

TOXIC CHEMICAL COMPOUNDS DETECTION FOR THE SOCIETY SOCIAL HEALTH CARE PREVENTION

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Abstract

Presently, there is no single detector which has all the desirable capabilities and performance functions, and currently available detectors all vary considerably in cost, performance and reliability. As such care must be taken to select a detector based on the abovementioned factors and operational requirements. Furthermore, many detector manufacturers make claims based on their own testing, some of which have not been thoroughly verified by third party laboratories. In this case we have only different stages of the same process: hazardous chemical is used in the production; concerning the hazards and subsequent problems with the legislative regulations of the finances, producers start to search for alternative technology; technology is developed and implemented; technology is used for making majority of the related product without the use of hazardous substance. In the example of phosgene – this process just begun in the near past, in the case of hydrogen cyanide – the process is near the end, and in case of other chemical process is at the end. The old technology with a hazards replaced by new one – more friendly to the environment and human health.

Keywords: detection, identification techniques, toxic chemical compounds, toxic industrial chemicals.

1. INTRODUCTION

The methods of electronic detection of any toxic chemical compounds (TCCs) and also any kind of toxic industrial compounds (TICs) vary because of the difference of their situational use. The present research is on the most effective electronic devices for detection of environmental exposed TCCs and TICs in order to achieve a better society social health care prevention. The TCCs electronic detection devices and used methods are described and analyzed by showing their advantages and disadvantages. Although incineration or other oxidative procedures are widely discussed methodologies for TCC detection and quantification, derive their widespread industrial use and environmental persistence from their resistance to oxidative degradation. The more highly chlorinated the TCC, the greater its resistance to oxidation, and the longer it will persist in the environment. Several detection methodologies for TCC remediation have been described, including treatment with:

- Ion Mobility Spectroscopy - IMS Technology, Ion Mobility Spectrometer 31, Chemical Agent Monitor (CAM), Raid-M and Raid-M-100, GID-3, LCD-3, AP2C72, AP2Ce;
- Colorimetric Technology;

- Mass Spectrometry, etc.

2. TOXIC CHEMICAL COMPOUNDS ELECTRONIC DETECTORS – CHARACTERISTICS, ADVANTAGES AND DISADVANTAGES FOR AN EFFECTIVE HUMAN HEALTH PREVENTION

Ion Mobility Spectroscopy (IMS).

- IMS Technology

IMS is a separation technique that allows ionised analyte molecules to be distinguished on the basis of their mass, charge and mobility in the gas phase. Hence, IMS instruments are quantitatively capable of detecting and identifying vapour-phase CAs and their degradation products (Creaser et al. 2004).

A typical IMS, shown in Figure 1, comprises a drift tube which is normally divided into an ionisation region and a drift region, which is where the separation and detection of ions occur. The ionisation and drift regions are separated by a gating or shutter grid which is used to pulse the ions produced in the ionisation region and inject them into the drift region (Eiceman, Karpas, 1994).

