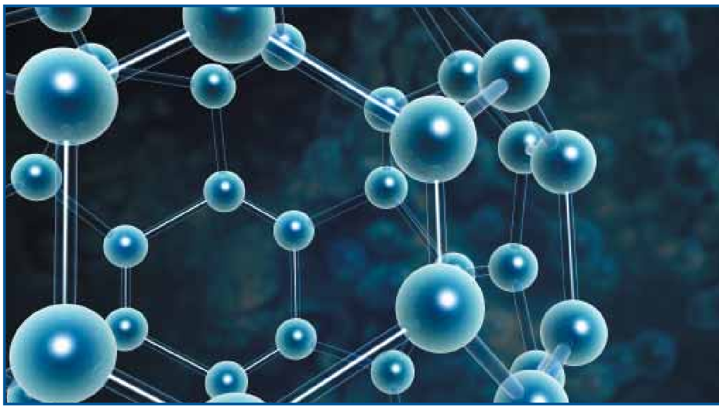
MNT Gas Sensor Roadmap



Prepared by the MNT Gas Sensor Forum

December 2006

Sensors & Instrumentation Knowledge Transfer Network

Opto Net Cem

CoGDEM The Council of Gas Detection and Environmental Monitoring

GAST

Nanotechnology Knowledge Transfer Network

Executive Summary

Why consider gas sensors?

Gas detection is important to the UK, not only because of the manufacturing industry but also because a number of wider societal benefits result from the use of gas sensors:

- 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**.

Scope and purpose

This application-led roadmap has been drawn together by the Forum's steering committee, **informing government-level decision makers** of this industry's needs and research challenges, and supporting **corporate decision-making.**

This UK MNT Gas Sensors Forum started with two DTI-sponsored workshops in 2005. The Forum links the gas detection community (industry, consultants and the research base) and micro and nanotechnology (MNT) technology providers.

Our approach

Fragmentation of the gas sensor market means that few niche applications can justify investment costs for step changes in technology. Fortunately there are many such niches, which together can provide broader justification. We generated a **matrix of gas detection applications / technologies,** agreeing on the potential impact for each area. This matrix is a useful market analysis tool in its own right.

Individual roadmaps were drawn together for fourteen application areas, and represent the current view of this steering group. The information contained within these roadmaps may be controversial, since predicting the future is impossible.

Finally, this **report** details our collective views of each market and each technology, considering the opportunities for both research and exploitation. We hope that you will provide feedback, refining this consensus view, captured within a living document.

The UK gas detection community has a strong heritage and is well served by several trade and government sponsored groups. We have drawn on the collective knowledge of the following:

- Sensors Knowledge Transfer Network (Sensors KTN)
- Gas Analysis and Sensing Group (GASG)
- Council of Gas Detection and Environmental Monitoring (CoGDEM)
- OptoCem.net KTN
- Members of the gas detection community

Gas sensing in the UK

- UK sensor research was considered by the 2002 Sensors Foresight study to give a healthy return to the treasury.
- The gas sensor industry is driven by high technology SMEs.
- Gas sensors, the enabling technology, are mostly developed and manufactured in the UK, while gas detection systems manufacture is frequently outsourced.
- This strong UK SME industry is at risk of missing out on the next generation of technology developments because of the investment cost barrier.
- Recent consolidation has brought some UK companies into US ownership, which is starting to weaken the UK sensor technology base.
- The 2002 Sensor Foresight study considered the UK to be weak in microengineered sensors, but government MNT investment has improved the infrastructure landscape.
- The opportunity now is for pre-competitive development, exploiting the MNT infrastructure and research base.

Market size and growth

Globally, the gas sensor market is £250 M/yr, with sensor systems totalling >£1.5 B. The principal markets are:

- **Fire and domestic gas detection:** £80M; a mature market, with growth in domestic CO.
- **Automotive (ignoring lambda):** £5M; rapid growth in cabin air quality monitoring, with large potential growth in emissions control.
- **Industrial safety:** £80M; a mature market with rapid expansion in developing economies.
- **Process control and emissions monitoring:** £20M; legislation- and efficiency-driven growth.
- **Breath and drugs:** £20M; large potential growth in medical diagnostics, but research is needed.
- **Environmental monitoring:** £5M; large potential growth, but technically challenging and legislation is not yet in place.
- **Security and military** £30M, with event-driven growth.

Technology priorities

High impact technologies include separation science, electronic components, optical light sources, nanomaterials, low cost/ integrated optics, microelectromechanical systems (MEMs), MEMs/ CMOS integration and electrochemical cells. Specific MNT priorities are:

- Nanomaterials
- Functionalised 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

- VOC characterisation 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 nanomaterial gas sensors.
- Combinatorial methodology for optimising 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.

Recommendations to the DTI and Research Councils

Fund a short series of one-day workshops on identified grand challenges, bringing together different skill areas to inspire new thinking.

Establish CASE awards in areas of common opportunity, through the Sensors KTN.

Fund a Global Watch gas sensor mission to North America, Russia or Far East, targeting technology priorities.

Develop funding mechanisms for Universities and Government Research Associations to engage with a diverse industry to work on the next steps to commercialisation – perhaps a DTI Knowledge Transfer version of EPSRC's successful fellowship scheme.

Use government bid requests to solve specific needs from MOD, DEFRA, EA, modelled on the USA SBIR contract procedure. Such contracts would supplement the use of development grants.

Authorship and affiliations

Author	Affiliation	Representing
Jane Hodgkinson	Cranfield University	Gas Analysis and Sensing Group
John Saffell	Alphasense Ltd	Council of Gas Detection & Environmental Monitoring
Jonathan Luff	SIRA, NPL	Sensors KTN
John Shaw	Tyco Safety Products	
Jeremy Ramsden	Cranfield University	
Carlos Huggins	e2v technologies Ltd	
Robert Bogue	Robert Bogue & Associates	Gas Analysis and Sensing Group, Optocem.net
Roger Carline	MNT Network	

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Contents

1 Introduction

The UK gas detection community has a strong heritage and is well served by trade and government sponsored groups. We have been able to draw on the collective knowledge of the following:

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- OptoCem.net KTN
- Members of the gas detection community

This Roadmap is written for:

Government decision makers who want guidance on where to concentrate funds for research and industrial exploitation;

(i) ***UK industry*** needing market or technology information to make corporate decisions;

(ii) ***Researchers*** who need to know market and technology requirements.

Gas detection is important to the UK, not only because of the manufacturing industry but also because a number of wider societal benefits result from the use of gas sensors-

- 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.

1.1 Purpose and scope

The MNT Gas Sensors Forum was established to inform both users and developers of gas sensor technology of the research activities and opportunities that may arise through developments in micro- and nanotechnology (MNT). It started with two DTI-sponsored workshops in 2005, which also established the steering committee who have written this document.

The scope of this roadmap is gas sensors and sensor systems using MNT. In order to develop a complete, application-led roadmap, this initial remit was broadened to include other current and emerging technologies. The diverse range of gas markets is hopefully inclusive.

1.2 Methodology

This roadmap was developed in three stages.

First, a matrix of technologies and market sectors was generated, agreeing on the potential impact for each area, taking expert input from a broad section of the gas detection community. This matrix was used to prioritise needs, but is also considered a useful market analysis tool in its own right. The importance of each market to the UK was analysed by considering two factors: (i) the potential market size, and (ii) the fit with strategic UK priorities identified by the 2002 Foresight exercise.

Second, diagrammatic, application–led roadmaps were compiled, again drawing on experts in different gas detection markets. These are presented in Appendix C. Specifying the technology and component developments that lead to final product is controversial, especially because we have defined timescales. Of course these timescales can slip, but the roadmaps act as a reference that can be corrected and updated, as required.

Third, this document details our collective views of each market and each technology, considering the opportunities for both research and exploitation. The opening sections review the overall gas detector/ gas sensor market in the UK, while later sections consider the technology in more detail.

Although other gas detection market surveys exist, this document is in the public domain, so please use this document to your advantage. Furthermore, your comments are needed to help us build an industry-wide consensus.

2 The importance of gas sensors to the UK

2.1 Market value and accessibility

Estimates of market value have been derived from various sources and are summarised in Table 1. A Sensors Task Force (STF) reported in 2002 on the present situation concerning all types of sensors for the UK Foresight exercise, uniting several market studies and analysing them from a UK perspective [1].The Task Force noted that:

- Exports accounted for 60% of the total, giving a positive trade balance of 10-20% of sales.
- UK production for all sensor types was estimated to be in 4th position globally, behind the US, Japan and Germany.
- Gas and chemical sensing were well-represented and the UK had a history of success in gas sensors.
- A conservative analysis of (i) R&D investment made by EPSRC, and (ii) the return to the treasury from identified spin-out companies, gave a real-terms rate of return of 15% pa; this did not include smaller companies or benefits to sales in existing companies, so can be regarded as an underestimate.

Market sector	Value pa	Source
Global - sensor components	£0.7 - £1.4 billion (10^9)	Sensors Task Force (STF) 2002 [1]
UK - sensors & instruments	£5 billion	
growth: new technologies	10%	
growth: established technologies	4%	
Global - gas detection instruments	$1.5 billion	Market study, major gas detector company (confidential)
Global - gas sensors	$250 M	
Global - gas detection instruments	£2.5 – 1.5 billion	Conservative estimate, UK gas sensor company (confidential)
Global - gas sensor modules (sensors & immediate electronics), excluding automotive Lambda sensors	£250 M	
growth: modules	10%	
Lambda sensors only (see section 5.3.2)	£1.2 billion	

Table 1. Estimates of annual market size and growth.

Figure 1 shows our conservative analysis of global market sizes for sensors modules (the sensor element and any immediate sensor-specific electronics) in different gas detection market sectors. The analysis also considers the level of technical maturity of each market sector, and its future development.

Mature markets often have barriers to entry, but nevertheless can offer opportunities for MNT, showing incremental benefits of reduced power and size. Although the market benefits may be incremental, at the component level this might require a step change in the underlying manufacturing technology. Less mature, smaller markets with high growth can offer opportunities for more revolutionary sensing techniques.

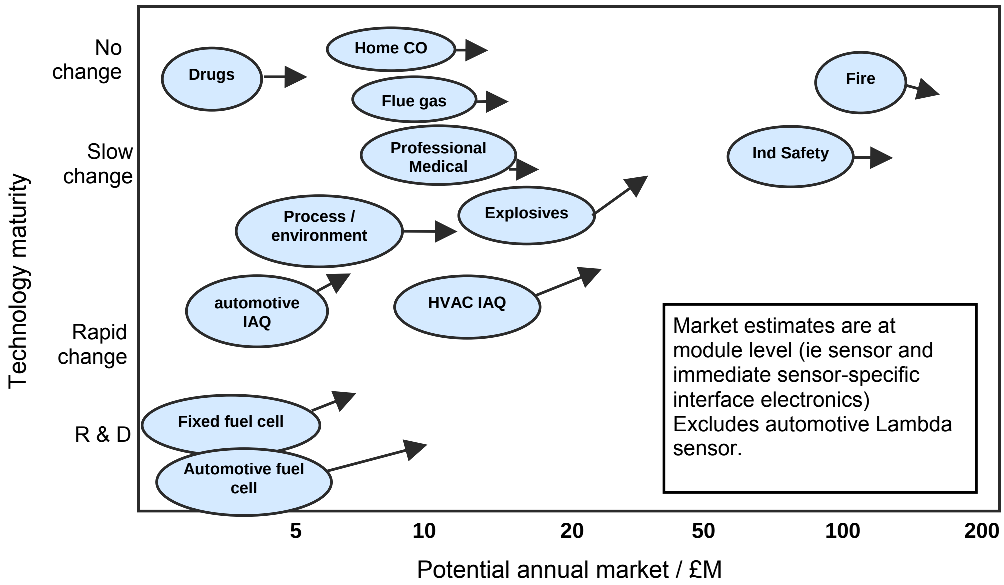


Figure 1. Maturity of different gas detection markets versus market size. Arrows show anticipated future development.

2.2 The global environment

The gas sensor market is geographically diverse.

- **D*omestic CO*** is a strong market in the USA and growing rapidly in Europe. Asia is more legislatively driven by domestic flammable gas detection.
- ***Automotive cabin air quality*** has become strong in Europe and will soon become ubiquitous worldwide. ***Engine management*** using gas sensing has worldwide demand.
- ***Industrial safety*** has been strong in North America, Africa and Europe for decades, and is now growing rapidly in Asia, especially China where multinational companies are demanding equivalent safety for all their employees worldwide.
- ***Indoor air quality*** (IAQ) is legislatively driven in Canada, some northern European countries and certain USA states such as Washington; Asia is a growing market for IAQ measurements.
- ***Urban air, medical diagnosis, and asthma*** and ***odour detection*** are not legislated adequately now, so the drivers are local and not geographically well defined.
- ***Homeland security*** research has been a focus of the US government, with limited tangible results. The USA expenditure in this area dwarfs that of all other countries.

Frost and Sullivan recently reported their analysis of this market [2]. The public domain summary estimated the size of the gas detection market and is worth repeating verbatim:

> "The size of the world industrial gas sensors market in 2005 was $48.5 million and is expected to reach $80.6 million in 2012, at a compound annual growth rate (CAGR) of 7.5 percent for the period 2005 to 2012.
>
> The world industrial gas detectors market was worth $680.0 million in 2005 and is expected to reach $947.3 million in 2012 at a CAGR of 4.9 percent for the period 2005 to 2012.
>
> The size of the world industrial gas analyzers market (NDIR, Zirconia, Paramagnetic and Electrochemical) in 2005 was $278.5 million and is expected to reach $376.1 million in 2012 at a CAGR of 4.4 percent for the period 2005 to 2012.
>
> The size of the other gas analyzers (Ultraviolet, thermal conductivity, PID, FID, Chemiluminescence and Laser) in 2005 was $74.8 million."

3 Characteristics of the gas sensor market

3.1 Fragmentation

The UK gas sensor market is fragmented and populated by small companies.
Recent consolidation has brought some UK companies into US ownership, which is starting to weaken the UK sensor technology base.
The UK gas sensor community is well served by a number of networks and groups.

It is generally recognised that the sensor market is fragmented [1], including that for gas sensors. For each market sector there may be as many as ten measurands (ie, the gas to be measured) for a range of applications, each with different requirements of sensitivity, reliability, gas selectivity, cost and market volume. To meet market requirements a range of technologies will often be used.

The UK gas sensor industry is characterised by small companies who excel in one or two technologies and markets. Companies that sell components have often started by concentrating on one technology, and then grown by extending their product line to meet new application requirements of existing customers and extending into similar technologies. Sensors tend to be manufactured in the UK under tight company control and arguably represent the area of highest technology input. Components making up the rest of a detection system (electronics, enclosures, sampling, etc.) are often outsourced but under UK design control. Companies that sell complete systems are often expert in understanding and meeting user needs within a very small niche application or technology.

Larger global companies encompass a wider range of technologies and in some cases (for example, Siemens) sell both components and fully developed instrumentation and products containing their sensor technology. In the past years there has been some consolidation of gas sensor companies in the UK, for example Halma, already owning Apollo and Crowcon, purchased Telegan. City Technology was bought by First Technology, who then added Sensoric and BW Technologies. Last year Honeywell, who already owned Zellweger Analytics, purchased First Technology, increasing its gas detector portfolio to four gas sensor companies and three gas instrumentation companies.

Acknowledging the fragmentation of the gas sensors market has been an important foundation of this study. We accept the need to work with and embrace this characteristic of the industry, and to ensure that conclusions and recommendations remain consistent within this fragmented industry. Organisations such as the Gas Analysis and Sensing Group (GASG), originally established by the DTI, the Council for Gas Detection and Environmental Monitoring (CoGDEM), Optocem.net KTN and the Sensors KTN play an important role in bringing together individuals and companies who each have expertise in different market and technology niches. The UK is unique in having these groups serving the gas detection market. We have been able to draw on their collective knowledge in assembling this document.

3.2 Development costs and risks

The small size of many niche markets makes it difficult to justify the scale of investment needed to generate a step change in technology, rather than funding incremental technology developments. Step change developments must be justified by applications in a range of market niches.

There are indications that the consolidation of some UK companies into US ownership may undermine the UK's technology base for the next generation of sensors, with manufacture sourced back to the US parent company. Recent UK government investment has improved the MNT infrastructure landscape, and there is a window of opportunity for UK sensor manufacturers to exploit this capability through product development.

The Intelligent Sensing Faraday Intersect Partnership (now Sensors KTN) completed a study in 2004 to estimate the cost of bringing a new technology to market [3]. Their findings, based on a model of development phases by Taylor [4], are shown in Table 2. The total investment of £1.4-3M is considered to be an underestimate of the true cost.
In the early stages the risk of losing one's investment is high, with each further stage of the development process having a decreasing risk level. Investors must take into account the probability of success as well as the time lag before the investment returns a profit and positive cash flow.

Phase	Time / months	Investment / $M	Milestone
1 Initial R&D. Limits are available capital, allowable risk, projected profit.	12-36	0.3-0.5	Lab prototype
2 Technical review and design concept selection. Limits are availability of assessment skills.	4-6	0.1-0.3	Development, commercialisation plan
3 Final design testing	6-10	0.3-0.6	Final design
4 Manufacturing prototype assembly and testing	6-10	0.3-0.6	Manufacturing prototype
5 Transfer to manufacturing	4-6	0.3-0.6	First production runs
6 Final production and product release	2-4	0.1-0.3	Market release
Total	**36-72**	**1.4-3**	

Table 2. Approximate times and costs assigned to different development phases for a new product. Data taken from ref [3], based on [4].

The small size of many niche markets makes it difficult to justify this scale of investment to generate a step change in technology, rather than funding incremental technology developments. Our approach has therefore been to identify developments that could impact across multiple markets, increasing the chance of success in at least one and hopefully many markets.

It was for this reason that we developed a matrix of market sectors versus applicable technologies, shown in 0. Sensor technologies that have application across large number of sectors are priorities for investment.

3.3 Generic market trends and drivers

MNT gas sensors have the potential to offer advantages over existing sensors for volume cost, compactness, power consumption and responsivity, and thus have the potential to open up new application areas, displacing existing technologies or creating new markets. The feasibility of displacing existing sensor devices and systems depends on the balance between investment costs and performance or functionality gain. However, in many cases the cost and uncertainty of moving to a new technology outweighs anything but a very substantial performance or cost advantage that may strengthen market position or open up new markets.

New markets for MNT gas sensors have been highlighted by the six technology strategies published by the DTI Technology Strategy Board on 26 April, 2006. These are based on the EU Seventh Framework Programme (FP7) which has specified the following specific research programmes: Health; Food agriculture and biotechnology; Information and communication technologies; Nanosciences, nanotechnologies, materials and new production techniques; Energy; Environment (including global warming); Transport (with aeronautics); Socio-economic sciences and humanities; Security; and Space. An MNT strategic area is bioscience and healthcare: ‘personalised therapy’, where cheap and widely available diagnostic breath sensors combined with knowledge-based systems would enable personal diagnosis of illness, would be attractive to consumers and may help ease the burden of an ageing population on the healthcare system. The environment and security categories include the safety and welfare of individuals, including protection from chemical and biological attack as well as from airborne pollutants. Existing sensors and sensor systems in these areas do not meet requirements in terms of performance, cost, ease-of-use and portability.

3.4 The role of legislation

Legislation can energise an application area and is a recognised success factor for the companies in that market. Standards often follow application development, increasing market size and consolidating market positions.

Companies have cited legislation as a success factor, particularly in the areas of environmental monitoring and health and safety. City Technology Ltd has noted the importance of the UK Health and Safety at Work Act (HASAWA) 1975 during its early development phase. This is an example of high level, goal-setting legislation that influences the way in which users manage their businesses. The Health and Safety at Work Act does not specify how companies should establish a safe working environment, but indirectly establishes a need for measuring specific gases.

In contrast, McGeehin [5] has pointed out that standards for sensors and systems often follow new applications. Such standards prescribe the performance requirements of sensors for particular measurands, once the application is established. An example is BS EN 61779 for portable detectors of flammable gases and vapours, used in support of compliance with the HASAWA. In these cases legislation increases the market size and consolidates the positions of existing suppliers.

Figure 2 illustrates a decision process for large users. It should be remembered that legislation is by no means the only driver: a need for monitoring can be decided by a user in the absence of legislation, especially for very large users that consider themselves to be at the forefronts of their fields.

We might conclude that companies with a timely combination of a developed technology base and an application that meets an emerging need will be successful, but the bigger question is how to increase the chance of success without increasing risk. One strategy is be to use good relations with existing users in order to better anticipate their reactions to forthcoming legislation and technology. It is hoped that by sharing information as a gas sensing community (for example via the roadmaps in 0) we might foster this awareness.

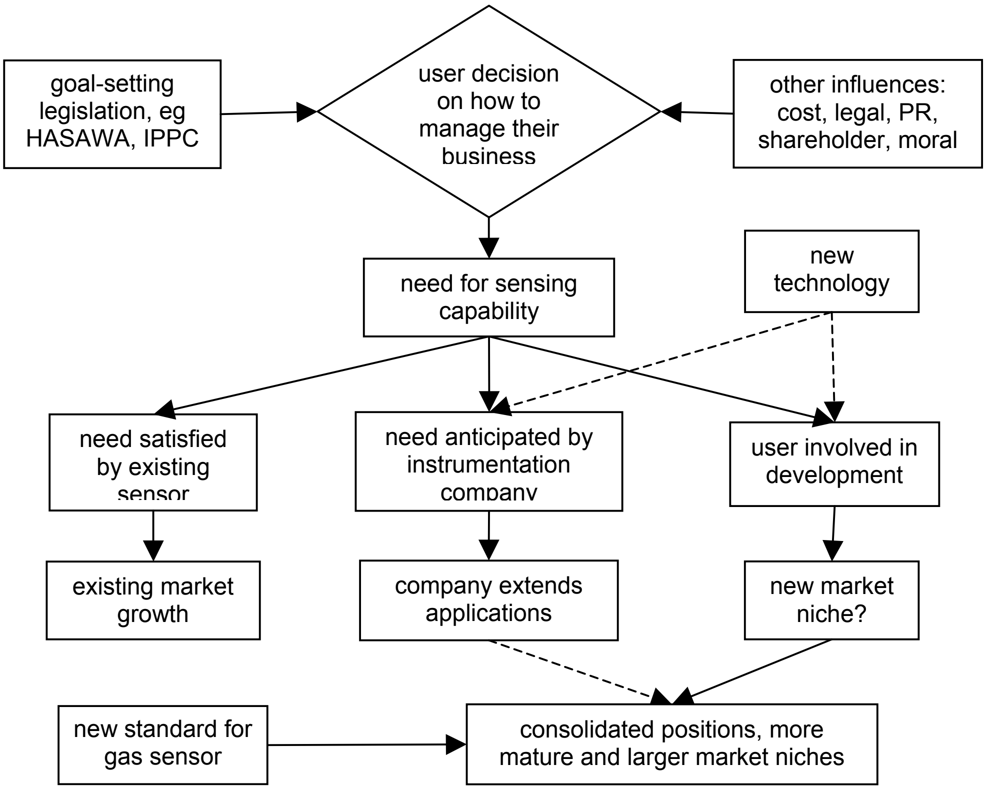


Figure 2. Simplified chart showing the effect of legislation as a driver for large users.

