



Gas chromatography–full scan mass spectrometry determination of traces of chemical warfare agents and their impurities in air samples by inlet based thermal desorption of sorbent tubes

Oliver Terzic*, Irvine Swahn, Gheorghita Cretu, Meehir Palit, Gary Mallard

Organisation for the Prohibition of Chemical Weapons, Johan de Wittlaan 32, 2517 JR The Hague, The Netherlands

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ABSTRACT

A sensitive gas chromatography–mass spectrometry (GC–MS) based analytical method was developed for detection of the chemical warfare agents (CWA) and related compounds in air/vapor samples. The method uses a Tenax TA packed GC liner as an air/vapor sampling tube and Programmable Temperature-Vaporization (PTV) GC inlet as the thermal desorber. This approach eliminates secondary focusing step and allows transfer of desorbed analytes as sharp bands directly to the head of GC column. Use of a Peltier element for rapid cooling eliminates need for an external coolant. Minimal logistic and hardware needs make the method relatively inexpensive and especially suitable for a mobile laboratory. The limits of detection (LODs) of 0.8–2.9 ng on tube for selected nerve and blister agents were achieved in the full scan MS mode. Simple derivatization method applied for detection of Lewisites 1 and 2 did not affect simultaneous analysis of other agents. The method was extensively evaluated with authentic CWA during the field trainings of the inspectors from the Organization for the Prohibition of Chemical Weapons (OPCW). The environmental area and personal samples were collected for a semi-quantitative determination of averaged airborne CWA concentration levels.

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1. Introduction

In the post World War II history, chemical warfare agents (CWA) use has been documented on several occasions. During the Iran–Iraq war in the 1980s, Iraqi military used CWA-filled offensive munitions on Iranian targets [1–3]. Japanese religious group Aum Shinrikyo used CWA as weapons of domestic terror in the 1990s [4–6]. On 29 April 1997, the Chemical Weapon Convention (CWC) entered into force prohibiting the member states from development, production, acquisition, stockpiling and use of chemical weapons (CW) [7]. By February 2011, the treaty had been endorsed by 188 countries. A unique feature of the CWC is its incorporation of the “challenge inspection” provisions, whereby any member state in doubt about another member state’s compliance can request the Director-General of the CWC administering body, the Organization for the Prohibition of Chemical Weapons (OPCW), to send an inspection team. Under the “challenge inspection” procedure, the member states to the CWC have committed themselves to the principle of ‘any time, anywhere’ inspections with no right of refusal. The CWC contains also provisions for investigation of allegations of use of CW and delivery of assistance to the member states. The assistance could be provided even for the

cases involving terrorist use or threat of use of CWA. In order to fulfill its mandate, the Technical Secretariat of the OPCW maintains constant readiness and operative capability for short-notice world-wide dispatch of an investigative team and mobile analytical laboratory. The readiness is regularly challenged through in-house and international exercises involving participation of other international agencies and national teams. These exercises and the OPCW inspectors’ trainings with authentic CWA serve as a platform to test analytical and other inspection equipment and procedures.

The analytical procedures followed by the OPCW inspection team were originally developed by technical experts of member states, working in expert and task force groups before entry into force of the CWC. These procedures covered different types of samples of industrial or environmental origin including solid, liquid and wipe samples, except air/vapor samples. One of the major expert contributors to the OPCW analytical capacity, Finnish Institute for Verification of the Chemical Weapon Convention (University of Helsinki, Finland) was intensively involved in the development of methods for air sampling for volatile CWC-related chemicals during the 1980s [8–10]. This work resulted in instructions for low-volume Tenax and XAD-2 air samples described in the recommended operating procedures for off-site analysis by the OPCW designated laboratories [11]. However, neither air sampling and analysis method nor air sampling equipment had been chosen for the OPCW on-site laboratory.

* Corresponding author. Tel.: +31 62 8425489.

E-mail addresses: oliver.terzic@opcw.org, oterzic@gmail.com (O. Terzic).

Air or vapor samples collected during an inspection may provide important verification and safety related information. With air sampling it is possible to screen large areas for CWA and related chemicals. It has already been shown that air sampling is a useful tool in detection of CWA in structures [12] where CWA were once manufactured or stored. The results from air analysis provide important information on the presence or absence of vapor hazards. Air sampling may also be used during the reconnaissance phase of a field investigation to confirm or reject the findings of the handheld detectors, known to be prone to false positives. Sampling of headspace above complicated sample matrix may resolve inconclusive results. There are numerous other possible inspection situations where air sampling may prove useful. This was the reason for the OPCW to undertake a method development described in this paper. The method was evaluated in the field with authentic CWA and it has been already included into the OPCW quality system documents.

Sampling of vapors has widely been accomplished by drawing air through a tube packed with adsorbent material having certain trapping efficiency for analytes of interest. Analytes are then removed either by solvent extraction or thermal desorption. Analysis is performed by gas chromatograph (GC) equipped with suitable detector. In the case of the OPCW, mass spectrometer is the only GC detector accepted and approved by the CWC member states for the on-site inspection activities [13].

Compared to thermal desorption (TD), solvent extraction has several disadvantages. First, it lowers sensitivity of a method by employing finite elution volume(s). Use of solvent may also introduce solvent based contamination and opportunity for analyte losses. Furthermore, extraction may require a preconcentration step extending further the overall sample preparation time. In the TD technique, samples are usually thermally desorbed from an external TD device and focused either into an adsorbent-trap or cryogenically cooled inlet of the GC. Ideally, the whole sample is transferred to the analytical system with no dilution or solvent interference. The major disadvantage of this approach is the inability to re-analyze the sample (a one-shot method). With the solvent extraction it is possible to repeat the analysis by injecting another portion of the extract. Once desorbed, the sampling tube can be reused [14]. TD–GC–MS has shown to be suitable for measurements of volatile organic compounds in the environment [15]. Tenax has been used as an effective sorbent material for TD–GC–MS analysis of a wide spectrum of CWA [10,14,16–18]. In fact Tenax TD–GC–MS has been in use for over 25 years now for historical monitoring and surveillance at chemical weapons storage and destruction facilities, and research laboratories [19]. In the design of TD–GC–MS equipment, much attention has to be paid avoiding cold spots, reducing the transfer time (path) and 'dead volume' [20,21]. These are common problems associated with many automated TD systems, especially when dealing with the less volatile compounds like O-ethyl S-2-diisopropylaminoethyl methylphosphonothiolate (nerve agent VX) [18]. One of the objectives of our work was to devise methodology that eliminates the secondary focusing step and allows transfer of desorbed analytes as sharp bands directly to the head of column. This was achieved by using a glass liner of a Programmable Temperature-Vaporization (PTV) GC inlet as a body of a TD tube. TD tube was prepared by packing of the liner with a small quantity of Tenax TA. Sampled TD tubes were desorbed directly into the GC inlet. The splitless operation of the inlet was used to transfer the maximum amount of analyte(s) into the GC column.

