Technology Sector – Security

Sub Sector – Detection

Segment - Chemical weapons

Author – Kshitij Aditeya Singh

Organisation – Institute of Nanotechnology

May, 2009

Table of Contents

1. Title

Detection of Chemical Weapons and Industrial Toxins

Keywords: nerve agent, blister agent, electronic nose, nanosensors, chemiresistors, chemicapacitors, conductive polymers, piezoelectric, sensor array, nanomaterials, spectroscopy

2. Definition of Technology Segment

The prevention of development, production, stockpiling, and use of chemical weapons was formed in 1992 by the Organisation for Prohibition of Chemical Weapons. Sarin gas was used in Matsumoto in 1994 and in the Tokyo subway in 1995 [1]. Civilian security is also threatened by malpractices in industry and accidents that lead to release of toxic industrial chemicals. Organisation for Prohibition of chemical weapons has classified chemical weapons into three categories - schedule 1, 2, and 3. Schedule 1 chemicals (nerve agents) have very limited industrial uses. Schedule 2 chemicals (example are Amiton, PFIB, dimethyl methylphosphonate precursor to sarin) have limited legitimate use on small scale. Schedule 3 chemicals (examples are chloropicrin, hydrogen cyanide and phosgene) are those which have large scale uses. The schedules limit the use of chemicals as identified in the conventions [2].

Table CW. 1 – A complied list of most harmful and common chemical warfare agents and industrial toxic agents [2,3]

Category of Toxin	Name
Nerve agent	Tabun, Sarin, Soman, Cyclosarin, VX, Novichok agents
Choking agents	Chloropiricn, chlorine, phosgene, diphosgene
Blister agent	Sulphur mustard, Nitrogen mustard, Lewsite, Phosgene oxime (CX)
Cytotoxic proteins	Ricin, Abrin
Industrial toxic agents	Phosogene , Hydrogen cyanide, Nitrous oxide, Carbon monoxide, Hydrogen Chloride, Methyl isocynate, Mercury, Lead, Benzene hexachloride, 1,3,5 trichlorobeneze , Dichloromethane, Chloroform

3. Short Description

Electronic Nose - Artificial noses also known as electronic noses are used to sense the presence of toxic gases and bio agents, and convey its presence by means of an electrical signal. These artificial or electronic noses are also used in detecting explosives. A number of physiochemical approaches are used in sensing, for example measurement of changes in conductivity for metals oxides and polymers, for piezoelectric materials changes in frequency are measured and fluorescent optical fibers changes in colour are measured. Nanosensors based on the human olfactory system have been studied in the United States for molecular recognition of species, pre-processing of the neural signal and transduction of the signal. Sensors based on the electrochemical are either conductance based or potentiometric (field effect transistor). Mass change based piezoelectric sensors are quartz crystal microbalance and for surface acoustic wave devices. Optical sensors are mainly either fluorescent based optical fibers or colorimetric [4].

Conductance sensors are based on a metal oxide or a conducting polymer where binding of a compound causes a change in the resistance between two metal contacts. The main material used for metal oxide sensors are tin, zinc, titanium, tungsten, and iridium. These could be doped with palladium or platinum. A gas sensor array the size of a thumb nail size can sense industrial gases that maybe potentially toxic gases such as ammonia, formaldehyde and carbon monoxide based on oxides of tin and tungsten. Sensor layer thickness can range from 2-20nm [5]. Nanoscale tin oxide based sensors and its variations, with grain size of 8 nm, have effectively demonstrated the recognition of combustible gases such as propane, butane, LPG within their explosion limits [6].

Conductive Polymer - Conductive polymers used as sensors use a polymer to connect two electrodes. The polymer acts as the active sensing agent, the sensitivity of the sensor is higher than metal oxide sensors. The main shortcomings of these types of sensors are the complexity of fabrication and reproducibility of sensing function between batches [4,7]. The active sensor element is used to detect volatile organic compounds. Polymers such as polypyrole, polyaniline, polythiophene, and polyacetate are used due to their high sensitive to vapour and gases. Nanometre sized carbon black has also been used to make polystyrene conductive for sensing application [8]. Carbon black composite sensing arrays have been used to detect explosives and chemical warfare agent such as sarin and soman [9].

Field effect transistors - Field effect transistors used as potentiometeric sensors have been demonstrated in detecting gases by making the gates sensitive to gases. A volatile organic compound produces a reaction in the sensing layer, which causes the physical property of the gate to change, thereby changing the threshold voltage and thus the channel conductivity. Noble metal catalysts such as platinum, palladium and iridium have been coated on metal oxide FET [10]. Nose on a chip concept of sensors arrays of polymer gated FET's is used for sensing different odours. The sensing element is combined with a signal processing component, which is used to detect the presence of a gas, identified by a train of spikes in the frequency [11]. Methods such as statistical pattern recognition, neural networks, chemometrics, machine learning, and biological cybernetics has been used to process electronic nose data [12].

