

A novel headspace sampler for field detection of chemical warfare agents and simulants connected to a commercial ion mobility detector

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Abstract A rapid and simple sampling technique for use in conjunction with commercial ion mobility spectrometric detectors is described. The technique may be used for the detection of chemical warfare agents in the field. A plastic syringe with a steel needle was attached to the nozzle of the detector, and the syringe shortened to reduce the dead volume in the interface. After heating samples of protective clothing in closed headspace vials to 70 °C for three minutes, the detector with the syringe and needle (called HS-LCD) was used to penetrate the vial and the overpressure was transferred to the detector via the simple interface. The detector response was registered in realtime. To demonstrate the possibilities with this technique, the HS-LCD sampler was tested in the field at relatively low temperatures on pieces of protective clothing contaminated by the chemical warfare agent simulants methyl salicylate and dipropylene glycol methyl ether. A significant improvement in detector response was observed utilising this technique compared to using the detector to survey the material in the open air. This improvement is believed to increase with decreasing ambient temperature and with decreasing analyte volatility. A more comprehensive list of possible interferences should be tested in the future.

Keywords Chemical warfare agents · Simulants · Field detection · Headspace · Ion mobility spectrometry

Introduction

The Geneva Chemical Weapons Convention (CWC) from 1997 bans production, stockpiling and use of chemical warfare agents (CWA) in armed conflicts [1]. The CWC has been ratified by most nations in the world, but there are still a few rogue nations remaining who have not signed or ratified the Convention. Also, as exemplified by the attacks in Matsumoto in 1994 and those in Tokyo in 1995, terrorists have demonstrated that they are capable of acquiring and using CWA [2].

Since most chemical warfare agents react quickly when entering the body, both by oral and dermal exposure, it is of vital importance to be in possession of rapidly reacting detection systems that can alert personnel to the potential presence of these agents. Among those at most immediate risk are first line personnel and military personnel. It is also beneficial to be able to check a possibly contaminated area before first responders enter into it to ensure that the area is safe.

There are a wide variety of vapour detectors on the market that can rapidly detect both chemical warfare agents and toxic industrial chemicals [3–5]. One such vapour detector is the Lightweight Chemical Detector (LCD) from Smiths Detection (Bushey, Herts, UK). This is an ion mobility spectrometric (IMS) detector that is currently in use in the armed forces of several countries. However, vapour detectors of this type will only respond if the vapour pressures of threat agents are large enough and if agent vapours are drawn into the detector in high enough quantities to trigger the alarm. The amount of vapour available for detection is therefore limited at low temperatures and in windy conditions where the wind blows the vapour away from the detector.

At this time there is very little field equipment on the market for the detection of threat compounds in liquid or solid form. The equipment mostly used today is detection paper that gives different colour spots when pressed against a liquid sample (for example the M8 and M9 detection paper from All

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Safe Industries, Louisville, KY, USA). These papers are slow and cumbersome to use and do not allow for the electronic transmission of detection results or alarms to neighbouring units. There are options for detecting CWA on solid surfaces by special heating devices that are scraped over the surface, thereby evaporating possible substances which are drawn into a vapour detector. One such device is sold by Proengin for the AP2C and AP4C handheld flame photometric detectors (Proengin, Saint Cyr l'Ecole, France). Such devices also take time to use and require the liquid agent to be physically present on the surface of the solid sample. The possibility to detect threat agents in liquid or solid form has therefore long been identified as a technology gap [6]. The availability of such technology would permit the detection of potential threat agents at a much wider range of temperatures and wind speeds.

The headspace (HS) sampling technique described by Røen et al. [7] [8], for example, could be used on a great variety of solid and liquid samples. In this technique, the sample is heated to a predetermined temperature for a given time in a closed vial and a vapour sample is subsequently taken and analysed by for example gas chromatography – mass spectrometry (GC-MS). The headspace GC-MS (HS-GC-MS) instrumentation used could be made transportable (this has been done for example by Inficon Inc. for the Hapsite GC-MS), but it is not ideal for use by military or civilian first-responders due to the high weight, high power consumption and large volume of the equipment. The search is therefore on to find more lightweight equipment with less power consumption that could be used as screening devices for liquid and solid samples.

