

GAS DETECTION- PREDICTING THE FUTURE

New markets are on the horizon, relying on the latest research to be turned into product. What are the market drivers and the potential opportunities from technology breakthroughs? We first consider new markets and then some technology opportunities for both emerging markets and existing markets.



The Council of Gas Detection and
Environmental Monitoring

Emerging Markets

Global politics and global consumer patterns are creating new markets, but the largest emerging market is health: personalised health, non-invasive health care and real time personal health monitoring.

Wearables and Smart Phone Sensors are needed urgently, we are told. The people spreading the message are the manufacturers of smart phones, tablets and lifestyle monitors. Accelerometers, GPS, temperature sensors and pressure/pulse monitors are well established but these manufacturers are looking for the next big thing and it is chemical sensors, biosensors and gas sensors. What gases do they want to measure? Smart phone breathalysers (ethanol) bad breath detectors (H_2S) and wearable air quality monitors (NO_2) are on their list.

Explosives/ IED detection became a significant market after 9/11. This demand is global and driven by the security requirements of every country. Attempts to detect explosives in the field at ppt concentrations in seconds is a challenge that has not yet been met. Organometallic and metal oxide arrays, fluorescence, FTIR and Raman spectroscopy, Ion Mobility Spectroscopy and "portable" GC and MS have all been tried, but with either slow processing time or inadequate selectivity or sensitivity. A significant breakthrough is required and either orthogonal multiple technologies or synthetic biology may provide the answer in years to come.

The health monitoring market is potentially a massive market, limited only by the available technologies. Non-invasive real-time personal health monitoring is the goal for support in assisted living, GP breath analysis for early detection of cancers and many other diseases, skin emissions to give a running diary of our wellbeing. These are just a few of the potential applications.

Sensor Technologies Have New Challenges

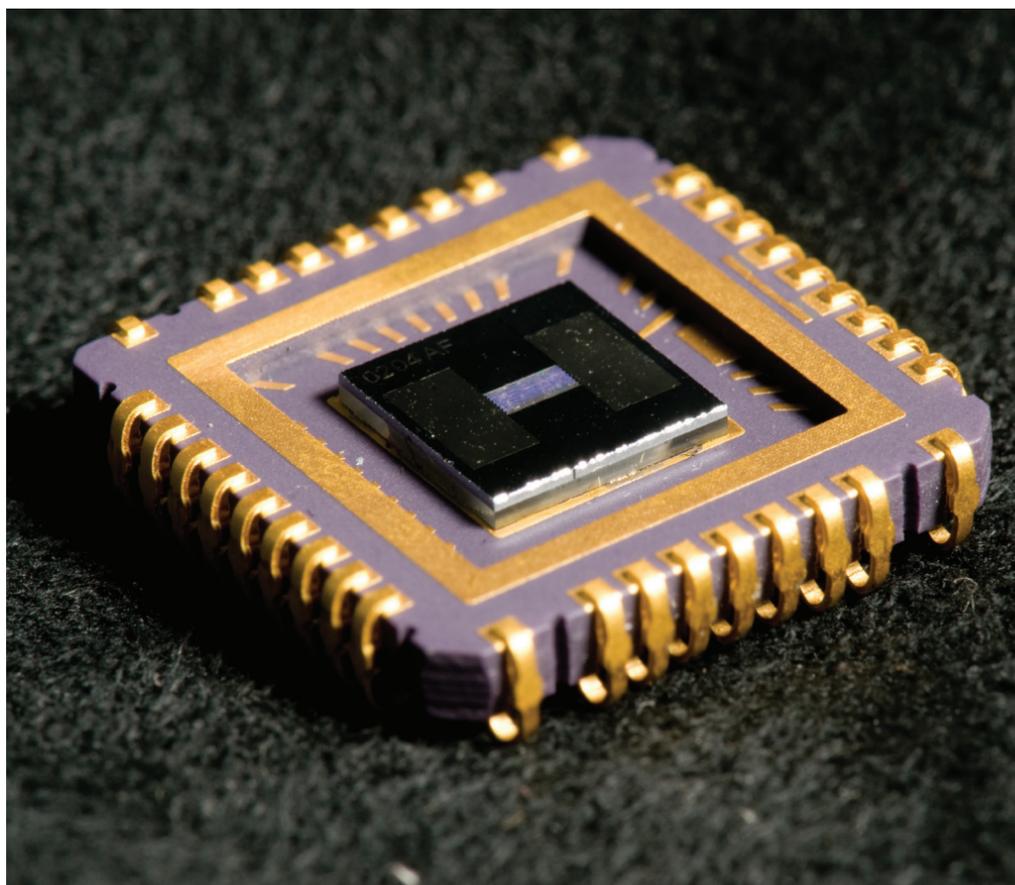
The path from basic research to applied research, then product development/ engineering has quickened and there is no lack of optimism on what can be achieved. Some of this optimism is justified, some is not.