Piezoelectric sensors - Piezoelectric devices working as an electronic nose work on the basis of measuring a change in mass. Piezoelectric crystals vibrate under the influence of an applied voltage, the mass of which determines the resonant frequency. Quartz crystal microbalance (QCM) and surface acoustic wave device are used as electronic noses [7]. QCM is used in explosive detection, wherein the adsorption of a gas molecule on the surface of polymer changes the resonant frequency. Quartz crystal microbalance with immobilised nanoscaled ZSM-5 zeolite film has been developed as a sensor for nerve agent. A minimum concentration of 1 part per million (ppm) was detected using the stimulant dimethylmethylphosphonate [13].

Surface Acoustic Wave sensors - Surface acoustic wave sensors are based on acoustic waves travelling on the surface of transducers. Adsorption of a gas molecule causes a change in the mass thereby causing a change in the frequency or phase shift. The advantage with these sensors is that they are easy to fabricate, while their drawback is that they are temperature sensitive, the noise in the signal increases with decreasing size [14]. IBM has demonstrated cantilever based sensors, in ambient air to detect ethenes, alcohols, natural flavours and water vapour using optical methods [15]. Microsensor systems Inc a leading producers of SAW sensors have demonstrated the nerve gas agents and blister gas agents, with a sensitivity of 0.04 ppm in 20 seconds and 0.01 ppm in 120 seconds respectively [16]. Polymer coatings such as polysiloxane films that allow diffusion of chemical agents into the bulk of the film for optimal mass loading. These have been used both for SAW and QCM sensors [17,18]. Thin film piezoelectric acoustic sensor works on the basis of change in thickness of the gas sorption layer on the substrate. These sensors can detect chemical and biological weapons with a sensitivity of 100 ppm [19,20].

Flexural plate wave sensors - Flexural plate wave sensors are similar to SAW and QCM sensors detect an agent based on mass absorbed on a coating deposited on the sensor. It is known to have one of the highest levels of detection sensitivity being in the range of parts per trillion (ppt) [21]. Chemical vapour detection and biosensor array based on flexural plate wave sensor has been demonstrated. A siloxane polymer coating 50nm thick is applied on the surface for the detection of specific chemical agents. A sensitivity of 10 ppm was demonstrated in the experimental study [22].

Sensor Arrays - Sensor arrays have been integrated with support vector machines for detecting organophosphate based nerve agents. Support vector machines serve the purpose of data extraction, pre-processing and classification of chemical biological agent [23]. MEMS based sensor arrays have been used to detect nerve agents such as tabun and sarin, with a sensitivity of 4 and 26 parts per billion (ppb) respectively. Blister agents such as sulphur mustard were detected with a sensitivity of 16 ppb. Oxides of tin and titanium were deposited as nanostructured thin films which act as the sensing element. These sensor arrays have demonstrated stability, high signal to noise ratio to the relevant chemical warfare agent [24].

Optical fibres - Optical fibres have been used in sensing application. The fibre is turned into a sensor by coating the end with sensing materials or by removing the cladding and coating it with the sensing material. The sensing material used is primarily polymers containing chemically active fluorescent dyes. The presence of a target agent causes a change in the polarity of the dye which further leads to a change in the wavelength [12]. These optical fibres have been used to detect explosives such as TNT at a sensitivity of 10-15 ppb, which is comparable to 1 ppb sensitivity of a dog's nose for the same agent. The sensitivity achieved was for a closed chamber however, field trials were not as successful in demonstrating the same result [25].

Cantilevers - Microcantilevers are similar in appearance to diving boards, and are machined from silicon or other materials. The length of these can vary from 100-200 microns and the thickness between 0.3 - 1 microns. Microcantilevers offer sensitivity at least an order of magnitude higher than QCM and SAW based sensors for chemical agents sensing [3]. Piezo resistive micro cantilever based sensors have been demonstrated to have excellent detection capabilities for chemical and explosive vapour detection. The cantilevers are coated with 4nm Ti film, 20nm gold layer and 4-mercaptobenzoic acid self assembled monolayer. Detection of dimethyl methylphosphonate (DMMP), a stimulant for the nerve agents was demonstrated with parts per trillion detection capability within 10 seconds of exposure [26].

Chemiresistors - Chemiresistors are sensors that monitor a change in the resistance continuously with exposure to vapours. Carbon nanotubes have been used for organic vapour sensing. Single walled carbon nanotubes with diameter of 15-30 nm have been demonstrated as effective sensors for nerve gas agents Sarin and Soman. A network of films 1-2 microns thick on a polyethylene terephthalate (PET) substrate can detect traces of chemical agent vapours with a sensitivity of 25 ppm. Strong sensors responses were obtained that were not affected by environmental conditions such as air quality and humidity does not interfere significantly [27]. Single strand DNA along with single walled carbon nanotubes field effect transistors have been used to detect chemical warfare agents. These sensors have show high sensitivity and stability up to 50 cycles of operation [28]. Detection of V type nerve agent has been experimentally demonstrated using carbon nanotubes. The detection is based on enzyme catalyzed hydrolysis of nerve agents and amperometric detection of thiol containing hydrolysis product that is performed at the carbon nanotube modified screen printed electrode. The sensitivity demonstrated for such sensors is 258 ppb [29].