Sample materials of interest in HS analysis are materials that easily adsorb CWA and retain the agents until analysis, but that also have the possibility to release the agents by heating during analysis. The samples should also be easy to collect during a sampling mission. Experiments carried out by the Norwegian Defence Research Establishment have shown that samples containing suspicious wet or stained spots on protective materiel (textiles, rubber, gloves, silicon materials, etc.) or on environmental samples (soil, sand, vegetation, etc.) are good choices. These experiments show that protective materials such as textiles and rubber are well suited for headspace analysis. Using this technique, the recovery of mustard gas from neoprene rubber after 14 days exposure in summer conditions was as much as 14 %. Similarly, the recovery of the nerve agent soman from silicone after 7 days exposure was up to 28 %, and up to 16 % after 14 days exposure under winter conditions [9]. In the present paper, a textile material with activated carbon is therefore used as a test material.

IMS-based detectors are well suited for field monitoring due to their small size, light weight and low consumption of power. Such detectors work under atmospheric pressure utilising ambient air as a drift gas, and could be used in various environmental conditions with a fast response and a relatively high sensitivity. IMS principles and applications have been described by for example Creaser et al. [10], Borsdorf and

Eiceman [11], Borsdorf et al. [12], Satoh et al. [13] or Maziejuk et al. [14]. Mäkinen et al. [15] have also described IMS and its application in the detection of chemical warfare agents and Armenta et al. [16] have made a review of recent unconventional applications of IMS. Holopainen et al. [17] have described different sample extraction methods for IMS in water analysis, but not using direct HS as an extraction technique. However, the Holopainen study did describe HS combined with solid-phase micro-extraction.

A review of sample introduction systems for IMS detectors, including HS, has been made by Arce et al. [18]. In this review, a need is identified to develop more efficient sample introduction systems. The HS-IMS interfaces described are either simple gas-tight syringes for the purpose of drawing vapour samples from the head space over a sample ([19] [20]) or a more complex carousel auto-sampler, where hourly samples were drawn from each sample vial using plastic syringes [21].

Eiceman et al. [22] have analysed petrochemical fuels in soil using a headspace sampler connected to IMS through a 20 cm long section of fused silica tubing. Kanu et al. have described a method to detect chemical warfare agent simulants and degradation products in which a thermal desorption IMS detector identifies these agents directly from a type of filter paper used to swab surfaces [6]. In addition, Rearden and Harrington [23] have developed a screening method for CWA degradation products by using solid-phase micro-extraction connected to a commercial IMS detector. The sample analysis time using this technique was less than 30 min.

Stach et al. [24] used an Erlenmeyer flask connected to an IMS detector through a Teflon tube to analyse samples from an old mustard production site. The sample was heated to 50 °C for 5 min and the IMS spectra were recorded continuously during the heating period. This technique was compared with a mobile GC-MS system and the results agreed with the GC-MS results in 95 % of the investigated samples. The technique described by Stach et al. has the potential to be miniaturised and simplified even further. This is described further in the present paper.

This paper describes a method in which a commercially available IMS detector (LCD 3.1B or LCD 3.2E from Smiths Detection) is used to rapidly detect certain CWA-simulants in liquid form from environmental samples materials by HS sampling. To the knowledge of the authors, no paper describing this method has been published before. The aim has not been to carry out a complete method development, but to demonstrate the possibilities and advantages that this method affords.