Planar Electrochemical Toxic Sensors have been on the market for a few years, with varying levels of success. The Ceramic-based structures appear to have been the first, but problems persist with the organic/ ionic liquid electrolyte. The first planar sensors based on aqueous electrolyte are completing UL approval. Planar designs allow for lower cost and better form factor for smart phone type designs and potentially wearable sensors, but sensitivity and selectivity must match the performance of standard 20.0 (dia) x 16,6mm (ht) sensors. Shrinking to smart phone and wearables dimensions and meeting their extended environmental requirements are further in the future.

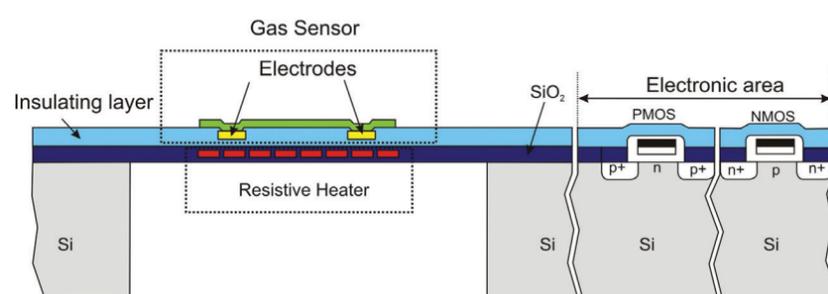
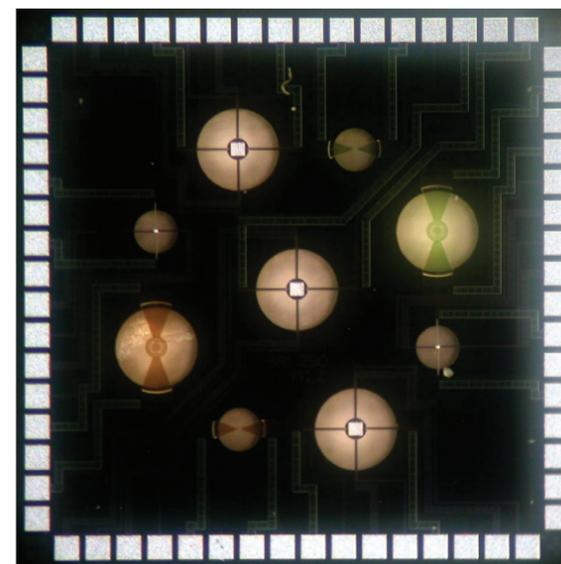
VOC Detection is more difficult than measuring inorganic gases: there are thousands of VOCs, and many are molecularly similar but very different in their toxicity. Current technology such as metal oxides and PIDs have adequate sensitivity (1-20 ppbv) but very little selectivity. The perennial question is whether to measure a family of VOCs (e.g. aromatics, amines, mercaptans) or target a specific VOC (e.g. formaldehyde, benzene, ethanol). Non-specific VOC indication is only useful as a relative indicator- for example, we can only confirm that there are more VOCs today than there were yesterday. Some technologies are now able to detect specific VOCs, using different forms of spectroscopy. They are still limited by high cost, restricted portability/ power and/ or poor sensitivity (also Limit of Detection: LoD).

Tunable Diode Laser Absorption spectroscopy (TDLAS/ TDLS) measures a single absorption peak, normally in the near-IR region. This peak must be chosen carefully to ensure it is measuring only the desired VOC and temperature control is critical. This method has been around for decades, but has been missing the diode lasers that are specific to the required wavelength and with better stability. These diode lasers are now becoming available at reasonable cost, so TDLS modules should soon be available for a cost of about £500-£800/ea for some common VOCs.

Ion Mobility Spectroscopy (IMS) has been used for decades in airports to screen for dangerous and illegal materials. By measuring the speed of drift of ionised molecules, it can identify a specific molecule from a small selection of molecules. Field Asymmetric IMS (FAIMS) offers more specificity and flexibility and the use of MEMS has shrunk the IMS to small dimensions. So IMS is a good opportunity, but sampling of the atmosphere requires smart engineering and preconcentration is required to achieve good sensitivity. Although IMS systems are available now, the cost



FAIMS microchip - courtesy Owlstone Nanotech Ltd



MEMS array - courtesy of the Department of Engineering, Warwick University

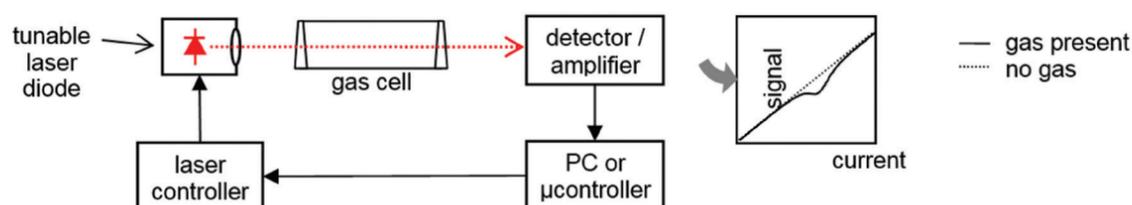
remains high and tuning to a specific molecule frequently requires knowledge of the local environment and competing VOCs.

