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Simple time weighted average level air-monitoring method for sulfur mustard in work places

M.V.S. Suryanarayana[a,*], R.K. Shrivastava[a], Diwakar Pandey[a], R. Vaidyanathaswamy[a],
Sumeet Mahajan[b], Debdas Bhoumik[b]

[a]*Defence Research and Development Establishment, Jhansi Road, Gwalior 474002, India*
[b]*Defence Research and Development Organisation, Nashik, India*

Abstract

A simple air-monitoring method was developed and validated for vesicant sulfur mustard (HD) in the work place at time weighted average levels. XAD-2 adsorbent was used for the collection of HD vapours for 8 h followed by liquid desorption with carbon tetrachloride. The trace level analysis was carried out by gas chromatography–photoionization detection and was confirmed by gas chromatography–mass spectrometric detection in the selected ion mode. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Monitoring of toxic chemical warfare agents during demilitarisation is of paramount importance to meet the Organization for the Prohibition of Chemical Weapons (OPCW) requirement and for occupational safety of personnel involved. Sulfur mustard [bis-(2-chloroethyl) sulfide, HD] is known to affect both men and material and has been documented as an antimitotic, mutagenic, carcinogenic and cytotoxic agent [1]. Because of the potential health hazards associated with sulfur mustard during handling, storage or destruction, the level exposure of workers should be assessed accurately to ensure safety.

Skin, eyes and respiratory tract are the principal target organs and deoxyribose nucleic acid (DNA) is the most important molecular target of HD toxicity. The acceptable time weighted average (TWA) for an 8-h day has been adopted as 0.003 mg/m^3 [2]. Presence of HD can be easily detected in the environment much above the TWA levels with many commercially available and OPCW adopted chemical agent monitors like the M-90 ACADA system (Environics, Finland), the CAM-GID-3 (Graseby Dynamics, UK), the AP2C (GIAT Industries, France), etc. However, these monitors can detect the presence of this chemical only when it is present about 100 times higher than the TWA levels. Moreover, these equipment cannot quantify the same. Earlier, reports on sorbent trapping of HD on Tenax and thermal desorption with gas chromatography (GC) were published, but none of these methods are accepted by the OPCW as the standard operating procedures to monitor chemical warfare (CW) agents. For this

*Corresponding author. Tel.: +91-751-341-980 ext. 311/173; fax: +91-751-341-148.

E-mail address: viro@drde.8m.com (M.V.S. Suryanarayana).

purpose complex and expensive equipment are required [3]. Moreover, thermal desorption–GC analysis has its inherent drawbacks like higher background generation from decomposition of agent during desorption process and being a one-shot analysis system, there is no provision for repetition of the observation.

Out of the available techniques for historical monitoring of toxic pollutants in the environment, adsorption of the chemical on to a sorbent (at lower flow-rates and longer sampling times) and its subsequent desorption using suitable solvent and the quantification by GC analysis with specific detection systems like flame-photometric detection (FPD) or photoionization detection (PID) is the most convenient for use in the workplace.

From our experience in developing portable [4] and continuous on-line (near real time) monitoring systems for CW agents, PID was found to be more suitable due to its simplicity of construction, ease of use, high sensitivity and greater linear dynamic range 10^6 for PID versus 10^3 for FPD. The relatively low specific surface area of Tenax GC (20 m^2/g), the wide use of Amberlite XADs (>500 m^2/g) for workplace air-quality monitoring, the low decomposition temperature of HD [5], lack of prior knowledge of probable HD concentration profile in work place air prompted us to device a foolproof and simple air-monitoring technique using the sorbent trapping and liquid stripping methodology. The present report describes a systematic study for the development of a simple historical monitoring protocol for HD in work places. We developed this method and validated it by generating standard atmospheres of HD concentrations. So far this approach is not reported for the other important CW agents [6].

2. Experimental

2.1. Gas chromatography

Standard atmospheres of known concentrations of HD vapours were generated using a slightly modified dynamic diffusion system for low concentrations and purging system for high concentrations [7]. The concentrations of the generated HD vapours were monitored and controlled by two methods: by trapping a portion of the flow in 3 ml of diethyl succinate followed by GC–FPD (in the S mode) analysis and also by on-line GC–PID before secondary dilution [8]. This system is regularly used in our laboratory to evaluate various chemical agent monitors [4,8].