Chemicapacitive sensor - A chemicapacitive sensor is a capacitor that has selectively absorbing materials such as a polymer, as a dielectric. Volatile organic compounds are absorbed into dielectric, changing the permittivity leading to an increase or decrease in the capacitance. Polymer dielectrics are a type of chemicapacitive sensor that are used for detecting chemical warfare agents. These demonstrate a sensitivity of detection of 100 ppm for toxic industrial solvents and 1 ppm for chemical warfare agent as well as explosives [30]. Chemicapacitive sensors for toxic industrial chemicals have demonstrated a sensitivity of 0.0006 – 720 ppm for analyte such as carbyl for the lower limit and carbon disulphide for the higher limit [31].

Spectroscopic Methods - Nerve gas agents such as sarin, soman, tabun, and VX, along with blister agents such as mustard gas, and lewisite were compared for their detection using techniques such as gas detection tube, flame photometric detector, ion mobility spectrometer, surface acoustic wave detector, photo ionisation detector, Fourier- transform infrared spectroscopy, gas chromatography – mass spectrometry for chemical warfare agents. Similar comparative study for biological warfare agents such as flow cytometry, bioluminescence detection, lateral flow immunoassay. Figure CW.1 below demonstrates the shortcomings of each of these techniques for onsite detection, according to the volatility and molecular weight. Some techniques proved to be suitable in detection of certain analytes while others resulted in false positives or a slow response to the nerve agent [32].

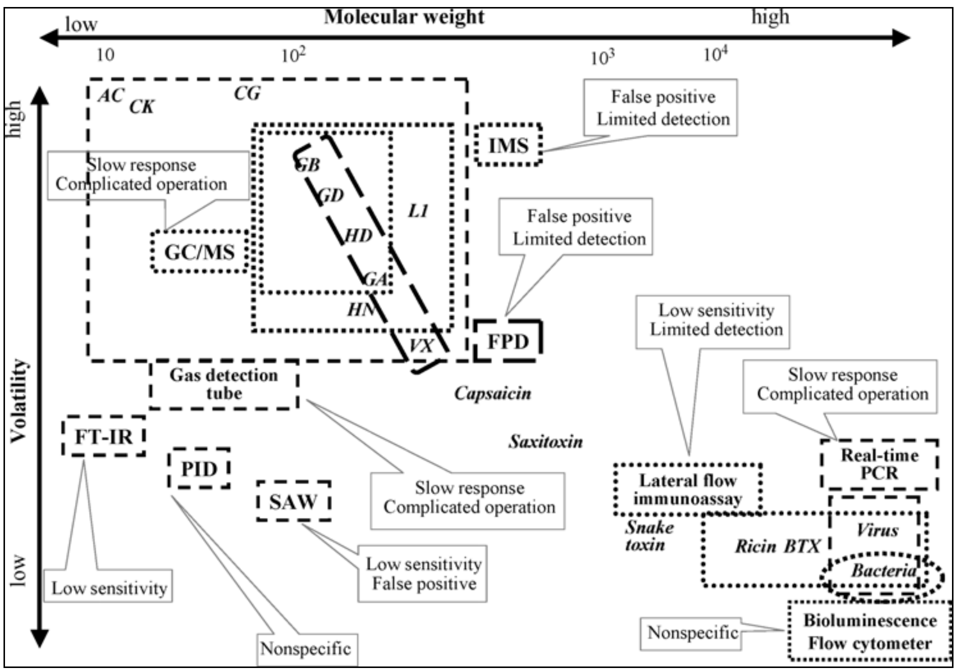

Figure CW.1 – Performance of onsite chemical and biological weapon detection [32]

In another study chemical warfare agents were comparatively detected by different analytical techniques such as gas chromatography–infrared detection–mass spectral detection (GC–IR–MS); liquid chromatography–mass spectrometry (LC–MS); nuclear magnetic resonance (NMR) using the nuclei H, C and P; and gas chromatography–atomic emission detection (GC–AED). It was observed in the study that each of the technique gave good identification of some of the components such as amines, phosphorous, or sulphur. Each of these techniques also missed out on several major components [33]. Separation and detection of organophosphorus type nerve agents by gas chromatography with inductively coupled plasma mass spectrometry has been demonstrated, less than 5 picogram sensitivity to river water and soil contamination [34].

Techniques such as laser photo-acoustic spectroscopy have demonstrated a detection of sarin with a sensitivity of 1.2 ppb, and with extremely low false positives of less than 1 in 1,000,000 in the presence of other trace gases [35]. Micro-X Ray fluorescence has unique capabilities suited to high throughput screening of combinatorial libraries of chemical warfare agents. High throughput screening of nerve agents such as VX has been demonstrated in nanogram quantities. These could be coupled with other spectroscopic techniques such as Raman and IR to give additional information [36]. Contamination of portable water with nerve agent Sarin can have serious consequences such as bronchospasm and even death under conditions if enough quantity is consumed. Diffuse reflectance infrared spectrum investigation, using nanoparticulate magnesium oxide as a preconcentration medium produced a sensitivity of 98 ppb for Sarin detection in water [37].

Laser induced breakdown spectroscopy has been used as a versatile sensory platform for detecting chemical agents, biological agents such as anthrax and improvised explosive devices. This sensory platform can be couple with robotic platforms for toxic environments and with fiber optics. The LIBS technique has demonstrated effectively to distinguish chemical agents especially in the soil [38]. Phosphorus containing nerve agent stimulant detection with LIBS has been demonstrated at a range of 20 meters [39].