Gas Chromatography and/ or Mass Spectrometry (GC/MS) is the laboratory method to identify and quantify specific VOCs. Advances occur continually for both of these analytical techniques and their combination. But shrinking them to be low cost and portable represents their own challenges including the view by some that the market size does not support a major R&D effort. Micro MS measuring systems exist, but the requirement for a vacuum pump and sampling system have been the stumbling blocks. The smallest battery powered vacuum system suitable for MS still costs about \$5,000. Miniaturised GC on its own, using a PID as the detector is available, with rapid advances expected: lower cost, smaller size and better separation.

FTIR and Raman Spectroscopy are already available as handheld tools for identifying solid and liquids but cannot yet achieve adequate sensitivity/ LoD for the gas phase. Costs start at typically \$8,000 and their performance is impressive, considering the complexity and required robustness of the optics. Multipass gas cells should be possible to improve resolution, but the current direction of developments means that these spectrometers will struggle to identify uniquely a single VOC if more than a few other known VOCs are present. This will be especially difficult if the chosen target analyte is present in a relatively low concentration, compared to other VOCs. As understanding of Surface Enhanced Resonant Raman Spectroscopy (SERRS) improves, there may be a more concerted effort to use SERRS for gas detection; current SERRS efforts are focusing on liquids and biological samples.

Sensor Transducers are simply platforms that measure changes in the property of a sensing layer. By themselves, they are not gas sensors—they require a sensing layer to complete the gas sensor system. We consider the future for three popular transducer structures.

Integrated Optic Sensors is a general term for a variety of technologies, usually centered around waveguides or optical fibers. Various combinations of light sources, Fibre Bragg Gratings to filter the light sources then a detection stage define an optical sensor. Evanescent waves are used frequently to detect small changes in the optical properties of a gas-sensitive sensing layer. Detection methods include Surface Plasmon Resonance (SPR), loss of light intensity, polarisation shift, single peak measurements such as Cavity Ring Down Spectroscopy (CRDS) and SERRS. These platforms allow silicon electronics to be integrated with the optics to provide potentially a low cost integrated package, so why don't we see these yet? Performance depends on sensitive, selective, reversible, fast-responding sensing layers—see below. Also, to



Conventional configuration for TDLS employing a laser diode. Ramping the laser current has the effect of scanning the emitted wavelength through the gas line, with the recovered signal shown to the right. Signal generation and recovered signal processing take place in a PC or microcontroller via DAC / ADC.

reduce cost the volume must be significant, so until the ideal sensing layer and integrated platform join up, volumes will remain low and prices high.

MEMS Sensor Arrays are a technology improvement over a sensing method that has been with us since the '90s. Sensor arrays were used in the early electronic noses with limited success. Moving to depositing organometallic and/ or semiconductor metal oxides in arrays theoretically offers sensitivity and selectivity; coupled with good correcting algorithms should provide the required stability. But if the sensing layer variants are not reversible, fast responding and sensitive, then many poor sensors formed into an array does not make a good sensor system, even with advanced analytic techniques. The capability of reliably depositing arrays of sensing layers onto MEMS platforms is becoming available; MEMS also helps with reproducibility, lower cost and reduced power demand. Like the optics platform, sensor array platforms need better sensing layers.

GasFETs are discussed regularly, so why are they not more commonly used? GasFETs offer theoretically the best sensing platform: Stephenson at MIT taught chemical FET sensing in the early '70s and Art Janata has been educating us since the early '80. But the difficulty and cost of manufacture and sensor irreproducibility have made this sensing platform still awaiting a breakthrough. Again, better sensing layers is the key.

Advanced Organometallic Sensing Layers and catalysts are the key to a breakthrough in the next generation of gas sensors; chemistry, materials and physics departments world wide are working on new gas sensing materials. This quick review cannot start to describe all the work undertaken to find better gas sensing materials. Research directions include unusual materials families such as chalcogenides and lanthanides, carbon

polymorphs (carbon nanotubes, graphene), 2-dimensional crystals, nanometal oxides and scaffolded organometallics. Such a variety of research is confusing but hopefully some successes will emerge, mainly targeted at VOCs and difficult gases such as ammonia and hydrogen. Only then will the transduction platforms be used to their full capabilities to provide the next generation of gas sensors.

Ignore the Internet at Your Peril

Advances in the use of cloud-based data storage/ access and more apps are going to change how we use gas detectors in the future. Two immediate developments are: (1) multilayer mapping where GPS information allows overlay of data layers—positions of persons, gas concentration maps, safety areas that can be redefined dynamically, weather conditions to predict plumes and subcontractor activity are just some layers that can be combined. (2) Each gas detection manufacturer has or will develop apps specific to their gas detectors. This can allow operators to change STEL and TWA levels in real time, for example when plant construction places new temporary safety constraints.

Emerging markets are pushing for gas detection breakthroughs. New materials and their understanding will provide us with better sensing layers. MEMS and optical integration production and assembly processes will reduce sensor systems' cost and improve performance. Advanced algorithms will improve sensor selectivity and stability. The internet will integrate gas detectors with other monitoring platforms and information systems.

The future looks bright. But when? We wait, watch, encourage and support.

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