VX is known to be a difficult compound to analyze in its free state due to its activity, low volatility and thermal instability. One approach to overcome this problem is to convert VX to the more stable G analog [22]. However, the procedure suffers from limited and variable efficiency and, failing to distinguish between the parental VX and G-series compound O-ethyl methylphosphonofluoridate, it

is not acceptable from the OPCW verification point of view. In this work, VX was analyzed in its free, underivatized form. Other CWA that commonly present a problem for direct GC–MS determination are Lewisites 1 and 2. Their highly reactive and corrosive nature originating from an arsenic–chlorine group leads to a poor method sensitivity and rapid deterioration of a GC column performance. Derivatization of the Lewisites prior to chromatography is therefore essential [23]. For this work, a simple in-tube derivatization procedure with an aliphatic monothiol was devised that enables Lewisites detection along with other selected CWA trapped into the TD tube. Contrary to the derivatization with dithiols, use of monothiois also enables differentiation between Lewisite 1 and Lewisite 2 species [24].

2. Experimental

2.1. Reagents and material

O-isopropyl methylphosphonofluoridate (GB, as 1 mg/ml solution in ethyl acetate) and O-ethyl S-2-diisopropylaminoethylmethyl phosphonothiolate (VX, as 1 mg/ml solution in ethyl acetate) were obtained from TNO Prins Maurits Laboratory (Rijswijk, Netherlands). Bis(2-chloroethyl)sulfide (HD, as 1 mg/ml solution in ethyl acetate), 2-chlorovinylchloroarsine (Lewisite 1, L1, as 1 mg/ml solution in n-hexane), and bis(2-chlorovinyl)chloroarsine (Lewisite 2, L2, as 1 mg/ml solution in n-hexane) were obtained from Spiez Laboratory, Swiss NBC Defence Establishment (Spiez, Switzerland). Lewisites derivatization reagent, 1 mg/ml 1-butanethiol solution in n-hexane (BUSH), was obtained from Finnish Institute for Verification of the Chemical Weapons Convention (University of Helsinki, Finland). Hexachlorobenzene (HCB) internal standard (50 µg/ml solution in dichloromethane) and the OPCW GC–MS Test Mixture, containing seven test compounds (trimethyl phosphate, 2,6-dimethylphenol, 5-chloro-2-methylaniline, tri-n-butyl phosphate, dibenzothio-phene, malathion, and methyl stearate) and nine calibration compounds (n-octane, n-decane, n-dodecane, n-tetradecane, n-hexadecane, n-octadecane, n-eicosane, n-docosane, and n-tetracosane), were also from Finnish Institute for Verification of the Chemical Weapons Convention. The concentration of each of the chemicals in the OPCW GC–MS Test Mixture was 10 µg/ml in dichloromethane solution. Deionized (D.I.) water was obtained from a Milli-Q system (Millipore, Bedford, MA, USA).

2.2. Instrumentation

A borosilicate GC liner (one ring restriction, 88 mm length, and 3 mm ID) packed with ~70 mg of Tenax TA, 60/80 mesh, was used as a TD tube. It was obtained from Joint Analytical Systems Benelux (Eindhoven, The Netherlands). For sample collection, TD tubes were transferred to the TDS³™ sampling/storage containers (Sigma-Aldrich, Zwijndrecht, Netherlands). The calibration/sampling train was assembled by connecting the TDS³™ container to the sampling pump using Tygon tubing. The sampling flow was adjusted by using a BIOS Defender 510M (Joint Analytical Systems Benelux, Eindhoven, Netherlands) digital gas-flow meter. Two types of the air samplers were chosen: dual channel diaphragm air sampler AirProSurveyor (Joint Analytical Systems Benelux, Eindhoven, Netherlands) and rotary vane air sampler SG 4000ex (Sysmex Nederland B.V., Etten-Leur, Netherlands). The AirProSurveyor air sampler can be fitted with two sampling tubes, each connected to the separate air inlet channel with independent flow-rate adjustment. The SG 4000ex air sampler has an in-built automatic volume flow regulation capability with a fault indicator and automatic shut-off.

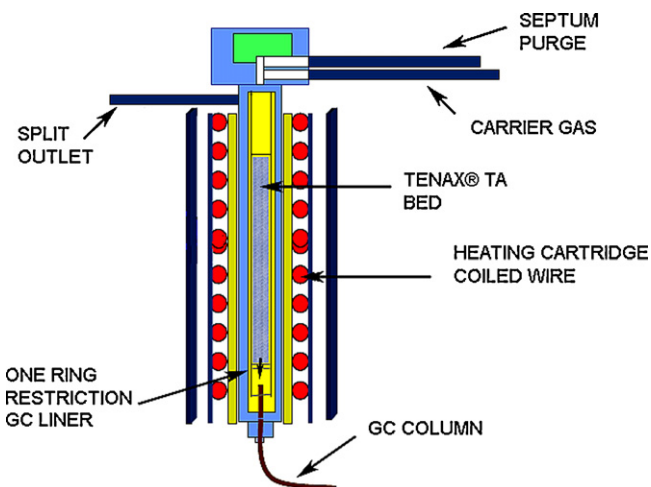


Fig. 1. Cross-sectional view of the UNIS 2000 inlet system with a TD tube (a one ring restriction GC liner packed with Tenax TA) placed into the position.

Tube conditioning, spiking, water removal and in-tube derivatization were performed using Six-Tube Conditioner Model 9600 (CDS Analytical Inc., Oxford, PA). The flow of nitrogen carrier gas was adjusted using Digital Flow Check™ (Alltech, Lokeren, Belgium).

TD–GC–MS analysis was performed with an Agilent 6850 GC/5973 or 5975 Inert MSD (Agilent Technologies, San Jose, CA, USA) equipped with UNIS 2000 inlet system and Peltier element (Joint Analytical Systems Benelux). The TD tubes were directly desorbed in the UNIS inlet system (Fig. 1) using a splitless mode and settings obtained after the optimization experiments. The purge flow was set at 50 ml/min at 2.0 min (GasSaver 20 ml/min at 4.0 min). The capillary column used was a RXI®-5MS (cross-bond, 5% diphenyl, 95% dimethyl polysiloxane) 30 m × 0.25 mm I.D. with 0.25 μm film thickness (Interscience, Breda, Netherlands). The carrier gas was helium and flow was maintained constant at 0.9 ml/min. The column temperature program was as follows: initial temperature 40 °C (held for 2 min), increased at a rate of 20 °C/min to 160 °C, then from 160 °C to 280 °C at a rate of 30 °C/min (final temperature held for 5.00 min) giving overall run time of 17 min. The MS interface was maintained at 280 °C, while the MS quadrupole and source temperatures were set at 150 °C and 230 °C, respectively. The solvent delay was set at 4.0 min or 3.0 min and the MS was operated in full scan mode (scanning mass range 40–450 amu, threshold 100 counts, sampling rate 3). The instrument tuning was performed with Autotune procedure using the instrument calibration compound perfluorotributylamine. Prior to analysis of each batch of samples, the instrument performance was tested with an OPCW Test Mixture spiked TD tube (1.0 μl) [25].