Nanomaterials - Nanocomposites of tin oxide and indium oxide have been demonstrated as excellent material for semiconductor gas sensors for toxic industrial gases. Addition of additives is shown to have enhanced sensitivity and selectivity performance significantly [40]. Toxic and explosive industrial gas such as methane, butane, propane, liquefied petroleum gas, and carbon monooxide have been detected by nanostructured tin oxide sensors. The sensor arrays demonstrated have a detection capability of less than 100 parts per million [6]. Tin, Niobium and Vanadium Oxide thin films have been developed for the detection of nerve gas agents Sarin. For agglomerates of the size of 40 nm, a sensitivity of 70 ppb was demonstrated. The stability of such thin films for gas sensing applications is being further researched [41].

Challenges of chemical sensing – Integration of large number of sensors in a limited area, providing high sensitivity, and selectivity of the toxin. Another challenge is the environmental conditions, whereby it is much easier to measure parameter in a laboratory condition as opposed to ambient air or in water [4]. Shortcomings of conductive polymers are that surface morphology is not predictable, therefore the surface conductivity and the sensing function are not reproducible between batches, and more importantly it sensitivity to water vapour [4, 7]. There is no one device that meets the need of onsite detection of both chemical and warfare agents for onsite detection [32]. Shortcomings of chemical agents sensors are that no polymer coating for sensors can display complete selectivity to all possible interferents [22]. The costs of using mass spectrometry, gas chromatography, ion mobility spectrometry are expensive and not as easy to use as electronic noses [26].

4. State of Research and Development

The sections give an overview of the technology development in relation to a specific technology. Fundamental Research is defined for this purpose as research with no particular goals of commercialisation. Applied Research is defined as research conducted in academia and industry directed towards a specific purpose and application. Prototype has been defined as Applied Research or Fundamental Research that has found a potential market application. Technologies that are in the field trial state are defined as those that are in the process of commercialisation, and are being tested. Deployed nanotechnologies are those that have found an early stage market. Mass Market has been defined as those technologies that have been adopted by large population and are attractive high growth markets. The technologies have been mentioned are those mentioned in the literature review for chemical detection. The scale of readiness mentioned ranges from fundamental research to mass market. The spread of research and development for a particular method indicates different applications, threat agents and devices that are being developed. A validation of their status is necessary from the economic and other technology sectors perspective. Table CW.2 gives an overview of all chemical weapon detection technologies enabled by nanomaterials.

Table CW. 2 – Comparative Research and Development Status for chemical weapons detection

	Fundamental Research	Applied Research	Prototype	Field Trials / Pilot plant (Pre-commercialisation)	Deployed (Commercialised)	Mass Market
Conductive polymers		▪	▪	▪		
Field effect transistors		▪	▪			
Piezoelectric		▪	▪	▪		
Surface acoustic wave		▪	▪	▪	▪	
Flexural plate wave			▪	▪		
Sensor arrays		▪	▪	▪	▪	
Optical fibres		▪	▪	▪	▪	
Cantilevers			▪	▪		
Chemiresistors			▪	▪	▪	
Chemicapacitors		▪	▪	▪		
Spectroscopic methods			▪	▪	▪	▪
Nanomaterials for detection		▪	▪	▪		

5. Additional demand for research

Specific research needs were mentioned in the literature relating to different detection aspects are as follows:

- SWCNT based sensors for detection of nerve gas agents have to be optimised for their performance. Performance optimisation is needed for tenability, stability, detection limit and elimination of false positives [27].
- No onsite detection equipment for capsaicin, lacrymating ingredient in pepper spray, and snake toxins is available. Further research is required in detection methods for these toxins [32].
- LIBS – further research is needed in reducing the number of false positives and negatives. Research is also needed in refining the model to include a range of materials and selection of detection limits [39].
- Research on properties of paper and its scanning through the postal system has also been suggested to protect civilians from biological or chemical attack [42].

6. Applications and Perspectives

In the expert engagement process for the technology segment, the following perspectives were observed:

- Funding research and development for detection of CBRNE and Narcotics was considered very important for society and economy of Europe.
- The most important drivers for research and development of '*detection of CBRNE and Narcotics'* were considered technological and social impact. The technological drivers relate to cost, performance, efficiency and absence of solutions. Other secondary drivers were indicated as competitive advantage in conflict situations, safety, productivity gains and regional security policy.
- The main drivers for R&D of *'chemical detection'* were mentioned to be 'cost of sensors, devices and instrumentation', 'sensitivity', 'time for detection', 'life time of operation' and accuracy of detection'. Other secondary drivers were identified as 'size of detectors', 'mobility of detection unit' and 'integration of detection platform'.
- The main barriers to research and development of *'detection of CBRNE and Narcotics'* were mentioned as 'availability of finance to early stage companies' and 'inadequate technology transfer from Universities'. Secondary barriers indicated were 'intellectual property conflicts', 'lack of tax incentives' and 'lack of supportive government policy'.
- Qualitative responses indicated to meet the challenges of 'availability of finance', EU needs to consider dual commercial use of security technology as the market was relatively smaller than US. While trends in US are towards government driven technology that is validated, EU grants are inadequate for proving technology. It was suggested that government validation of systems was necessary as laboratory systems not scaled for field use.
- The main barriers to R&D of *'chemical detection'* were indicated as 'inadequate research funding', 'lack of skilled personnel availability' and 'lack of reproducible results'. Other secondary barriers were mentioned to be 'poor detection limit', 'failure in integrating devices', 'robustness of field trials' and 'limited target acquisition'.