Materials and methods

Chemicals and materials

The chemicals used were: Dipropylene glycol methyl ether (DPM) [34,590–98-8] (97 %), a mixture of isomers from

Aldrich, Milwaukee, WI, USA; Methyl salicylate (MS) [119–36–8], synthetic, extra pure, from Merck KGaA, Darmstadt, Germany; Acetone [67–64–1], Emsure® from Merck KGaA; Ethylene glycol [107–21–1], technical grade, from VWR International, Fontenay-Sous-Bois, France; 2-propanol [67–63–0], Ultra Resi-analyzed® from J.T. Baker, Deventer, The Netherlands.

In addition to the above, diesel oil, unleaded gasoline and engine oil from Statoil, Stavanger, Norway and Break Free CLP weapon oil with NATO Code S-758, 9150–01-327-9631 (FSD-7717) from Safariland, Ontario, CA, USA were used in the study.

The septa used to close the headspace vials were silicone/PTFE seal, part number 20-AC-ST3 (aluminium crimp cap with 20 mm silicone/PTFE liner) from Chromacol Ltd., Welwyn Garden City, Herts, UK; PFTE silicone seal (aluminium crimp cap with 20 mm PFTE/silicone liner) from Agilent Technologies, Santa Clara, CA, USA; and butyl rubber/PFTE seal (steel crimp cap for SPME with 1,3 mm butyl rubber/PTFE liner) from Gerstel GmbH & Co.KG, Mülheim an der Ruhr, Germany.

The textile used as test material was a combination consisting of one layer of polyester and one layer of cotton with small spherical particles of activated carbon in between, type CD2870 from GENTEX, Rancho Cucamonga, CA, USA. The simulant was applied to the outer polyester layer of the material.

Instrumental design

The IMS detectors used in the experiments were the LCD versions 3.1B and 3.2E from Smiths Detection. The LCDs have two separate drift tubes, one measuring positive ions and the other measuring negative ions, and the detector alternates between the two polarities. The LCDs are equipped with a corona discharge ionisation source and use air as a drift gas. The detectors present the detected concentration as bar readings. LCD 3.1B has no bar readings on the detector itself, but the number of bars from one to eight can be read out using software from Smiths Detection (TrimScan2 version 0.6.9, Smiths Detection – Watford). On the LCD 3.2E it is also possible to see the bar reading on a display on the outside of the detector. There is an approximate doubling of agent concentration in the air when the detector reading has increased by one bar level.

LCD version 3.2E was used in the laboratory experiments, whereas LCD version 3.1B was used during the experiments carried out outdoors. The built-in libraries in the two LCD versions were used, which means that only agents that are present in the libraries should give a positive response.

A small fan is mounted in the LCD sample inlet to draw air into the detector. The air sample then enters the ionisation region through a pinhole inlet where ions are generated by a

corona discharge ioniser. A moving diaphragm is used to pump the sample into the drift region of the IMS where the generated ions are separated. The LCD draws a new sample into the detector every 5 s (measuring cycle) whereas each measurement only takes 20 milliseconds. The remaining time of each measuring cycle is instrument relaxation time, during which the LCD prepares for the next cycle.

Connection of headspace needle

The normal rain cap in front of the sample inlet was in the present experiments replaced by a survey nozzle from Smiths Detection. A shortened 5 ml plastic syringe (Becton, Dickinson and Company, Franklin Lakes, NJ, USA) with a luer lock was then put on the outer end of the survey nozzle (see Fig. 1). The syringe was shortened in order to reduce the dead volume in the inlet system as much as possible. An interchangeable steel needle was mounted at the end of this shortened syringe by using the luer lock. In the present paper this assembly is referred to as a headspace LCD (HS-LCD) connection.

Steel needles with a diameter of 16G (1.194 mm ID), 18G (0.838 mm ID), 21G (0.495 mm ID) and 23G (0.318 mm ID) from Becton, Dickinson and Company were tested in the experiments. Needles of 194 mm ID × 40 mm in length (16G) were used if not otherwise specified.