2.3. Procedure for TD tube spiking

Method development was carried out using a liquid spiking method. This convenient technique generally shows better precision than loading of tubes using a vapor generator [26]. The injection port option of CDS Analytical six-tube conditioner was assembled with a TD tube (a glass restriction end/sampling side) inserted into a thumbwheel nut and a Viton o-ring placed under the thumbwheel ferrule. A liquid spike was introduced into the tube using standard 10 μl GC syringe and nitrogen flow of 60 ml/min. The syringe needle was pushed all the way through the septum until the needle tip was touching the metal screen of the TD tube. The tube was purged for 2 min after the injection in order to transfer the sample and/or derivatization agent further into the sorbent bed.

2.4. Method development for CWA

Three compounds were selected for use in the optimization study according to their volatility and CWA classification: GB as a more volatile nerve agent; HD as a semi-volatile vesicant; and VX as a low volatile nerve agent. TD method was developed by optimizing the maximum TD inlet temperature and GC oven starting temperature. TD tubes were spiked with 1 μl of 4 μg/ml GB, HD, and VX mixture in DCM and analyzed. Three replicates were run for each of the data points.

Selection of the optimum thermal desorption temperature was performed by setting an initial temperature of UNIS inlet system at 40 °C, a ramp rate at 720 °C/min, and then varying the maximum ramp desorption temperature in 10 °C increments, starting from 250 °C to 300 °C.

For the optimization of GC oven starting temperature, following settings were selected: 35 °C, 40 °C, 45 °C, and 50 °C. The resulting chromatographic peak widths of the agents were considered.

2.5. Reverse desorption of the spiked TD tubes

Reverse desorption of the spiked TD tubes was performed to simulate an operational mistake by the on-site laboratory personnel and complete migration of the agents down the Tenax bed. TD tubes were spiked with 1 μl of 4 μg/ml mixture of GB, HD, and VX in DCM, respectively. The spiked tubes were desorbed into the GC in a “reverse” manner (spiked sampling side positioned upwards in the inlet) and analyzed. The results were compared to the data obtained by the analysis of parallels desorbed in the “proper” manner. Three replicates were run for each of the data points.

2.6. Effects of sampling flow/volume

TD tubes were spiked with 1 μl of 3, 5 and 10 μg/ml mixture of GB, HD, and VX in DCM, respectively. The tubes were fitted with the TDS³™ sampling container and connected with Tygon tubing to the AirPro Surveyor pump. The sampling flows of 200 and 400 ml/min were tested in durations of 15 and 60 min. Four replicates were produced for each of the data points. The tubes were subjected to the TD–GC–full scan MS analysis. The acquired GC–MS data were processed using the Automated Mass Spectral Deconvolution and Identification System (AMDIS) in the default OPCW settings [25].

2.7. Effects of a complex airborne matrix

TD tubes were spiked with 1 μl of 100 μg/ml Diesel solution in DCM and 1 μl of 4 μg/ml of mixture of GB, HD, and VX in DCM. The liquid Diesel spike was used in order to simulate a complex airborne matrix. The tubes were subjected to the TD–GC–full scan MS analysis. The acquired GC–MS data were processed using AMDIS.

2.8. Effects of water and TD tube drying treatment on agents recovery

In this experiment, TD tubes were spiked with 2.5 μl of D.I. water. After 1 min purging under nitrogen flow of 60 ml/min, the tubes were spiked with 1 μl of 2 and 4 μg/ml mixture of GB, HD, and VX in DCM, respectively. The tubes were purged for one additional minute before repeating the water spiking step. In order to remove water, a tube heater was placed over the tubes and tubes were heated for 5 min at 60 °C under 60 ml/min He flow. Three replicates were run for each of the spiking levels tested. The experiment was repeated using freshly prepared tubes and omitting the water spiking steps. TD tubes were then thermally desorbed into the GC and analyzed. The agents recoveries were estimated by comparing

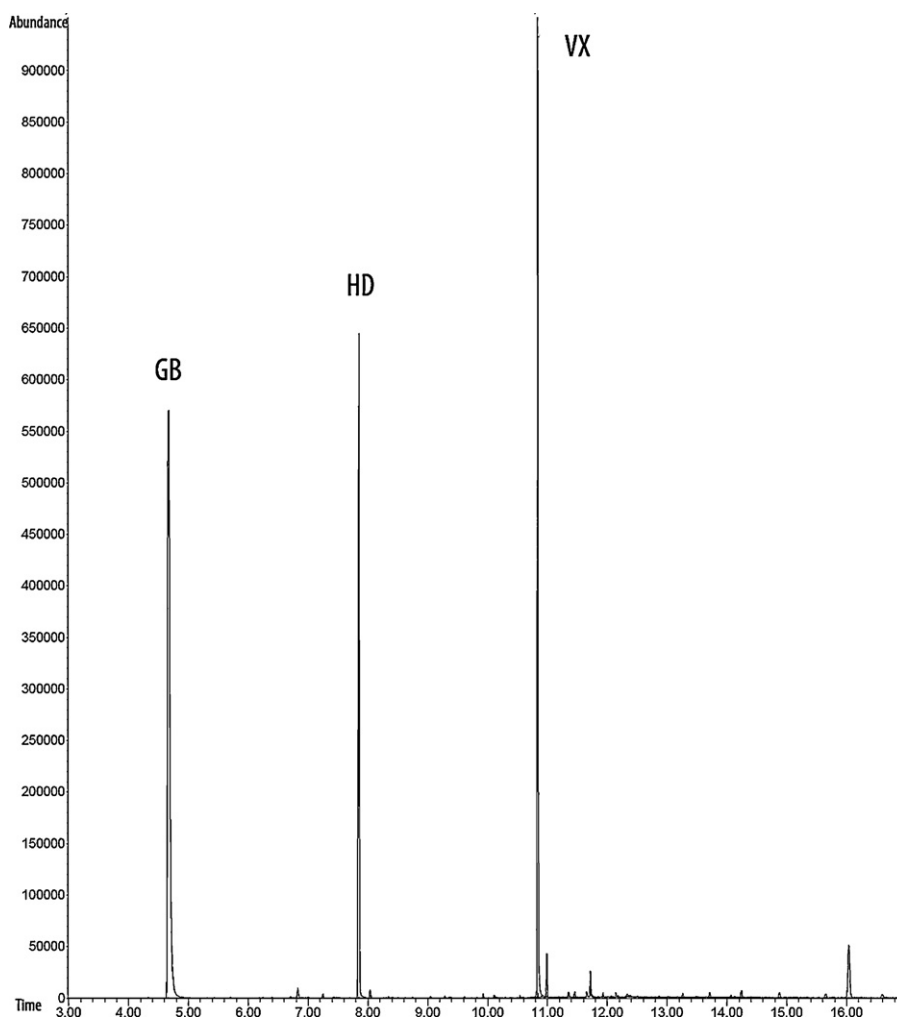


Fig. 2. TD-GC-MS extracted ion chromatogram of GB (m/z 99), HD (m/z 109) and VX (m/z 114) at 10 ng load in the TD tube.

their peak areas to the results obtained with tubes spiked with the agent mixture and desorbed without any further treatment.

2.9. Stability of GB, HD and VX during TD tube storage

TD tubes were spiked with 1 μ l of 4 μ g/ml mixture of GB, HD, and VX in DCM. The parallels were stored at room temperature (24 $^{\circ}$ C) and in a refrigerator (4 $^{\circ}$ C). These were analyzed by TD-GC-MS at 1, 7 and 15 day intervals. The results were compared with those obtained for the tubes spiked on the day of analysis. All experiments were run in duplicates.