All other quantification studies including breakthrough check up were performed on the GC–PID system (Nucon Engineers, New Delhi, India) with further confirmation by a Hewlett-Packard HP 6890 series GC system equipped with HP 5973 mass-selective detector (Hewlett-Packard, Singapore) using selected ion monitoring (SIM). The instrumental conditions for the Chemito 1000 series GC system equipped with FPD (Toshniwal Instruments, Nashik, India) for all analyses of HD were as follows: the carrier gas was helium at a flow-rate of 15 ml/min and the inlet temperature was 250°C. The column used was an SGE BP-5 (Australia), 30 m× 0.53 mm, with a 1.0 μm film thickness. The GC oven program was 50°C (1 min hold), 10°C/min to 280°C (1 min hold). The detector temperature was 260°C.

The on-line gas chromatograph, a NUCON-1000 series instrument, was equipped with a 10.2 eV photoionization detector and a 1-ml heated sample loop with a provision for a liquid injection facility for calibration and analysis. A 30 m×0.53 mm I.D. SGE fused-silica BP-5 wide bore capillary column (Australia), 1.0 μm film thickness was used in the analysis. Zero-grade nitrogen at a flow-rate of 15 ml/min was used as carrier gas. The temperatures of the injection port, oven and detector were maintained at 170, 140 and 150°C, respectively. The injection volume was 2 μl throughout the experiments in the splitless injection mode.

A Hewlett-Packard GC–MS system 5973 (USA) equipped with a 30 m×0.32 mm I.D., 0.25 μm thickness BPX-5 (SGE) capillary column was used for breakthrough check-up studies. The oven temperature program was similar to that of the GC–FPD system. Helium (99.9999%) was used as carrier gas at a flow-rate of 1.2 ml/min. The electron impact (EI) ion source temperature was 230°C with electron impact energy of 70 eV and the quadrupole analyser temperature was 150°C. The injection port and GC–MS interface temperatures were 280°C each.

HD (>99% GC) was prepared in the laboratory. Amberlite XAD-2 was purchased from Supelco (Bellefonte, PA, USA). The resin was thoroughly cleaned by repeated refluxing with water, methanol and carbon tetrachloride (eluent) sequentially in a Soxhlet assembly. Carbon tetrachloride, chloroform, dichloromethane and methanol (analytical-grade reagents) procured from E. Merck, India were used as solvents for the extraction of HD from the adsorbent. HD and carbon tetrachloride are highly toxic chemicals and the necessary safety precautions must be taken while handling these chemicals.

3. Results and discussion

3.1. Method development

In developing a sorbent tube trapping protocol for air-monitoring of a toxicant, it is imperative to select a suitable sorbent, desorbing solvent, check the desorption efficiency, adsorption capacity of the sorbent as well as validation of the method by active sampling methods. To optimise the above-mentioned variables, it is prerequisite to define the action level as well as determine the minimum detection level. The action level was determined by multiplying the TWA exposure limit for the agent to be determined (3 ng/l for HD) by the sampling rate (0.5 l/min) with the sampling time optimised for 8 h (480 min). The sampling rate has been optimised so that the agent can still be detected amongst the background. This also facilitated minimum change of tubes in the field. The minimum detectable quantity (signal-to-noise ratio 3:1) of PID was 0.8 ng and by GC–MS in the SIM mode it was 0.1 ng of HD in carbon tetrachloride. The action level was computed as 720 ng (1 TWA). The calibration graph for the HD for the investigated concentration range of 0.5–1250 μg/ml in carbon tetrachloride was linear and gave a correlation coefficient of 0.9998 ($n=10$; $y=2.1012x+3.5998$) for a plot of the peak area ratio for 10 concentrations.