3.5 UK funding and support for gas sensor technologies

The UK is strong in gas sensing.
Total EPSRC expenditure on academic research projects related to gas sensing runs at around £1500k pa. Industrial expenditure on R&D is between 2% and 10% of sales.
The 2002 Sensor Foresight study considered the UK to be weak in microengineered sensors, but government MNT investment has improved the infrastructure landscape.

The UK Sensors Foresight study reported that EPSRC's estimate of annual investment for all sensor research was £13M, with gas sensing making up 15 out of 255 projects spread over an average of 3 years [1]. Assuming that projects in gas sensing are of similar size to projects in other areas, this means that in 2002 a total of £760k was spent on academic gas sensor research projects. Our analysis, based on public domain information available through the EPSRC website, shows a higher total, illustrated in Figure 3, because we include work on basic technologies (for example, optical components and semiconductor oxides) that were not explicitly aimed at developing gas sensors, but had a clear downstream application to gas sensing. Research funded by other Research Councils (NERC, BBSRC and MRC) has not been included.

The UK Foresight study also noted two salient points:

(i) The UK was considered weak in microengineered sensors.
This might have been due to a lack of silicon manufacturing capacity, in which case recent investment in facilities may have rectified this situation. Groups such as CAPE in Cambridge and Warwick Electronics Department are addressing this shortfall.

(ii) A large body of research on optical sensors had been under-exploited.
This may be due to the high capital cost of many optical systems compared with their traditional counterparts, limiting the niche areas in which they are beneficial.

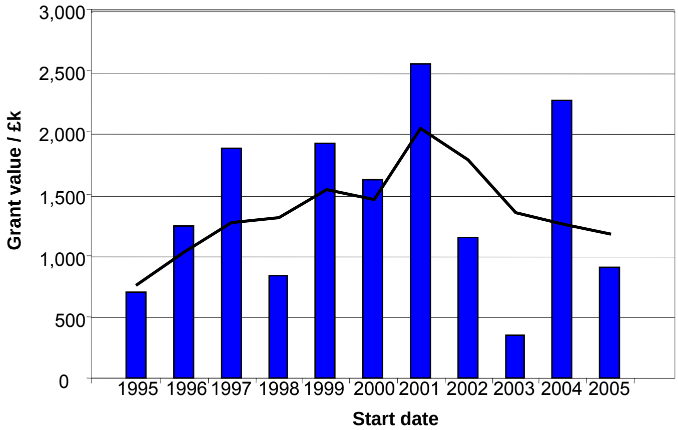


Figure 3. Breakdown of EPSRC grants with a main application in gas sensing, taken from public domain information on the EPSRC website. Grants are organised by start date and the trend line indicates a three year moving average, chosen because grants typically last for three years.

Table 3 shows the level of R&D investment reported by large gas and other sensor manufacturers. Gas detection is one of their target markets, but is not the only target market for these large companies.

Company	R&D investment / £M [a]	R&D : Profit / % [b]	R&D : Sales / % [c]	Total sales / £M	Profitability / % [d]
Honeywell	477.63	42.4	3.6	13,300	8.5
Tyco International	408.36	15.6	2.0	20,400	12.5
Invensys	124	-	4.2	3,000	-1.6
Drägerwerk	73.51	104.1	6.8	1,000	6.6
Hamamatsu Photonics	44.58	12.4	22.3	200	11.8
Spectris Group	34.9	66.4	5.7	612	8.6
FLIR systems	23.85	42.8	9.5	250	22.3
Kidde	17.00	15.9	1.7	1,000	10.8
Halma	11.7	26.2	3.9	300	15.0
e2v technologies	5.42	55	5.6	100	10.1
The companies below are now part of the Honeywell group					
First Technology	7.5	49.7	6.3	120	12.7
Zellweger Analytics	1.59	70.5	5.6	30	7.9

Key
a R&D investment for the latest financial year in £M.
b R&D as % of operating profit.
c R&D as % sales = R&D intensity.
d Operating profit as % sales = profitability.

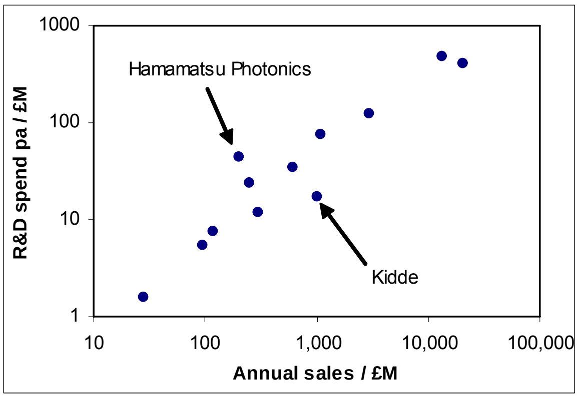
Table 3. Indicators of R&D investment for a selection of companies involved in gas sensing and instrumentation. Taken from the DTI R&D scoreboard, 2005 [6].

It is useful to plot R&D spending vs. annual sales, revealing a slight trend where the higher the turnover, the more spent on R&D, but this is generally a smaller proportion of sales.
We can conclude that either:

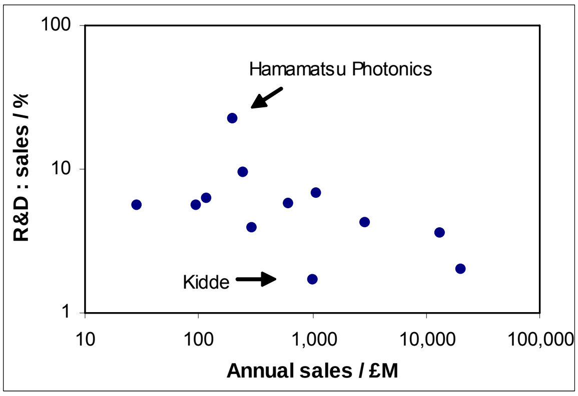
i) Smaller, less mature companies spend a greater proportion of their income on R&D, or

ii) Gas sensing is R&D intensive and larger companies are more likely to rely on other industries in their portfolio to maintain turnover.

Most companies are re-investing between 15% and 50% of their profits and between 2% and 10% of their sales into R&D. Photonics based companies tend to be more R&D-intensive than those based in other technologies.



(a)



(b)

Figure 4. Larger companies tend to invest more in R&D (a), but this can represent a smaller overall proportion of their sales (b).

Pre-competitive development is the most urgent area requiring investment so that the gas detection community can take advantage of recent investment in manufacturing infrastructure (FP7 priority) Such development may require additional basic research such as process control or nanostructure reproducibility, yet would yield widespread benefits in many sectors including gas detection.

Government level funding is required because individual SMEs simply can not justify the scale of investment required in a technology, especially in generic areas that also benefit their competitors and other market sectors. We should take advantage of mechanisms that enable companies to come together to steer projects to their mutual advantage. Applied R&D may also be seen as too incremental or insufficiently disruptive to win funding through EPSRC's competitive "responsive mode" funding. Therefore where basic research is needed, specific calls or schemes may be needed.

We recommend the following measures to help fill these gaps.

- Establish a short series of one-day workshops to identify research challenges, bringing together different skill areas to inspire new thinking, following a smaller scale version of the Future Intelligent Transport Systems (FITS) model used by EPSRC.
- Increase CASE awards in areas of common opportunity, specifically allocated through Sensors KTN. CASE awards are a popular and successful mechanism to promote R&D that is relevant to SMEs, but they can be hard to secure in some

RDAs. This measure would ensure their use by industry sector, possibly replacing some regional allocation.

- Develop funding mechanisms for Universities and Government Research Associations to engage with a diverse industry to work on the next steps to commercialisation – perhaps a DTI Knowledge Transfer version of EPSRC's successful fellowship scheme. Funding for people helps ensure continuity across a programme of shorter projects and allows researchers to develop continuing relationships with their communities.
- Use the mechanism of bid requests to solve specific needs for government departments such as the MOD, DEFRA, EA, modelled on the USA SBIR contract procedure. Use of contracts would promote product development specific to government needs and should be viewed as a supplement to grants which remain the cornerstone of academic-industry cooperation.
- Set a Global Watch mission for gas sensors to North America, Russia or the Far East. Target our technology priorities, to open the UK's eyes and to test our roadmap conclusions against the global context.

4 General technical trends

Table 4 shows a simplified breakdown of commonly used gas detection technologies, the gases to which they respond and typical applications. The table has been simplified and expanded from a similar version in reference [26]; further detail on different types of optical sensors can be found in that publication.

Sensor technology	Measurand	Typical applications
Catalytic (Pellistors)	Combustible gases (non-selective)	Fire and explosion prevention, especially in enclosed spaces
Wet electrolyte (Electrochemical)	Oxygen, toxic gases and environmental pollutants	Occupational health and safety, combustion and emissions monitoring, medical
Solid electrolyte (zirconia)	Oxygen	Industrial combustion monitoring and control, vehicle exhausts
Metal oxide semiconductor	hydrocarbons (HCs), CO, O_3, H_2S, organic vapours, odours.	Leak detection, health and safety monitoring, cabin and indoor air quality
Paramagnetic	Oxygen	Medical, process control and monitoring
Thermal conductivity	Binary gas mixtures (often a known gas in air)	Leak detection, process control
Flame ionisation detectors (FIDs)	Methane, organic vapours (non-selective)	Landfill site monitoring, occupational health and safety
Photo-ionisation detectors (PIDs)	Organic vapours (non-selective and excluding methane)	Occupational health and safety, indoor air quality, security
NDIR (non-dispersive infrared)	Many IR absorbing species, e.g. methane, CO_2	Stack emissions, health & safety, food storage & processing, medical, ventilation control
Tunable diode laser absorption spectro-scopy (TDLAS)	Small molecule IR absorbing species eg CO_2, CO, CH_4, NO, small HCs, H_2S, NH_3, O_2	Emerging high value uses (stack emissions, trace moisture analysis etc.)
UV absorption spectroscopy	UV absorbing species: O_3, H_2S, SO_2, BTEX. Excludes alkanes	Ambient indoor and urban air quality (AQ) monitoring (fixed and transportable instruments)
UV fluorescence	SO_2 (modified for H_2S), BTEX	Outdoor and urban AQ monitoring
Chemiluminescence	NO_x	Outdoor and urban AQ monitoring

Table 4. Established gas sensors and their uses.

We have identified general trends in gas detection technology:

(i) Widespread use of cheap, single point sensors with either sensitivity to a broad range of gases or reasonable selectivity to one gas.

(ii) Smaller, lower power traditional sensors, with higher sensitivity to target gases.

(iii) Displacement of traditional solid state or electrochemical sensors by optical sensors in applications where a high degree of gas selectivity is needed, coupled with less frequent calibration requirements where cost is not critical.

(iv) Technologies able to discriminate specific gases in both well understood environments (eg process control) and complex environments (eg volatile organic compound (VOC) measurement, homeland security).

The technologies able to support (i) and (ii) will be used in the emerging networked sensor market.
The technologies able to support points (i)-(iii) are developments of existing generic techniques that are described in Table 4.

New technologies are emerging in response to needs described in point (iv), summarised in Table 5.

Sensor technology	Measurand	Typical applications
Micro (optical) spectrometer	UV or IR absorbing gases listed above	Process control (high concentrations, known matrix)
Micro mass spectrometry	VOCs	Process control, homeland security, air quality
Micro gas chromatography		
Widely tunable solid-state lasers	Small molecules with consequently narrow optical absorption bands	Emissions and stack gas monitoring, process control, small VOCs, odours
Differential Ion Mobility Spectroscopy (DMS, FAIMS)	Volatile organics, explosive and drug residues [7]	Homeland security, occupational health and safety, process control

Table 5. Emerging gas sensors able to discriminate between multiple gases.

As well as technologies specific to gas sensors, several important supporting technologies and components will fuel growth in gas sensor development. Gas sensor advances will ride on improved technology in the following fields:

- networked communications
- batteries
- displays
- computer electronics

We are already seeing use of mixed signal ASICs and FPGAs to improve sensor sensitivity, error and selectivity. The pace of change in battery and communications technologies gives instrument companies technology opportunities that must be cherry picked, and the gas sensor market must adapt what is available from these fast-moving telecoms and consumer markets.

5 Markets for gas detection and measurement

5.1 Introduction

Gases are necessary to humans to stay alive, remain healthy and for our industries. Therefore, it is no surprise that the gas sensor industry is diverse, including domestic safety, industrial safety, personal comfort and health, security and medical diagnostics.

5.2 Domestic CO, flammables and fire

Drivers are competitive advantage by cost saving and/ or higher specification products, especially reducing false alarms.
Significant price constraints arise from strong competition and the “grudge” nature of the purchase.
The world market for fire detectors was estimated to be around £2B in 2003.

Fire detection primarily uses non-gaseous indicators (smoke, heat), but gaseous emissions are also recognised as possible, though not well-characterised targets. Carbon monoxide is a recognised product of many but not all nuisance fires and fire detectors incorporating CO sensors are being increasingly deployed. Characterisation 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 useful targets may be small organic molecules including:

(i) methane, ethane, ethylene and acetylene

(ii) partially oxidised derivatives including formaldehyde, formic acid, acetaldehyde and acetic acid

(iii) possibly some aromatics and inorganic species such as NO_x, SO_x, HCl and Cl_2. The sensor types required for fire detection will expand as targets are 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 “nature of the purchase. Sensors are constrained by the need for low power (with power less than 2mW), 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 [8], 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 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 non-electrochemical devices.

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, possibly piggy-backed onto fire detection. There is increasing (US) state legislation requiring CO detector deployment in residential and other occupied buildings, plus activity by advocacy groups that 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 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 2034 [9] 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, being more directed by commercial safety and heath and safety requirements. However, it is a common building requirement in Asian countries such as Korea and in specific industries such as leisure craft (including boats).

The world market for fire detectors was estimated to be around £2B in 2003 [10], of which the US represented 38% and the 7 largest EU countries represented 28%. The market for ionisation 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%.

5.3 Automotive

There is a relentless downward pressure on costs, but volumes are large enough for micro- and nanoprocessing economies of scale.

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. On average, 30 to 40 sensors of all types are utilised in a typical economy car. For luxury models, where the electronic content is already high, the number of sensors is already around 120 and set to grow further.

An increasing number of these sensors, including gas 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, the automotive sector is attractive in that manufacturing volumes are large enough to take advantage of micro- and nanoprocessing economies of scale. Bosch and similar physical sensor suppliers are now active in the gas sensor automotive market, as discussed below.**Cabin air quality**

Detection of target gases (CO at present, VOCs in future) gives efficient control of HVAC recirculation levels.

Increased drive 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 now uses an air quality sensor located in the main air inlet duct of the HVAC system. When the threshold for the target gases (at present CO) is reached, the sensor tells the HVAC system to switch to recirculate and prevent further ingress of pollutant. In the future this system will be extended to monitoring NO_x and VOC nuisance odours. These microhotplate sensors are currently being supplied by companies such as MicroChem SA in this very competitive niche sensor market.

5.3.2 Exhaust gas emissions

Candidate sensors including resistive metal oxides are being evaluated, but are currently limited by cross-sensitivity to other gases and extreme environment survivability.

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, O_2, CO, CO_2 and NO_x.

Lambda sensors use a zirconia (or sometimes titania) element to monitor oxygen in a car's exhaust. Oxygen concentration is used by the engine management system to control the fuel/ air mix in the intake. Bosch, the market leader, claims to have manufactured over 300M sensors since inventing Lambda sensors in 1976. All new European cars are fitted with a minimum of two Lambda sensors.

Due to more stringent emission standards for heavy vehicles, the EU automotive industry has decided to adopt the ammonia selective catalytic reduction gas after treatment process, which involves the addition to the exhaust of ammonia-forming substance such as urea-water solutions. To optimise the conversion process, a closed loop control system using an ammonia exhaust gas sensor is desirable, and several possible types of sensor are being considered by the industry, including those based on resistive metal oxides. These types of sensors are currently limited by cross-sensitivity to other gases.

5.3.3 Particulates

Particulate sensors optimise the lifetime of exhaust filters that must be regenerated through heating.

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.

5.4 Industrial health and safety

We have a good understanding of target species, but less so of matrix interferents.
Sensor technology must be fail-safe and auditable.

Gas sensor systems are designed to alert personnel of possible health and safety hazards to both themselves and to their workplace. The chemical process industry and energy industry are particularly safety conscious, handling large quantities of both toxic and explosive materials including gases and vapours. Our roadmaps include utilities' response to leaks from the gas distribution system. In general, requirements are characterised by a good understanding of the target species in a relatively controlled environment, but matrix interferents 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 energised, so validation systems 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.

Different countries have different management cultures, for example US companies adopt prescriptive standards, whereas UK procedures are often based on risk analyses, offering more scope for flexibility in achieving a goal. For example, 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.

In the past, larger companies have developed safety systems and robust internal standards that are more stringent than international standards, pushing their internal standards to 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 might stifle innovative product development in smaller companies.

5.4.1 Flammable leak detection

Very low power catalytic sensors or optical detection of hydrocarbons is at the top of the wish list.
Development of a ppb detector for odorants is also underway.

Most flammables are alkanes, subsequently burnt to provide power. Methane is an important target gas 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%vol in air for methane, compared with only 2.8%vol in air for ethane [11]. 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.

There are different requirements and drivers for permanently installed and portable detectors, as summarised in two different diagrammatic roadmaps. Permanently installed monitors must be sited carefully to maximise 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 top of the wish list for many gas detector manufacturers.

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, as 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 ppb mercaptan detector is underway, but needs more concentrated research to achieve market requirements in a reasonable period.

5.4.2 Toxic gases

Regulatory limits vary, but are linked by a global understanding of toxicity levels, with slow convergence to a common limit. Emphasis is moving from short-term to long-term exposure.

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 EH 40 [12] as Workplace Exposure Limits (WELs). Drivers in different countries are different, but are linked by a global understanding of toxicity levels, with a slow convergence of permitted exposure levels.

Historically workers were 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 long term damaging. 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 to the measurement of the BTEX compounds (see BTEX roadmap), which have very different toxicities but often similar levels of sensor response.

5.4.3 Asphyxiants and oxygen

Oxygen sensors require high accuracy and continuous operation.
New standards follow increased emphasis on CO_2 monitoring, for example near boilers.

Oxygen is the most important gas for humans; our bodies need oxygen levels between 19% and 23% oxygen; the oxygen concentration in dry air is normally 20.9% oxygen. 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 oxygen concentration with good accuracy from -30°C 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 dilution of oxygen, a serious health concern. New standards are being written to enforce the need to monitor CO_2, especially where boilers are used, either in homes or industry. A draft British standard for CO_2 portable 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 recognised 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 oxygen concentration can be dangerously low. CO_2 is toxic at high concentrations (as demonstrated in the Apollo 13 moon mission).

5.5 Process industries and process control

The process industries are strong in the UK and have historically driven new developments, but are under increasing cost pressures. New environmental legislation will drive emissions measurement.

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 employ combustion processes.

These industries are major users of sensor and control instrumentation which fulfil 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 under mounting financial, legislative and other pressures:

- 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;
- 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 ("Feed back combustion control" and "Feed forward combustion control, fuel quality and metering" diagrammatic roadmaps);
- ***Environmental legislation*** and emission trading schemes will necessitate improved stack emission monitoring technologies ("Stack emission monitoring" diagrammatic roadmap);
- ***Public concerns* and legislation** will require improved odour monitoring and control ("Odour monitoring" diagrammatic roadmap);
- ***Health and safety*** considerations will result in sensors for real-time monitoring of toxic organics in the workplace ("BTEX" diagrammatic roadmap);
- Continual drive ***to improve productivity***, combined with rising raw material costs will drive the development of improved techniques for characterising feedstock materials ("Feedstock processes" diagrammatic roadmap);
- 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.

5.5.1 Food quality, production, transportation and storage

A conservative industry that has a tendency to 'get by' on existing practices. Measurands include contaminant origins, micro-organisms, allergens and waste monitoring, many of which are not gases. The 'electronic nose' for monitoring freshness has not realised its early promise.

The food processing industry is characterised by the need for rapid development of new products, so tends to be product-led rather than process-led: there is a tendency to 'get by' on existing practices rather than risk the introduction of new technologies that may not be readily applicable to new or improved product lines. However, there are some generic needs in the industry that may be addressed through the application of new technologies and would find ready acceptance if the sensors were reliable and inexpensive. Those relevant to gas sensors include:

- Freshness and other aspects of quality monitoring (see below)
- Detection of micro-organisms (may result in generation of a distinctive gas or mixture of gases; otherwise a DNA-based approach of traditional bacteriology is likely to be used)
- Foreign body/contaminant detection—mostly not gases
    - Must be non-invasive to reduce risk of further contamination
    - Plastics and insects in particular are not readily detected using current techniques
    - Tracing the origin of contaminants (e.g. lubricants) to a point in the production process is important
- Detection of allergens that 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. See also §5.6.4
- Monitoring environmental and process control waste (see also §5.6.4)

Useful indicators for quality, e.g. in connection with fish spoilage (volatile amines), fruit ripening (ethylene) and wine production (alcohols) are often gases or vapours. Gas sensors therefore provide a technology for rapid quality assessment. However, successful application requires some knowledge of the complex mixture of components likely to be present in the gas phase, and this knowledge still requires both academic and industrial research. The 'electronic nose' approach has not been successful, at least not until now, due to the complexity of food aromas, typically leading to misleading sensor responses, and the expense and difficulty of calibration of these instruments. Some of the issues are currently being addressed through the application of MNT.

5.5.2 Bioreactors and landfill

In closed bioreactors, target gases include oxygen, ammonia and carbon dioxide, with secondary interest in methane, hydrogen and some important ions such as acetate vapour. In landfill, targets are methane, hydrogen, heavier alkanes and VOCs.

