

A Survey On Chemical Agent Detectors

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ABSTRACT

In an environment it is very important to detect the hazardous chemicals which causes harm to the human and also damage the environment. So an instrument chemical agent detector is used to detect chemical agents. It operates continuously in real-time environment. It provides an alert to the human by immediate sounding of an alarm upon detection of hazardous chemicals. This is useful in many applications like military, civilian, agriculture and medical. In this paper different types of chemical agent detectors are listed. The advantages and disadvantages of different chemical agent detectors are discussed. The operational features of each and every chemical agent detectors are discussed.

1. Introduction

Chemical warfare (CW) involves using the toxic properties of chemical substances as weapons. This type of warfare is distinct from Nuclear warfare and Biological warfare, which together make up NBC, the military acronym for Nuclear, Biological, and Chemical (warfare or weapons), all of which are considered "weapons of mass destruction" (WMD). None of these fall under the term conventional weapons which are primarily effective due to their destructive potential. Chemical warfare does not depend upon explosive force to achieve an objective. Rather it depends upon the unique properties of the chemical agent weaponized. A lethal agent is designed to injure or incapacitate the enemy, or deny unhindered use of a particular area of terrain. Defoliants are used to quickly kill vegetation and deny its use for cover and concealment. It can also

be used against agriculture and livestock to promote hunger and starvation. With proper protective equipment, training, and decontamination measures, the primary effects of chemical weapons can be overcome. Many nations possess vast stockpiles of weaponized agents in preparation for wartime use. The threat and the perceived threat have become strategic tools in planning both measures, and counter-measures [1]. For military forces, the threat of chemical weapons has existed for decades and can radically affect operations, particularly on land and sea. That threat is increasingly spreading to the civilian population. The ability to detect an attack by chemical agents or toxic industrial chemicals (TICs), rapidly, is therefore vital to protect those in the front line and the public at large [2].

2. Techniques for Chemical Agent Detection

Analytical methods that are currently used for the detection and identification of chemical warfare agents are reviewed and classified by the number of dimensions of information they provide.

Single-dimensional sensors target specific compounds or classes of compounds. Although they can be less expensive and more portable than multidimensional sensors, multidimensional sensors detect a broader threat spectrum with greater precision and accuracy.

Under the Chemical Weapons Convention (CWC), it is recommended to use simple two-dimensional analytical methods, such as gas chromatography (GC) or ion mobility spectrometry (IMS), for on-site screening of chemical weapons (CW) agents [3].

2.1 One-Dimensional Sensors (Selective Detectors)

The simplest approach for chemical detection is to target the specific compound of interest and selectively detect it in the presence of other background compounds and interferences [3].

2.1.1 Surface acoustic wave (SAW) sensors

One of the most popular approaches for selective sensing of CW agents is the SAW sensor. First reported by Wohltjen and Dessy in 1979[4] and based on the GC piezoelectric response demonstrated by King in 1964 [5], this sensor detects absorption of an analyte on the surface of a piezoelectric crystal.

When a time-varying electric field is applied to one side of a piezoelectric material, it sets up an acoustic wave that is propagated along the surface of the piezoelectric material and detected by electrodes located at the other end of the material. Changes in amplitude or phase of this wave occur when an analyte absorbs onto the surface of the piezoelectric material. When the surface is coated with a thin film, which absorbs chemicals selectively, a selective sensor is produced.

The major advantage of SAW detectors is that they can be made small and portable. The U.S. Military has developed a small sensor based on SAW technology called the joint chemical agent detector (JCAD).

The draw-back of these sensors is sensitive to moisture and may suffer from de-wetting effects that reduce responsiveness.

2.2 Two-Dimensional Sensors

Due to the complex nature of the agents and their matrices, non-separation based analytical methods often experience interferences, which result in false positive or negative responses. Thus, some type of separation method is often coupled to an analytical detector to provide more specificity of response and a broader range of application.

The most common separation devices are GC, liquid chromatography (LC), capillary electrophoresis (CE), IMS, and mass spectrometry (MS).

2.2.1 Gas chromatography (GC)

For vapour-phase chemical warfare agents, GC is usually the analytical separation method of choice. In general, a high-resolution gas chromatographic separation can require up to 30 min for complete separation and detection of a complex mixture.

However, when selective detectors are used in combination with GC, the separation time can be reduced significantly [6].

2.2.2 Liquid chromatography (LC)

For compounds that are not volatile or thermally labile, LC rather than GC is often the method of choice for separation prior to detection. However, high pressures and small particle sizes limit column length and therefore, the ultimate resolving power possible by LC. In addition, low diffusion rates in liquids make LC a relatively slow analytical method for the detection of CW agents.