- The most important functionality for detection were indicated as ‘sensitivity of specie being detected’, ‘reproducibility of accurate results’, ‘retaining functionality in wide operating conditions’, and ‘long operating life with minimum maintenance’. ‘Collection and sampling’ and ‘specificity’ were considered other very important functional requirement.

- Other secondary desirable functionalities were indicated as ‘stability of detection’, ‘multifunctionality’, ‘signal transduction’, ‘minimal sample preparation’, ‘integration of detector into monitoring unit’ and ‘low cost’. ‘Reversibility’ was considered relatively less important functionality.

- The application trends were mentioned as:

    - The charecteristics of a detector application are mission and scenario dependent.

    - Development of portable and sensitive detection devices. There is a present lack of portable instruments with good sensing characteristics. Trend is towards miniaturising chemical sensors.

    - Application development trend directed toward broad based technologies primarily for transportation hubs.

    - Development of nanostructured functional materials and interfaces for high performance detection of chemical agents.

    - Systems integration is a gap in technology development for detection.

    - Low false positives and low false negatives are the most important application requirement.

    - Response time was entirely application dependent. While in border situation 2-3 seconds response time is ideal, several seconds at the port, it should be within milliseconds in crowded locations.

    - Functionalities such as detection limit are dependent on application and scenario where ppm might be adequate.

    - Operational constraints were identified as environmental changes such as temperature, humidity and large number of interferants. Mobility of detection device, and calibration for temperature and humidity were mentioned as constraints.

    - Other operational constraints were mentioned to be calibration of measurement, skills and interpretation needed from operator. The need for simpler interfaces that are tailored for operation setting was mentioned specially for less qualified operators.

    - Processing constraints were identified as lack of basic understanding to control nanomaterials in a precise manner.

    - Improving cost effectiveness by controlled large scale production and improve laboratory infrastructure for mass scale production.

    - Long development life cycles for applications are characterised by delivering scientific results, establishing performance and establishing cost effective performance of detection technologies.

- The sensing methods for chemical detection that are presently deployed are chemicapacitive, chemiresistors, surface acoustic wave, sensor arrays, optical fibres, mass based, and spectroscopy based detection.

- Methods for chemical detection that are expected to be deployed in the next 5 years are nanomaterials based detectors, conductive polymers, field effect transistors, and piezoelectric sensors. Certain types of sensor arrays and specific optical fibres are also expected to be in the market in 5 years.

- Application issues for surface acoustic wave sensors were mentioned to be sensitivity and functionalisation. Development barriers for sensor arrays were mentioned as availability of diverse sensors at the required selectivity and sensitivity. Limitations of spectroscopy as a practical field technique were also mentioned. Reproducibility, selectivity and pattern recognition were development challenges for a majority of sensors. The factors determining the uptake of conductive polymers were mentioned as reproducibility, stability, durability and selectivity. For field effect transistors it was mentioned as robustness, selectivity and sensitivity. Important factors in uptake of piezo - electric sensors were mentioned to be robustness and stability.

- Methods for chemical detection that are expected to take over 10 years to be deployed were mentioned to be cantilevers.

- The very attractive and relatively higher growth markets were expected to be sensor arrays, biosensors, surface acoustic wave, flexural plate wave, chemiresistors and nanomaterials for detectors.

- The moderately attractive growth markets were expected to be field effect transistors, piezoelectric transistors, optical fibres and cantilever based detection.

- North America was considered relatively better than Europe which was considered better than Asia for fundamental and applied research, industrial technology development and commercialisation. While Asia was considered better for cost effectiveness for technology, EU was considered better for governmental policy for innovation. Qualitative responses mentioned that EU research was complimentary to US for chemical detection. It was mentioned that Europe had existing sensor deployment relatively better than other world regions, it lacked research and development for future leadership.

- Qualitative suggestions on improvement of capabilities were :

    - collaborative research between security agencies, academia and industry
    - encouraging tax exemptions
    - basic research to understand nanomaterials better
    - technology transition from science to implemented demonstrators is gap that needs to be addressed
    - creation of multinational, multidisciplinary fund for development
    - creating a centre for standardised testing for different sensors

The theme of integrated platform for detection of chemical, biological, explosive, radiological and nuclear threats was conducted at Dusseldorf in March 2009. The following outcome and recommendations resulted from the discussion:

- Technology was not sufficiently advanced to achieve single platform detection.
- An integrated modular system that focuses on Chemical, Biological and Explosive as one unit and Radiological-Nuclear detection as a separate module is a better approach.
- One of the main weaknesses for CBRNE detection was considered to be systems integration. It was suggested that a statement of requirements to be produced taking nanotechnology into consideration.
- Accuracy and reliability of measurement was considered to be most important characteristic. Reproducibility of measurements and operating life of sensor were considered to be poor for modular systems of detection.
- The cost of false positives are very high, therefore operational definition should be developed on a case by case basis for a modular system.
- The need for greater fundamental research in understanding the sensing mechanism was emphasised.
- It was recommended that communication between materials and sensing community be improved in order to create mutual awareness of technical breakthroughs.
- The first area of application is expected to be transportation hub for such a modular system.
- Technology penetration and application driven by state for CBRNE detection.
- It was recommended that sensor requirements for the EU are critically examined.