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

(a) vessels in which microorganisms 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—these are termed here as "open" and "closed" bioreactors, respectively, also known as thermodynamically open and closed systems.

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 production capacity. Demand for cultured organs and tissues such as skin is also pushing the development of bioreactors, in which growth proceeds by division of precursor cells. 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, so losing a batch is potentially very costly, and monitoring is vital to ensure batch success.

At present the 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 so 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 non-ionized, volatile forms. Near infrared spectroscopy and semiconductor gas sensors are currently popular.

Open bioreactors

Pressures on available landfill volume in many countries have led to strong increase 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 is an informative way of ensuring that the process targets are kept on track. Monitoring the gas profile of methane, hydrogen, heavier alkanes and VOCs allows us to age the landfill, which is important for district council determination of the stage of the landfill. Spectroscopy is being developed because it can monitor a range of compounds simultaneously.

5.6 Air quality

5.6.1 BTEX (benzene, toluene, ethylbenzene, xylene)

Toxicity levels for specific BTEX compounds are very different, yet they are difficult to measure separately; research is needed to select the best measurement technology. Benzene levels frequently exceed EU limits (1ppm), especially at petrol stations.

The family of aromatic and polyaromatic hydrocarbons can be measured separately using laboratory analytical equipment, but it is difficult to separate BTEX mixtures using field or on-line methods; unfortunately. the individual carcinogenic impact for each hydrocarbon is very different. Specifically, benzene is classed as carcinogenic at the 1ppm level, while other aromatics are not dangerous until the concentration exceeds hundreds of ppm. The BTEX family is present in common situations such as petrol stations and fuel tanker bunkers, where the benzene level frequently exceeds EU legislated limits. Detecting benzene is a difficult challenge, with disposable stain tubes the only crude technology currently available, but 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, which is not trivial: deconvolution of the spectra will be a challenge. Research is required to select the preferred technology, and in parallel to determine whether the market volume and regulatory market pull is adequate for the investment costs.

5.6.2 Outdoor air quality and emissions monitoring

Emissions monitoring is best done at source, using dedicated gas detectors integrated with small weather monitoring stations.
New EU legislation requires continually audited improvement of on-site emissions.
Enforcement agencies need more sensitive and geographically wider gas detection networks for remote detection of automotive and urban air emissions.

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.

Dilution from the emissions source is rapid, so measurement of the emission is technically easiest at the source, with cross-stack instruments designed to detect particular measurands in a reasonable well-known background matrix. See the “Stack emissions monitoring” roadmap. 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 CO_2 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 measurands are based on their concentration at a fixed distance from the source, the position selected by where they can cause harm to staff or residents.
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 ppb level;

(ii) To make cross-stack measurements and combine them with weather monitors and dispersion modelling software.

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 3-d anemometry at the point of emission or at 10m height (the standard height for dispersion models).

Recent EU Integrated Pollution Prevention and Control (IPPC) legislation now requires companies to show a continuous improvement in their emissions, not just to stay within defined limits. Acceptable levels of pollution are determined by industry best practice, therefore setting a flexible standard that is intended to move ever downwards in emission levels, following industry leaders. The drive is for self validation, forcing companies to demonstrate the validity of their data, which may require periodic independent audits. The first step towards this European model is the UK MCERTS programme. Government monitoring requires low level (ppb) detection of a range of indicative measurands, usually with a single instrument for each target species. See the “Outdoor air quality” roadmap. 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 (ppb) detection;

(ii) lower capital cost to afford wider geographical coverage with a larger network of monitoring stations.

Automotive emissions are measured by government enforcement agencies by controlled sampling of the exhaust (eg UK annual MOT test), but this does not accurately reflect emissions in use. Therefore there is also increasing interest in monitoring emissions at the side of the road, in which case again target species must be measured relative to the main gaseous emission, CO_2. Automotive emissions can be measured using remote optical detection as cars drive past. See also section 5.3, *Automotive*.

Certain measurands still present major challenges for monitoring. Heavy metals require improvements in sampling as they can be present in many phases, within airborne particles or as vapour (eg Hg, lead). Molecules such as dioxins also present sampling challenges because they need detection at sub ppb levels and yet are very “sticky”. The Stack Testing Association (STA) leads the UK by training operators in stack monitoring, and writing standards and establishing best practice.

5.6.3 Indoor Air Quality (IAQ)

Targets include ozone, nitrogen oxides, cleaning solvents and formaldehyde.

Both asthmatics and at-risk employees 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 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 detection of organic classes such as aldehydes or alcohols through NIR spectroscopy is needed, to show whether it may be possible to detect some classes of VOCs at ppb levels with reasonable cost.

5.6.4 Asthma in the home

Targets are ozone, nitrogen oxides and airborne bioparticulates, the latter being a major challenge.

Asthma and rhinitis are human response 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 ppb level, but lower cost, more prevalent sensors are required. Detection of airborne bioparticulates may remain a technical challenge for years to come; real time monitoring of biological systems can use:

- molecular imprinting for specific proteins or simple sensitisers (MIPS);
- toxic particulate broadband detection by monitoring respiration in simple or complex biological systems;
- electrochemical or optical detection using synthetic enzyme sites.

5.6.5 Nuisance odours

Challenges are point detection of offending gases and mapping dispersion from complex sites.

High throughput site models could drive the gas sensors market by improving applications knowledge.

This section considers odorous emissions from sites such as landfill and waste water treatment works (WWT), which can be a nuisance for residents, and are considered in the "Odour monitoring" diagrammatic roadmap. Problems arise with point detection of the offending gases and with mapping of the gas plume using either predicative computer models of the site, working from local wind and precipitation measurements or using a network of point sensors feeding into a computer model.

Odours that are excluded form this section include the odorants that are added to natural gas in the distribution system (see section 5.4.1*, Flammable leak detection)* and odour monitors used in food quality control (see section 5.5.1 *Food quality, production, transportation and storage).*

Site operators are driven by a need to:

(i) defend claims of nuisance odour, requiring a zero trace and / or quantified level of odour at a particular time in the past and 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 sites often comprise a non-odorous carrier gas in large concentrations, together with smaller levels of odour 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 characterising the composition of the odour (eg by measuring mercaptans) close to its source, measuring the concentration of the higher concentrations of odourless carrier gas (methane for old landfill matter and WWT, H_2 for recently disposed landfill matter) at the site perimeter, then modelling the gas dispersion using wind monitors and software models. The latter requires a good understanding of the topology of the site, which can be costly to develop and may only have been achieved to date for "problem" sites. Developing high throughput site models, possibly based on newly available digital elevation maps from satellites, could provide an improvement in applications knowledge that drives the market for gas sensors.

5.7 Homeland security

A technically challenging area that has driven much R&D, but translation into solutions and sales remains uncertain.

In recent times, the level of attention paid to homeland security has risen rapidly, generating a rapid increase in R&D expenditure in academia and industry, and helping to establish the case for a number of start-up companies. Translating this requirement into markets and sales remains more uncertain until specific niche markets emerge.

Homeland security is the most technically challenging of all gas detection markets. The technologies suited to homeland security applications are few, given the rare combination of generally fast-moving media (humans and baggage), variable environments (airports and the open field), the low concentrations of the materials present in the ambient air or 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 derivatives of high resolution (and expensive) laboratory techniques, for example Ion Mobility Spectroscopy. The specific opportunities and advantages presented by MNT are summarised below for explosives, drugs, and chemical, biological or nuclear attack.

5.7.1 Explosives and drugs

Opportunities may lie in improving traditional policing methods. MEMS based optical absorption sensing and micro-mass spectrometry with increased sensitivity could be of interest. Terahertz (THz) spectroscopy for standoff detection of explosives is a strong contender.

In the USA, the major homeland security spend immediately following the events of 9/11 was focused on explosives detection at airports. A small number of chemical sensor or bench-sized spectroscopy systems is 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 pose major problems to the countries that produce and consume them- both to the user's health, and in the encouragement of international crime. The existing technology is essentially supported by IMS type systems, with challenges as described above, but the user base has limited confidence in technology and other policing methods are perceived to be more reliable: questioning suspects, identifying behaviour patterns or 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 with traditional policing methods and improving their efficiency, especially at the point of investigating a suspect criminal or item of baggage.

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

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 stand-off 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 bench top type gas detectors without dilution. Developments in standoff detection would also solve this problem.

(ii) ***Improvements in discrimination ability*** since highly sensitive, broad band 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 [13], 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.

However, 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.

A diagrammatic roadmap has not been prepared for this area, because the field is considered event – driven, and the real market pull has not yet emerged.

5.7.2 Chemical, biological or nuclear attack

First responders need networked sensors with a range of measurands of interest to characterise and map releases after the event: known high toxins, hazardous industrial chemicals, DNA or RNA based identification of biohazards and alpha particle identification.

This class of material can be seen as having the properties of being both harmful and easily transported or ingested. 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 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 first responders.

It is likely that the core sensor capability for chemical analysis will, as in section 5.7.1, involve a combination of MEMS sensors, and the use of microfluidic 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 more traditionally used in industrial health and safety.

Biological detection emphases rapid identification of the DNA or RNA of the airborne species through rapid sequencing, and to this end a major programme is underway in the USA.

For nuclear materials, the detection of radioactive emissions will be achieved through “gamma cameras” utilising sensitive optical detectors and spectrum-changing scintillators. In contrast, the direct detection of radioactive materials is unlikely to be amenable to MNT other than by use of a sensing process using standard inorganic chemistry. Alpha particle detection could be used after seizure of the material, to allow fast determination of the radioactive material. Beta particles are rarely specifically measured because most materials that generate beta particles are also picked up by gamma detectors.

With all of these sensors, communications via a network is a key element, and so low cost integrated 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.

5.8 Medical diagnostics

Basic research is required to determine gaseous markers of disease and their variation in normal populations, between individuals, and in any one individual.

The opportunity to determine health using breath analysis is growing continually. Capnography is the measurement of exhaled breath as a function of time, and is a useful diagnostic tool, especially in anaesthetics. For a single exhaled breath, the final gas concentrations reached are considered to give a direct indication of the partial pressure of those gases in the blood. In its simplest implementation, variations in carbon dioxide levels are also used to monitor breathing.

Newer applications include detection of *H. pylori* in the gut – a precursor of stomach ulcers. For diagnosis, the patient must drink a solution of food containing ^{13}C, which is subsequently metabolised by *H. pylori* to $^{13}CO_2$. Sensitive optical spectroscopy can be used to determine the $^{12}CO_2$: $^{13}CO_2$ ratio. At present the high capital cost of the test equipment demands that testing is performed in specialist units in hospitals. It should noted that in this example, gas detection gives no information about the nature of the bacterial colonies. More precise information is required for a definitive diagnosis and at present is obtained by endoscopy. Gas sensing can be used in screening to give an indication that further tests are necessary, and is vulnerable to displacement by future measurement alternatives.

One long term goal is to provide GPs with non-invasive analysers that detect the out-gassing from either the gut or lungs of by-products of chemical / biochemical processes that mark diseases. Many years of basic research are required to determine these gas markers, their significance with respect to the normal population, required detection levels and interferents. Once the gas markers are defined by research, then gas detector manufacturers must step in, providing either marker-specific hand-held devices or spectrometers with signal processing to detect the required gas.

Variations in some exhaled gas marker concentrations (for example, ethane) have been anecdotally observed to vary between individuals and for one individual at different times of day or following exercise [14]. If substantiated, such variations could preclude these techniques from being used in general population screening, but gas analysis might still be a useful method to monitor changes within a single patient, for example during intensive care.

5.9 Niche markets

The following markets are considered to be small and specific at present, but have sufficient growth potential to warrant their own sections.

5.9.1 Hydrogen

Hydrogen sensors for leak detectors and process control are driven by interest in hydrogen fuel cells. Strong candidates are sensors based on semiconductors, carbon nanotubes and palladium.

There is considerable activity 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, the latter often being sporadically available or not always available in the right locations. 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, H_2 is used to generate electricity in a fuel cell or by enzymatic biological systems—the latter of which will remain in research for many years.

Gas sensors will be required:

(i) For ***safety***, to detect hydrogen leaks and quantify H_2 concentration with respect to its lower explosive limit (LEL) in air (4 %vol [11]).

(ii) For ***process control***, to check the purity of hydrogen as it is formed. Assessment of the level of H_2 formed by electrolysis may be conveniently assessed by monitoring the internal pressure.

(iii) To ***measure contaminant gases*** that arise in the production of H_2 from natural gas, examples are carbon monoxide (CO) [15] and hydrogen sulphide (H_2S) in the presence of high concentrations of H_2. Bringing H_2S levels down to 1ppb would extend the lifetime of proton exchange membrane fuel cells [16].

(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 (see sections 6.2 *Nanometal oxides* and 6.3 *Carbon nanotubes (CNTs))* is often considered a problem for the detection of other gases. H_2 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 [17]. These developments are reducing but not eliminating a fundamental issue with such broad spectrum detectors. Gas detectors used for both H_2 leak detection and measuring contaminants in an H_2 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. H_2 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 [18], 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 ageing of Pd [19] 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. (See sections 6.7, *Thermal conductivity, enthalpy and catalytic sensors* and 7.1.6, *Micro hotplates*.)

(ii) *Thermal conductivity* (see section 6.7).

(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.

5.9.2 Ammonia for refrigerants and intensive farming

Ammonia detection is driven by their use in refrigerants and emissions from intensive animal breeding. Low cost, ppm detection of ammonia at -40ºC is a technology challenge not yet met.

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 (1-5ppm) background ammonia whilst being always ready to detect a breakthrough of 10 to 20ppm. 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 of ammonia at -40ºC is a technology challenge not yet met. We could be years away from an electrochemical solution, but 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 biotechnology are also being researched [20].

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.

6 Enabling technologies

Most enabling technologies involve either new materials or material advances, but we do consider other enabling technologies including lower cost temperature measurements, electrochemistry, separation science and optical property changes.

6.1 Micro ElectroMechanical Systems (MEMS)

> There is a lack of capability in the UK for processing non-silicon materials.
> Research is needed on deposition of active sensing layers, especially those with high surface areas.

Silicon isthe 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, making silicon unsuitable as it is opaque at wavelengths below 1.1μm. High temperature applications (>400°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 non-silicon 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 non-silicon 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.

Microfluidics refers to the generic technology of manipulating fluids on a chip, including the integration of pumps, valves, mixers and reaction chambers that enable the fabrication of microreactors and lab-on-a-chip devices. Incorporation of microfluidics offers the following advantages for sensor products:

- compactness
- reduced reagent volumes (hence lower cost)
- faster response times
- well-controlled reaction conditions and delivery of reagents
- low power consumption

However, possible disadvantages of this technology that may impact its commercialisation in some areas are:

- how representative are small sample volumes?
- device fouling
- interfacing to the macro-world
- high electric fields required for electrophoretic pumping systems

6.2 Nanometal oxides

Use of nano-structured materials improves responsivity and lowers operating temperatures, but does not improve issues such as gas selectivity, sensitivity to humidity or slow recovery times.

The gas sensing properties of conventional metal oxide semiconductor based sensors are mainly dependent on their surface chemistry. The sensor response relies on oxidation / reduction reactions of gases that diffuse into the surface and subsurface of the oxide material. This causes a change in the depth of an electronic depletion layer at the material's surface, detected as a change in the material's bulk plus surface resistivity. Therefore the use of nano-particulate materials, by increasing the surface to bulk ratio, give improvements in responsivity and lower operational temperatures, but unfortunately provides no improvement in selectivity.

The problems of humidity sensitivity and dosimeter type response (or very slow recovery) at low temperatures or powers may not be addressed by changes in particle/crystallite size for many materials. The advantages of nano-structured materials may be best realised by opening up use of new compositions such as perovskites. Nano-sized forms of some photochemically active compositions, e.g. titanium oxides, may also open up new sensing capabilities.

6.3 Carbon nanotubes (CNTs)

The electrical properties of a carbon nanotube can be sensitive to a single molecule. Control of growth processes is being studied to develop tailored, uniform structures, but also requires a link to gas sensing characteristics.

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 the conduction in high-quality semiconductor nanotubes means that even the adsorption of a single molecule can produce significant changes in the electrical properties of the nanotubes, 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.

The potential of carbon nanotubes and indeed of other nanomaterials will not be realised until synthesis and post-processing methods have been developed which generate materials with selected electronic and structural properties. Sensors require well-defined metallic and 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 (where Rice University presently leads the world), 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 onto other studies such as morphology and growth, semiconductor behaviour, mechanical properties and methods of analysis of this unusual material.

6.4 Quantum dots and wires

More basic research is needed to establish viability of quantum dots for gas sensing, and to explore semiconductor or electrochemical transduction.

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, with limited success: QDs are popular in biotechnology as photonic tags, but use of QDs as gas sensors 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, losing their advantage as nanoparticles. The preferred transduction method for these particles is photonics. 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.

6.5 Polymer sensing layers

Molecular imprinted polymers may provide airborne biological detection in a more robust format than their biological equivalents.

Molecular imprinted polymers (MIPs) are produced by inducing polymerisation around a target template molecule. Removal of the template theoretically results in a material containing specific recognition sites for the template. MIPs may be able to perform the function of biological recognition in sensor devices (e.g. replacing immunochemical reactions). MIPs are more robust than biological systems in terms of longevity, reusability, use in extremes of pH, pressure, temperature and solvent polarity, although they may have lower specificity compared to biological equivalents.

Recent work has addressed some of the significant issues hindering full exploitation of these materials, such as productionisation, heterogeneity, reproducibility and leaching. Recent attempts to join MIPS with active site implantation have improved target recognition, as shown by Ken Shea at Irvine, California.

6.6 Separation science

Many gas detection systems suffer from poor selectivity; add-on active layers therefore have an important role, but there is little specific research in this area.

Many low cost gas sensors have a broadband sensitivity to a range of molecular species. Since selectivity is frequently required, sensor manufacturers must either revert to alternative, more selective analytical technologies or provide a separating front end technology. Considering the second option, there are several front end separation technologies available.

i) ***Chemical filtering*** is typically tied up in industrial know-how, so leading-edge technology is not accessible, and could be something of a black art. Most sensors use unsophisticated adsorption on carbon to remove unwanted gases. Targeted, functionalised materials are not available commercially, despite the large and widespread potential.

ii) ***Gas chromatography*** (GC) has been an accepted technique for decades, but the purchase and maintenance costs of the instruments have been prohibitive. However, the materials and know-how used for gas separation might find a use as gas-selective overlayers.

iii) ***Micro GC*** has been under development for years, but frequently misses the performance requirements. More research is required.

iv) On-the-fly separation and detection systems such as ***ion mobility spectroscopy*** (IMS) and ***micro mass spectroscopy*** (MS) offer new opportunities. Each has its technological and cost challenges, but both concepts have been proven in the laboratory. Field trials are underway with micro MS (Microsaic) and IMS has been used by NATO forces for years. However, industrial and homeland security applications are still under development or too expensive for broad acceptance.

6.7 Thermal conductivity, enthalpy and catalytic sensors

This range of technologies offers great opportunities for low cost MEMS devices, and is the subject of much current research and development.

Temperature change is the most reliable transduction method we know – in fact many sensors exhibit an unwanted response to temperature changes. We can detect temperature changes cheaply, sensitively and reliably, so why not develop sensors that use this transduction method? For decades the enthalpy generated by catalytic combustion of flammable gases (in the well-known pellistor) has been the preferred detection technology in mines and other high risk areas for detection of explosive gases. Building on this technology of a catalyst on a ceramic substrate, opportunities arise for measuring high concentration gases reliably. Two opportunities are the most obvious: carbon dioxide for carbon emissions monitoring and helium / hydrogen in high technology applications. Current sensors can detect these gases, but performance and negation of transients and humidity problems is not to requirements - further research is required, either from universities or industry. This measurement technology is most cheaply employed using MEMS devices, similar to the structures used in digital mass flow controllers.

6.8 Electrochemistry

Research is needed on nano-structured catalysts and non-aqueous electrolytes and solvents.

Electrochemical sensors are the backbone for detection of oxygen and toxic gases. Well established in the safety and combustion industries, this technology has new opportunities arising from developments in catalysts. Current technology uses noble metal and carbon based catalysts, but has much to learn from well funded fuel cell technology. Also, the scientific challenge is to develop chemical-electrochemical sensors, using intermediate chemistry to indirectly detect molecules such as ammonia.

Further research is required in novel catalysts based on nanotechnology and using non-aqueous electrolytes and solvents, based on organics and ionic liquids. Many companies are pursuing electrolyte development but government assistance is required for new catalysts, solvents and electrolytes, which can be part of research programmes into nanomaterial chemistry.

6.9 Optical absorption

Most optical gas sensors are based on measurement of optical absorption. Work is needed to lower the capital cost and improve field robustness.

For further details about specific optical detection technologies, consult reference [26].

Measurement of optical absorption is the most widely used optically-based gas detection technique. Many gases of interest exhibit absorption in characteristic regions of the spectrum, the strength of the absorption at a particular wavelength giving the concentration of the gas. The fact that this is a direct, physical effect gives this technology an advantage in that it can be a more reliable indicator of gas concentration than other techniques based on property changes of a sensing layer.

Spectral region	Gas species	Basis of absorption	Characteristics
mid IR	CO, CO_2, CH_4, NO, SF_6, NH_3, H_2O, HCl, N_2O	molecular vibrations (fundamental)	strong absorption, many narrow lines
near IR	CO, CO_2, CH_4, NO, SF_6, NH_3, H_2O, HCl, N_2O, O_2	molecular vibrations (overtone)	weak (~ 1/100) absorption, many narrow lines
UV	O_3, H_2S, SO_2, NO, NO_2, NH_3, BTEX, Cl_2	electronic transitions of energy states in bonds	strong absorption, broader lines

Table 6. Some gases commonly detected by optical absorption.

Absorption is characterised by the well-known Beer-Lambert absorption law [21] and thus the basic optical response is highly predictable. At low gas concentrations, the response is proportional to the optical pathlength of the gas cell, the characteristic absorption strength of the gas species and the concentration of the gas itself. Thus it is important in many applications to increase the optical pathlength within practical limits.

The more important techniques that exploit absorption are described briefly in Table 7; for further details see reference [26].