For sample heating in the laboratory, a standard 20 ml headspace vial with a flat bottom (Part number 5182–0837 from Agilent Inc., Santa Clara, CA, USA) was loaded with the sample and heated in a water bath. After the sample was loaded into the vial, it was sealed with a crimp cap with septum.

Due to the low pump capacity, the LCD is unable to draw much gas out of the HS vial without vial overpressure. Detection is therefore only possible as long as overpressure exists in the HS vial to push the sample into the detector. The heating of air from 20 °C to 70 °C will theoretically give an overpressure of 0.17 atm in the HS vial. This overpressure will only last for a few seconds when the HS septum is pierced by the HS-LCD needle.

Sample preparation

Before analysis, circular pieces measuring 1 cm² in size were cut out of the test material and placed at the bottom of



Fig. 1 LCD 3.1B detector connected to a survey nozzle and syringe with a 16G needle. This combination is here called the HS-LCD connection

headspace vials that could hold a volume of 20 ml. One drop-let of the test agent was placed on top of the material sample using a 10 μl syringe from SGE.

During some of the experiments, the liquid test agents were diluted in acetone and a droplet of the solution placed directly on the glass wall of an otherwise empty HS vial using an adjustable 2–20 μl Finnpi-pipette from Thermolabsystems.

The closed HS vial was allowed to stand for one hour at room temperature before being heated to a thermostating temperature of 70 °C. This temperature was also used by Johnsen et al. [25] and Røen et al. [8] in an earlier study and was used without further investigation. At the end of the thermostating time, the HS-LCD needle was quickly pressed through the vial septum to release the overpressure into the LCD.

Results and discussion

Determination of optimal thermostating time

The first experiments were carried out to find the optimal heating time for DPM and MS in the headspace vials (thermostating time). For field use, it would be advantageous if a relatively short thermostating time could be achieved. An amount of 1 μl pure DPM (0.95 mg) or MS (1.2 mg) was placed on a piece of 1 cm^2 test material in a closed glass chamber (volume 6 L) and allowed to equilibrate for 60 min at room temperature (approximately 25 °C). The test material pieces were then transferred to headspace vials and closed with crimp caps before thermostating at 70 °C. Analysis of control samples of the test material without added simulants gave no LCD response. A plot of detector response for DPM and MS as a function of thermostating time is shown in Fig. 2.

The mean LCD response is relatively constant from both DPM and MS when the thermostating time is varied from one to ten minutes with a maximum at two minutes. The standard deviation (SD) of the response is, however, quite large for MS at two minutes.

The maximum numbers of measuring cycles with a positive LCD response during these experiments were mostly 1–2

for MS and 2–3 for DPM (not shown in Fig. 2), which is in agreement with the higher vapour pressure for DPM compared to MS. The highest number of measuring cycles with a positive response was observed with a thermostating time of three minutes. Consequently, a thermostating time of three minutes was selected for further work. This thermostating time is short enough for practical use in the field.

Evaluation of different needle diameters

With the relatively large needles (16G) used in the previous experiments, a short duration of the MS or DPM peak was observed. In most of the cases a maximum of four measuring cycles were observed, corresponding to 20 s for one peak. It was suggested that a narrower needle connected to the LCD might produce a longer duration of the alarm due to a slower release of the overpressure in the sample vials. This was explored by testing needles with an inner diameter ranging from 1.2 mm (as used in the earlier experiment) to 0.32 mm and using 1.2 mg of MS as a test substance placed on pieces of test material (Fig. 3). The thermostating time used in these experiments was three minutes.

The results in Fig. 3 show that the number of cycles with a positive LCD response is highest using a 0.84 mm ID needle. The narrowest needle also gave the lowest LCD response. These two numbers are statistically different (95 % t-test). The reason for this is unclear, but it was observed that some air leaked out from the HS vial during penetration of the septum due to the tapering of the needle. Use of other types of syringes with different tapering might improve the response from the narrowest needles.