2.10. Procedure for derivatization of Lewisites 1 and 2

TD tubes were spiked with 5 μ l of 1 and 10 μ g/ml solution of Lewisites 1 and 2 in DCM, respectively. After 2 min of purging, the tubes were spiked with 3 μ l of BUSH derivatizing agent. The tubes were purged for two additional minutes and subjected to the TD-GC-MS analysis. Six replicas were run for each of the spiking levels tested.

2.11. Calibration, limits of detection (LODs) and quantification (LOQs), repeatability

A series of standard solutions containing GB, HD, VX, L1 and L2 were prepared in concentrations of 1.0, 3.0, 5.0, 7.0 and 10.0 μ g/ml

in DCM. TD tubes were first spiked with 1 μ l of the standards followed by injection of 3.0 μ l of BUSH derivatizing agent. The tubes were purged for 2 min with helium and thermally desorbed into the GC-MS. The data were acquired using full scan mode operation of MSD, while extracted ion chromatograms (ion m/z 99 for GB, ion m/z 109 for HD, ion m/z 114 for VX, ion m/z 314 for butanethiol derivative of L1, ion m/z 164 for butanethiol derivative of L2) were used for integration. Each concentration standard was run in triplicate and linear regression analysis was performed.

Detection and quantification limits were calculated using Eqs. (1) and (2), respectively [27].

$$LOD = \frac{3 \cdot RMSE}{slope} \quad (1)$$

$$LOQ = \frac{10 \cdot RMSE}{slope} \quad (2)$$

Root mean square error (RMSE) and slope terms refer to parameters obtained by performing linear regression analysis. The repeatability of the method was assessed by replicate analysis ($n=6$) of the tubes spiked with the standard agent solutions at 3.0 and 5.0 ng in tube levels as described above.

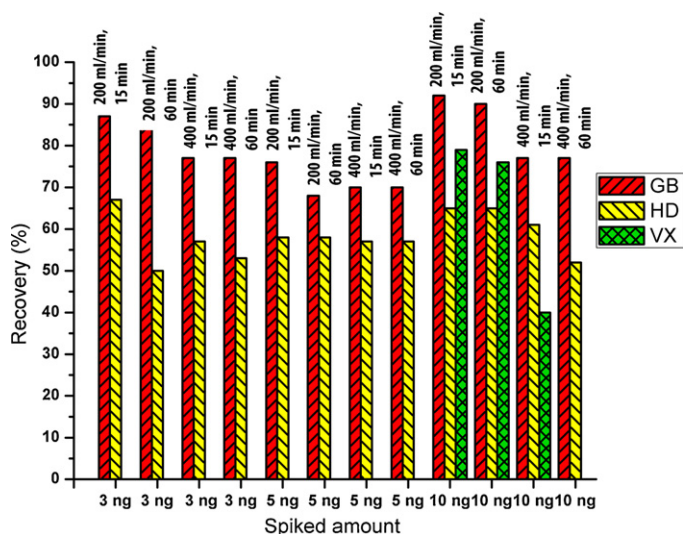


Fig. 3. Effects of sampling flow/volume on recovery of GB, HD and VX from spiked TD tubes.

3. Results and discussion

3.1. Optimization of the thermal desorption parameters

Increasing the maximum ramp desorption temperature from 250 °C to 270 °C resulted in 29% increase in the average peak area for GB, 30% increase in the average peak area for HD, and an insignificant increase in the average peak area for VX. Increasing desorption temperature further led to a slight decrease in the average peak areas for the three compounds. The temperature of 270 °C also led to 35% reduction in the peak width for GB, while peak widths for HD and VX were not notably affected. Therefore, the maximum ramp desorption temperature of 270 °C was selected as the optimal for the analysis.

Optimum GC oven starting temperature is required to provide focusing of the analytes on a GC column. Increasing the oven starting temperature from 35 °C to 40 °C caused slight increase in the peak width for GB and 10% decrease in the peak width for HD and VX. Increasing temperature further for 5 °C did not affect the peak widths for HD and VX but it caused 60% increase in a peak width for the more volatile GB. The oven starting temperature of 40 °C was hence selected as the optimal. A TD–GC–MS extracted ion chromatogram of GB, HD and VX at 10 ng in the tube is shown in Fig. 2.

3.2. Reverse desorption of the sampling tubes

Forcing of the analytes through a whole length of Tenax bed resulted in 70–80% reduction in the signals from GB and HD, while the signal of VX failed to increase above the baseline for the spiking level tested.

3.3. Effects of sampling flow/volume

When injecting liquid standards onto the sorbent bed, a small narrow plug of the analytes is formed that migrates down the bed under the flow of carrier gas/air. Although this model does not correspond to the case when collecting analytes continuously from a gas stream, it is practical in predicting the behavior of analytes on the adsorbent bed. In the experiments performed, the best retention behavior was observed for GB at all spiking levels (Fig. 3). Passing of 24 l of ambient air (~47% RH) through spiked tubes with flow rate of 400 ml/min amounted to ~30% decrease in the signal

from GB. In the case of HD, ~45% decrease of the signal was measured. With default OPCW settings, AMDIS was able to identify VX only at the spiking amount of 10 ng per tube and sampling volumes of air lower than 24 l. Drawing of 6 l of air at flow rate of 400 ml/min led to a 36% lower recovery of VX comparing to drawing 12 l of air at flow rate of 200 ml/min.

3.4. Effects of a complex airborne matrix

This experiment was performed to assess an ability of the automatic AMDIS analysis in default OPCW settings [25] to identify target analytes at relatively low concentration level in a complex background. AMDIS successfully reported presence of all agents despite a visibly high hydrocarbon background. A TD–GC–MS total ion chromatogram of this run is shown in Fig. 4.

3.5. Drying of wet TD tubes

Water can interfere with a process of adsorption of organic compounds even when using hydrophobic sorbents like Tenax TA [28,29]. Moreover, majority of CWA are susceptible to hydrolysis yielding non-volatile or less-volatile degradation products [30]. The experiments performed simulate “the worst case scenario” with water droplets drawn into a TD tube or condensed out of the gas phase. The treatment applied for water removal did not have a notable effect on the recovery of the agents from “dry” tubes. It appears that the hydrophobic environment provided by polymer matrix protects the agents from the action of water. The highest variation in recovery values was obtained for VX.

3.6. Effects of TD tube storage on GB, HD and VX recovery

Percentage recoveries of the analytes during storage stability tests are displayed in Fig. 5.

In the case of GB, no significant difference in recovery was observed between room temperature and refrigerator storage. Storing of the tubes up to 7 days did not have any effect on the recovery of this compound, while a storage time of 15 days halved the recovery values. In the case of HD, a storage time of 7 days at room temperature resulted in a significantly lower recovery then storage at reduced temperature. Storing of the tubes for 8 more days decreased further recovery for refrigerator storage, while no change in recovery value for room storage was observed. The results suggest that sampled TD tubes should be kept in a refrigerator unless the analysis is to commence in a period of no more than 24 h after the sampling. For spiking level tested, VX was not recovered in the storage trials. Therefore, the air samples suspected to contain low levels of VX should be analyzed in a shortest possible period after the sampling.