Technique	Principle of operation
Non-dispersive infra-red, (NDIR) or ultra violet (NDUV)	IR (or UV) light is absorbed by the target gas in path between a broadband source and detector. The absorption waveband is selected using optical filters. A second reference beam can be used in a neighbouring (non-absorbing) waveband. Good for low cost, single component detection where there is little spectral interference from other species.
Spectrophotometry	Light from a broadband source is dispersed, for example using a grating or in a Fourier Transform Infrared (FTIR) interferometer. The entire spectrum is measured at a defined resolution. Good for multi-component sensing.
Tunable diode laser absorption spectroscopy (TDLAS)	IR absorption using a tunable diode laser as the source. Resolution is very high enabling measurement of a single gas line. A high sensitivity technique often using multi-pass cells to increase the optical pathlength and hence the signal to noise ratio.
Cavity ringdown spectroscopy (CRDS)	Light is multiply reflected between two mirrors within a cell containing the gas sample. The decay time of the light is measured as it is absorbed with each pass. Effective pathlengths of several km lead to high (ppt) sensitivity.

Table 7. Commonly used absorption-based gas sensing techniques.

Optical gas detection techniques offer a number of advantages over traditional techniques, depending on the specific method of implementation. These advantages include:

- high degree of gas specificity
- low maintenance requirement
- potential for self validating measurements and measurements that require no calibration potential for non-contact or remote measurement
- greater ease in designing intrinsically safe systems, especially when absorption cells are linked using optical fibre
- potential for remote standoff gas detection, using thermal imaging, perimeter detection, backscatter detection or LIDAR (LIght Detection And Ranging), an optical analogue to radar giving full 3-D gas cloud information.

Disadvantages include a comparatively high capital cost and lower level of field robustness. These issues are linked, in that optical systems can require high tolerance alignment, which makes their manufacture expensive (many components are aligned by hand) and increases the cost of maintaining that alignment in the field. Optical techniques with high spectral resolution have a greater robustness against fouling (dirt, dust etc) on the windows exposed to the sample, but lower resolution techniques are susceptible to fouling-related errors. Condensation of moisture on the optics in the field is a problem in many applications.

6.10 Optical pathlength and refractive index changes

Active layers change their refractive index on absorption of gas, and can be interrogated with a variety of optical methods at lower cost than for optical absorption.

The presence of a gas can induce a change in the refractive index of an active layer, which can be interrogated optically. These changes may be caused by actual changes in the film dimensions due to etching or deposition, or to changes in the film refractive index due to swelling, shrinkage or diffusion of analyte from the environment into the film.

In comparison with optical absorption, this is an indirect detection technique. However, it has the advantage that there is no need to match the light source with the absorption spectrum of the indicator, and the approach is well suited to employing the very cheap light sources made in vast quantities for telecommunication applications.

Many devices use the principle of optical interferometry to detect the refractive index changes with high sensitivity. One configuration is to end-coat an optical fibre with the responsive thin film, and the interference pattern generated by light reflected from both the fibre end-film and film-environment interfaces changes according to changes in the optical path length of the film. Other interrogation methods include:

- (i) surface plasmon resonance in a thin film of noble metal
- (ii) probing a thin layer at the surface using an evanescent optical field
- (iii) polarisation interferometry
- (iv) long period gratings on integrated waveguide structures or in optical fibres
- (v) modification of laser emission via a distributed feedback (DFB) grating, using the laser gain medium to amplify the signal.

Gas specificity arises from the design of the active layer. Points of debate include whether such devices would be fail-safe, the robustness of the active layers and what might happen when exposed to contaminants. It has been suggested that disposable devices would avoid some of these problems.

6.11 Chemiluminescence

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.

6.12 Biosensors

Most biosensors are used for sensing in liquid media but there is some interest in gas sensing. Biomolecules can offer a high degree of selectivity, but are relatively fragile in long service.

Biosensors are defined as sensors incorporating one or more biological molecules in order to carry out one or more functions of the sensor. The most famous biosensor, the glucose sensor, is made by combining an enzyme, glucose oxidase, with an oxygen electrode. The enzyme is typically present in a membrane in the vicinity of the electrode and selectively oxidizes glucose, thereby diminishing the partial pressure of oxygen, which is monitored by the electrode.

Any biomolecule able to respond to a gas by changing a characteristic parameter can be incorporated into a gas sensor. For example, the membrane protein bacteriorhodopsin changes not only its optical absorption spectrum upon exposure to gases such as ammonia, but also the kinetics of the photo-activated transitions from one of its states to another. These phenomena can in principle be exploited to yield sensors whose sensitivity could be better than existing technologies. In effect, one is exploiting the complexity of biomolecules in order to enhance both selectivity and sensitivity.

The limiting factor at present is designing suitable measurement schemes in order to fully benefit from these features of biomolecules. The downside to the use of many biomolecules is their relative fragility. While this problem can be evaded in disposable devices (it is then only sufficient to ensure that their storage before use does not take place under overly harsh conditions), it could be problematical in devices designed for long service. On the other hand, there is a huge variety of potentially useful biomolecules available from organisms (especially the archaea) growing under extreme conditions, including boiling water, non-aqueous solvents and high pressures. Bacteriorhodopsin is one example of a molecule extracted from such a so-called extremophile. Furthermore, it is possible to produce it relatively cheaply on a large scale using standard bioreactors.

While much of the above applies to liquid sensing, there is some interest in developing biosensors for airborne spore detection, for example anthrax, but their potential as yet is unproven.

7 Component technologies

New components for use in gas sensing mostly have their origins in either MEMS or new opto-electronic components.

7.1 MEMS and silicon components

Many devices have shown great technical advances but limited commercial progress, possibly because none have found a "killer application" in high volumes that allow low cost manufacture.

The term MEMS (micro-electromechanical system) is something of a misnomer in that not all so-called MEMS devices are 'electromechanical' and few are 'systems'. Nevertheless, the term is now widely applied to all manner of miniaturised devices, generally 3-D microstructures of one sort or another, which are mostly fabricated from silicon using techniques which are derived from the microelectronics industry. These include isotropic and anisotropic etching ('microengineering'), thin film deposition, anodic bonding and the well known masking and doping techniques employed in IC manufacture. Devices such as silicon microsensors, 'lab on a chip' and Micro-TAS (micro-total analytical systems) can all be viewed as MEMS sub-sets.

MEMS/ silicon technology has been outstandingly successful for sensing physical variables, yielding small, rugged and inexpensive devices (eg accelerometers, pressure sensors and Hall effect position sensors) but its impact on gas sensing has been less dramatic, with few products yet in high volume production. Silicon GasFETs only satisfy niche applications and have so far failed to meet their early promise. Silicon's major contribution in gas sensors to date has probably been its growing use as a substrate for metal oxide gas sensors. Nevertheless, research is widespread and varied and some topics include:

- Porous and nanoporous silicon layers
- Micro-hotplates using Si and SiC (for high temperature operation)
- Integrated metal oxide sensor arrays/ electronic noses
- Resonating, coated Si cantilevers
- Micro-thermal conductivity and paramagnetic sensors
- GasFET variants such as MISiCFETs (metal insulator silicon carbide), HSGFETs (hybrid suspended gate), PolFETS (FETs with polymer-coated gates) and GasFET arrays.

The aim is to yield families of miniaturised devices that offer economic and operational improvements over conventional gas sensor types. Some have enjoyed a limited degree of exploitation, e.g. GasFETs and FET arrays by Applied Sensor AB (Sweden) but commercial progress has been slow, perhaps reflecting in part the failure to identify high volume applications where the benefits of the technology can be fully exploited. Indeed, this has been the case with some physical sensors: silicon accelerometers were developed in the 1970s but only enjoyed real commercial success with the advent of vehicle air bags.

Another major research theme is the development of MEMS-based analytical instruments for gas sensing and some examples include:

- Miniaturised silicon photoacoustic sensors
- MEMS Fourier transform and other spectrometers
- Integrated NDIR sensors
- Miniaturised IMS
- MEMS-based GCs, MSs and FIDs.

Again, market penetration has been slow; despite that the first silicon GC was developed in the 1970s and several of the above MEMS devices have recently enjoyed a limited degree of commercial success. Part of the problem lies with the fact that miniaturisation is not always particularly beneficial: miniaturised optical sensors suffer from low sensitivity due to the necessarily short optical path-lengths; silicon photoacoustic sensors cannot offer the low limits of detection that characterise their conventional counterparts; and as yet, MEMS spectrometers only offer low resolution.

Another critical issue is cost: this must fall if MEMS devices such as spectrometers are to exert a real commercial impact. This is something of a "chicken and egg" dilemma: prices will only fall if volumes increase. Indeed, Yole Développement have recently predicted that, by 2008, the global market for MEMS spectrometers will reach a relatively modest $96 million/annum [22]. Their report notes that the "spectrometer market appeared in 2000 and is growing slowly because current applications volumes are small and new high volume applications have to be found". In many ways, this comment is true for most of the devices listed above. In the fullness of time, however, the availability of improved devices with lower costs is expected to allow techniques such as FTIR and perhaps UV absorption spectroscopy to be more widely deployed.

Interesting longer term prospects may arise from the discovery of IR lasing in nanoporous silicon in 2005 which may lead to the development of families of fully integrated optical MEMS-based gas sensors.

7.1.1 Micro gas chromatography (micro GC)

Research and engineering is needed into developing compatible gas sampling stages.

Considered by many as the most reliable separation method for gas analysis, GC is a well developed technology. First shrunk 30 years ago by HP, the micro GC has had a few niche market successes, but needs better sampling and integration with the detection stage which can be a simple FID or thermal detector or more interestingly a micro MS. Recently the Technical Research Center of Finland has produced the integrating silicon to connect micro GC to micro MS. More research and engineering of the sampling stage is now required to commercialise micro GCs.

7.1.2 Micro mass spectrometers

This area has great potential. Research is needed into each application to characterise the background matrix and sensitivity to the target against this background.

Micro mass spectrometers are discussed in reference [3]. MNT versions of mass spectrometers are now beginning to appear, including magnetic sector, Wien filter, travelling wave and QMS (quadrupole mass spectrometer) types. The advantages of microengineered mass spectrometers are:

- Lower cost of manufacture since a batch of several mass analysers can be made simultaneously on a single silicon wafer.
- High-pressure operation: small size means that ion mean free path length can be reduced which allows operation at higher pressures (up to 10^{-2} mbar). The small size/higher pressure combination avoids the use of an expensive and bulky vacuum pumping system, leading to compact instruments.
- Low power operation is possible since the electrode voltages can be reduced.

Potentially, microengineered MS arrays can become disposable.

Research groups in the UK developing MNT MS technologies for sensor applications include:

- Imperial College, Optical and Semiconductor Devices Group: Silicon-based MNT QMS with hot filament sources; stable and reproducible QMS operation has been demonstrated for gases in the mass range 0-150 Da. Work is also being carried out on arrayed mass filters, for enhanced sensitivity and/or selective multipeak ion monitoring. Microsaic Ltd is a UK company that is developing MNT MS devices, and is closely linked with the group at Imperial College.
- University of Liverpool, Department of Electrical Engineering and Electronics: Working on QMS in collaboration with Imperial.
- University of York, working on novel microfabricated electron spectrometers and ion trapping mass spectrometers.

7.1.3 Micro IMS

Research is needed into sampling systems and analysis of VOC combinations.
There is an opportunity for a non-radioactive ionisation source.

Graseby (now Smiths Detection) has dominated the ion mobility spectroscopy industry (IMS) industry, mainly through military contracts. In the last few years two companies, Scionex (Mass. USA) and Owlstone (Cambridge UK) have developed patent protected technologies that bypass Graseby IP, shrink IMS and exploit the new variant, Field Asymmetric Ion Mobility Spectroscopy (FAIMS), also known as Differential Mobility Spectroscopy (DMS). The UK, along with USA and Germany dominate this technology, and the MEMS DMS from Owlstone looks promising. More research for sampling systems and analysis of specific VOC combinations is required, in parallel with product development. There is an opportunity for a non-radioactive (eg deep UV) ionisation source.

7.1.4 Micro spectrophotometers

The UK opportunity is to integrate components into systems for niche markets, but not to compete with the USA to build MEMS based spectrometers.

Spectrometry in the near IR can be used to analyse either single VOCs or families of VOCs, depending on the spectrometer resolution: more expensive, high resolution spectrometers can isolate single VOCs, but MEMS-based spectrometers, which are dropping in price rapidly, are still only capable of isolating VOC families.

The MEMS components used to separate wavelengths are patented technologies owned mainly by USA corporations, so the UK opportunity is to integrate these proprietary components into niche market spectrometers, if the owners of the MEMS components will cooperate.

7.1.5 Quartz micro balance (QMB), surface and bulk acoustic wave (SAW and BAW) devices

These MEMS devices use resonance to detect small mass or compliance changes to a sensing layer as the gas is absorbed or adsorbed. Devices are commonly integrated with microhotplates because the technologies are compatible. QMB, SAW and BAW transduction technologies are well-developed and available; gas sensing requires the introduction of new sensing layer materials.

7.1.6 Micro hotplates

There are significant opportunities for low power devices, when combined with functionalised, high surface area sensing layers.

Microhotplates have been shrunk to MEMS for many years. Companies such as Capteur and Microchem SA have commercialised these devices. To date, the shrinkage has not achieved the low power requirement (less than 10mW for 550°C), but recent UK academic advances [23] have shown that low power can be achieved. Low power opens up significant, new markets in domestic, portable and sensor array gas detection. This work should continue, acting as the base for integration of emerging sensing layer deposition technologies.

7.1.7 Sensor arrays and electronic noses

Early UK developments didn't meet their promise, but take-up is slowly growing in food, automotive and health sectors.

Arrays of chemical or biochemical sensors with varying degrees of response are utilised in artificial olfaction (electronic nose) systems. The individual sensor elements themselves include many of those described above. Artificial olfaction has potential in numerous application areas, including food quality control, personal healthcare and security as well as air quality monitoring in the automotive sector. Significant research on artificial olfaction is carried out at the University of Warwick (Sensors Research Laboratory), including the development of CMOS-based array gas sensor, and at the University of Manchester (Bioanalytical Science).

The UK was a leader in commercialising electronic noses with companies such as Neotronics and Aromascan in the early '90s. Both attempts failed because the target markets were not well selected and the sensor was not sufficiently repeatable. A research network under FP6 (GOSPEL) has continued to advance the technology, and now there are many companies active in this technology; with 18 major companies active in 2002 [24]. Companies using or investigating electronic nose technology included Nestle, Danone, Starbucks, E&J Gallo, El Castillo, Wild, Fonterra, Kyowa, Merck, Coors, Ford, VW, Henkel, Procter and Gamble, Swedish Match, Basell, KCL, Korea Tobacco & Ginseng, Brystol Myers Squibb, Cardinal Health, Takeda and The International Group [25].

Nexus have estimated the annual value of the market for electronic noses to be 1,000 units or around £5M in 2000, with a predicted rise to 36,000 units or £100M in 2005 [3]. We have no evidence to confirm whether this promise has been realised.

7.2 Microfluidics components and micro total analytical systems

Microfluidic devices are currently made using the same kind of subtractive top-down processing technology routinely used in the semiconductor industry. This technology can also be used to make master dies with which synthetic polymer blanks can be hot embossed, offering a low-cost route for the high-volume production of components that will typically be used for disposable devices. Other low-cost routes are moulding and sheet stamping.

The field has also come to be known as lab on a chip, or micro total analytical systems (μTAS). The channel sizes are typically in the 10 to 100 μm range. Much effort is expended in fluid dynamic modelling for efficient mass transfer and mixing in low Reynold's number environments.

The use of microfluidics in a gas sensor might be considered as rather esoteric. There has been limited work on gas absorption in microfluidic gas/liquid systems, in order to provide gas sensing capability were a suitable chemistry is operating in the liquid phase, combined with typically optical detection. For example, ammonia-containing gas flowing above a fluorescent indicator-containing liquid results in a fluorescent product dependent on the concentration of ammonia. Until now however, such systems are laboratory curiosities rather than useful prototypes.

7.3 Microprocessors, FPGAs, PICs, ASICs, DSPs

Many gas sensors provide complex signals that require deconvolution and transforms to obtain the required information. As the market for mobile and computing technology expands, the gas sensor industry is riding on the back of newly available components to analyse received signals in real time.

An area of difficulty is the requirement for high volume, low cost mixed signal chips: gas sensors need both analogue and digital signal processing, whereas the high volume entertainment and telecoms markets are strictly digital. So suppliers of mixed signal designs are few, but growing. Hence, gas detector manufacturers are reverting to FPGAs and discrete analogue components- not ideal, but the best currently available.

The following opportunities exist:

(i) Wireless (Zigbee or equivalent) system, added to an analogue interface and fast DSP single chip- this requires government support to pay for the high cost of chip development and cooperation when designing the interface so that many companies can use the ASIC.

(ii) High temperature analogue pre-amplifier that could be used with a number of different sensors types in, for example, automotive applications. To avoid pick-up, pre-amplifiers are best placed as close to the sensor as possible, and therefore experience the same high temperatures. This type of project should be joined with other industrial needs for high temperature electronics to share research costs across multiple industries.

(iii) Low cost, flexible mixed signal ASICs and FPGAs optimised for electrochemical, metal oxide and/or optical gas sensors.

7.4 Optical and optoelectronics components

7.4.1 Light sources

QCLs are gradually winning the race for room temperature tunable mid IR lasers, with prices slowly falling. Opportunities for better quality UV sensing will open up with LED and laser sources replacing discharge lamps. Tunable light sources still cost too much for many applications.

Many of the most commercially important optical gas sensing techniques are based on absorption at mid-IR wavelengths (e.g. ~3-15 μm) but still use incandescent filament lamps as the light sources. These are subject to drift and cannot be modulated faster than around 10Hz because of their high thermal mass. New developments of incandescent technology include very thin, platinum plate emitters (for faster modulation) and emitters with microstructured surfaces that enable more efficient emission of plasmon-generated light at the wavelengths needed for gas IR measurement. LEDs offer much greater light efficiency, more stable output and faster (kHz) modulation, but until recently their continuous wave (cw) output has been too low for commercial use, and a reliable commercial supply is yet to be established, especially at wavelengths longer than 2.2um.

Tunable lasers have long been available in the near IR region as developments of telecoms technology in wavebands centred on 1.3 and 1.55 μm. Such tunable lasers emit in a narrow band able to resolve a single gas absorption line, providing a high degree of gas specificity with a superior signal : noise ratio. Tuning over a wider wavelength range is of interest because it could allow gas-specific multi-component gas detection with a single instrument. At telecoms wavelengths, a driver for wider range tuning comes from the need for single devices able to tune their emission across the ITU grid of wavelengths around 1.55 μm. In the mid IR, where gas absorption lines are strongest, there is a race to develop a room temperature tunable solid-state laser with three contenders; quantum cascade lasers (QCLs), room temperature lead salt lasers and devices based on periodically poled lithium niobate.

In the case of QCLs, the wavelength is governed by the thickness of the material layers rather than the bandgap of the material itself. QCLs are now available that operate at room temperature and prices are falling; it is anticipated that they could fall below £1k by 2009 (but this may be dependent on their finding a sufficiently large market). Market leaders such as Hamamatsu have recently joined in the fray.

Relatively few gases are routinely detected at UV wavelengths (i.e. λ ~ 200-380 nm) and most instruments use UV sources such as xenon or mercury vapour lamps. Smaller and inexpensive UV laser diodes and LEDs are anticipated within the next few years, offering more stable output and faster modulation leading to sensitivity gains. Laboratory sources already exist, and BlueRay and other new DVD technologies are driving the reliability of UV lasers. Very short wavelength, intense but low power sources are also seen as key to the future of photoionisation detectors.

Laser type	Wavelength	Power	Comments
Galium nitride (GaN)	Blue/violet to near UV (400-480 nm)	< 5 mW	-
AlGaInP	Red (630-690 nm)	10 mW	Room temp., low cost
Aluminium gallium arsenide (AlGaAs)	NIR or visible (750-1,000 nm)	10 mW	Room temp., low cost
Vertical cavity surface emitting lasers (VCSELs)	NIR or visible (650-1,680 nm)	-	Room temp., low cost, widely tunable
InGaAsP for comms	NIR (1,200-2,000 nm)	10 mW	Room temp., fibre optic
Antimonide	NIR to mid-IR (2-4 μm)	≥1 mW	Room temp. or cooled
Quantum cascade lasers (QCLs)	Mid-IR (4-12 μm)	tens of W pulsed, tens of mW CW	Falling prices, no need now for cryogenic cooling
Lead salt	Mid-IR (3-30 μm)	<1 mW	Require cryogenic cooling

Table 8. Summary of lasers with the potential to be used in gas sensing (from [26]).

7.4.2 Photodetectors

Improved detectors are also the topic of a significant research effort and as with mid-IR sources, the key requirements for detectors within this wavelength range are room temperate operation and low cost. Photovoltaic and photoconductive detectors fabricated from compound semi-conductors such as InAsSb, HgCdTe arrays on Si (Qinetiq), PbSe and InSb which operate to 10 μm and, for near IR, to 2.2 μm with extended InGaAs have recently been demonstrated.

Currently low cost detectors are available as either thermopile arrays or pyroelectric arrays, used for standard thermal imaging. More widespread use in gas camera requires either an improvement in sensitivity of the cheaper manufacturing technologies, or a reduction in price of the higher specification arrays. High specification IR array technology is controlled mainly by North American companies, following long term military funding, and recent consolidation has resulted in FLIR dominating this market.

Silicon carbide (SiC) and diamond UV detectors covering the range ~200-400 nm exist but as with the mid-IR region, novel detectors with higher sensitivities and which are more wavelength-specific may be required if this spectral region is to be exploited to the full.

Microspectrometers (see also section 7.1.4) have, as yet, only exerted a minor impact in certain process control applications, are still relatively costly and offer limited resolution, but there is great competition and prices are falling rapidly. If these issues can be resolved, however, they could play a role in, for example, portable multi-gas sensing instruments.

7.4.3 Gas cell design

Specialist optical fibres may offer longer term prospects:

1. Hollow fibres have been used to increase the effective pathlength and thus sensitivity in an experimental TDLAS systems [27].
2. Tapered fibres allow a small proportion of the light from the core to access the fibre coating.
3. Emerging families of nano-fibres exhibit the interesting property of guiding light around their outsides, also suggesting the ability to interact with gases over a long pathlength within a small volume.

More generally, techniques that can extend the effective absorption pathlength without recourse to long physical paths could pave the way to higher sensitivity optical gas sensors.

8 Summary of detailed conclusions

The following section summarised detailed conclusions made throughout the roadmap document.

8.1 Market Evaluation

Market value and accessibility

- A recent market study by a major gas detector company valued the industrial gas detection market at $1.5 billion annually, with gas sensors worth $250M in sales, while Frost and Sullivan (2006) valued the industrial gas sensor market at approximately $50M and total gas detector and analyser market at approximately $1billion annually.
- Globally, the UK production is estimated to be 4th worldwide, behind the US, Japan and Germany.
- The UK has a history of success in gas sensors.