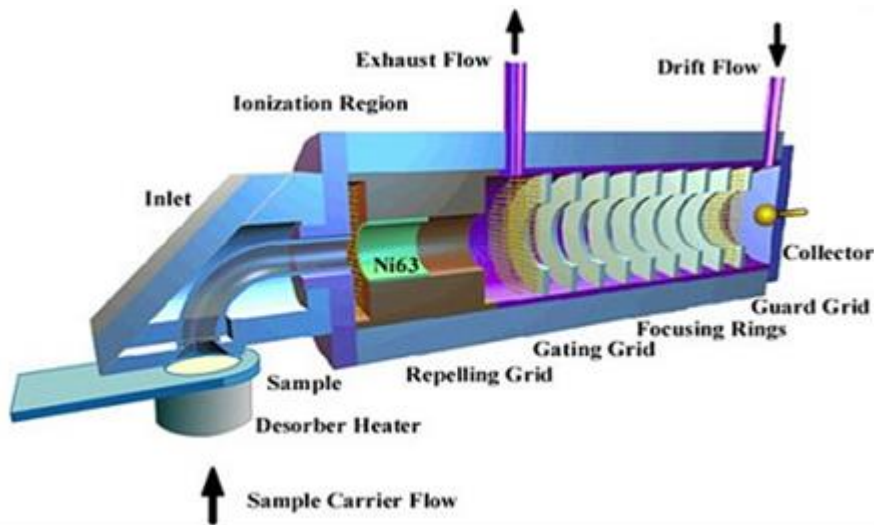


Figure 1: Schematic of Ion Mobility Spectrometer 31.

IMS operates by drawing a sample vapour into the detector via an inlet (1999). However, for a detector to perform optimally, the detector must be operated in clean, dry air (Sun, Ong, 2005; Brittain, Brokenshire). Membrane inlet interfaces and/or molecular sieve packs have been used extensively in CA monitoring as they limit the entry of moisture, dust and other particulates into the drift cell whilst allowing compounds of interest to pass through. These membranes allow chemicals in the sample to diffuse through them into the ionisation region whilst water molecules and other chemicals that have a low permeation rate will be carried away by the exhaust flow¹⁰. One disadvantage with these membranes is that they may also lead to diminished sensitivity and increased response time (Hofacre et al.2004a).

- Chemical Agent Monitor (CAM)

The CAM, shown in Figure 2, is manufactured by Smiths Detection (Watford, UK) and was the first mass produced, reliable hand-held instrument capable of detecting nerve and blister agents. It is now heavily deployed around the world⁶. A number of variants have been manufactured which have incorporated product improvements, including the Improved Chemical Agent Monitor (ICAM), Enhanced Chemical Agent Monitor (ECAM), CAM-2 and CAM Plus (Hofacre et al.2004a).



Figure 2: Chemical Agent Monitor (CAM)

The CAM is not able to identify a specific agent, but gives an indication of the class of agent present. As a result, it is mostly used to survey an area exposed to a CA and confirm the extent and relative concentration of any contamination. It can also be used to monitor chemically exposed personnel, vehicles, equipment and terrain to determine the extent of any cross contamination, and confirm the effectiveness of decontamination (ECAM; CAM).

CAM is easy to use with a simple ON/OFF switch and a mode button to switch from blister ('H' mode) to nerve ('G' mode) agent detection. However, the required mode must be manually selected as the CAM is incapable of simultaneously detecting nerve and blister agents. The hazard level is shown on a liquid crystal display (LCD), via an increasing number of lighted bars. The number of bars indicates the degree of hazard which can also be related to the relative concentration, with one to three bars indicating a low concentration, four to six bars a medium to high concentration and seven to eight bars indicating a very high concentration (Longworth, Ong, 2001).

According to the manufacturer, the CAM is a lightweight, handheld detector that can detect and differentiate between low levels of nerve and blister agents. It requires minimal training, has a simple user interface and is easy to maintain (Longworth, Ong, 2001a). Evaluation of the CAM by scientists at Edgewood Chemical Biological Center (ECBC) found that it can detect nerve and blister agents below the IDLH level of 0,03 mg/m³ (nerve agents), but cannot detect them at the AEL concentration level, which is 0,0001 mg/m³ and 0,003 mg/m³ for nerve and blister agents, respectively. The detectors were also found to successfully detect CAs at different temperatures and humidities. However, the CAM was found to produce an alarm in the presence of a number of interfering vapours, giving a visual bar warning with no audible warning (Longworth, Ong, 2001).

- Raid-M and Raid-M-100

The RAID-M-100 pictured in Figure 3 (A) (Technologies: RAID-M Handheld Chemical Agent Detector), is based on the RAID-M which is shown in Figure 3 (B) (Technologies: RAID-M Handheld Chemical Agent Detector). Both detectors are manufactured by Bruker Daltonics, Inc. (Bremen, Germany) and are currently in use by the German and Danish military. These detectors are IMS-based and are able to detect, classify, quantify and continuously monitor concentration levels of dangerous vapours specified in their library, whilst being operated single handedly (Daltonics; Technologies: RAID-M Handheld Chemical Agent Detector).