2.2.3 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. Different methods of chemical agent detectors are as follows:

Conventional IMS: A conventional ion mobility spectrometer consists of the reaction region, including the ion source and ion gate, and the drift region and detector. The sample compounds are ionized by proton transfer or electron capture reactions. The electronic gating grid (ion gate) introduces the ions into the drift region, where the ions travel along the electric field gradient. Ions are separated according to their velocities in the neutral, counter-flowing drift gas. Ions create a drift time related signal through collision and neutralization at the detector (a Faraday plate).

Aspiration IMS: Another type of IMS used to detect CWAs is aspiration IMS (AIMS). The ionization occurs at ambient conditions in the presence of a relatively high amount of water, which affects the kinetics of ionization reactions. The principle of operation of the AIMS instrument is Ions travel through an orthogonal electric field in which they are deflected to multiple channels located on the collecting electrode. Ions with a faster velocity collide earlier than slower ions; the detection in AIMS is based on characteristic signal patterns and utilizes pattern recognition methods. A Finnish company, Environics Oy, is a specialized manufacturer of the ChemPro handheld AIMS instrument.

Field Asymmetric IMS: The mechanism of field asymmetric IMS (FAIMS), also known as differential mobility spectrometry (DMS), is closely related to AIMS, but the ion separation process differs. In FAIMS, ions pushed by the gas flow travel through a perpendicular electrical field. The electrical field is generated by an asymmetric

AC dispersion voltage but also has a compensation voltage called the DC component. This radio-frequency (RF) region works as a filter and ions of both polarities are collected behind it. Ion mobility is a function of field strength, especially in the case of high fields; hence, ion drifts caused by the asymmetric field can be compensated for with a suitable compensation voltage. The advantages of this instrument are its small and simple construction and potentially high resolution. Detection is based on the signal peak position and intensity in the RF-voltage- Compensation Voltage (Vrf-CV) plane.

2.3 IMS Advantages

The principle advantages of IMS are its simplicity and sensitivity. IMS-based detectors are portable and provide rapid analysis and response. Furthermore they are highly sensitive, have low limits of detection and are relatively inexpensive to manufacture. IMS detectors have a simple design and are quite rugged. They contain few moving parts, are lightweight, have low power consumption and use limited consumables [7].

IMS utilises a weak radioactive ionisation source to provide the ionisation energy thus enabling the instrument to be miniaturised for field operations. In addition the detectors do not require any specialised power supplies, additional carrier gases or vacuum pumps. The general operation and maintenance of an IMS detector is also quite simple, requiring minimal training.

The initial setting up of a detector requires a battery pack to be inserted and the detector to be turned on. After a warm-up period, the detector will perform a self-test, which verifies that proper operational parameters are satisfied. It can then be calibrated using stimulants. If a target substance is detected, an alarm is triggered thus allowing minimal or no data interpretation [7].

2.4 IMS Disadvantages

Although IMS, as a technique, is fast, relatively sensitive, and instruments can be hand portable if necessary, it can suffer from poor selectivity and is prone to interferences which produce false alarms. IMS uses a non-discriminatory ionisation process and therefore is subjected to potential interferences by non-target compounds. Thus, it may be necessary to use more than one peak for substance identification which will improve a detector's identification capability and minimise its potential for false alarms. Furthermore, limitations on the resolution or separation capacity of IMS detectors which are the result of short drift tubes, means that the number of targeted compounds programmable for detection must be limited to avoid peak

overlapping. This leads to detection interference and frequent false alarms.

2.5 Mass spectrometry (MS)

Unlike IMS, MS is an ion separation method in which gas-phase ions separate according to their mass to charge ratio as they move through a vacuum. Due to the lack of ion-molecule interactions and the rapid analysis time (on the order of μ s), typical mass spectrometers have resolving powers 1 to 2 orders of magnitude better than IMS and chromatographic instruments. However, the complexity of requiring a vacuum limits the practical application of MS as a field analytical technique.

An ion trap mass spectrometer with a high-pressure negative ion source and selected reactant negative ions has been used to insure unambiguous detection of phosphorus- and nitrogen-containing chemical warfare agents.

3. Joint Chemical Agent Detector (JCAD)

The Joint Chemical Agent Detector (JCAD) will provide state of the art chemical warfare agent detection capability to ground vehicle operators.