Fragmentation

- The UK gas sensor market is fragmented and populated by small companies.
- Recent consolidation has brought some UK companies into US ownership, which is starting to weaken the UK sensor technology base.
- The UK gas sensor community is well served by a number of networks and groups.

Development cost and risks

- The small size of many niche markets makes it difficult to justify the scale of investment needed to generate a step change in technology, rather than funding incremental technology developments.
- Step change developments must be justified by applications in a range of market niches.

Generic market trends and drivers

- New markets for MNT gas sensors have been highlighted by the DTI Technology Strategy: manufacturing processes, consumer products and services, environmental monitoring, transport, structural monitoring, security and healthcare.

The role of legislation

- Legislation can energise an application area and is a recognised success factor for the companies in that market.
- Standards often follow application development, increasing market size and consolidating market positions.

UK funding and support for gas sensor technologies

- The UK is strong in gas sensing.
- Total EPSRC expenditure on academic research projects related to gas sensing runs at around £1500k pa. Industrial expenditure on R&D is between 2% and 10% of sales.
- The 2002 Sensor Foresight study considered the UK to be weak in microengineered sensors, but government MNT investment has improved the infrastructure landscape.

8.2 Specific markets

Domestic CO, flammables and fire

- Drivers are competitive advantage by cost saving and/ or higher specification products, especially reducing false alarms.
- Significant price constraints arise from strong competition and the "grudge" nature of the purchase.
- The world market for fire detectors was estimated to be around £2B in 2003.

Automotive

- OEMs do not want to pay more than €1- €2 for a sensor, no matter how complex. However, the automotive sector is attractive in that manufacturing volumes are large enough to take advantage of micro- and nanoprocessing economies of scale.

Cabin air quality

- Detection of target gases (CO at present, VOCs in future) gives efficient control of HVAC recirculation levels. In the future this system will be extended to monitoring VOC nuisance odours. These needs are being met using microhotplate in this very competitive niche sensor market.

Exhaust gas emissions

- Candidate sensors including resistive metal oxides are being evaluated, but are currently limited by cross-sensitivity to other gases and extreme environment survivability.

Particulates (PM10, 2.5)

- 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 two regeneration events, offering an opportunity for nanomaterials in conductimetric-type particle sensors.

Industrial health and safety

- We have a good understanding of target species, but less so of matrix interferents.
- Sensor technology must be fail-safe and auditable.

Flammable leak detection

- There are different requirements and drivers for permanently installed and portable detectors. Very low power catalytic sensors or optical detection of hydrocarbon are top of the wish list for many gas detector manufacturers.
- Development of a reliable ppb mercaptan detector is underway, but needs more concentrated research to achieve market requirements in a reasonable period.

Toxic gases

- Regulatory limits vary, but are linked by a global understanding of toxicity levels, with slow convergence to a common limit.
- Emphasis is moving from short-term to long-term exposure.

Asphyxiants and oxygen

- Oxygen sensors require high accuracy and continuous operation.
- New standards follow increased emphasis on CO2 monitoring, for example near boilers.

Process industries and process control

- The process industries are strong in the UK and have historically driven new developments, but are under increasing cost pressures. New environmental legislation will drive emissions measurement.

Food quality, production, transportation and storage

- A conservative industry with a tendency to get by on existing practices rather than risk the introduction of new technologies.
- Measurands include contaminant origins, micro-organisms, allergens and waste monitoring.
- The ‘electronic nose’ has not realised its early promise.

Bioreactors and landfill

- In closed bioreactors, target gases include oxygen, ammonia and carbon dioxide, with secondary interest in methane, hydrogen and some important ions such as acetate vapour.
- The gas profile of methane, hydrogen, heavier alkanes and VOCs characterises landfill ageing, important for district council determination of the state of the landfill.

BTEX (benzene, toluene, ethylbenzene, xylene)

- Toxicity levels for specific BTEX compounds are very different, yet they are difficult to measure separately; research is needed to select the best measurement technology.
- Benzene levels frequently exceed EU limits (1ppm), especially at petrol stations.

Outdoor air quality and emissions monitoring

- Emissions monitoring is best done at source, using dedicated gas detectors integrated with small weather monitoring stations.
- New EU legislation requires continually audited improvement of on-site emissions.

- Enforcement agencies need more sensitive and geographically wider gas detection networks for remote detection of automotive and urban air emissions.

Indoor Air Quality (IAQ)

- Dangerous gases or vapours are ozone from photocopiers, nitrogen oxides from heating sources, cleaning solvents and formaldehyde released from new buildings, furniture and carpets.
- Building control systems now use carbon dioxide monitoring to optimise ventilation control
- Specific VOC detection is unlikely to emerge in the short term. Research into detection of organic classes such as aldehydes or alcohols through NIR spectroscopy will show whether it may be possible to detect classes of VOCs at ppb levels.

Asthma in the home

- Targets are ozone, nitrogen oxides and airborne bioparticulates, the latter being a major challenge.

Nuisance odours

- Odorous emissions are emitted mainly from landfill sites and waste water treatment works (WWT).
- Problems arise when using point detection of the offending gases and then mapping of the gas plume using predicative computer models of the site. Networks of sensors are needed.
- Developing high throughput site models, possibly based on newly available digital elevation maps from satellites, could provide an improvement in applications knowledge that drives the market for gas sensors.

Homeland security

- A technically challenging area that has driven much R&D, but translation into solutions and sales remains uncertain until specific niches emerge.

Explosives and drugs

- There may be more realistic opportunities for gas and vapour sensors to gain market entry for drug detection by assisting with traditional policing methods and improving their efficiency,
- MEMS processes (for volume production capability) with an optical absorption sensor or micro-mass spectrometry sensor (for specificity and stand-off 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 need improvements in sampling technology, Improvements in discrimination ability
- There has been substantial interest in the development of terahertz (THz) spectroscopy for detection of (solid) explosives either by using standoff cameras to detect packages or by analysing suspect samples with THz spectroscopy.

Chemical, biological or nuclear attack

- Major programmes are trying to develop MNT based sensors networked together to give area coverage and fast feedback for first responders.

- A combination of MEMS sensors, and the use of microfluidic techniques would seem sensible.
- Lower toxicity but more widely available hazardous chemicals as might be found in the chemical process industry are a real threat.
- Rapid field identification of the DNA or RNA of the species through rapid sequencing is needed.
- Detection of radioactive emissions is achieved through “gamma cameras”, while alpha particle detection is used after seizure of the material, to allow fast determination of the radioactive material.

Breath analysis and capnography

- The goal is ultimately to provide GPs with non-invasive screening tools for disease, based on breath analysers that detect the out gassing of by-products of chemical or biochemical processes from either the gut or lungs.
- Much basic research will be required to determine these gas markers and their variability.

Hydrogen

- Development of hydrogen fuel cells for energy storage is a strong driver for the development of better hydrogen gas sensors. Sensors will be required for safety, process control, during production of H2 from natural gas and to monitor leakage in future hydrogen cars.
- The selected technology will depend on the application. Strong candidates are sensors based on semiconductors, carbon nanotubes, hydrogen absorption into palladium (Pd) and its alloys, pellistor hydrogen response and Pt catalytic amperometric electrochemical cells.

Ammonia for refrigerants and intensive farming

- Ammonia detection is driven by their use in refrigerants and emissions from intensive animal breeding.
- Low cost, ppm detection of ammonia at 40ºC is a technology challenge not yet met.

8.3 Enabling Technologies

Micro ElectroMechanical Systems (MEMS)

- There is currently a significant lack of capability in the UK for processing non-silicon materials, but this is being addressed.
- Deposition of sensing layer materials on MEMS devices requires more research, especially where high surface area layers on small hotplates are required.

Nano-metal oxides

- Nano-particluate materials give improvements in responsivity and lower operational temperatures by increasing the surface to bulk ratio, but unfortunately offer no improvement in selectivity.
- The problems of humidity sensitivity and dosimeter type response (i.e. very slow recovery) at low temperatures may not be addressed by changes in particle/crystallite size for many materials.

Cabon nanotubes (CNTs)

- Adsorption of a single molecule can produce significant changes in the electrical properties of the nanotubes, resulting in potentially high sensitivity and fast response.
- 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. We wish them luck.
- Gas sensing is not the primary CNT research focus; rather, gas sensing is often bolted onto other CNT studies because it can frequently benefit with little additional research costs.

Quantum dots and wires

- Use of QDs as gas sensors needs more fundamental research.
- 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.

Polymer sensing layers

- MIPs may be able to perform the function of biological recognition in sensor devices (e.g. replacing immunochemical reactions), but are not proven reliable. Recent attempts to join MIPS with active site implantation have improved target recognition.
- PEDOT studies by major display companies such as Epson, Philips and Kodak have moved conductive polymer behaviour understanding from the lab to industry. We need to see if this can be exploited by the gas sensor industry.

Separation science

- Chemical filtering is frequently used.
- Gas chromatography (GC) has been an accepted technique for decades, but Micro GC has been under development and needs further research, especially sampling and connection with the detection (ideally micro MS or IMS).
- On-the-fly separation and detection systems such as ion mobility spectroscopy and micro MS offer new opportunities.

Thermal conductivity, enthalpy

- Enthalpy generated by catalytic combustion of flammable gases has been the preferred detection technology in mines for decades.
- Two opportunities of low cost thermal conductivity measurements are: carbon dioxide for carbon emissions monitoring and helium/ hydrogen in high technology applications.
- This measurement technology is most cheaply employed using MEMS devices, similar to the structures used in Digital Mass Flow Controllers.

Electrochemistry

- Electrochemical sensors are the backbone for detection of oxygen and toxic gases.
- Current technology uses noble metal and carbon based catalysts, but has much to learn from well- funded fuel cell technology.

- Further research is required in novel catalysts based on nanotechnology and non-aqueous electrolytes and solvents, based on organics and ionic liquids.

Optical absorption

- Measurement of optical absorption is the most widely used optically - based gas detection technique. Advantages include high degree of gas specificity, low maintenance requirement, potential for self validating measurements and measurements and greater ease in designing intrinsically safe systems.
- Disadvantages include a comparatively high capital cost and lower level of field robustness.

Optical pathlength and refractive index changes

- This method uses various techniques to sample the refractive index (RI) of a sensing layer. The method is very sensitive to RI changes, with overall similar sensitivity to BAWs and SAWs.

Chemiluminescence

- Attaching a QD to chemically reactive matrices can lead to strong emissions at specific wavelengths at low gas concentrations.

8.4 New Components

Gas sensor advances will ride on improved components in the fields of networked communications, batteries, displays and computer electronics.

MEMS and silicon components

- Devices such as silicon microsensors, ‘lab on a chip’ and Micro-TAS (micro-total analytical systems) can all be viewed as MEMS sub-sets.
- Silicon’s major contribution in gas sensors to date has probably been its growing use as a substrate for metal oxide gas sensors. Nevertheless, research is widespread and varied commercial progress has been slow, perhaps reflecting in part the failure to identify high volume applications where the benefits of the technology can be fully exploited. major research theme is the development of MEMS-based analytical instruments for gas.
- The MEMS spectrometer market appeared in 2000 and is growing slowly because current applications volumes are small and new high volume applications have to be found. Interesting longer term prospects may arise from the discovery in 2005 of IR lasing in nanoporous silicon, which may lead to the development of families of fully integrated optical MEMS-based gas sensors.

Micro gas chromatography (micro GC)

- More research and engineering of the sampling stage is now required to commercialise micro GCs.

Micro mass spectrometers

- The advantages of microengineered mass spectrometers are:
- Lower cost of manufacture;
- High-pressure operation;
- Low power operation;

- Potentially, microengineered MS arrays can become disposable.

Micro IMS

- More research for sampling systems and analysis of specific VOC combinations is required, in parallel with product development.

Micro spectrophotometers

- The UK opportunity is to integrate these proprietary components into niche market spectrometers, if the owners of the MEMS components will cooperate.

Quartz mass balance (QMB), surface and bulk acoustic wave (SAW and BAW)

- These well-developed transduction technologies are available as soon as new sensing layer materials are introduced.

Micro hotplates

- Low power (<10mW) opens up significant, new markets in domestic, portable and sensor array gas detection.
- This work should continue, acting as the base for integration of emerging sensing layer deposition technologies. The UK is currently leading this technology.

Sensor arrays and electronic noses

- A research network under FP6 (GOSPEL) has continued to advance the technology, and now there are many companies active in this technology.

Microfluidics components (aka lab on a chip, or micro total analytical systems (µTAS).

- Channel sizes are typically in the 10 to 100 µm range. Much effort is expended in fluid dynamic modelling for efficient mass transfer or mixing in low Reynold's number environments. We do not expectany gas sensing breakthroughs in the short term.

Microprocessors, FPGAs, PICs, ASICs, DSPs

- The gas sensor industry is riding on the back of newly available components to analyse received signals in real time.
- Gas sensors need both analogue and digital signal processing, whereas the high volume entertainment and telecoms markets are strictly digital
- Opportunities exist: wireless (Zigbee or equivalent) systems, high temperature analogue pre-amplifier ,low cost, flexible mixed signal ASICs, FPGAs optimised for electrochemical, metal oxide and/or optical gas sensors.

Light sources

- Many of the most commercially important optical gas sensing techniques are based on absorption at mid-IR wavelengths (e.g. ~3-15 µm) but still use incandescent filament lamps as the light sources.
- In the mid IR, where gas absorption lines are strongest, there is a race to develop a room temperature tunable solid-state laser with three contenders; quantum cascade lasers (QCLs), room temperature lead salt lasers and devices based on periodically poled lithium niobate.
- QCLs are now available that operate at room temperature and prices are falling; it is anticipated that they could fall below £1k by 2009.

- Smaller and inexpensive UV laser diodes and LEDs are anticipated within the next few years, offering more stable output and faster modulation leading to sensitivity gains.

Photodetectors

- The key requirements for detectors within this wavelength range are room temperate operation and low cost. Photovoltaic and photoconductive detectors.
- If IR arrays can operate with better sensitivity, then gas cameras will become commonplace- this IR array technology is controlled mainly by North American companies.
- Silicon carbide (SiC) and diamond UV detectors cover the range ~200-400 nm.

Gas cell design

- Specialist optical fibres may offer long term prospects.

9 Main conclusions and recommendations

Technology Priorities

High impact technologies include separation science, electronic components, optical light sources, nanomaterials, low cost/ integrated optics, microelectromechanical systems (MEMs), MEMs/ CMOS integration and electrochemical cells. Specific MNT priorities are:

Nanomaterials

- Functionalised 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 characterisation 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 nanomaterial gas sensors.
- Combinatorial methodology for optimising sensing materials.
- Integrated MEMS using combinatorial sensing arrays with widespread applicability.
- Room temperature Mid-IR, Far-UV low cost, tunable light sources.
- Detector for specific precursors and sources of asthma in the home.

Recommendations to the DTI and Research Councils

The following measures are recommended to fill funding gaps and enable the industry to take advantage of new developments and investments in infrastructure.

- Establish a short series of one-day workshops on identified research challenges, bringing together different skill areas to inspire new thinking, following a smaller scale version of the Future Intelligent Transport Systems (FITS) model used by EPSRC.
- Increase CASE awards in areas of common opportunity, specifically allocated through Sensors KTN. CASE awards are a popular and successful mechanism to promote R&D that is relevant to SMEs, but they can be hard to secure in some

RDAs. This measure would ensure their use by industry sector, possibly replacing some regional allocation.

- Develop funding mechanisms for Universities and Government Research Associations to engage with a diverse industry to work on the next steps to commercialisation – perhaps a DTI Knowledge Transfer version of EPSRC's successful fellowship scheme. Funding for people helps ensure continuity across a programme of shorter projects and allows researchers to develop continuing relationships with their communities.
- Use the mechanism of bid requests to solve specific needs for government departments such as the MOD, DEFRA, EA, modelled on the USA SBIR contract procedure. Use of contracts would promote product development specific to government needs and should be viewed as a supplement to grants which remain the cornerstone of academic-industry cooperation.
- Set a Global Watch mission for gas sensors to North America, Russia or the Far East. Target our technology priorities, to open the UK's eyes and to test our roadmap conclusions against the global context.

10 Acknowledgements

We would like to thank the following individuals and organisations, without whom we could not have assembled this document:

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The MNT Network and SIRA, in sponsoring and organising the initial brainstorming meetings that started this activity. The MNT Network has also supported a web site for dissemination, with url www.gas-sensor-roadmap.com. Thanks in particular to Toby Gill for helping us set up the website and use the Interwise teleconferencing software.

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Finally, thanks in advance to the readers of this document who, we hope, will comment further to help us establish a solid consensus for each topic.

11 References

[1] 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.

[2] *World Industrial Gas Sensors Detectors and Analyzers Markets*. Frost and Sullian, August 2006. Availale from http://www.frost.com.

[3] J Luff, P Cumpson, M Cross and R Brook. *SENSCOPE Strategic Scoping Study on the Convergence of Enabling Technologies: Microsystems, Nanotechnology and Sensors, Report and Roadmap*. Faraday Intersect Intelligent sensing Faraday Partnership, 2004.

[4] R F Taylor. Chemical and biological sensors: markets and commercialisation, in *Handbook of Chemical and Biological Sensors*, Ed R F Taylor and J S Schultz, IoP Publishing, Bristol, 1996.

[5] P McGeehin. New sensor businesses: expectations and realities. *Proc GASG Colloquium*, 2002.

[6] DTI. *The 2005 R&D Scoreboard. The top 750 UK and 1000 global companies by R&D investment*. Volume 2: company Data, Available from DTI, http://www.innovation.gov.uk/rd_scoreboard/downloads/RD_Analysis_20051%20-%20FINAL.pdf , 2005.

[7] B Boyle. Enabling new detection scenarios with button sized spectrometers. *Proc 37th GASG colloquium*, April 2006.

[8] Underwriters Laboratories. *Standard for Smoke Detectors for Fire Alarm Signaling Systems.* Standard 268 edition 4, Underwriters Laboratories Inc, Northborok, IL, USA, 1996.

[9] Underwriters Laboratories. *Standard for Single and Multiple Station Carbon Monoxide Alarms.* Standard 2034 edition 2, Underwriters Laboratories Inc, Northbrook, IL, USA, 1996.

[10] *Fire detection systems, the European market 2003-2008. Intelligent controls in buildings*. i&i Limited – Proplan, Watford, UK, 2004.

[11] *Dealing with reported gas escapes*. Publication SR/20, the Institution of Gas Engineers and Managers, 1998.

[12] *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.

[13] K Kawase, Y Ogawa and Y Watanabe. Non-destructive terahertz imaging of illicit drugs using spectral fingerprints. *Optics Express* **11** (20), 2549-2554, 2003.

[14] C Patterson. Comments made during presentation. C Patterson and K Skeldon. From the desert to the clinic - the diverse applications of a compact trace ethane gas sensor. *Photonex, Stoneleigh Park, Warwick, 2006*.

[15] CT Holt, PK Dutta, A-M Azad, SL Swartz and RR Rao. Carbon monoxide sensor for PEM fuel cell systems. *Sensors and Actuators B* **87** (3), 414-420, 2002.

[16] IJ Mathiak, W Benz, IK van der Saar and IM van Doeselaar. Hydrogen desulfurization extends fuel cell life. *Hydrocarbon Processing* **86** (2), 107-10, 2006.

[17] T Weh, M Fleischer and H Meixner. Optimization of physical filtering for selective high temperature H_2 sensors. *Sensors and Actuators, B* **68** (1), 146-150, 2000.

[18] S Okuyama, Y Mitobe, K Okuyama and K Matsushita. Hydrogen gas sensing using a Pd-coated cantilever. *Japanese Journal of Applied Physics* **39** (6) 3584-3590, 2000.

[19] A Chtanov and M Gal. Differential optical detection of hydrogen gas in the atmosphere. *Sensors and Actuators B* **79**, 196-199, 2001.

[20] JP Sharkany, SO Korposh, ZI Batori-Tarci, II Trikur and JJ Ramsden. Bacteriorhodopsin-based biochromic films for chemical sensors. *Sensors and Actuators B* **107**, 77–81, 2005.

[21] JD Ingle and SR Crouch. *Spectrochemical Analysis*. Prentice Hall, 1988.

[22] *"OMEMS": Analysis of Optical MEMS applications for non telecom markets.* www.yole.fr, Yole Développement Lyon, France, 2005.

[23] MS Haque, SP Oei, KBK Teo, F Udrea, JW Gardner and WI Milne. CMOS compatibility of carbon nanotubes on SOI Devices. *Nanotech 2006* **1**, *Technical Proceedings of the 2006 NSTI Nanotechnology Conference*, NSTI, 2006.

[24] E Vanneste. *Handbook of Machine Olfaction*. Wiley-VCH, 2002.

[25] J Mitrovics. *Market Survey Artificial Olfaction 2004*. Available from NOSE II – 2nd Network On Artificial Olfactory Sensing, www.nose-network.org, and JLM Innovation, Tübingen, Germany, 2004.

[26] RW Bogue. *Technology roadmap: Optoelectronic gas sensors in the petrochemicals, gas and water industries*. Published on www.OptoCem.Net , August 2006.

[27] GJ Fetzer, AS Pittner, WL Ryder, and DA Brown. Tunable diode laser absorption spectroscopy in coiled hollow optical waveguides. *Applied Optics* **41**, 3613-3621, 2002.