7. Current Situation within EU

NANOS4 was a research and technology development project which was completed last year. The objective of the project was the development of metal oxide gas sensing system based on mesoscopic sensor. The thin film sensors were to be developed using lithography techniques, for applications in transport safety, monitoring environmental variables. TERAEYE is another framework project that aims to develop an innovative range of inspecting passive range of systems based on Terahertz wave detection. The two dimensional array of detectors are expected to detect harmful explosive, biological, and chemical agents at airports, railways hubs and civilian zones.

The following framework 7 projects have been funded by the European Commission in the Security theme that are relevant to biological weapons detection:

- CBRNE related testing and certification facilities - a networking strategy to strengthen cooperation and knowledge exchange within Europe (CREATIF) was initiated early in 2009. The project aims to create a network of product testing facilities for CBRNE detection [43].
- Integrated mobile security kit (IMSK) was initiated in 2008. The objective of the project is to combine technology solutions from Detection of CBRNE, area surveillance, and check

point control for additional sensitive security locations. The sensor data is expected to be integrated with communication and data module to a command centre [44].

The following Preparatory Action for Security Research Funded projects were funded by the European Commission and are relevant to chemical detection:

- European Security: High level study on threats responses and relevant technologies (ESSTRT). The support action project has provided a comprehensive overview of necessary responses to security challenges. These include technologies for detecting chemical weapons and hazardous materials at airports and travel hubs [45].

- The active terahertz imaging for security (TERASEC) project, that aims to develop terahertz detection. The detection of threats, explosives, pathogens and chemicals in person, luggage or post were the focus of the project. The Terahertz imaging systems were developed and evaluated in the 24 month period [46].

- Hazardous Material Localisation and Person Tracking (HAMLeT) project demonstrated an indoor security system using sensors to give real time decision information. This was done by classifying, tracking and localising potential threats. Chemical sensors were used for detection of hazardous materials such as explosives [47].

- On-line monitoring of drinking water for public security from deliberate or accidental contamination (WATERSAFE) project aimed to use nanotechnologies in sensing and detoxification to protect drinking water systems for potential terrorist attacks or accidental spillage [48].

8. References and Literature

[1] Y. Seto, N. Tsunoda, M. Kataoka, K. Tsuge, T. Nagano, “Toxicological Analysis of Victims Blood and Crime Scene Evidence Samples in the Sarin Gas Attack Caused by the Aum Shinrikyo Cult,” in Natural and Selected Synthetic Toxins—Biological Implications, A.T. Tu, W. Garfield, eds, Washington: American Chemical Society, 2000, p. 318.

[2] Organisation for Prohibition of Chemical weapons, “Chemical warfare agents – An overview of chemicals defined as warfare agents,” September 2007, http://www.opcw.org/resp/html/cwagents.html

[3] L.A. Pinnaduwage, H. Ji and T. Thundat, “Moore’s Law in Homeland Defense: An Integrated Sensor Platform Based on Silicon Microcantilevers,” IEEE Sensors Journal, vol. 5, pp. 774 - 785, August 2005.

[4] B. Rolfe, “Toward nanometre-scale sensing systems: natural and artificial noses as models for ultra-small, ultra-dense sensing systems,” MITRE Nanosystems Group, USA, Tech. rep. MP 04W0000169, 2004

[5] C. Arnold, M. Harms, and J. Goschnick, “Air Quality Monitoring and Fire Detection With The Karlsruhe Micronose KAMINA,” IEEE Sensors Journal, vol. 2, pp. 179-188, June 2002

[6] D-S Lee, D-D. Lee, S-W Ban, M. Lee, and Y. T. Kim, “SnO2 Gas Sensing Array for Combustible and Explosive Gas Leakage Recognition,” IEEE Sensors Journal, vol. 2, pp. 140-149, June 2002.

[7] H. T. Nagle, R. Gutierrez-Osuna, and S. S. Schiffman, “The How and Why of Electronic Noses,” IEEE Specturm, vol. 35, pp. 22 – 31, Sep 1998.

[8] T. C. Pearce, S. S. Schiffman, H. T. Nagle, J. W. Gardner, eds. Handbook of Machine Olfaction, Weinheim, Germany, Wiley-Vch Verlag GmbH & Co., 2003.

[9] N.S. Lewis, "Electronic Nose Chip Microsensors for Chemical Agent and Explosives Detection,” California Institute of Technology: Noyes Laboratory, Pasadena, California 2001.

[10] J. Janata, “Electrochemical Microsensors,” Proceedings of the IEEE, vol 91, pp. 864-869, June 2003.