The JCAD will provide a small (40 in³), lightweight (2 lb.) chemical agent detector for vehicle interiors, aircraft, individual personnel, shipboard, and fixed site locations. The system provides a common detection component across multi-service platforms. This common detector system will allow the Joint Services to use the same operational and support concept for more efficient utilization of resources. The JCAD will detect, identify, quantify, and warn of the presence of chemical agents prior to onset of mitosis. Upon detection of chemical agents, the detector will provide local and remote audible and visual alarms to the operators. Advance warning will provide the vehicle crew with the time necessary to protect themselves from the lethal effects of chemical agents. The JCAD will also be capable of being upgraded to protect against future chemical agent threats. The JCAD will provide the vehicle operators with the warning necessary to survive and fight in a chemical warfare agent threat environment.

3.1 Description

The detector unit weighs two pounds and is 40 cubic inches (4 in. wide by 7 in. tall by 1.5 in. deep) in volume. The unit is capable of worldwide operations from -32 to 49°C and in any environment. The JCAD detector unit will operate on either platform power or an internal battery. The

unit will use the BA- 5800 battery which is the same one used in the Rockwell PLGR. The battery life is expected to be greater than 18 hours on the primary battery or approximately 12 hours on a rechargeable being provided by the JCAD prime contractor.

The JCAD uses surface acoustic wave (SAW) technology to detect the chemical warfare agents. The SAW sensor is a small, piezoelectric quartz crystal that is coated with a proprietary polymer. The SAW crystals are part of a high performance oscillator circuit and eight SAW crystals form the chemical sensor array in the detector unit. The base frequencies for the SAWs are 275 MHz. Each polymer is specifically designed to attract nerve, blister, or blood CW agents. The CW agents are selectively absorbed by the polymer, thus changing the resonant frequency of the SAWs. The frequency changes from the SAW array are processed by a neural network algorithm to determine the type and concentration of the chemical agent. The neural network algorithm can also be upgraded as new threat agents are identified.

3.2 JCAD View

The heart of the JCAD is the detector unit shown in Figure 1



Figure 1. JCAD detector unit

3.3 JCAD Operational Features

The JCAD detector unit will provide immediate operator feedback in the event of chemical agent detection. The operator will be notified via the liquid crystal display (LCD), light emitting diode (LED), and an audible signal. The LCD is night vision system compatible and all of the operator alert functions may be adjusted to match the desired mission requirements. The JCAD will also interface with the Joint Warning and Reporting Network (JWARN). Up to 10 JCADs may be

“strung” together at distances up to 400 meters apart. The base unit functions as a control unit to provide chemical alerts and mal-function signals for the other 9 units that are deployed [8].

4. APD2000 Detector Description

Environmental Technologies Group, Inc. (ETG) manufactures the APD2000 detectors. The detector is marketed as a lightweight (approximately 6 pounds, including the batteries), handheld, portable detector designed for surveying the environment to identify specific CW agents and irritants. It contains a 10-millicurie Nickel 63 radioactive source. The detector can be operated in CW or irritant mode. For this evaluation, only the CW agent mode was considered. The APD2000 detects nerve and blister agents simultaneously in its CW mode. It also has data logging features to record monitoring events.

The APD2000 employs ion mobility spectrometry (IMS) detection techniques. Sample air passes through the heated membrane and then is drawn into the cell assembly. The molecules are ionized by the radiation source. The resulting ions are swept down the drift tube where they become separated according to their mass and mobility toward the collector electrode. An electronic signature is produced for each ion, based on the time required to reach the collector electrode. The APD2000 will sound an alarm if the sample signal “matches” the required signature criteria.

In addition to the audible alarm, the detector also has a visible display that shows “reference level” readings and the “identity” of the substance detected. The reference level is a number between zero and 100 for the “specific CW agent” or the “class of CW agent” that caused the detector to alarm. Larger numbers indicate the presence of a higher concentration of vapour is suspected. The numeric values (26-50, 51-75, and 76 -100) are relative indications for low, medium, and high agent concentration responses, respectively, and will trigger the audio alarm.

Response value below 25 indicates there is a detection of the displayed substance at low concentration levels below the alarm set point. The audio alarm will not sound when below the threshold set point. The reference class for this detector response can be either “nerve” or “blister”, with or without a specific agent (GA, GB, GD, VX, HD, HN or L) identified. This feature, despite occasional mislabels, distinguishes this detector from others tested thus far. The detector also contains a back-flush pump that reverses the sample flow path to protect the cell assembly from gross contamination. Back-flush mode is activated when the detector displays a “high (76-100)” concentration detection. The detector cannot detect

when it is in this “back-flush” mode until its sensor has been sufficiently purged.