Appendix A Glossary

ASIC	Application Specific Integrated Circuit
Asphyxiant	substance that causes unconsciousness or death by suffocation
BAW	Bulk Acoustic Wave
BBSRC	Biotechnology and Biological Sciences Research Council
billion	10^9
BTEX	Benzene, Toluene, Ethylbenzene, Xylenes
CAGR	Compound Annual Growth Rate
Capnography	exhaled breath measurements
CASE	Cooperative Awards in Science and Engineering – 3 year postgraduate research awards with industrial co-funding
CFC	Chloro fluoro carbons
CH_4	methane
Chemiluminescence	chemical reaction causing emission of light. Used as marker.
Cl_2	chlorine
CMOS	complementary metal oxide semiconductor (Si device process)
CNT	Carbon nanotube
CO	carbon monoxide
CO_2	carbon dioxide
CoGDEM	Council of Gas Detection and Environmental Monitoring
CRDS	cavity ringdown spectroscopy
Da	Dalton (molecular weight unit)
DEFRA	Department for Environment, Food and Rural Affairs
DMS	Differential Mobility Spectroscopy (IMS variant)
DSP	Digital Signal Processing
DTI	Department of Trade & Industry
DVD	Digital Video Disc
EA	Environment Agency
EH40	Environmental Health requirements and guidelines
EPSRC	Engineering and Physical Sciences Research Council
EU	European Union
FAIMS	Field Asymmetric Ion Mobility Spectroscopy (IMS variant)
FET	Field Effect Transistor
FID	Flame ionisation detector (mainly for GC)
FITS	future intelligent transport systems.
Fluorescence	light emission following absorbance of (usually shorter wavelength) radiation. Used as marker by linking to a reaction process.
FPGA	field programmable gate array
GasFET	Gas sensitive Field Effect Transistor
GASG	Gas Analysis and Sensing Group
GC, microGC	Gas Chromatography
GP	General Practitioner (doctor)
HASAWA	(UK) Health and Safety at Work Act (1975)
HC	hydrocarbons
HCl	hydrochloric acid
H_2O	water (vapour)
H_2S	hydrogen sulfide
HSGFET	Hybrid suspended gate Field Effect Transistor
HVAC	Heating Ventilation and Air Conditioning
Hz	Hertz – frequency – as in THz terahertz
IAQ	Indoor Air Quality
III-V materials	compound semiconductor – group III and V elements e.g. GaAs
IMS, microIMS	Ion Mobility Spectroscopy

IPPC	Integrated Pollution Prevention and Control
IR	Infra red
KTN	Knowledge Transfer Network (e.g. Sensors KTN)
LED	Light Emitting Diode
LEL	Lower Explosive Limit
LIDAR	Light Detection and Ranging
MCERTS	the UK Environment Agency's Monitoring Certification Scheme
measurands	property or thing to be measured, eg chemical species
MEMS	Micro ElectroMechnical Systems
Microfluidic	pertaining to fluid flow in microstructures and channels
Microhotplate	low thermal mass heated sensor substrate
Micro-TAS	Micro Total Analysis Systems (μTAS, Lab on a Chip)
MIP	Molecularly imprinted polymers
MISiCFET	Metal Insulator Silicon Carbide Field Effect Transistor
MNT	Micro and Nano Technology
MOD	Ministry of Defence
MRC	Medical Research Council
MS	Mass Spectrometry
NERC	Natural Environment Research Council
NDIR	Non-Dispersive Infra Red (detection)
NDUV	Non Dispersive Ultra Violet
NH_3	ammonia
NIOSH	National Institute for Occupational Safety and Health
N_2O	nitrous oxide
NO	nitric oxide
NO_2	nitrogen dioxide
NPL	National Physical Laboratory
O_2	oxygen
O_3	ozone
OptoCem.net	KTN covering optoelectronic chemical sensing research and exploitation.
OSHA	Office of Safety and Health
PEDOT	Poly(3,4-ethylenedioxythiophene) – a conducting polymer
Pellistor	gas sensor relying on heat release by combustion of target gas on a heated catalyst, increasing its temperature and thereby its resistance.
Photoacoustic	gas sensed by acoustic effect of heating following light absorption
PIC	Peripheral Interface Controller
PID	Photo-ionisation detector
PM 10, PM 2.5	Particles –10 and 2.5 micrometre sizes
PolFET	Polymer (coated) gate Field Effect Transistor
ppm	parts per million
ppb	parts per billion
QCL	Quantum Cascade Laser
QD	Quantum Dot
QMB	Quartz microbalance
QMS	quadrupole mass spectrometry
Reynolds Number	Dimensionless number in fluidics. Ratio of inertial to viscous forces. Laminar flow at low values, turbulent at high.
Rhinitis	inflammation of the mucous membranes of the nose
RI	Refractive Index
SAW	Surface Acoustic Wave
SBIR	Small Business Innovation Research program
SF_6	sulfur hexafluoride
SIRA	Business with Sensors KTN functions now transferred to NPL

SME	Small and Medium sized Enterprise. For a full definition see http://fp6uk.ost.gov.uk/documents/lsgb/Jane_Watkins_SME_Definition.pdf
STF	Sensor Task Force
STA	Stack Testing Association
SVOC	Semi-Volatile Organic Compound
TDLAS	Tunable diode laser absorption spectroscopy
Toxic gas	Gas that can cause death by poisoning at low concentrations
TWA	Time Weighted Average
UV	Ultra violet
VOC	Volatile Organic Compound
WEL	Workplace Exposure Limits
Wien filter	velocity filter in mass spectroscopy using orthogonal electric and magnetic fields
WWT	Waste Water Treatment

Appendix B Market-Technology Matrix

The potential of each technology in each market sector was ranked from 1 to 5, with 1 representing either low potential or possibly a very small market, and 5 representing significant potential. Rankings were provided initially by the authors of this report and then by various invited contributors, including those attending a meeting of the Gas Analysis and Sensing Group. From the combined rankings a consensus emerged, shown below.

The scores have been totalled for each technology area and market sector. These scores are not considered definitive and we are seeking further comments - this matrix is considered to be a live document, and in the public domain. Organisations considering investment decisions should conduct their own market studies in greater depth and form their own opinions; our rankings can only be considered a starting point in this process.

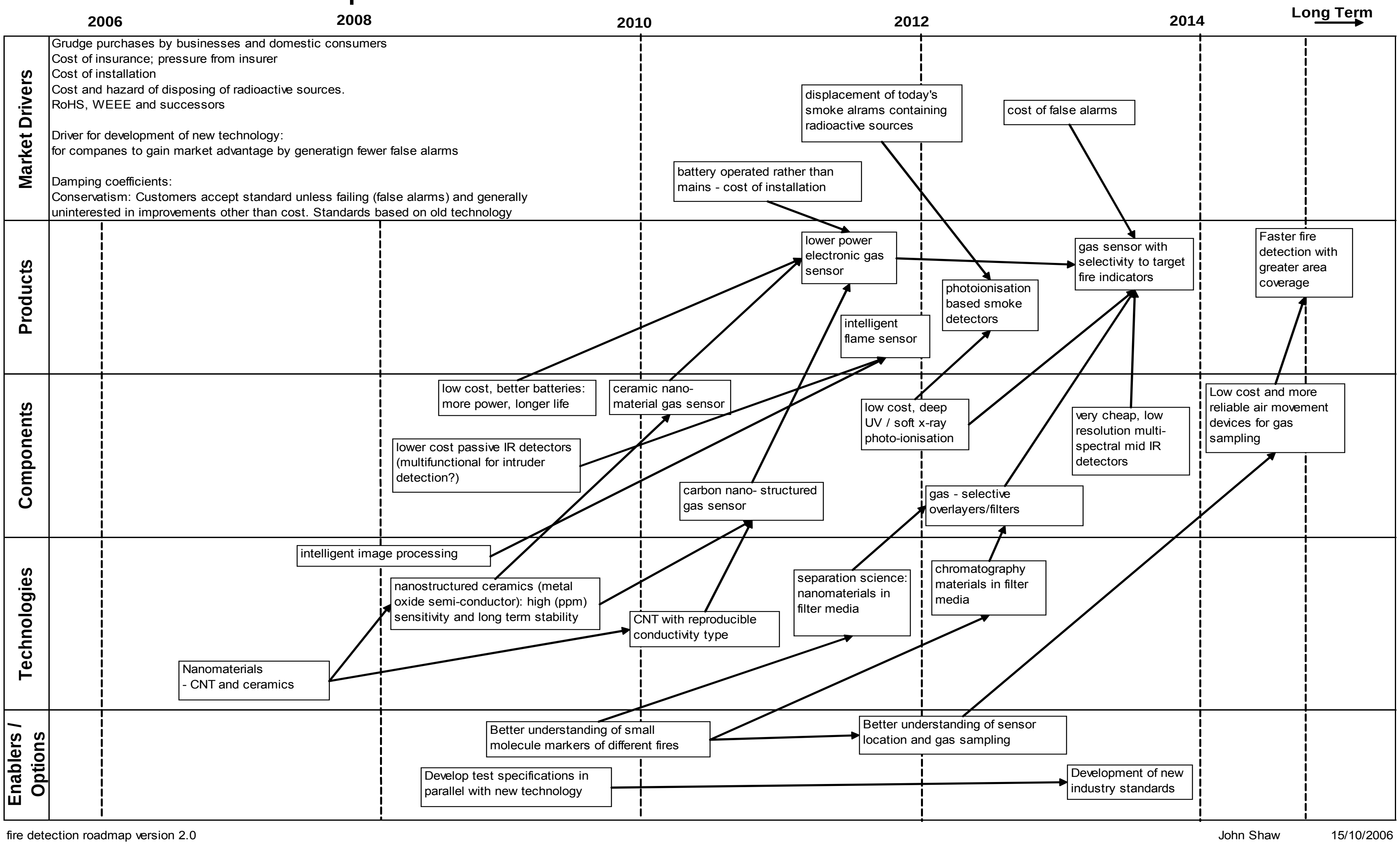
This matrix was then analysed as follows:

- ***A high total for a technology*** means that it could have widespread impact, increasing the justification for investment. High impact technologies include separation science, electronic components, optical light sources, sensor arrays, nanomaterials, low cost/ integrated optics, microelectromechanical systems (MEMs), MEMs/ CMOS integration and electrochemical cells.
- ***A high total for a market sector*** may justify investment in applications engineering or fundamental understanding. Some market sectors may be held back by technology immaturity or missing analytical knowledge. Favoured markets include indoor air quality, VOCs, medical diagnostics, food quality and production control.
- If a market sector is considered important or of high value, ***a low market total*** could mean that there is little opportunity for alternative technologies, but if a technology is able to meet a market need then it will have a secure market position. An example would be asthma in the home, which is rated as important but has few applicable technologies.
- ***A low technology total*** does not imply that it does not fit a niche; rather, at present the consensus is that large scale investment is not justified. There could still be a "killer application", or a technical development which, if successful, could change the picture. Two technology examples would be ion mobility spectrometry (IMS) with potential use for indoor air quality and homeland security, or micro total analytical systems (microTAS), with potential use in predicting asthma in the home.

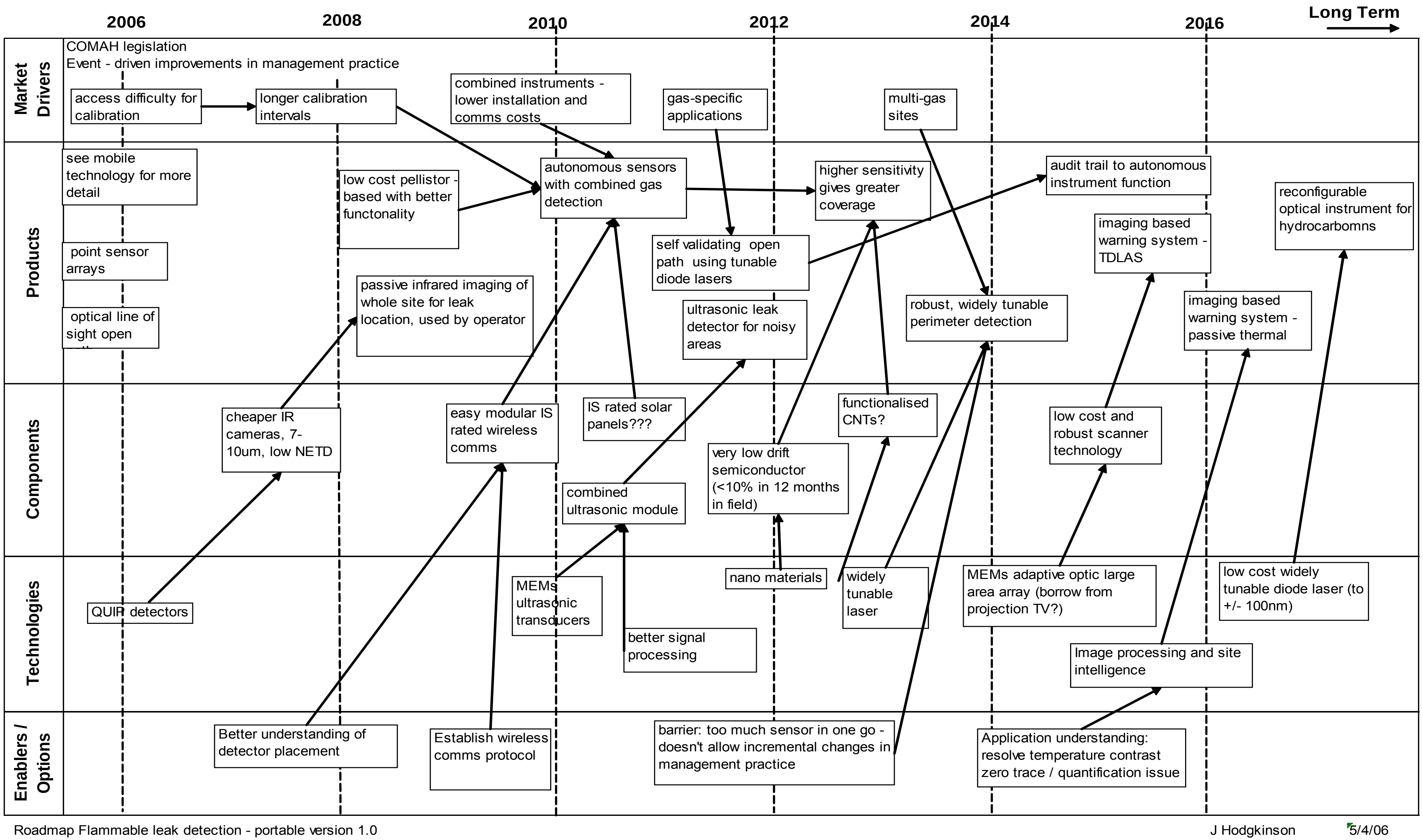
Key: 5 - highly applicable / high potential 1 - generally poor potential		Domestic safety		Auto-motive		Industrial safety		Process control			The Law		Niche			Air quality					Homeland security	Medical	
However, technologies with low ratings might nevertheless find good application in a very small niche	**Existing markets**	Fire and home safety	Utilities leak detection	Car emissions	PM10, PM2.5	Industrial safety & LEL	Confined space entry	Stack emissions	Process control and analysis	Food processing, transport and storage	Breathalyser / alcohol & drugs	**Emerging markets**	Hydrogen: fuel cells	Extreme environments (planetary, oil)	Ammonia	Benzene, BTEX	Outdoor air	Indoor air	Asthma, allergies	Nuisance odours	Explosives/ terrorism	Breath analysis & capnography	Total
Components																							
Lasers and optics		2	5	4	4	4	3	5	5	3	3		2	4	4	1	5	5	1	4	5	5	74
UV, IR, microplasma sources		4	3	4	4	5	4	5	5	3	5		1	3	4	4	4	5	1	4	4	5	77
Wavelength separation MEMS		3	2	4	1	2	2	3	5	4	3		1	3	4	4	2	4	2	4	2	4	59
Low cost optics, detector arrays		4	3	3	4	4	3	3	3	4	4		1	2	3	4	2	5	1	2	1	4	60
Fibre optics		1	3	2	4	4	3	4	4	4	2		3	5	1	3	2	2	1	2	3	4	57
Micro GC		1	2	3	4	2	2	3	4	3	3		1	2	1	5	3	4	1	3	5	3	55
Micro MS		1	2	1	1	1	1	4	4	4	3		5	5	1	3	1	2	1	1	4	3	48
PID, IMS		1	4	2	1	4	4	2	4	4	3		2	1	3	5	2	5	2	4	5	3	61
QMB, SAW, BAW		1	2	1	1	1	1	1	4	3	2		1	2	3	3	1	1	1	3	4	3	39
Sensor arrays		4	4	2	1	3	4	4	4	4	3		3	3	4	4	3	4	4	5	3	4	70
Microprocessors/ FPGAs/ PICs/ ASICs		3	1	5	5	5	5	3	5	5	3		3	4	3	5	4	5	5	4	5	5	83
Wireless		3	3	2	3	4	4	3	3	3	1		3	1	2	3	5	5	2	5	4	4	63
Technologies																							
MEMS		3	2	2	3	2	2	2	4	4	3		4	2	4	5	5	3	4	4	4	4	66
Nanomaterials (QDs, CNT, nano MO)		2	2	2	1	2	2	2	3	3	2		4	4	4	5	3	4	4	3	3	3	58
Polymers, liquid crystals		2	1	2	1	2	1	2	2	4	3		1	2	3	3	2	4	1	3	2	3	44
Electrochemistry		4	2	4	1	5	4	4	4	2	4		4	4	4	2	4	5	4	4	2	3	70
Separation science		3	5	5	3	5	5	1	3	5	4		4	5	5	5	2	3	5	4	3	4	79
Physical chemistry (enthalpy, speed of sound)		2	4	3	1	4	4	2	2	1	1		4	4	1	2	1	3	1	1	1	2	44
Products																							
NIR spectrometers		2	2	3	1	3	3	3	5	5	4		1	3	1	4	2	5	1	5	2	5	60
IR single line absorption		2	5	4	4	3	3	5	5	5	5		2	5	5	1	4	5	3	5	4	5	80
IMS		3	3	2	1	1	1	2	5	2	1		2	1	2	4	2	1	2	1	5	2	43
Micro GC/MS		1	2	3	3	1	1	5	5	3	3		3	3	1	4	3	2	3	2	5	3	56
Nanoparticle fluorescence		2	1	2	1	2	2	3	4	4	2		3	5	3	2	2	2	5	3	5	4	57
IR, Visible, THz gas cameras		1	5	4	1	4	3	3	2	1	3		1	2	1	2	3	3	1	4	5	2	51
Ultrasound, thermal conductivity imaging		4	5	1	1	1	1	2	3	2	1		4	5	1	1	1	3	1	1	1	2	41
Electrochem/ optical/polymer/ nano arrays		4	1	2	1	4	4	2	5	5	4		2	5	2	1	2	2	2	5	4	4	61
Total		57	66	64	48	69	65	68	92	84	67		62	78	62	80	61	82	57	78	82	83	