3.7. In-tube derivatization of Lewisites 1 and 2

Fig. 6 demonstrates an efficiency of the in-tube 1-butanediol derivatization procedure. Both derivatives were obtained with relatively high signal-to-noise (S/N) ratio. An underivatized Lewisite 2 was not detected.

3.8. LODs, LOQs and repeatability

Results showed good linearity for GB, HD, L1 and L2, with the product-moment correlation coefficients $r \geq 0.9900$. In the case of VX, a lower value of $r = 0.9781$ was calculated. A significance of the coefficient was checked using a two-sided t -test performed with the null hypothesis that there is no correlation between the peak areas (x) and spiking levels (y). The calculated value of t [31] was greater than the critical t value for $p = 0.05$ and $(n - 2)$ degrees of

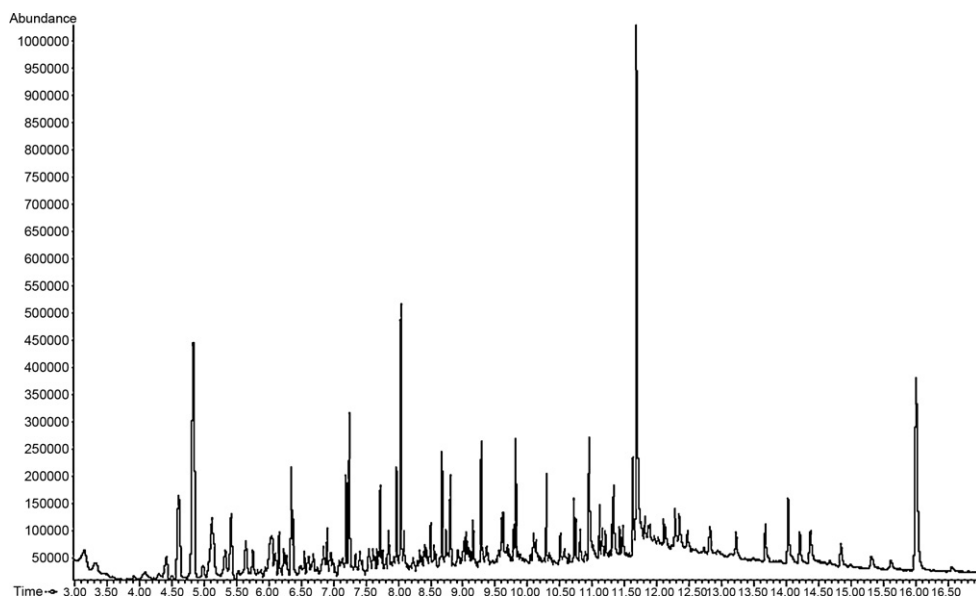


Fig. 4. TD-GC-MS total ion chromatogram of GB, HD, and VX at 4 ng and Diesel oil at 100 ng load in the TD tube.

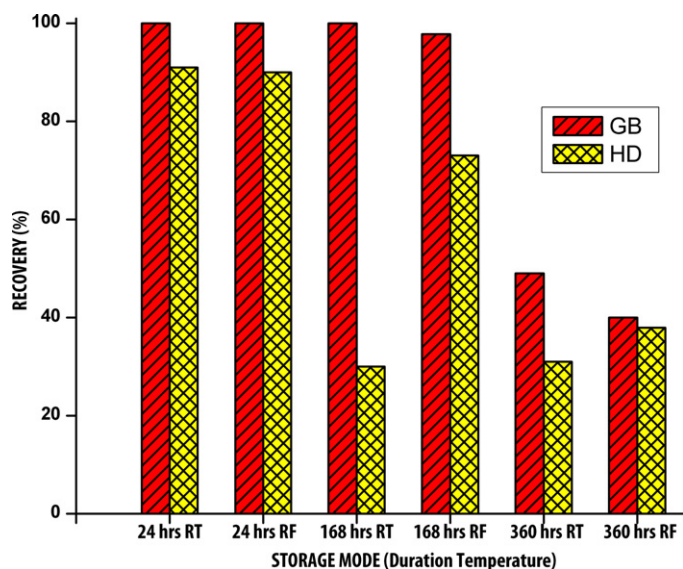


Fig. 5. Effects of TD tube storage on GB, HD and VX recovery at 4 ng load in the TD tube. Key: RT = room temperature storage; RF = refrigerator storage.

freedom. Therefore the null hypothesis was rejected, leading to a conclusion that a significant correlation does exist. The LODs, LOQs and relative standard deviations (RSDs) for the agents are listed in Table 1. No noticeable effects of use of 1-butanethiol derivatization reagent and mixed agent standard solutions on LOD and LOQ values

Table 1

Method limit of detection, limit of quantification, and repeatability for the selected CWA.

Agent	LOD (ng in tube)	LOQ (ng in tube)	RSD (%) for $n=6$	
			3 ng in tube	5 ng in tube
GB	0.8	2.6	7.7	6.1
HD	0.9	2.9	3.9	8.7
VX	2.9	9.6	10.5	6.3
L1	2.0	6.8	36.1	14.0
L2	1.0	3.5	8.6	2.1

were found when comparing the results with separate calibrations, constructed using single component solutions.

Butanethiol derivative of Lewisite 2 had a superior LOD (LOQ) to butanethiol derivative of Lewisite 1. The RSD values also followed this trend. This could be explained with presence of two derivatizable groups in Lewisite 1 and steric effects leading to a higher uncertainty in the reaction yield.

4. Validation of the method during the OPCW inspectors' trainings with authentic CWA

The method was validated during two OPCW inspectors' toxic chemical trainings. The first training was carried out during a winter season on the ranges of Vyskov Garrison Training Base, Czech Republic. The second was carried out during following spring on the ranges of NBC Training and Test Centre Zemianske Kostol'any, Slovak Republic. The OPCW inspectors, wearing adequate personal protective equipment, exercised in a toxic chemical environment (hot zone) their protocols for detection and decontamination.

Small amounts of CWA of unknown purity were applied on separate metal plates placed in metal trays in roofed outdoor CWA working areas. Area air samples were collected using sampling tubes positioned at two heights and different distances downwind from the metal tray sources. The samples were collected in duplicates using dual channel AirProSurveyor pump. The personal air samples were collected during the decontamination and detection exercises. Selected trainees and exercise instructors were equipped with a sampling train. The trays with agent samples were lifted on CWA working tables at a waist height. The sampling tubes were clipped at the chest pocket of the Saratoga type permeable suit with air sampler placed either in the pocket of the suit (SG 4000ex) or hanging on a strap over the individuals' shoulders (AirProSurveyor). The sorbent tubes were placed in a vertical position, with the inlet directed upwards during sampling to avoid channeling. This way air samples were collected from the breathing zone (air that would nearly represent that inhaled by the individual). The breathing zone is usually defined as being within 30 cm of the nose and mouth [32]. The instructors were chosen as those who are expected to have the longest entry time into a hot zone due to their job task. Selection of trainees was based on a random selection method. Meteorological parameters were recorded automatically in 30 min intervals.