Power sources to operate the APD2000 include six standard or rechargeable C batteries, AC adapter, or 9-18 Volt DC supply. Six C-type batteries can sustain approximately seven hours of operation at ambient temperature. The APD2000 operating specifications give the operational temperature range from -22°F to 126°F (-30°C to +52°C) and the relative humidity range from zero to 95%. Battery life decreases sharply at lower temperatures. DC power supply was used through the evaluation to ensure that the detector performance would not be affected by battery condition.



Figure 2. Digital photograph of the APD2000 detector

5. Flame Spectrophotometry

Flame Spectrophotometry is a method which is used to determine intensity of radiations of various wave-lengths in a spectrum emitted by a chemical inserted into a flame. Initially, air is drawn into a reaction chamber by an air pump (B and A, respectively, in Figure 3). 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.

A basic schematic of a portable FPD device is shown in Figure 3.

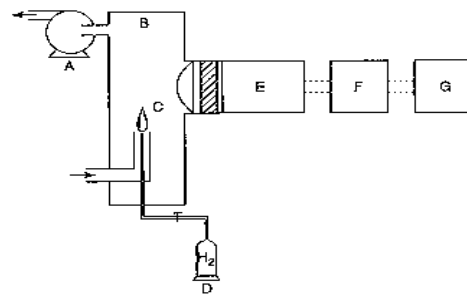


Figure 3. Schematic Representation of an FPD Device (A=air pump, B=reaction chamber, C=flame, D=hydrogen supply, E=photometric cell, F=electronics, G=display)

6. Detection Process of Chemical Agent

The target detection and identification algorithm is generally based on three key factors: the composition of the analyzed pixel, the type of model used to estimate the variability of the target and background spaces, and the model used to describe the pure and mixed pixels [9].

A. Background Estimation

The mathematical representation of a mixed pixel depends on whether the background (or target) space is estimated statistically or geometrically.

The considered sub-pixel target detection algorithms are of a stochastic nature. When the background is entirely represented by its statistics, the detection problem consists in extracting the targeted spectral signatures from a background noise term [11]:

$$H_0 : x = \epsilon_b$$

$$H_1 : x = T_a + \epsilon_b$$

Here, a is a weighting vector to be estimated and T is a matrix of “ k ” targets: $[t_1, t_2, t_3, \dots, t_k]$. It is assumed that the noise component has a mean value of zero and covariance C .

B. Clutter-Matched Filter: a Stochastic Mixed Pixel Model

The basic idea behind is to minimize the response to the unknown background signatures while accentuating the response to the target spectrum. To do so, the following mathematical operator was developed:

$$q_i = \frac{C^{-1}t_i}{\sqrt{t_i^T C^{-1}t_i}}$$

where q_i is the related to the i th target t taken from the matrix of targets T and the $N \times N$ estimated covariance matrix, C .

7. Results

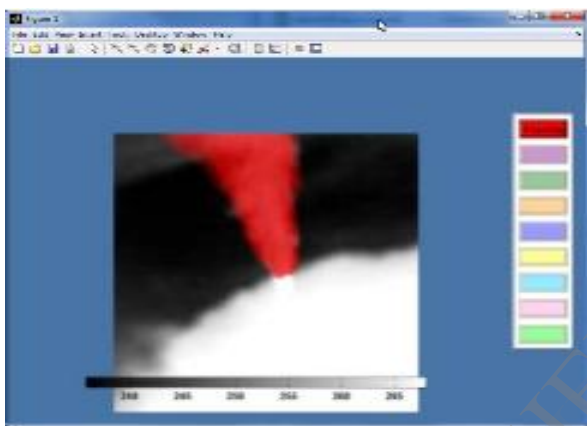
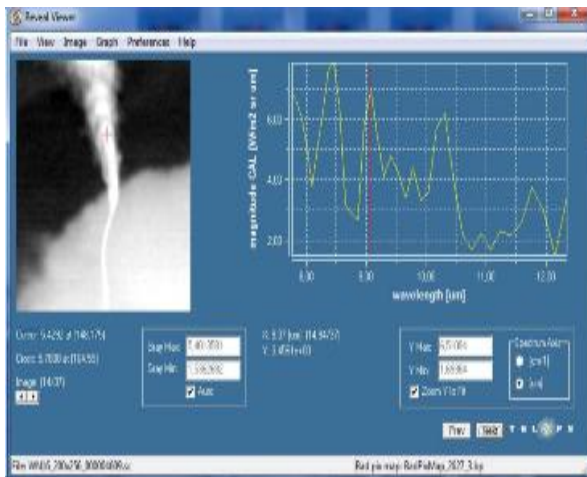


Figure 4. The results of freon 134 measurements (concentration 3%, distance 60 m, T atm = 18°C, v wind = 8 m/s, p atm = 992 hPa): (a) spectral characteristics, (b) results of analysis in Matlab.