A

B



Figure 3: (A) Raid-M-100, (B) Raid-M.

Both detectors have been designed to automatically alternate between positive and negative mode every two to three seconds. As such they can both be used to monitor TCC and TIC contamination on personnel or equipment in the field and within collective protection facilities (Hofacre et al. 2004a). Once the detector is switched on, it will perform a self test and if successful will automatically start measuring in "sample" mode. Once in this mode, the detector's operation is checked with the confidence samples provided; no other daily instrument calibration is required (Baranoski, Longworth, 2003). Detected substances can be displayed as the agent class or specific agent, simulant or TIC, with hazard levels being indicated by an 8-bar incremental display. Each bar corresponds to a certain concentration level depending upon the chemical vapour detected. When an agent is identified the RAID-M gives a visual and audible alarm, which can be muted if required (Daltonics; Technologies: RAID-M Handheld Chemical Agent Detector). When the amount of CA or simulant reaches a preset level, the RAID-M will automatically enter back flush or purge mode which contributes to its short recovery time of between 15 and 70 seconds. Scientists at ECBC have evaluated the RAID-M and found that it can detect CAs below the IDLH levels but higher than the AEL levels, in response times of less than one minute.

Temperature and relative humidity have been found to have a minimal effect on response times for detecting CAs. However, at extreme low and high operating temperatures, as stated by the manufacturer, there was a decrease in sensitivity for certain agents. For example, there was approximately a six-fold and a 17-fold loss of sensitivity for HD at the low and high temperatures, respectively. However, it was noted that the detectable levels were still at or below the IDLH.

Although the RAID-M offers fast and sensitive detection, the number of false responses to interferences still poses a concern. It is not known as yet whether the selectivity has been improved with the RAID-M-100 version.

- GID-3

The GID-3, also referred to as the M22 ACADA, shown in Figure 4 (GID-3), is manufactured by Smiths Detection (Watford, UK) and has been described as being the most advanced CWA detector fielded by the US Armed Forces (GID-3). The GID-3, also referred to as the M22 ACADA, shown in Figure 4 (GID-3), is manufactured by Smiths Detection (Watford, UK) and has been described as being the most advanced CWA detector fielded by the US Armed Forces (GID-3).



Figure 4: GID-3.

The GID-3 was originally developed after the Gulf War (1990-91) to overcome perceived weaknesses in existing detectors, namely the inability of detectors to simultaneously detect nerve and blister agents. As a result, this detector contains design features that have improved its agent detection capability, reduced false alarms, allowed for better agent discrimination and identification and improved ease of use by deployed troops (GID-3). The GID-3 has two completely independent spectrometers, shown in Figure 5 (Lancaster, 2006), both of which have their own ionisation sources allowing the GID-3 to detect positive and negative ions simultaneously. It responds to agents in real time and is capable of being reprogrammed to meet further threats from blood and choking agents (GID-3).

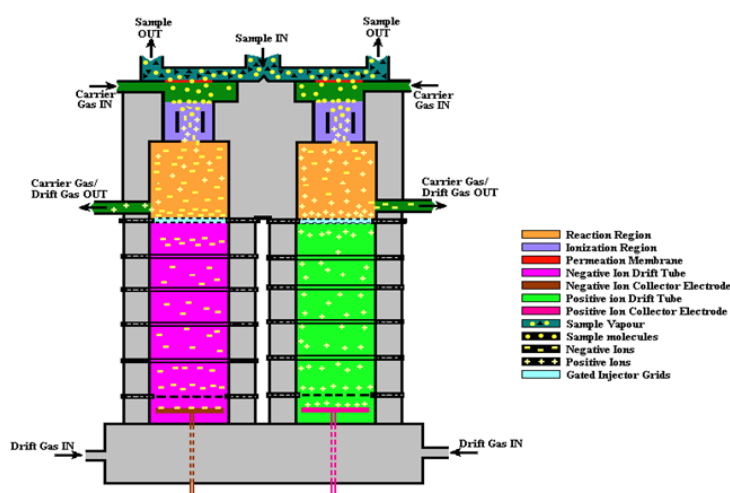


Figure 5: GID-3 schematic.