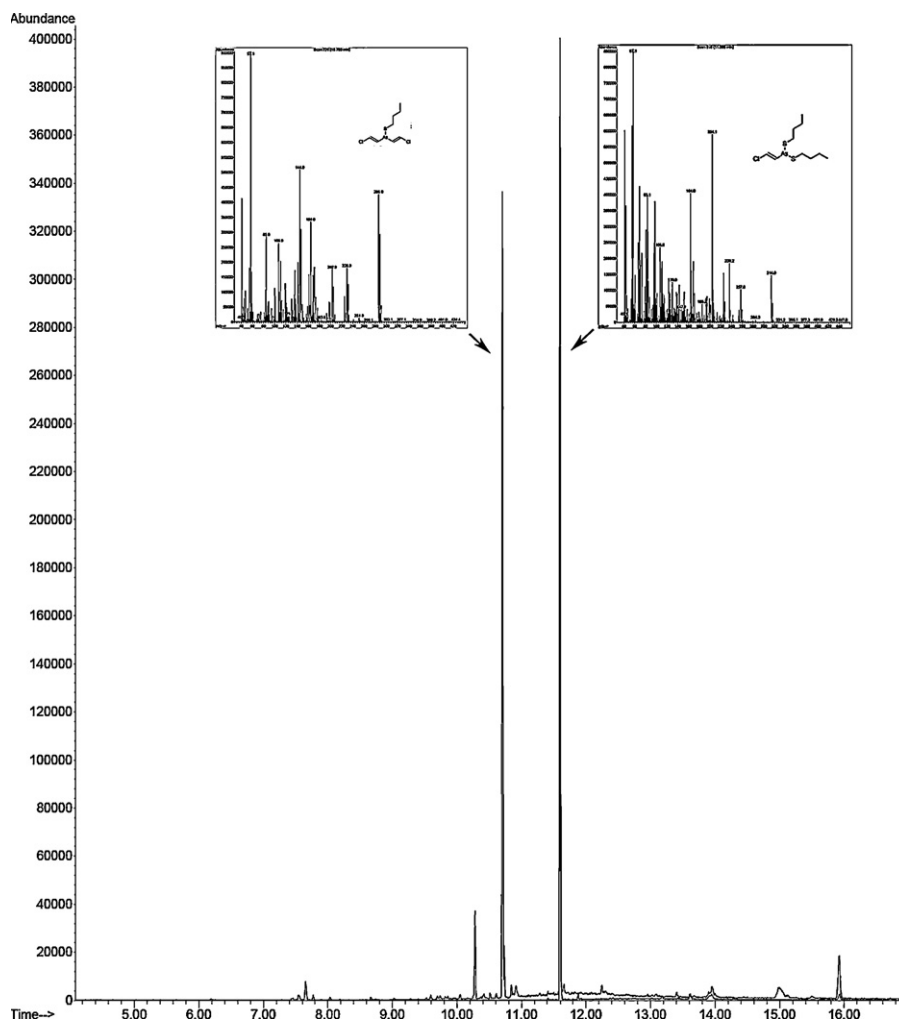


Fig. 6. TD-GC-MS extracted ion chromatogram of butyl bis(2-chlorovinyl)arsinothiolite (m/z 164) and dibutyl 2-chlorovinylarsonodithiolite (m/z 314) at 8 ng load in the TD tube.

The pump, connection tubing and sampling tubes enclosed in the sampling tube holders were calibrated as a unit. These items were separated only after completion of sample collection and final flow check. The sampling tube holder was detached and sampling end caps exchanged with storage end caps. The tube storage assembly was over packed, processed through the decontamination station and transferred to the OPCW mobile laboratory set up in immediate vicinity of the training sites.

Semi-quantitative TD-GC-full scan MS analyses of the tubes were performed upon their receipt using the calibration curves constructed as described in Section 2.10, with a difference in an extended calibration range of up to 80 ng of agent spike on the TD tube. Prior to analysis, sampled tubes were spiked with 0.5 μ l of 50.0 μ g/ml HCB internal standard solution and 3.0 μ l of BUSH derivatizing reagent. Although the air/vapor sampling and analysis method described has been primarily developed for the OPCW verification use, i.e. determining the absence (qualitative analysis) of the CWC related compounds, the semi-quantitative analyses were performed in order to produce an estimation of airborne levels of CWA used during the OPCW trainings. The calculated airborne concentration for a sample represents the average concentration for the sampling period. In the case of the personal air samples, the airborne concentration is denoted as the Time-Weighted Average (TWA).

4.1. Area air sampling at a height of 0.20 m, the OPCW inspectors training in the Czech Republic

For the first trial, separate steel plates were contaminated with 75 μ l of neat GB, VX, and HD, respectively. The air samples were collected up to a maximum downwind distance of 3.0 m. An overall 22 l of air was passed through the tubes with a flow rate of 300 ml/min. Meteorological conditions are summarized in Fig. 7a. The results showed that sample volume chosen was too high in respect to GB for sampling distances of 0.25, 0.50 and 1.00 m from the source. The maximum sample volume was exceeded with collection of so much of the analytes that the calibration range was no longer valid. The airborne concentrations were highest closest to the source, with lower concentrations as the agents disperse further away. It is interesting to note that HD was still detected at a distance of 1.00 m, despite a fact that air temperature was below HD freezing point (14 °C). GB, the most volatile of the agents used, was detected at a maximum distance of 3.00 m from the source. VX was not detected, even from the shortest sampling distance. This is not a surprising result, considering low environmental temperature and very low vapor pressure of VX (0.0007 mmHg at 25 °C compared to 2.2 mmHg for GB or 0.11 mmHg for HD) [33]. However, by performing a qualitative analysis it was possible to detect one VX impurity along with

