tunable light sources.
- Detector for specific precursors and sources of asthma in the home.

Even modest **sensorization** in the gas detection field will have clearly perceivable benefits:

- Providing early diagnostics in **healthcare**
- Monitoring complex processes that ensure a **sustainable economy**
- Monitoring and reducing pollutants in the **environment**
- Providing early detection and forensic analysis for **security**
- Reducing pollution by improving efficiency in **transport**.

The benefits are directly applicable to the developed economies, but are possibly even more pressing for those economies rapidly developing on a large scale, such as Brazil, China and India. Although the market may ultimately deliver what is required, the process might be significantly accelerated by judicious government-organized funding of obvious science and technology gaps with clear economic payback, since nowadays any manufacturer of gas sensing devices will find that the market is global.

Acknowledgments

This article (together with the preceding one) originated from the MNT Gas Sensors Roadmap,² prepared by the MNT Gas Sensors Forum (constituted by the authors). We especially thank the Microsystems and Nanotechnology (MNT) network,³⁰ SSIRA,³¹ the Sensors and Instrumentation Knowledge Transfer Network (SIKTN), the Gas Analysis and Sensing Group (GASG), the Council for Gas Detection and Environmental Monitoring (CoGDEM), the OptoCem.net KTN, and individual members of the gas detection community, for their contributions to the Roadmap, which have been further distilled into this article. J. Hodgkinson is supported by an EPSRC Advanced Research Fellowship, reference GR/T04595/01.

³⁰ See H. Clare, The UK microsystems and nanotechnology network. *Nanotechnol. Perceptions* 2 (2006) 213-216.

³¹ SSIRA went into voluntary liquidation in March 2006.