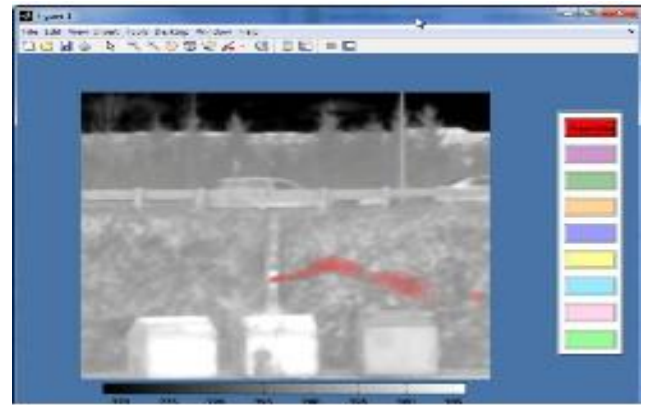
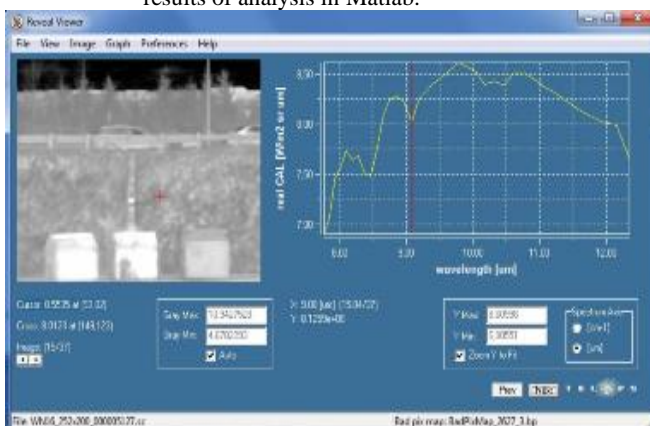


Figure 5. The results of freon 136 measurements (concentration 3%, distance 63 m, T atm = 18°C, v wind = 10 m/s, p atm = 996 hPa): (a) spectral characteristics, (b) results of analysis in Matlab.

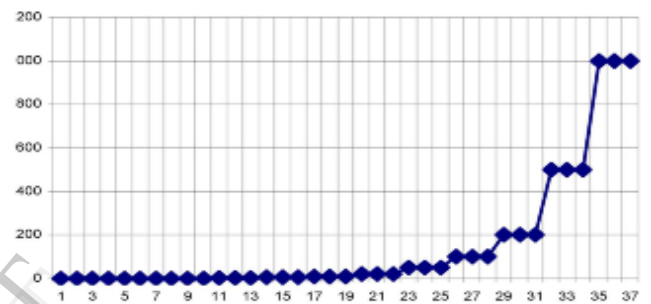


Figure 6. TBP concentration profiles for files SPME-TBP

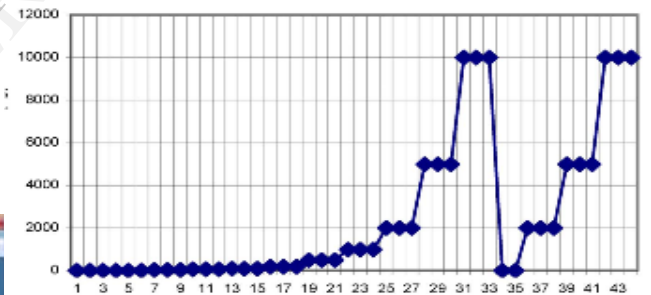


Figure 7. TBP concentration profiles for aqueous injection (closed-port) files

8. Conclusion

To protect the human and make them survival from the chemical warfare, detection of chemical agent is much required. So a warning system is needed in all the applications as soon as a chemical agent is detected. The above techniques that are implemented are the best and easy methods to detect the chemical agents that are present in the environment. Therefore chemical agent detector has become one of the important in all applications like military, medicine, agriculture etc. So as soon as the chemical agent is detected which causes harm to the public and nature, a communication system has to be involved in the detector in order to save the lives of human.

9. References

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