The GID-3 is easy to use, rugged, reliable and the most widely deployed detector currently in production (GID-3). It indicates the presence of CAs and the level of threat, whilst operating continuously with quick response and clear down times. It also provides a visible and audible alarm both locally and at remote

locations. The GID-3 can be installed on vehicles and can be deployed for use in man-portable or static locations (GID-3). In a reconnaissance role the GID-3 is normally fitted in the crew compartment of a vehicle where it samples the external atmosphere via a sensor head (GID-3).

- LCD-3

The LCD-3, shown in Figure 6 (LCD-3), is a personal chemical detector, manufactured by Smiths Detection (Watford, UK) (LCD-3). It has been designed to act as a local warning alarm for individuals and small groups of soldiers and can be handheld whilst wearing IPE or can be operated inside its carry pouch which can be attached to clothing (LCD-3; LCD). It can withstand the stresses and shocks associated with both operational use and transport by road, sea and air (Taylor, 2002).



Figure 6: LCD-3.

It detects, identifies, quantifies and warns personnel of CA threats at/or below attack concentrations (LCD-3; LCD). It is generally operational within five minutes of switching on, including warm up time and self testing, and requires no daily calibration. Operating performance is verified by using the confidence samples provided³⁷. In operation the LCD- 3 samples the air continually, and can thus simultaneously detect nerve and blister agents and simulants, usually within 10 seconds (LCD). It has an audible and visual alarm which alerts personnel to the need for IPE and because it operates continuously, it recovers rapidly thereby providing constant real time detection of CAs (LCD).

Flame Photometry

Flame Photometry is an important CA detection technique that has been successfully used for a number of years (Sun, Ong, 2005). Flame Photometric Detectors (FPDs) are deployed in military forces and civil agencies worldwide, however they are more commonly found integrated with a gas chromatograph (GC) in the laboratory (Sun, Ong, 2005; 38; Nieuwenhuizen, 2006). GC-FPD is used routinely for clinical, biological and environmental analyses. To date, GC-FPD has been one of the most useful methods in determining the TCC concentrations in samples sent to a laboratory for confirmatory analysis (Sun, Ong, 2005).

- Flame Photometric Detection Technology

Flame photometry is an atomic spectroscopy technique based on the light emission properties of excited atoms or clusters as they return to lower energy states¹⁰. A basic schematic of a portable FPD device is shown in Figure 7 (Nieuwenhuizen, 2006a).

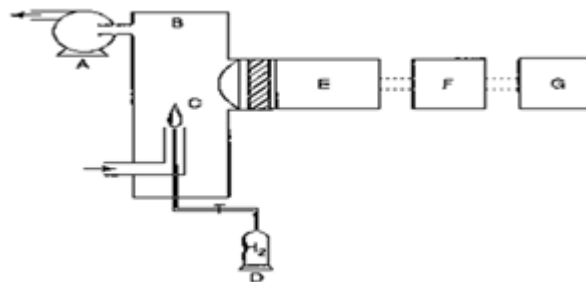


Figure 7: Schematic Representation of an FPD Device (A=air pump, B=reaction chamber, C=flame, D=hydrogen supply, E=photometric cell, F=electronics, G=display).