Appendix C Diagrammatic Roadmaps

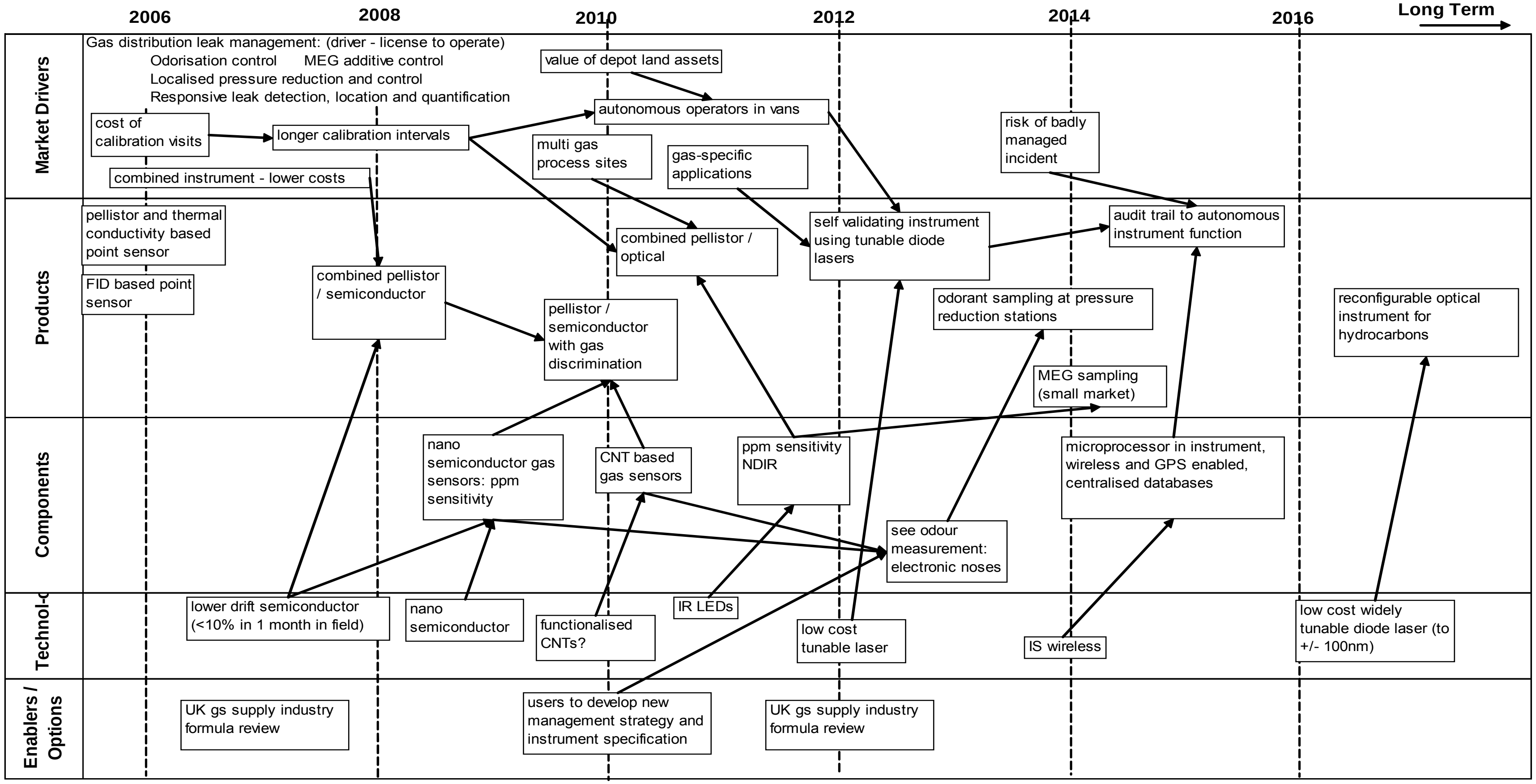
C 1. Fire detection roadmap



C 2. Flammable leak detection roadmap – permanent installations



C 3. Flammable leak detection roadmap – portable equipment and leakage control



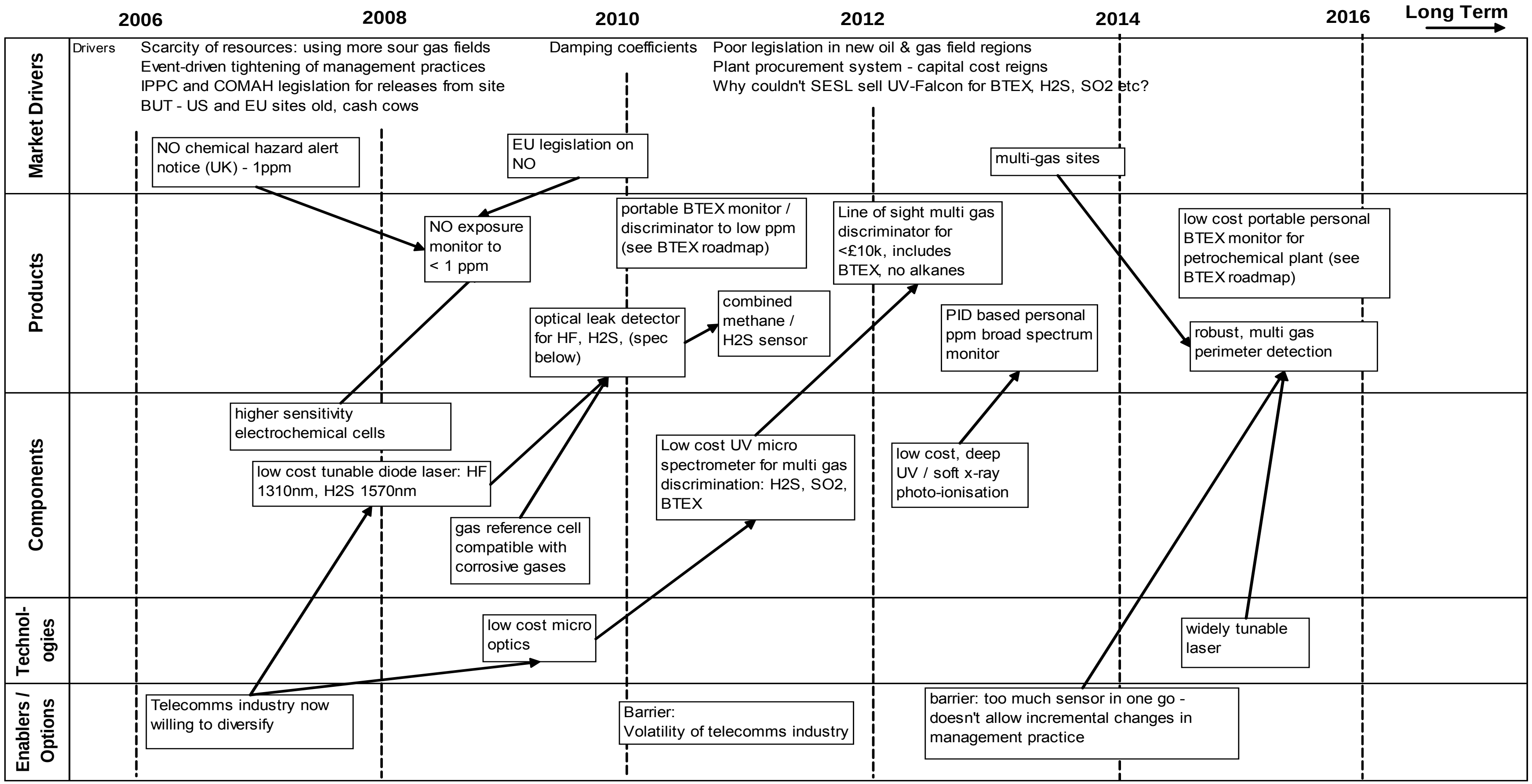
<u>Portable gas leak detectors (natural gas / methane)</u>
Concentration range 10 ppm – 100%
Accuracy ± 15% at 0-1000 ppm; ± 1% LEL at 20% LEL; ± 2% vo
Response time T90: 1-15 sec, depending on mode of use
Rechargeable batteries with 8 hour life
Life between recharges 8 hours
IS. Ex II 1G (ATEX 100A Directive), Eex ia s IIC T4 (Cenelec)
£3-4,000 for full functionality
market size ~ 30,000

<u>Spec for odorant sampling:</u>
Responds to Mixtures of BM and DMS or characteristic odour arising from this
Typical concentrations 6 mg/m3 (~ 3 ppm)
Limit of detection ~0.1 ppm

Specifications Ref R Bogue "Needs and opportunities for new and improved gas sensors", Issue D, Optocem.net, Feb 2006

Roadmap Flammable leak detection - portable version 1.0 J Hodgkinson 5/4/06

C 4. Toxic leak detection roadmap

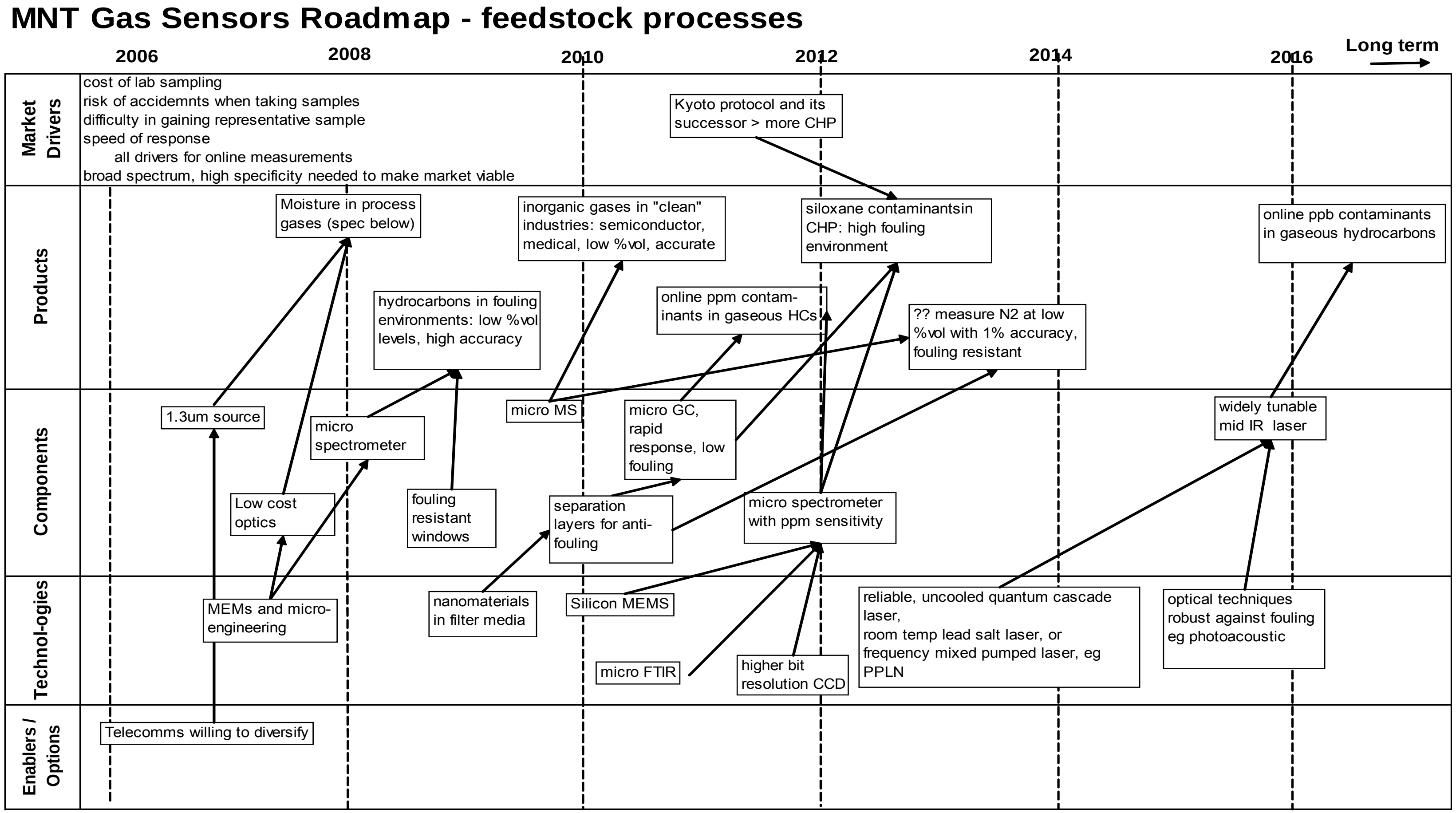


HF leak detector:	H2S sensor (and combined with methane):
Range ~ 0-20 ppm	Range 0-1000 ppm H2S
Limit of detection ≤ 1 ppm	Minimal cross-reactivity to chlorine, CO etc.
Response time < 1 min, ideally a few sec	Operate to 100% RH and 90-100°C
Lifetime > 1 year (ideally maintenance-fre	Operating over 1 year continuous, unattended
Certified IS	£1k cost per measurement point
1000 point sensors x £1500, or	£5k per open path line of sight
50 line-of-sight systems x £50k	market of low 10's thousands

Specs Ref R Bogue "Needs and opportunities for new and improved gas sensors", Issue D, Optocem.net, Feb 2006

J Hodgkinson 5/4/06

C 5. Feedstock processes roadmap



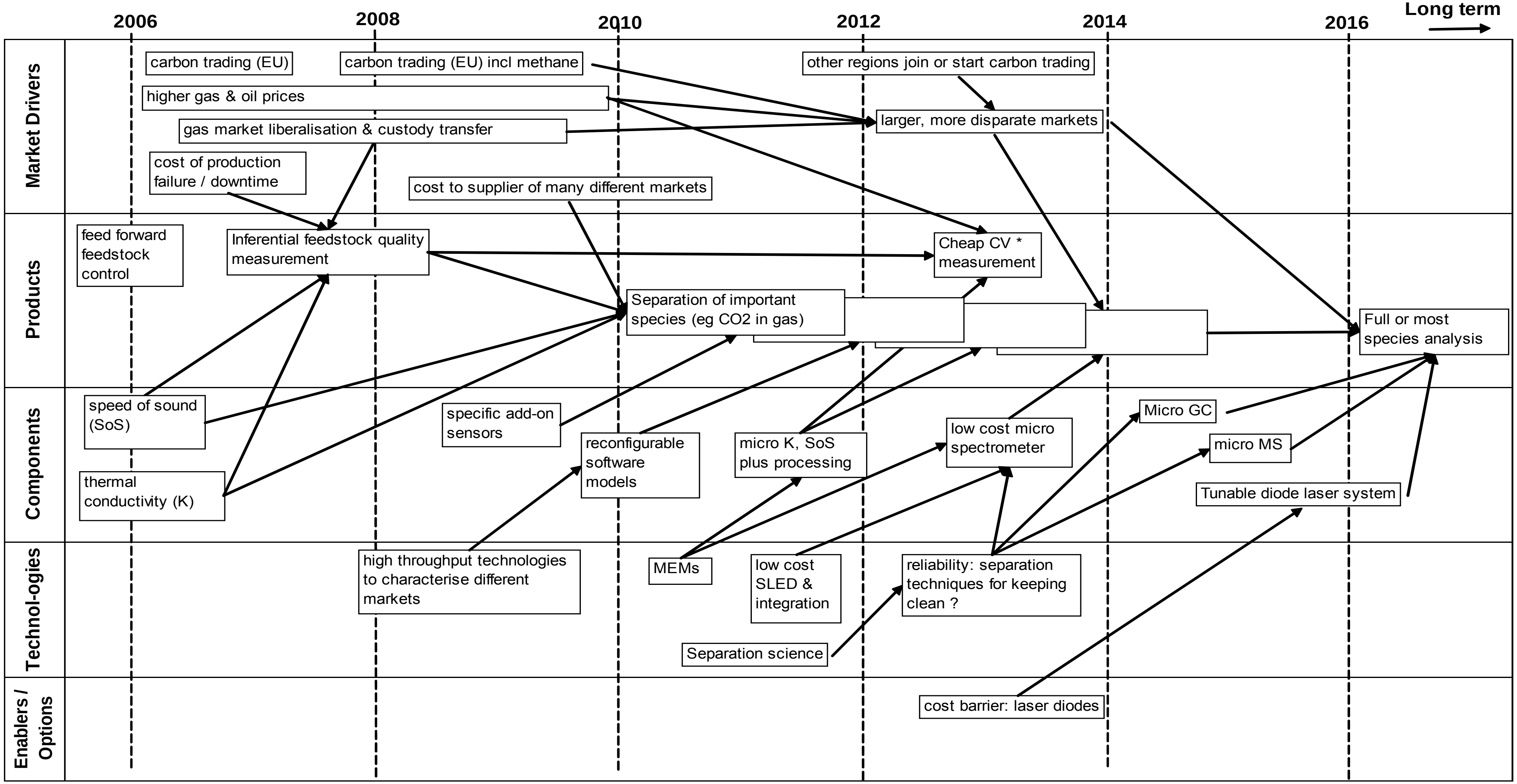
Moisture in natural gas
spec
Range <1 to >100 ppm
Resolution <1 ppm
Not affected by CO_2, H_2S, glycol or other contaminants
Response ideally seconds
Certified IS (gas & oil industry), non IS (semiconductor, medical industry
£20-30k for installed system on a plant

spec for siloxanes:
range 0-100ppm
lod 1ppm
cost £5k
market ~ 5,000 for water treatment alone

spec for contaminants in process streams:
ppm to ppb detection of H_2S, mercaptans, NH_3, ethers, esters, alcohols
in hydrocarbon matrix
robust against fouling or cleanable
IS rating not necessary
cost £50k for ppb
market several 100's

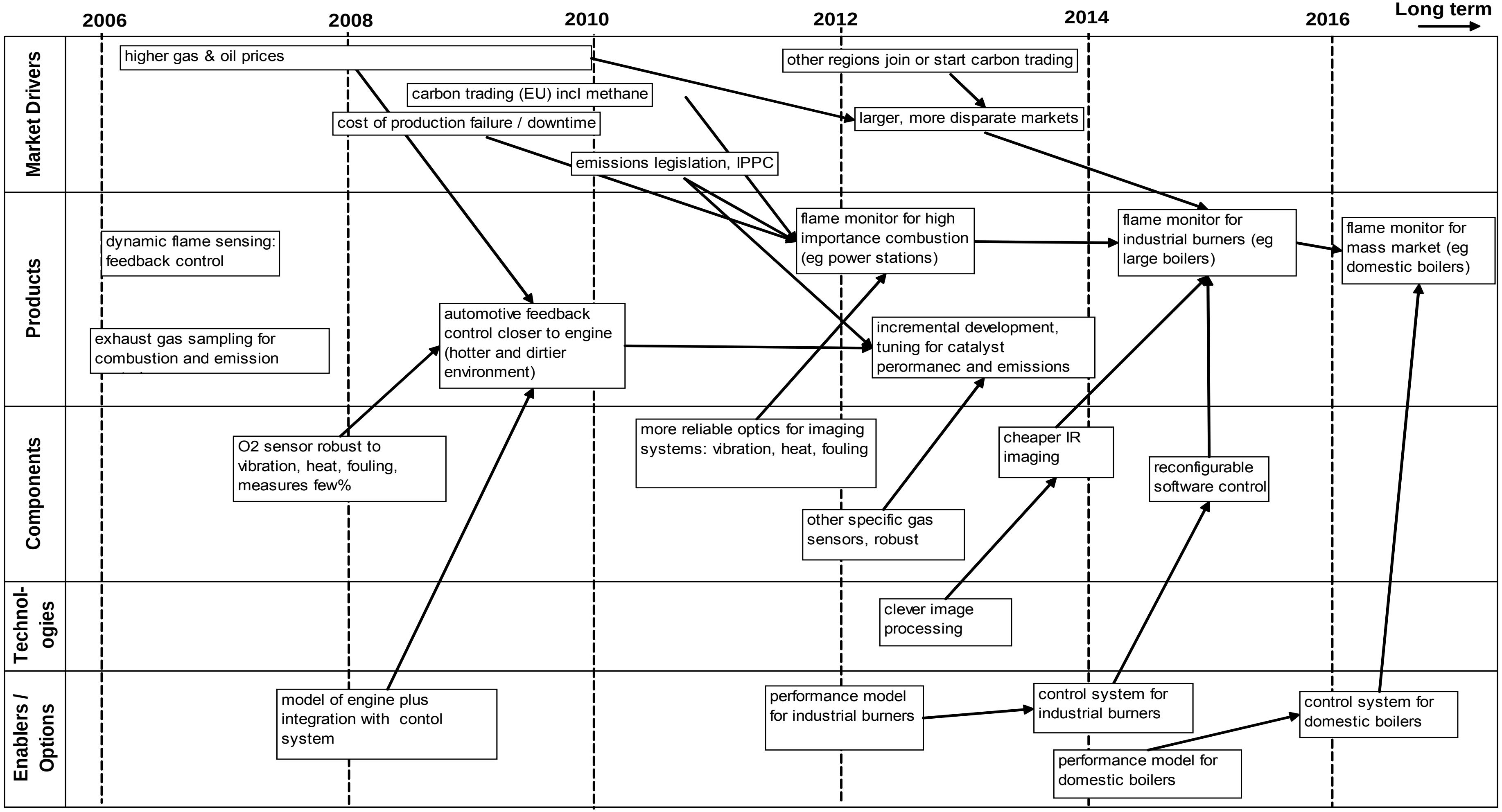
Specifications Ref R Bogue "Needs and opportunities for new and improved gas sensors", Issue D, Optocem.net, Feb 2006