Method repeatability

The measuring cycle of the LCD 3.1B and LCD 3.2E is 20 milliseconds every 5 s. Since the concentration will decrease over time after the septum is penetrated, the detector response will depend upon the exact time of the penetration in relation to the measuring cycle. The repeatability of the method is therefore quite low. In order to quantify repeatability during different

Fig. 2 Detector response (mean \pm SD, $n = 3$) for 1.2 mg methyl salicylate and 0.95 mg dipropylene glycol methyl ether, placed on a piece of test material as a function of thermostating time

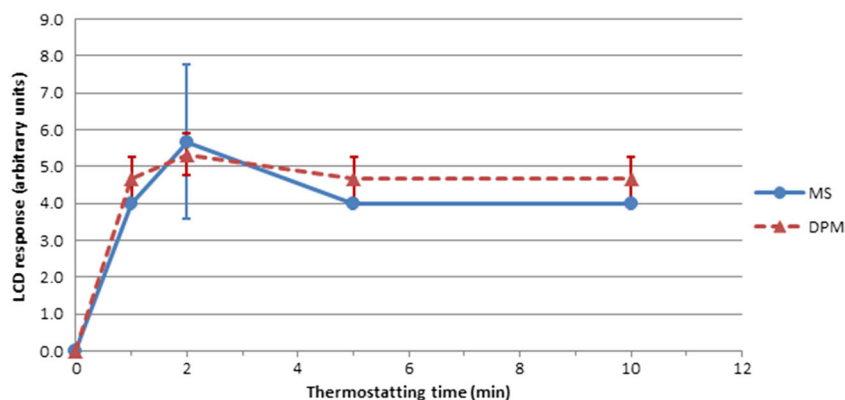
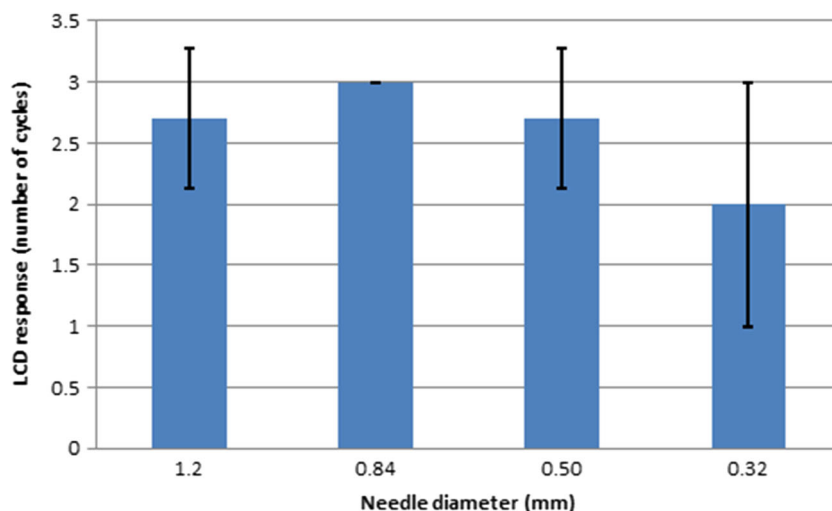


Fig. 3 Number of LCD measuring cycles (mean \pm SD, $n = 3$) with a positive response using needles with different inner diameters. MS is used as the test substance (1.2 mg) and is placed on pieces of test material



septum penetration times, the LCD response was measured using different times between the point of vial penetration and LCD measurement. Two sets of experiments were conducted with 12 μg of MS dissolved in 2 μl of acetone placed in empty HS vials. The experiments were done as described earlier in this paper (60 min of equilibration time at room temperature and 3 min of thermostating time at 70 $^{\circ}\text{C}$).

In the first set of experiments, the septum was penetrated just after (< 1 s) one measuring cycle, i.e. almost five seconds before the next measurement took place. In the second set, the septum was penetrated just (< 1 s) before the next measuring cycle. Five replicates were performed for each set alternating between the two sets.