Initially, air is drawn into a reaction chamber by an air pump (B and A, respectively, in Figure 7) (Nieuwenhuizen, 2006a). The sample is then burned in a hydrogen-rich flame and the compounds present emit light of specific wavelengths. This, in turn, produces a characteristic emission spectrum that serves as a fingerprint for the atoms in the compound analysed (Creaser et al. 2004, Traeger, 2006; Davis; Nieuwenhuizen, 2006a). Figure 8 (Davis) shows an example of the main emission bands for sulfur, phosphorus, sodium and potassium.

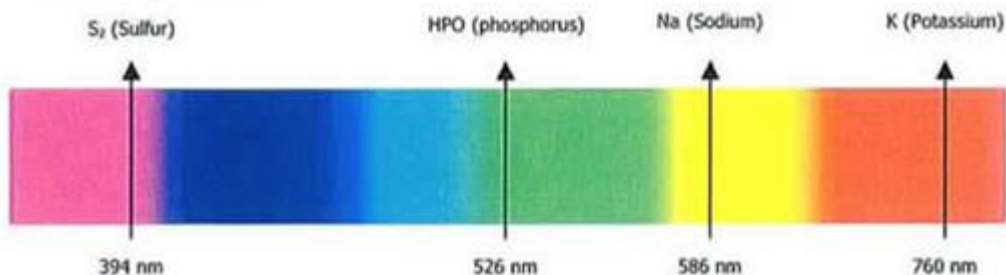


Figure 8: Example of main emission line (or band) from sulfur, phosphorus, sodium and potassium between 350 and 800 nm.

An optical filter is selected to allow a specific wavelength of light to pass through it and a photosensitive detector then produces a representative response signal. Since most elements emit a unique and characteristic wavelength of light when burned in this flame, the detection of specific elements is facilitated (Sun, Ong, 2005; Nieuwenhuizen, 2006).

Phosphorus and sulfur are the key components in nerve agents and HD, respectively. Hence CA detectors based on FPD have optical filters that are specific for these two elements. When phosphorus-containing compounds are burnt in a hydrogen-rich flame, excited phosphorus (in the form HPO^*) species are formed, whereas sulfur-containing compounds form excited S_2^* species. When these species fall back to their ground state light is emitted near 526 nm for the HPO^* species and 394 nm for the S_2^* molecule (see Figure 8) (Sun, Ong, 2005; Nieuwenhuizen, 2006).

- Existing Flame Photometric based Field Detectors

Although most of the major instrumentation used for field analysis of TCC is based on IMS, the next most predominant technology is flame photometry. The French AP2C monitor and the updated version, AP4C use FPD technology as does the MINICAMS (Sun, Ong, 2005).

- AP2C

The Proengin SA (Saint Cyr l'Ecole, France) AP2C, shown in Figure 9 (A), is the most notable detector based on flame spectrometry. It is a handheld CWA detector which detects most CWAs, including degraded and homemade agents (Sun, Ong, 2005). The AP2C is in service with the French, Swedish, Israeli and Australian military forces, civil defence agencies, and US federal government agencies and fire departments (2007). The AP2Ce, seen in Figure 9 (B) (2008), is a version of the AP2C which has additional heating systems to enhance the safety and performance of this detector in flammable atmospheres.

A



B



Figure 9: (A) AP2C72, (B) AP2Ce.

The AP2C can also detect liquid surface contamination using the S4PE Surface Sampler Probe accessory shown in Figure 10 (Longworth, Ong, 2001a). If liquid contamination is present, the S4PE, equipped with a

sampling tip, is used to wipe the contaminated surface. This is then analysed by the AP2C fitted with the shorter sampling pipe nozzle (Longworth, Ong, 2001a).



Figure 10: S4PE Surface Sampler Probe.

Colorimetric

Colorimetric detection is a wet chemistry technique formulated to indicate the presence of a CA by a chemical reaction that causes a color change when agents come into contact with certain solutions or substrates³. Colorimetric detectors have been employed by the military for a number of years as they are the fastest, cheapest, lightest and easiest type of detector to use in the field (Creaser et al. 2004). The most common colorimetric detectors come in the form of detection tubes, papers or tickets, each of which can detect TCC.