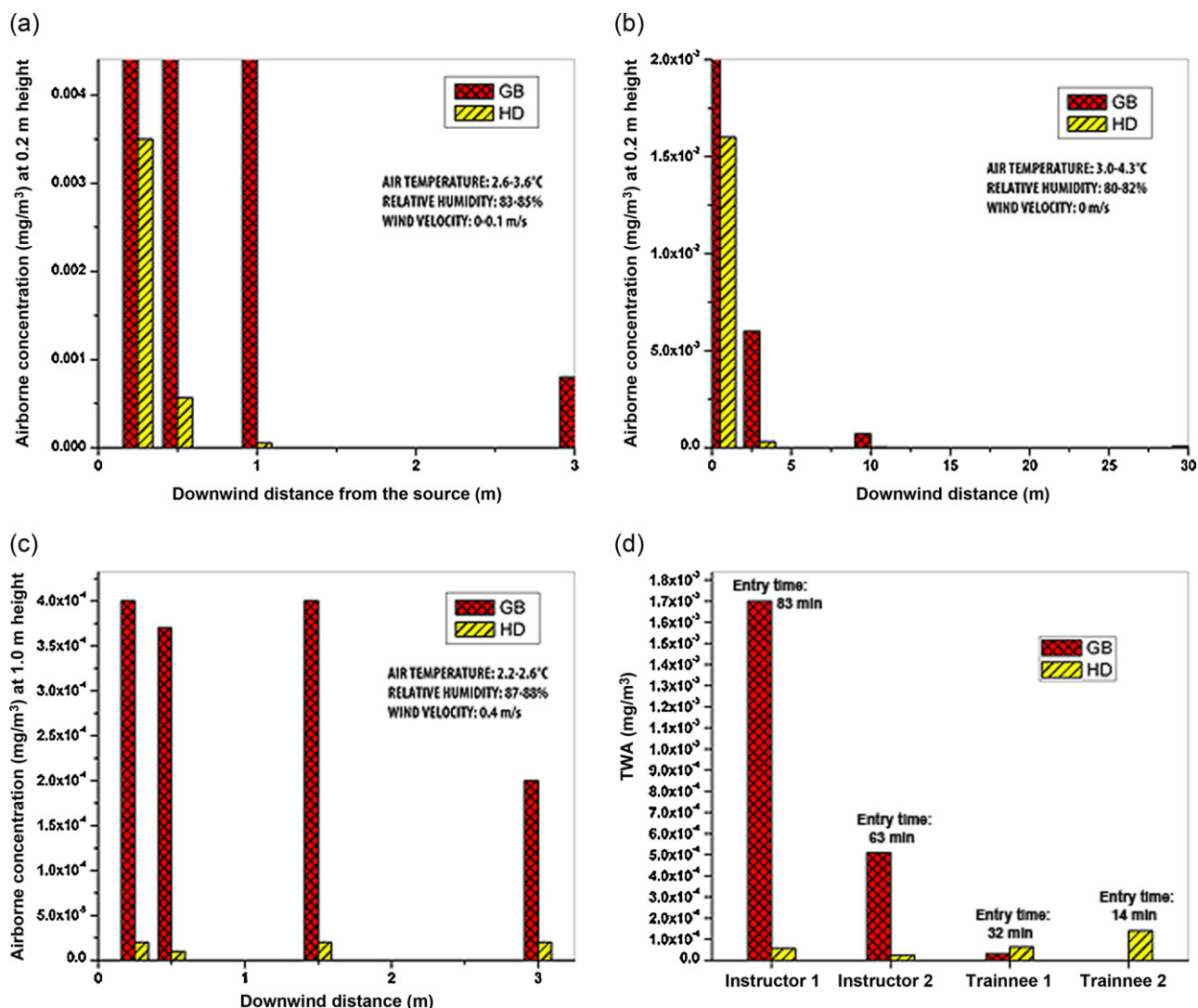


Fig. 7. Averaged airborne concentration levels measured during the OPCW inspectors training in the Czech Republic. (a) Area air sampling, 75 μ l of neat GB, HD and VX applied; (b) area air sampling, 1.0 ml of neat GB and 25.0 ml of neat HD applied; (c) area air sampling, 50 μ l of neat GB, HD and VX applied; (d) personal air sampling, 50 μ l of neat GB, HD and VX applied at the detection station and 50 μ l of neat HD applied at the decontamination station.

two GB impurities. O,O-diethyl methylphosphonate is a common VX impurity originating from a production process or degradation of VX. The compound was detected at 0.25 and 0.50 m distances from the source. Traces of O-propyl methylphosphonofluoridate, GB production impurity, were detected at a distance of 0.25 m. Another common GB impurity, O,O-diisopropyl methylphosphonate, was detected at distances of 0.25, 0.50 and 1.00 m from the source. The presence of these impurities in neat agent samples was confirmed by independent GC-MS analysis of liquid agent samples coming from the same batch as the agents used in experiments.

In a separate experiment, steel plates were contaminated with 1.0 ml of GB and 25.0 ml of HD, respectively. This time, a maximum sampling distance was set at 30.0 m, while the sample volume for a shortest distance was reduced to 5 l only. The analysis results are summarized in Fig. 7b. Even reduced sample volume at 0.5 m distance was too high in respect to GB. Traces of GB were detected as far as the maximum sampling distance of 30.0 m. From impurities, only O,O-diisopropyl methylphosphonate was detected at distances of 0.5 and 3.0 m.

4.2. Area air sampling at a height of 1.0 m, the OPCW inspectors training in the Czech Republic

Separate steel plates were contaminated with 50 μ l of neat GB, HD, and VX. A sample volume was set at 22 l with pump flow rate at 300 ml/min. The analyses results are shown in Fig. 7c. Compared to the results in Fig. 7a, an order of magnitude lower airborne concentration values were obtained. This could be explained by lower volumes (for 33%) of agents used. Higher vapor density of the CWA relative to air could also contribute to the observed trend. GB has a vapor density of 4.9, and HD of 5.4 relative to air [34]. The agent vapors tend to sink and accumulate closer to the ground. Probably from the same reason, no agent impurities were detected at a height of 1.00 m.

4.3. Personal air sampling, the OPCW inspectors training in the Czech Republic

Two groups of trainees exercised at separate CWA stations. At the detection station, sample surfaces were contaminated with