C 6. Feed forward process control, fuel quality and metering



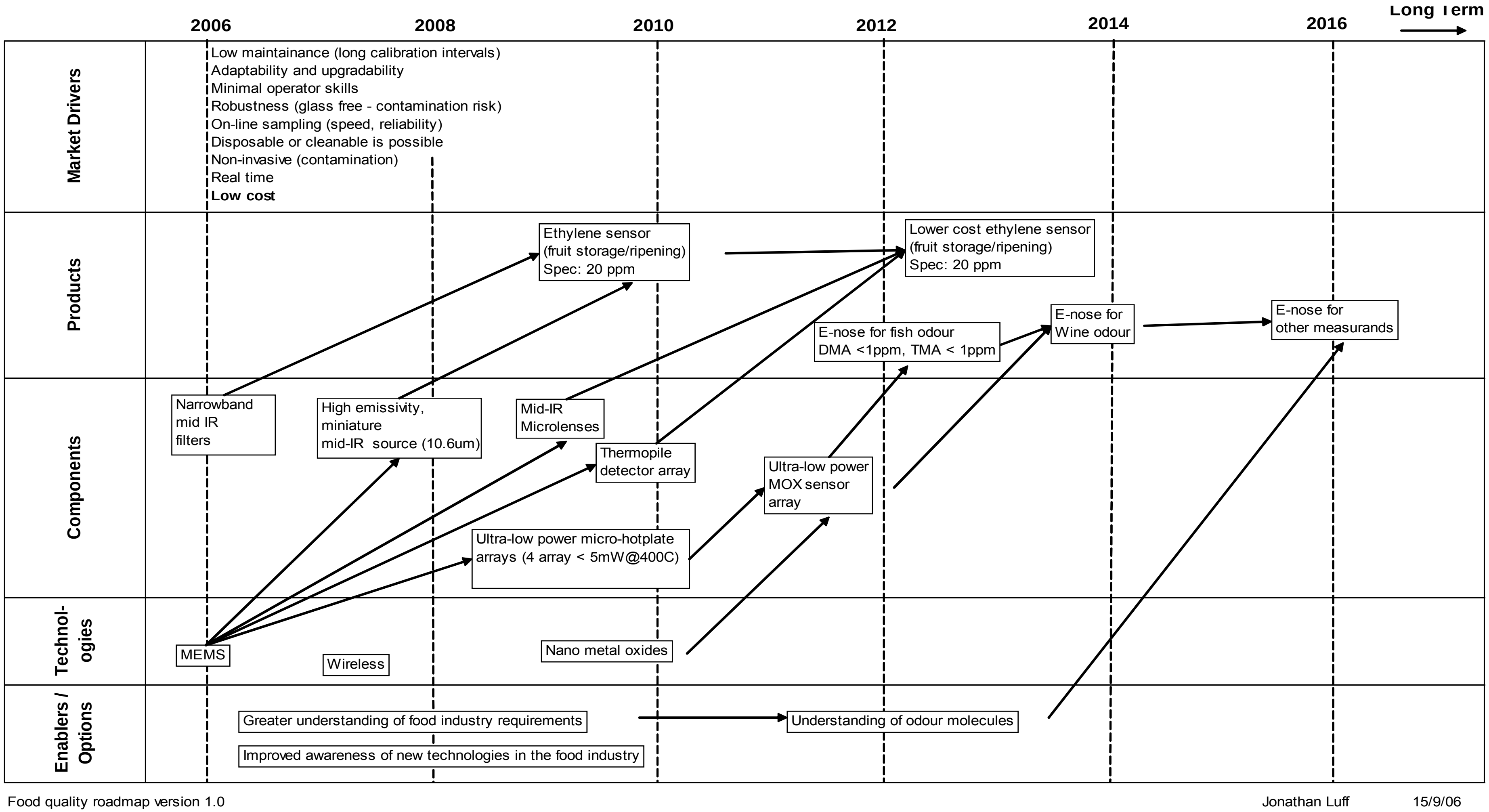
CV: calorific value

C 7. Feedback combustion control

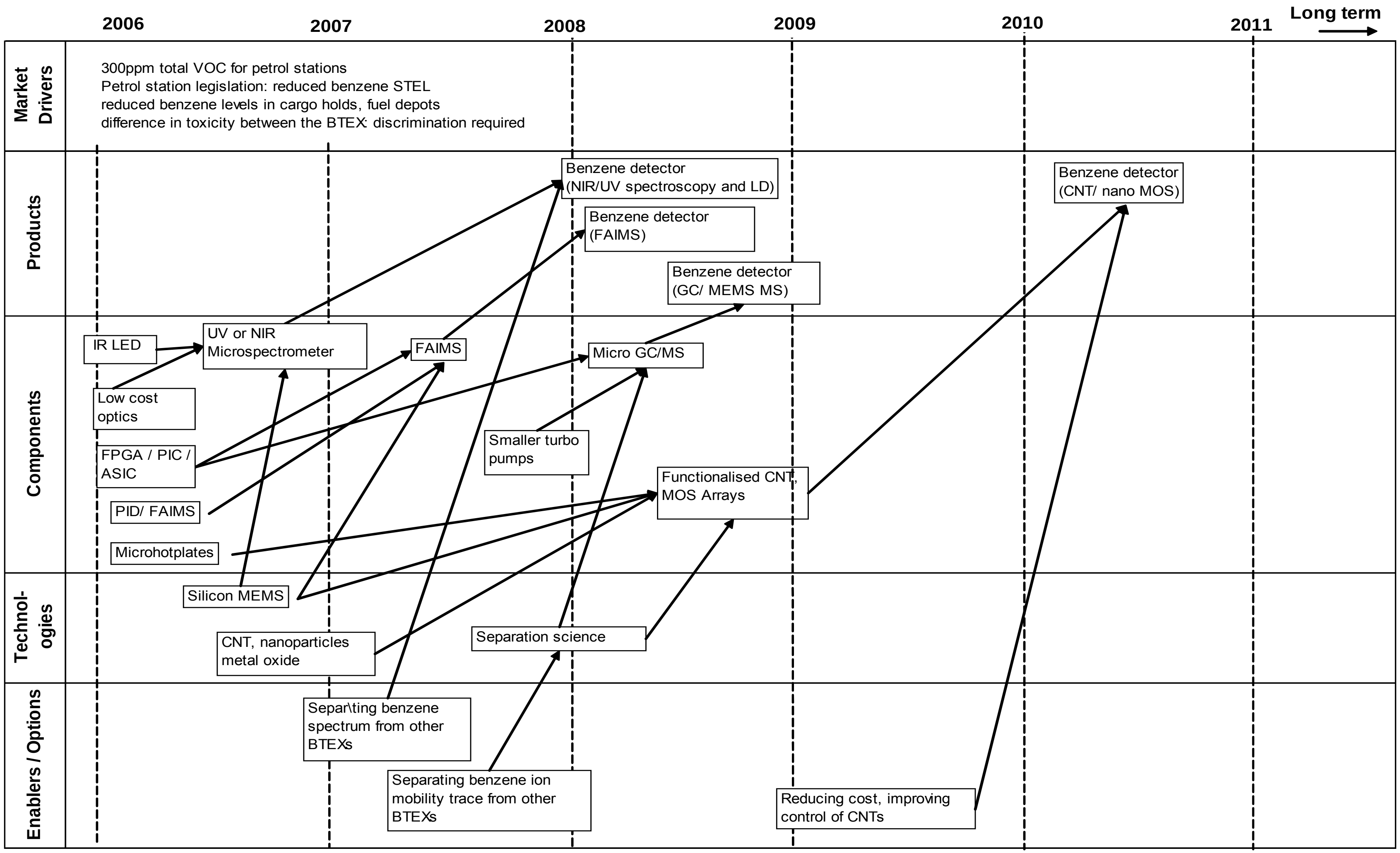


Roadmap Feedback combustion control version 2.0 J Hodgkinson 5/4/06

C 8. Food quality roadmap

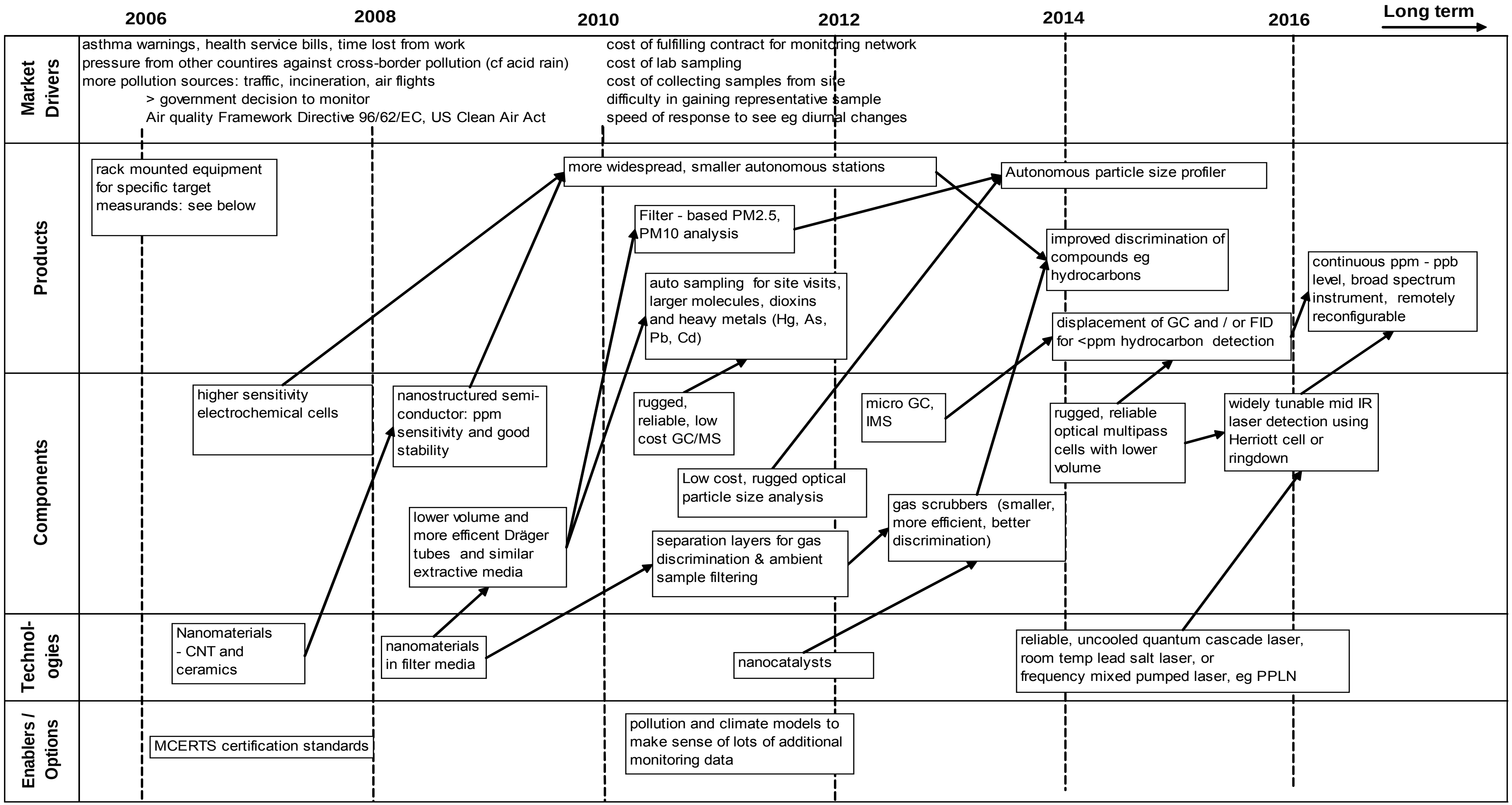


C 9. BTEX roadmap



BTEX Roadmap version 2.0 John Saffell 21/4/06

C 10. Outdoor air quality roadmap

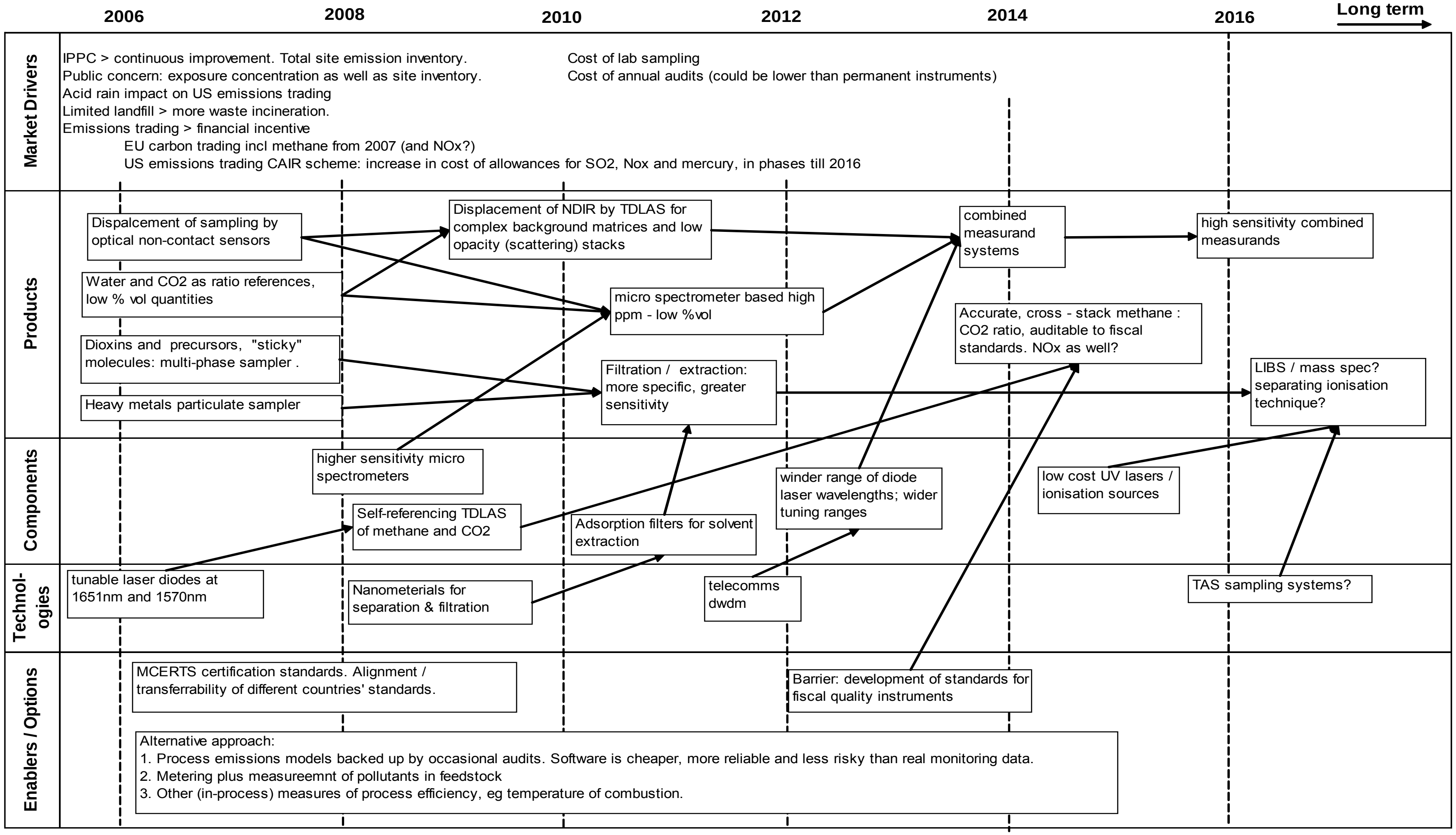


Limits of detection:	CO	0.1ppm	benzene	0.25ppb	Equipment cost approx £10k per measurand.
	NO2	2.5ppb	hydrocabons	100ppb	Zero drift is an issue.
	O3	1ppb	SO2	2.5ppb	

Outdoor air quality roadmap version 2.0

Jane Hodgkinson 11/12/06

C 11. Stack emissions monitoring

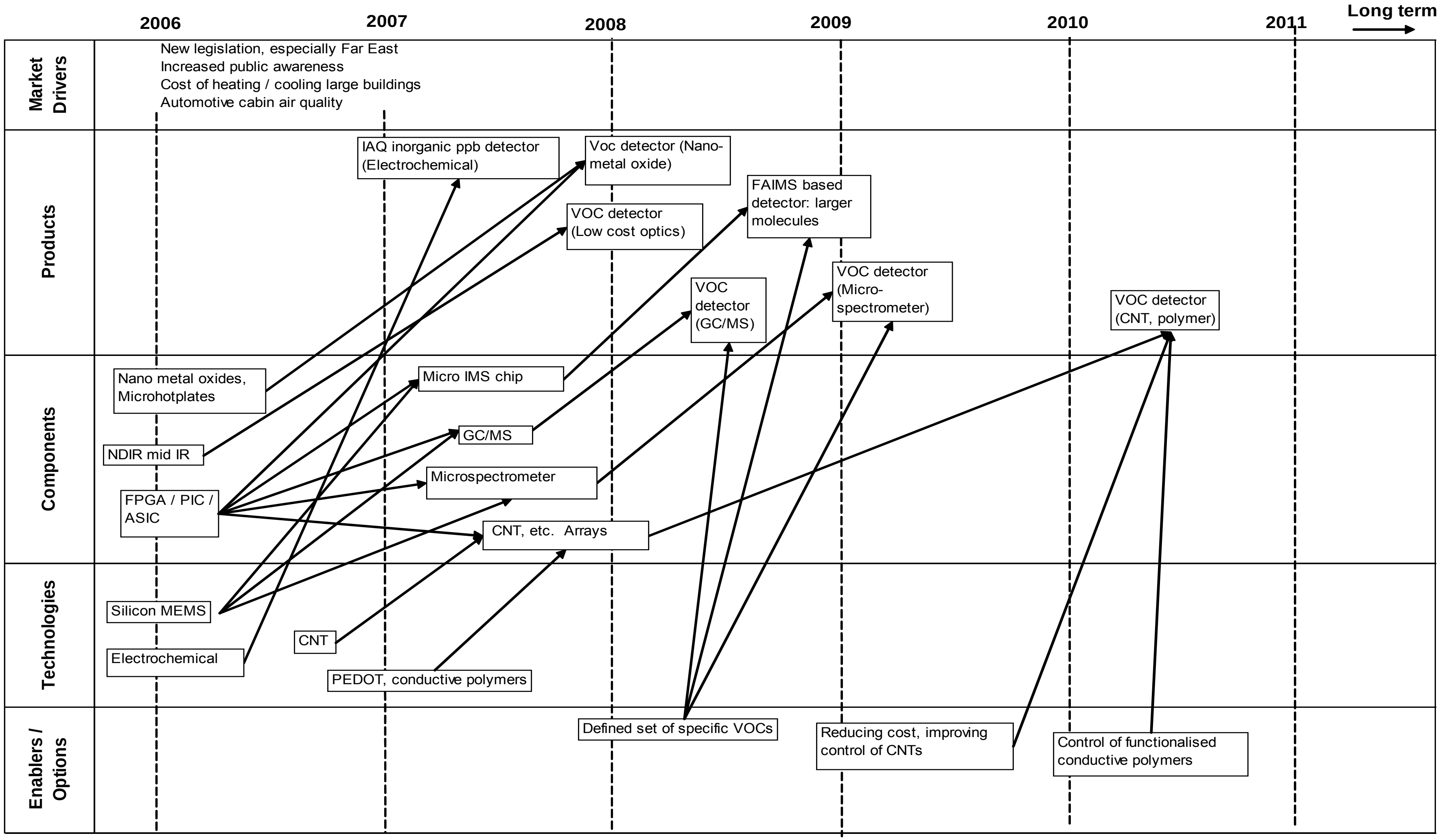


Accuracy can be important in this application, ratioed to eg CO2 emissions (absolute levels of which are determined by metering)

CO2	range 5% or more	SO2	range 20ppm	CL2	range 50ppm
H2O	range 10%	NO2	range 20ppm	HCl	range 50ppm
CO	range 200ppm	NO2	range 20ppm	HF	range 50ppm
		NH3	range 20ppm	H2S	range 50ppm

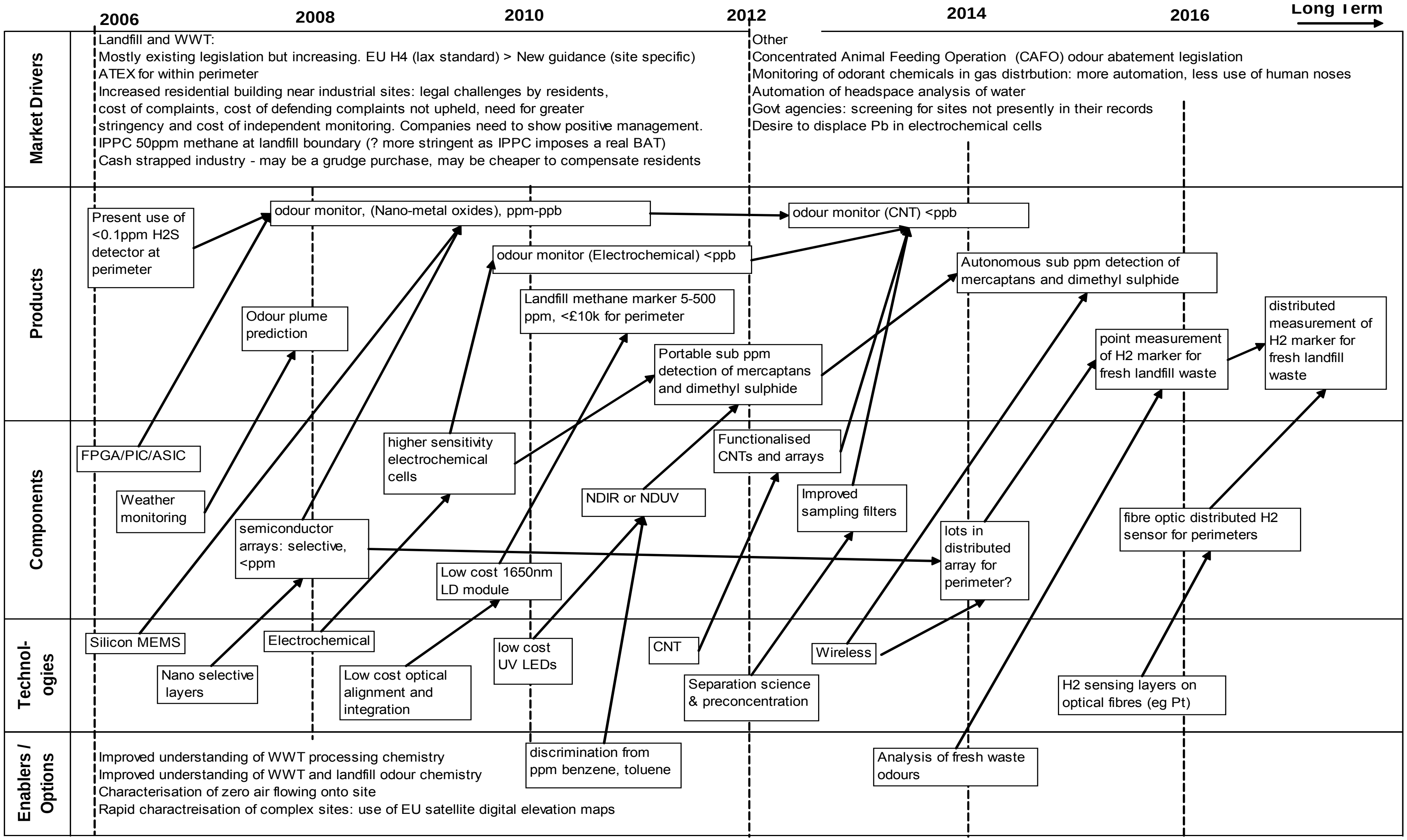
Stack emissions monitoring roadmap version 1.0 Jane Hodgkinson 10/4/06

C 12. Indoor air quality roadmap



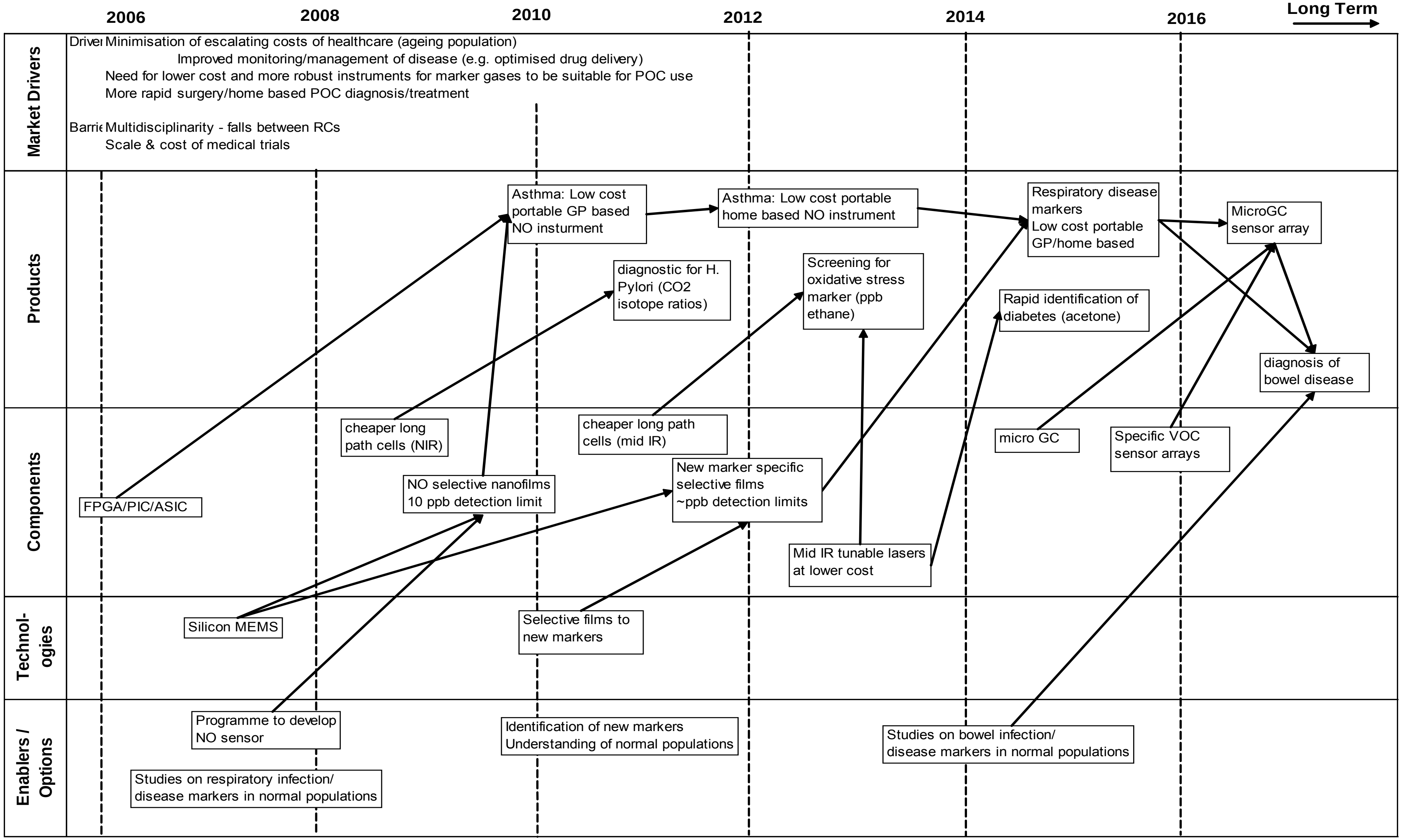
Indoor air quality roadmap version 1.0 John Saffell 21/4/06

C 13. Odour monitoring roadmap



Odour monitoring roadmap version 2.0 Jonathan Luff and Jane Hodgkinson 28/4/06

C 14. Medical diagnostics roadmap



Medical diagnostics roadmap version 1.0 John Saffell and Jonathan Luff 7/4/06