- **Colorimetric Technology**

Colorimetric technology is based upon specific chemical reactions that occur when the TCC interact with certain substrates and solutions (Coutant, 1999a). Colorimetric detectors are commonly made with sorbent substrates, such as paper and paper tickets, to which a reagent has been applied¹⁰. When the targeted chemical comes into contact with the substrate, it will react with the reagent to produce a distinctive colour change which can be visually detected (Sun, Ong, 2005). The concentration of the targeted chemical in the sample can also be estimated based on the intensity of the developed colour over the exposure time (Sun, Ong, 2005). These detectors are considered to be quite specific and usually come in the form of kits. The kits are quite complex as they include multiple tests for specific chemicals or specific toxic chemicals.

- **Advantages**

The major advantages of colorimetric detectors are that they are easy to use, low-cost and provide relatively fast responses (Sun, Ong, 2005). Also because most colorimetric detectors are designed to be selective, that is, the selected reagent will only react with a specific class of chemical compound to produce a colour change, they suffer from low false alarm rates (Sun, Ong, 2005).

- **Disadvantages**

Although selectivity is one of the major advantages of these detectors, it can also be one of the major disadvantages. Due to their selectivity, many different colorimetric detectors would be required in field applications. However to overcome this problem, some companies have produced kits which incorporate several different tests for detecting specific classes of compounds (Sun, Ong, 2005).

The colour changes produced by colorimetric detectors rely on visual signal processing which may also be problematic. Firstly, each person has a slightly different colour perception and some people may suffer from some degree of colour blindness thus impairing their ability to observe certain colour changes. It is also difficult to observe colour in dim or bright light which may limit the effectiveness of colorimetric detection devices. Detection may also become unreliable if any moisture is lost or absorbed by the sensor spots during use or storage (Sun, Ong, 2005).

Mass Spectrometry

Mass spectrometry is a powerful analytical technique used to quantify known materials, to identify unknown compounds within a sample, and to elucidate the structure and chemical properties of different molecules.

The complete process involves the conversion of the sample into gaseous ions, with or without fragmentation, which are then characterized by their mass to charge ratios (m/z) and relative abundances. This technique basically studies the effect of ionizing energy on molecules. It depends upon chemical reactions in the gas phase in which sample molecules are consumed during the formation of ionic and neutral species.

- Basic Principle

A mass spectrometer generates multiple ions from the sample under investigation, it then separates them according to their specific mass-to-charge ratio (m/z), and then records the relative abundance of each ion type. The first step in the mass spectrometric analysis of compounds is the production of gas phase ions of the compound, basically by electron ionization. This molecular ion undergoes fragmentation. Each primary product ion derived from the molecular ion, in turn, undergoes fragmentation, and so on. The ions are separated in the mass spectrometer according to their mass-to-charge ratio, and are detected in proportion to their abundance. A mass spectrum of the molecule is thus produced. It displays the result in the form of a plot of ion abundance versus mass-to-charge ratio. Ions provide information concerning the nature and the structure of their precursor molecule. In the spectrum of a pure compound, the molecular ion, if present, appears at the highest value of m/z (followed by ions containing heavier isotopes) and gives the molecular mass of the compound.

- Components

The instrument consists of three major components (Figure 11):

Ion Source: For producing gaseous ions from the substance being studied.

Analyzer: For resolving the ions into their characteristics mass components according to their mass-to-charge ratio.

Detector System: For detecting the ions and recording the relative abundance of each of the resolved ionic species.

In addition, a sample introduction system is necessary to admit the samples to be studied to the ion source while maintaining the high vacuum requirements ($\sim 10^{-6}$ to 10^{-8} mm of mercury) of the technique; and a computer is required to control the instrument, acquire and manipulate data, and compare spectra to reference libraries.