[11] Space Daily, “World’s smallest electronic nose,” March 2002, http://www.spacedaily.com/news/future-02a.html

[12] Ricardo Gutierrez-Osuna, “Pattern Analysis for Machine Olfaction: A Review,” IEEE Sensors Journal, vol. 2, pp. 189-202, JUNE 2002

[13] H.F. Xie, Q.D.Yang, X.X. Sun, T. Yu, J. Zhou, Y.P. Huang, “Gas sensors based on nanosizedzeolite films to identify dimethylmethylphosphonate,” Sens Mater, vol17, pp 21-28, 2005.

[14] K. Bodenhoefer, A. Hierlemann, G. Noetzel, U. Weimar, and W. Göpel, “Performances of Mass-Sensitive Devices for Gas Sensing: Thickness Shear Mode and Surface Acoustic Wave Transducers,” Analytical Chemistry, vol. 68, pp. 2210-2218, 1996.

[15] H.P. Lang, M.K. Baller, F. M. Battiston, J. Fritz, R. Berger, J.-P. Ramseyer, P. Fornaro, E. Meyer, H.-J. Guntherodt, J. Brugger, U. Drechsler, H. Rothuizen, M. Despont, P. Vettiger, Ch. Gerber, J.K. Gimzewski, “The Nanomechanical Nose,” 12th IEEE International Conference on Micro Electro Mechanical Systems, 1999, pp 9-13.

[16] J. C. Cajigas, T. L. Longworth, N. Davis, K.Y. Ong, “Testing of HAZMATCAD Detectors Against Chemical Warfare Agents: Summary Report of Evaluation Performed at Soldier Biological and Chemical Command,” Microsensor Systems, Inc, Bowling Green, Kentucky. p. 1-12, 2003

[17] A. J. Ricco, R. M. Crooks, and G. C. Osbourn, “Surface acoustic wave chemical sensor arrays: new chemically sensitive interfaces combined with novel cluster analysis to detect volatile organic compounds and mixtures,” Accounts Chem. Res., vol. 31, pp. 289–296, 1998.

[18] A .Ulman, “Formation and structure of self-assembled monolayers,” Chem. Rev., vol. 96, pp. 1533–1554, 1996.

[19] L.M. Dorozhkin, V.A. Nefedov, A.G. Sabelnikov, V.G. Sevastjanov, “Detection of trace amounts of explosives and/or explosive related compounds on various surfaces by a new sensing technique/material,” Sens. Actuators B, vol. 99, pp 568 - 570, 2004.

[20] L.M. Dorozhkin, G.N. Dorozhkina, A.V. Fokin, I.A. Rozanov, A.G. Sabelnikov, V.G. Sevastjanov, “Thin-film piezoelectric acoustic sensor (TFPAS): further experimental validation of the theory of resonance sensitivity, ” Sensors and Actuators B, vol. 106, pp. 529–533, 2005.

[21] Q. Y. Cai, J. Park, D. Heldsinger, M. D. Hsieh, and E. T. Zellers, “Vapor recognition with an integrated array of polymer-coated flexural plate wave sensors,” Sens. Actuators B, vol. 62, pp. 121–130, 2000.

[22]B. Cunningham, M. Weinberg, J. Pepper, C. Clapp, R. Bousquet, B. Hugh, R. Kant, C. Daly, E. Hauser, “Design, fabrication and vapor characterization of a microfabricated flexural plate resonator sensor and application to integrated sensor arrays,” Sensors and Actuators B, vol. 73 pp. 112 -123, 2001.

[23] W. H. Land, Jr., D. Leibensperger, L. Wong, O. Sadik, A. Wanekayab, M. Uematsu, M. J. Embrechts, “New Results Using Multi Array Sensors and Support Vector Machines for the Detection and Classification of Organophosphate Nerve Agents,” in Systems, Man and Cybernetics IEEE International Conference, Oct. 2003, pp 2883- 2888.

[24] D. C. Meier, C. J. Taylor, R. E. Cavicchi, Edward White V, M. W. Ellzy, K. B. Sumpter, and S. Semancik. IEEE Sensors Journal, vol. 5, pp 712 -725, August 2005.

[25] R.J.Davenport, “Crossover Research Yields Scents and Sensitivity,” Science, vol. 291, pp. 2071- 2072, March 2001.

[26] L. A. Pinnaduwage, A. C. Gehl, S. L. Allman, A. Johansson and A. Boisen, “Miniature sensor suitable for electronic nose applications,” Review Of Scientific Instruments, vol. 78, 055101 1-3, 2007.

[27] K. Cattanach, R. D. Kulkarni, M. Kozlov and S. K. Manohar, “Flexible carbon nanotube sensors for nerve agent simulants,” Nanotechnology, vol.17, pp 4123–4128, 2006.

[28] C. Staii, A. T. Johnson, M. Chen, A.Gelperin, “DNA decorated carbon nanotubes for chemical sensing,” Nanoletters, vol. 5, pp 1774 -1778, 2005.

[29] K. A. Joshi, M. Prouza, M. Kum, J. Wang, J. Tang, R Haddon, W. Chen, and A. Mulchandani, “V-Type Nerve Agent Detection Using a Carbon Nanotube-Based Amperometric Enzyme Electrode,” Anal. Chem. vol. 78, pp 331-336, 2006.

[30] S.V. Patel, T.E. Mlsna, B. Fruhberger, E. Klaassen, S. Cemalovic, D.R. Baselt, “Chemicapacitive microsensors for volatile organic compound detection,” Sensors and Actuators B, vol 96, pp. 541–553, 2003.