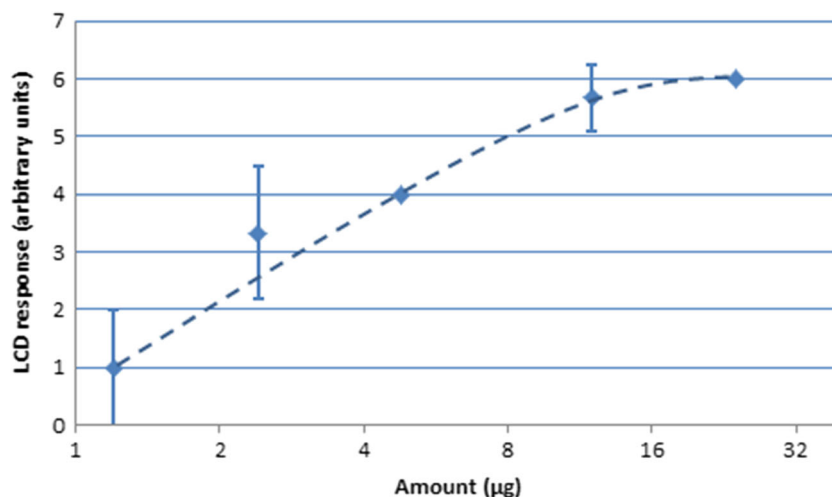
When septum penetration occurred almost five seconds before the measurement, the average maximum LCD response was 3.8 bars \pm 11 % with (1.2 \pm 0.4) positive measuring cycles. If the measurement was made just after penetrating the vial septum, the average maximum LCD response was 5.0 bars \pm 20 % with (2.4 \pm 0.6) positive measuring cycles. This shows

that the timing of vial penetration in relation to the LCD measuring cycle is important in obtaining the best response from the detection. It is not possible to reduce the time between each measurement in the present detectors. If sensitivity is critical, it is advisable to time penetration of the septum to just before the measurement is performed by the LCD, which is indicated by the green tick icon light in the detector display.

Response curves for methyl salicylate and dipropylene glycol monomethyl ether

Response curves were constructed by diluting different amounts of MS and DPM (separately) in acetone. Small (2 μl) aliquots of the dilutions were placed in empty HS vials and closed. Three replicates were analysed for each amount. The vials were equilibrated for 60 min at room temperature (approximately 25 $^{\circ}\text{C}$) before thermostating. A thermostating time of 3 min at 70 $^{\circ}\text{C}$ was used in this experiment. An approximately semi-logarithmic (base 2) response curve for

Fig. 4 Detector response for methyl salicylate as a function of applied amount in empty HS-vials (mean \pm SD, $n = 3$). The trend line is manually inserted. Note the semi-logarithmic scale (base 2) on the abscissa



MS (from 1.2 μg to 24 μg) is shown in Fig. 4. Amounts down to 1.2 μg could be detected in empty glass vials. It is believed that the use of other syringe needles and survey nozzles without air leaks will improve the linearity of the response curve.