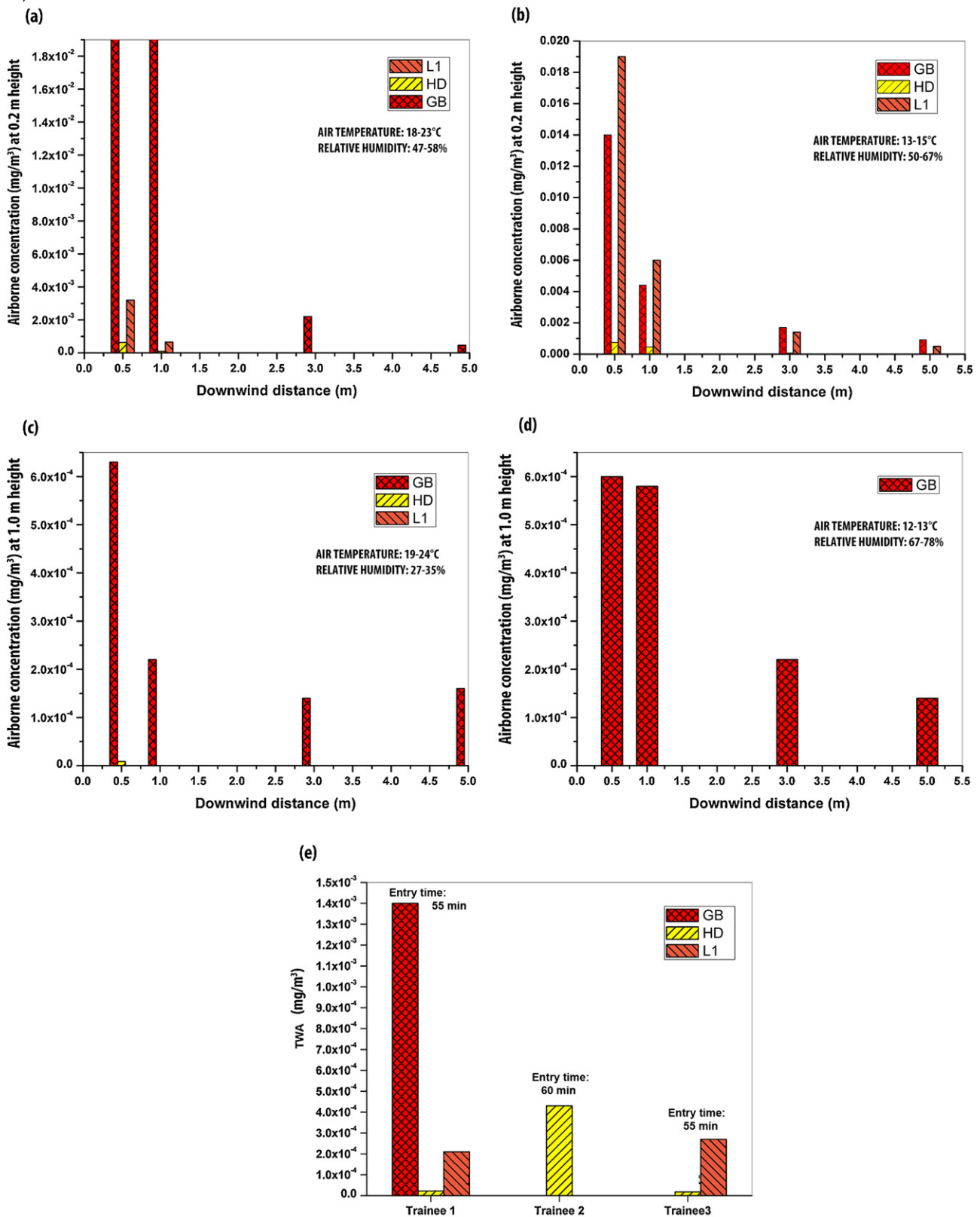


Fig. 8. Averaged airborne concentration levels measured during the OPCW inspectors training in the Slovak Republic. (a) Area air sampling, 50 μl of neat GB, HD, VX and L1 applied; (b) area air sampling, 100 μl of neat GB, HD, VX and L1 applied; (c) area air sampling, 50 μl of neat GB, HD, VX and L1 applied; (d) area air sampling, 100 μl of neat GB, HD, VX and L1 applied; (e) personal air sampling, 50 μl of neat GB, HD, VX and L1 applied at the detection station and 50 μl of neat HD applied at the decontamination station.

50 µl of GB, HD and VX. At the decontamination station, 50 µl of HD was transferred into a glass dish. The sampling flow rate was set at 300 ml/min in all cases, while the sampling time was equal to the entry time into the hot zone (Fig. 7d). The results showed that “Instructor 1”, who was present during the application of the agents and had a longest entry time into the hot zone, aggregated the highest concentration values. During sampling, two drops of condensation water from air purifying respirator worn by “Instructor 1” were accidentally drawn into one of the sampling tubes. Water was removed prior to analysis by heating the tube on a tube conditioner to 60 °C under helium flow of 60 ml/min for 6 min. A comparison with the analysis results obtained with non treated duplicate sample showed that no noticeable loss of analytes occurred during the drying process. “Instructor 2” was not present during the application of the agents, and his entry time was 15 min shorter. Both of the instructors performed activities that could bring them in a contact with atmosphere containing low levels of HD and GB vapors. “Trainee 1” performed the detection exercise and that explains for both HD and GB detected in his personal samples. “Trainee 2” performed the decontamination exercise and HD only was detected in his personal samples. VX was not detected in any of the personal samples.

4.4. Area air sampling at a height of 0.20 m, the OPCW inspectors training in the Slovak Republic

Separate steel plates were contaminated with 50 µl of neat GB, HD, VX and L1.

Sampling volume was set at 25 l with a flow rate of 300 ml/min. Relatively high airborne levels of GB were determined at 0.50 and 1.00 m distances from the agent source (Fig. 8a). Airborne levels of L1 were higher than of HD, as expected taking into the account higher volatility of L1. Traces of L2 were detected in the samples collected at distance of 0.50 m.

In a separate experiment, 100 µl portions of neat agents were applied. A sample volume was reduced to 13 l, while flow rate remained 300 ml/min. In this case, L1 was detected at all distances, while L2 was detected at the distance of 0.50 m with averaged concentration level of 1.3×10^{-3} mg/m³. The results are displayed in Fig. 8b.

4.5. Area air sampling at a height of 1.0 m, the OPCW inspectors training in the Slovak Republic

With 50 µl of agents applied, an airborne concentration of GB dropped sharply in a first 1.0 m, with slower decrease to 5.0 m (Fig. 8c). A low concentration of HD vapors was still measured at the distance of 0.5 m. It is interesting to note that L1 was not detected despite the fact that it is more volatile than HD. Higher vapor density of L1 (7.1) compared to the vapor density of HD (5.5) [35] could contribute to the observed trend. L1 vapors accumulated closer to the ground, while HD vapors dispersed higher.

With 100 µl of agents applied, sampling time was reduced giving overall sampling volume of 13 l. Airborne levels of GB gradually dropped to 5.0 m distance and no other agent was detected (Fig. 8d).

4.6. Personal air sampling, the OPCW inspectors training in the Slovak Republic

“Trainee 1” performed the detection exercise at the stations with 50 µl of GB, HD, VX and L1 applied on different types of surfaces. “Trainee 2” performed the decontamination exercise with 50 µl of neat HD applied. “Trainee 3” performed the detection exercise, but with no GB applied. The entry times and measurement results are as displayed in Fig. 8e. All agents used, except VX, were detected in the personal air samples of “Trainee 1”. HD only was detected

in the samples collected with “Trainee 2”. The TWA values for HD and L1 obtained with “Trainee 3” were comparable to the values obtained with “Trainee 1”.

5. Conclusions

Use of the Tenax TA packed GC liner as an air/vapor sampling tube and PTV GC inlet system as a thermal desorption unit has shown to be a viable and robust method for the field analysis of CWA and their impurities in air. The benefits of the approach were numerous. The packed GC liners were a low cost alternative to the commercial sampling tubes. In combination with storage/sampling system, the liners were easily handled and used for sampling in hazardous environments. The whole sample was introduced into the GC, lowering the detection limits and enabling the full scan MS trace analysis. The maximal settable temperature ramp rate of 720 °C/min in PTV mode allowed for fast transfer of compounds from the adsorption tube directly to the column resulting in good peak shapes for the analytes. The approach eliminated a need for an often expensive external TD unit, while the transfer path and ‘dead’ volume were reduced to a minimum. Use of a Peltier element with good heating and cooling properties eliminated also need for an external coolant and enabled a rapid cycle time for the analysis (~22 min). With minimal hardware needs, the method did not add much to the logistic burden of the field analytical laboratory. Change from the standard liquid injections mode to the PTV TD mode and back was accomplished fast and easily by loading of an adequate GC–MS method in the control software package. Although the method has been primarily developed for the qualitative analysis (analytical screening), the tests and validation exercises have shown that it has the potential to be a quantitative method for a range of CWA. The procedure adapted for derivatization of Lewisites was fast and simple, enabling the simultaneous determination of other CWA. VX at low spiking levels (≤ 5 ng on tube) was found to be very susceptible to storage and air flow through the tube. Since this could be partially due to the interaction of VX with the active silanol groups on the inner surface of the GC liner, future studies should look at using of deactivated/inert liners to enhance the sensitivity of the method.

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