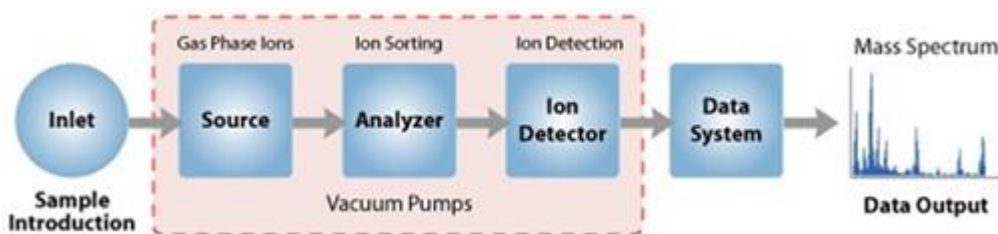


Figure 11: Components of a Mass Spectrometer.

With all the above components, a mass spectrometer should always perform the following processes: Produce ions from the sample in the ionization source. Separate these ions according to their mass-to-charge ratio in the mass analyzer (Terziev, Petkova - Georgieva, 2019-a).

Eventually, fragment the selected ions and analyze the fragments in a second analyzer.

Detect the ions emerging from the last analyzer and measure their abundance with the detector that converts the ions into electrical signals.

Process the signals from the detector that are transmitted to the computer and control the instrument using feedback.

3. CONCLUSION

All of the TCCs currently considered to be a threat have been known for decades, with the simplest and most prolific TCC being the vesicant, sulfur mustard which was first synthesised in 1823 (2001b; Eiceman, Karpas, 1994). As a result, the patterns of defence have also been fairly conservative, with detector technology being somewhat reactive rather than proactive (Eiceman, Karpas, 1994). Most detectors are designed to respond only when a threat is directly imminent and therefore tend to 'detect to respond' or 'detect to react' rather than "detect to warn" (Kosal, 2003).

The term "CA detection" can be defined as the systems and methods utilised for detecting and monitoring CAs and providing early warning of an imminent danger (Kosal, 2003). In the event of an attack by CAs, this capability is essential to enable the potential number of casualties to be reduced, or perhaps eliminated (Sun, Ong, 2005). With respect to the military, early warning of an attack can provide commanders with enough time to plan appropriate courses of action and warn adjacent units (CAM; GID -2A; Sun, Ong, 2005). Early warning will also give troops time to don individual protective equipment (IPE), with the basic items being the respirator (gas mask) and protective suit, both of which were originally developed at the end of World War I (Eiceman, Karpas, 1994).

IPE is still utilised as the main form of protection against a chemical weapons attack as it has been proven to provide effective protection for an individual whilst the agent is neutralised or eliminated (Petkova - Georgieva, 2018). Whilst IPE does provide adequate protection for the individual it also reduces the effectiveness of the wearer. Therefore, it is critical to monitor the level of hazard in the environment so that the IPE can be removed once it is safe to do so thereby reducing the physiological stress imposed through the wearing of full protective clothing (Pearson, 1990; Eiceman, Karpas, 1994). Hence detection equipment is not only crucial for the effective early warning of a potential CA attack but also for the continual monitoring of the environment to allow an individual to assess when it is safe to remove their IPE (Sun, Ong, 2005).

Many of the current CA detectors have technologies that are adapted from classical analytical chemistry techniques and although these technologies have progressed significantly, progress is still lacking in some areas (2004; 1996; Kosal, 2003). For example, detection technologies have not yet been developed to permit detection of lowest level concentrations under the AEL criteria (Sun, Ong, 2005).

The focus of most international research and development activities is now in the area of agent detection and identification and in the field of response via command and control systems (Eiceman, Karpas, 1994). However, there is a need to improve and expand the use of sensors in countering terrorism and minimising the impact on a civilian population should an incident occur. Beyond point sampling devices, it is of the utmost importance to develop sensors which will help provide sensitive and rapid detection and advanced warning of toxic vapours at fixed sites such as buildings, train stations and airports or air bases (Petkova - Georgieva, 2018).

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