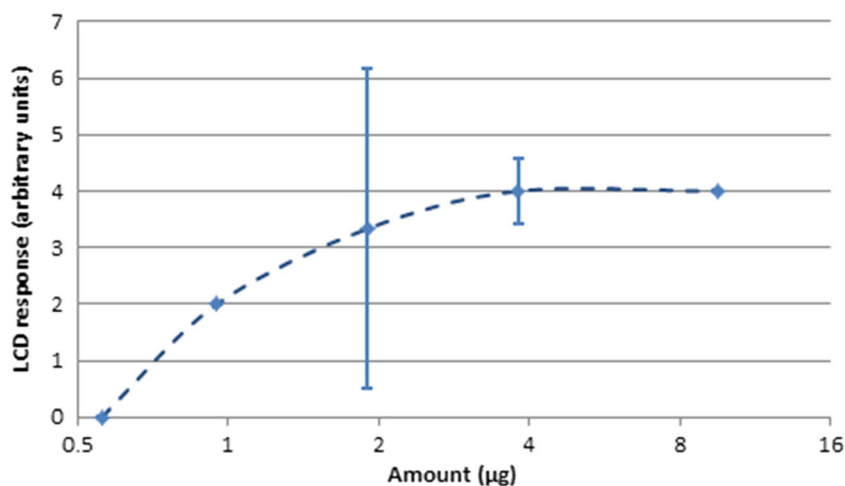
A similar experiment was conducted with 2 μl aliquots of DPM (from 0.38 μg to 9.5 μg). Amounts down to 0.56 μg could be detected in empty glass vials. For this compound, the observations did not fit a semi-logarithmic response curve as well as in the case of MS. The maximum detector response was almost constant from 1 μg DPM up to the maximum amount used in this experiment (figure not shown). If, instead, the LCD response from the second measuring cycle is plotted against the concentration of DPM in the HS vial, a smooth curve which levels out after 4 μg is observed (see Fig. 5). The second measuring cycle gave more consistent results compared to the first cycle, probably due to variations in septa penetration time in relation to the LCD measuring cycle (see discussion on method repeatability).

The detection limits obtained in these experiments (0.56 μg for DPM and 1.2 μg for MS) are good enough to be used for field measurements in a hot zone. They are also comparable with the detection limits for the M8 and M9 detection paper, which in favourable cases are 5 mg/m^2 [26].

Interferences

During a field mission, soldiers will encounter many liquids or wet spots from the many different kinds of chemicals that are present in the normal environment. Only a small fraction of the suspicious spots in a contaminated area might be chemical warfare agents or toxic industrial chemicals. It is therefore important that the detector does not respond to most of the normal chemicals that may be present. Therefore the HS-LCD detector was tested against the liquids acetone, 2-propanol, petrol, diesel, ethylene glycol, engine oil and weapon oil. For each simulant, three parallels with 100 μl of the chemical were placed in empty HS vials, allowed to stand at room temperature

Fig. 5 Detector response at the second measuring cycle for dipropylene glycol monomethyl ether as a function of the applied amount in empty HS vials (mean \pm SD, $n = 3$). The trend line is manually inserted. Note the semi-logarithmic scale (base 2) on the abscissa



for one hour and then heated to 70 $^{\circ}\text{C}$ for three minutes. The septum was then penetrated with the HS-LCD needle and the detector response observed for a minimum of 30 s.

Of the tested chemicals, only weapon oil gave a positive response using the built-in libraries of the LCD. This oil gave up to the maximum number of bars that lasted more than 15 s. One should therefore be aware that weapon oil could give a false positive response on the LCD.

Field experiments

In order to test the HS-LCD technique in a more realistic situation, an outdoor test during winter conditions was conducted of the technique. The temperature during the experiment started at -0.1 $^{\circ}\text{C}$ and rose to 4.3 $^{\circ}\text{C}$ during the test with MS. During the test with DPM, the temperature started at 9.4 $^{\circ}\text{C}$ and ended at 12.3 $^{\circ}\text{C}$. The relative humidity during the tests dropped from 78 % to 45 % during the day.

Circular pieces of test material (1 cm^2) were cut out and placed on open glass plates. One microliter of the test substances (0.95 mg DPM or 1.2 mg MS) was placed on top of each of the pieces of test material, loosely fitted with a glass cover and exposed to the prevailing weather conditions. After one hour, one half of the samples were analysed directly by LCD without the headspace sampler by holding the survey nozzle 2–3 cm above the sample. The other samples were placed in HS vials, closed with crimp caps and analysed by HS-LCD after heating to 70 $^{\circ}\text{C}$ for 3 min. Five replicates were analysed for each test substance and each cover (open glass plate or closed HS vial). A specially made, small and easily portable headspace vial heater running on a 12 V battery was used for this purpose (see Fig. 6).