[31] T. E. Mlsna, S. Cemalovic, M. Warburton, S. T. Hobson, D. A. Mlsna, S. V. Patel. Sensors and Actuators B, vol. 116, pp 192–201, 2006.

[32] Y. Seto, M. Kanamori-Kataoka, K. Tsuge, I. Ohsawa, H. Maruko, H. Sekiguchi, Y. Sano, S. Yamashiro, K. Matsushita, H. Sekiguchi, T. Itoi, and K. Iura, “Development of an on-site detection method for chemical and biological warfare agents,” Toxins Review, vol. 29, pp. 299-312, July 2007.

[33] M. D. Brickhouse, W. R. Creasy, B. R. Williams, K. M. Morrissey, R. J. O’Connor, H. DuPont Durst, “Multiple-technique analytical characterization of a mixture containing chemical-weapons simulant from a munition,” Journal of Chromatography A, vol. 883, pp. 185–198, 2000.

[34] D. D. Richardson and J. A. Caruso, “Derivatization of organophosphorus nerve agent degradation products for gas chromatography with ICPMS and TOF-MS detection,” Analytical and Bioanalytical Chemistry, vol 388: pp 809–823, 2007.

[35] M. B. Pushkarsky, M. E. Webber, T. Macdonald, C. Kumar, N. Patel, “High-sensitivity, high-selectivity detection of chemical warfare agents,” Applied Physics Letters vol. 88, 044103 pp 1-3, 2006.

[36] G. J. Havrilla, and T. C. Miller., “High-throughput screening with micro-x-ray fluorescence,” Review of Scientific Instruments, vol 76, pp 062201: 1-6, 2005

[37] K. J. Ewing and B. Lerner, “Infrared Detection of the Nerve Agent Sarin (Isopropyl Methylphosphonofluoridate) in Water Using Magnesium Oxide for Preconcentration,” Applied Spectroscopy, vol. 55, pp 407 – 411, 2001.

[38] F. C. DeLucia, A. C. Samuels, R. S. Harmon, R. A. Walters, K. L. McNesby, A. LaPointe, R. J. Winkel, Jr., and A. W. Miziolek, “Laser-Induced Breakdown Spectroscopy (LIBS): A Promising Versatile Chemical Sensor Technology for Hazardous Material Detection,” IEEE Sensors Journal, vol. 5, pp 681 – 689, Aug 2005

[39] J. L. Gottfried, F. C. De Lucia, C. A. Munson, and A. W. Miziolek, “Standoff Detection of Chemical and Biological Threats Using Laser-Induced Breakdown Spectroscopy,” Applied Spectroscopy, vol. 62, pp. 353- 363, 2008.

[40] C. Aifan, H. Xiaodong, T. Zhangfa, B. Shouli, L. Ruixian, L. C. Chiun, “Preparation, characterization and gas-sensing properties of SnO_2–In_2O_3 nanocomposite oxides,” Sensors and Actuators B, vol. 115, pp 316–321, 2006.

[41] A. Ponzoni, E. Comini, G. Sberveglieri, I. Alessandri, E. Bontempi, L.E. Depero, “Tin, Niobium and Vanadium mixed oxide thin films based gas sensors for chemical warfare agent attacks prevention,” in IEEE Sensors Conference, 2007, pp 1322 – 1325.

[42] T. G. Maréchaux, “Better Materials Can Reduce the Threat from Terrorism,” JOM, vol. 53, pp 12 – 13, December 2001.

[43] Cordis, “CBRNE related testing and certification facilities - a networking strategy to strengthen cooperation and knowledge exchange within Europe,” 16th April 2009, http://cordis.europa.eu/search/index.cfm?fuseaction=proj.document&PJ_LANG=EN&PJ_RCN=10422186&pid=28&q=FD8A9BBC079BD5FCECD584ADBD3CE6A7&type=adv

[44] Cordis, “Localisation of threat substances in urban society ,” 6th of April 2009, http://cordis.europa.eu/search/index.cfm?fuseaction=proj.document&PJ_LANG=EN&PJ_RCN=10453356&pid=35&q=FD8A9BBC079BD5FCECD584ADBD3CE6A7&type=adv

[45] Directorate General for Enterprise and Industry European Commission, “ ESSTRT – European Security: High level study on threat responses and relevant technologies,” 15th April 2009, http://ec.europa.eu/enterprise/security/articles/article_2007-02-23_en.htm

[46] Directorate General for Enterprise and Industry European Commission, “ TERASEC – Active Terahertz imaging for security,” 5th April 2009, http://ec.europa.eu/enterprise/security/doc/project_flyers_2007/TERASEC.pdf

[47] Directorate General for Enterprise and Industry European Commission, “Hazardous Material Localisation and Person Tracking,” 15th April 2009, http://ec.europa.eu/enterprise/security/doc/project_flyers_2007/HAMLeT.pdf

[48] Directorate General for Enterprise and Industry European Commission, “On-line monitoring of drinking water for public security from deliberate or accidental contamination,” 15th April 2009, http://ec.europa.eu/enterprise/security/doc/project_flyers_2007/Watersafe.pdf