Analyses of MS at 4.3 $^{\circ}\text{C}$ gave no LCD response from the samples analysed directly on open glass plates. When the test material pieces were put HS vials, heated and analysed by the HS-LCD technique, a response of 4–6 bars (5.0 ± 0.7 bars) lasting 2–4 measuring cycles (10–20 s) was observed.



Fig. 6 A small and easy portable headspace vial heater used in the field experiments

Analyses of DPM at 12.3 °C gave a small response of 0–4 bars (1.5 ± 1.2 bars) lasting 1–2 measuring cycles (5–10 s) when the test material samples were analysed directly on open glass plates. When the test material pieces were placed in HS vials, then heated and analysed by the HS-LCD technique, a response of 4–5 bars (4.4 ± 0.5 bars) lasting 1–2 measuring cycles was observed.

The experiments carried out outdoors at relatively low temperatures show that the HS-LCD technique is much more effective in detecting the CW-simulant MS compared to using the LCD with survey nozzle directly on the same samples without heating. The improvement was not so pronounced for DPM, since this compound is more volatile than MS (DPM has Bp 190 °C vs 223.3 for MS). Furthermore, the experiments with DPM were carried out at a higher outdoor temperature (12.3 °C), which made it easier to detect the compound from the sample without heating. One would also expect a greater improvement for DPM if the samples were analysed at lower ambient temperatures.

Conclusions and suggestions for further work

A novel, rapid and simple sampling technique for use in conjunction with commercial IMS detectors has been developed. This technique is easy to use in the field and does not require solvents or lots of extra equipment. The technique is also fast, since an optimal thermostating time of only three minutes for the chemical warfare agent simulants MS and DPM has been established.

Since the vial overpressure obtained by heating the sample vial is rapidly released into the IMS detector, the duration of the LCD response is quite short (5–20 s). However, this rapid response time will be an advantage during field operations where short analysis times are critical. Since the analytical cycle from sample introduction to final result is very short (less than four minutes), it would be easy to analyse a new sample, if necessary.

An approximately semi-logarithmic (base 2) response curve for MS in an otherwise empty glass vial was obtained from a detection limit of 1.2 µg to 24 µg calculated from the maximum number of bars. For DPM, the response curve was exponential from a detection limit of 0.5 µg and levelled out at 4.0 µg when the number of bars in the second measuring cycle was plotted against DPM amount. The reason for the difference in the shape of the response curve between MS and DPM in the detector response is not known.

In order to obtain the highest sensitivity, a release of the HS vial overpressure just before one of the LCD measuring cycles is necessary. Since this degree of timing could be difficult to perform accurately in the field, the repeatability varies from 10 to 20 %.

Tests carried out on some common interferents that might be present in a field environment showed a low occurrence of false alarms. Of the tested chemicals, only weapon oil gave positive response on the LCD.

The field experiments carried out with the HS-LCD at relatively low temperatures showed large improvements in the detection limits for MS and DPM from samples of protective materials compared to using the LCD with the survey nozzle directly on the samples without heating. More experiments are needed to quantify the improvements and to establish detection limits for different combinations of sampling materials and analytes. The technique should also be evaluated for real chemical warfare agents and toxic industrial chemicals.

The present interface between the LCD survey nozzle and the headspace needle needs improvement before it is suitable to be used in the field. The needle is very sharp, with the ensuing possibility that a person could be stuck by it during operations. Due to its large tapering, the needle sometimes is sometimes blocked by small pieces of the septa used to close the HS vial. This may be easily overcome by using new needles for each injection. More robust needles that are not so easily blocked may be desirable in the future.

The survey nozzle itself and the connection between the nozzle and the plastic syringe are not airtight in the present configuration. This may have caused leaks and less reproducible results than wanted during the experiments carried out. A more airtight interface is therefore to be preferred.

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