3.2. Selection of sorbent

Pyrex glass tubes of 5 mm O.D.×3 mm I.D. filled with approximately 220–230 mg of XAD-2 resin and plugged with silanised glass wool at both ends were used as the sorbent tubes for sampling throughout this study. XAD-2 resin was selected as the sorbent system owing to its suitability for trapping organothiophosphates [9]. Moreover, during our experiments XAD-2 was found to be better than other Amberlites like XAD-4 or XAD-7 for trapping HD in air. Though some reports are available suggesting the use of XAD-2 for air-monitoring of CW agents, no systematic and in-depth studies have been carried out so far [10–13].

3.3. Selection of a suitable solvent system

With the use of PID, selection of a suitable solvent system is more critical. The criteria should be: (i) the solvent should be less sensitive to PID (of higher ionization potential (I.P.) value than 10.2 eV), (ii) recovery efficiency in the solvent should be more than 75% [6,14] and (iii) at ambient temperature, it should not be highly volatile (i.e., during the course of extraction and the GC analysis process).

The above limitations restricted us to test a few solvents for the recovery efficiency and the results are shown in Table 1. Though the extraction efficiency of dichloromethane is comparable to carbon tetrachloride, its high volatility as well as the presence of a significant impurity at the same retention time of HD prompted us to select carbon tetrachloride as the solvent system for further studies.

3.4. Procedure for determining desorption efficiency

Five sorbent tubes were spiked with HD stock solution at concentrations of 360, 720, 1440, 2160 and 2880 ng. A 20-l volume of dry air at a flow-rate of 500 ml/min was drawn through all the sorbent

Table 1
Recovery of HD from XAD-2 tubes spiked at 1 TWA[a]

Solvent	Recovery (%) ($n=4$)
Dichloromethane	89±2
Carbon tetrachloride	94±3
Chloroform	83±3
Methanol	53±4

[a] TWA, Level at which HD was spiked. 1 TWA=720 ng.

Table 2
Desorption efficiency of HD from XAD-2 adsorption tubes

TWA level	Mean recovery (%) ($n=8$)	SD	True mean for 95% confidence interval
0.5	91.0	7.7	91.0±8.1
1.0	94.2	4.9	94.2±5.2
2.0	95.5	5.7	95.5±3.9
3.0	94.3	6.9	94.3±7.3
4.0	95.3	9.5	95.3±6.6

tubes to simulate an air-sampling situation. All the five tubes along with a blank sorbent tube (not spiked with HD) were kept in the open at ambient temperature (25±2°C) for 1 h. After this period each of the above six sorbent tubes that included the blank tube were desorbed in 1 ml of carbon tetrachloride with vigorous shaking for 5 min on a cyclo-mixer and were analysed simultaneously by GC–PID and GC–MS in the SIM mode. This experiment was performed in duplicate for 5 consecutive days and the results are outlined in Table 2. The average desorption efficiency was always more than 91%

with relative standard deviations (RSDs) generally less than 10%, much below the specified 25% [6,14].

There was a linear response in the recovered amount, when a graph (Fig. 1) was drawn between the spiked and the recovered HD concentrations. This ensured that: (i) even at as low as 0.5 TWA level HD can be monitored and analysed and (ii) linearity was maintained thus validating the desorption efficiency.

3.5. Air-flow experiments

Six different sets of samples (five sorbent tubes per set) with each sample spiked at different levels, i.e., 0.5, 1, 2, 4 and 10 TWA were prepared for this study. In addition to each set of sample, additional tubes used as control samples were placed in specially designed sample trains that contained a small vacuum pump and a rotameter. Air (temperature 25±2°C, relative humidity 55±5%) was drawn through two batches of three sets of tubes at a flow-rate of 500 ml/min for 8 and 16 h. In this experiment, the rear end of the spiked tube was connected to an unspiked sorbent tube, which was periodically removed and analysed by both GC–PID and GC–MS-SIM techniques for the breakthrough of HD from the upstream (spiked) tube. All sorbent tubes were extracted and analysed as described above for the desorption efficiency study. It became clear from the results (Table 3) that average loss during air-flow was less than 5%. The conditions of breakthrough experiment were more stringent than the actual sampling situation.

3.6. Active sampling

To further assess the capabilities of the method that mustard vapour could be collected (adsorbed)
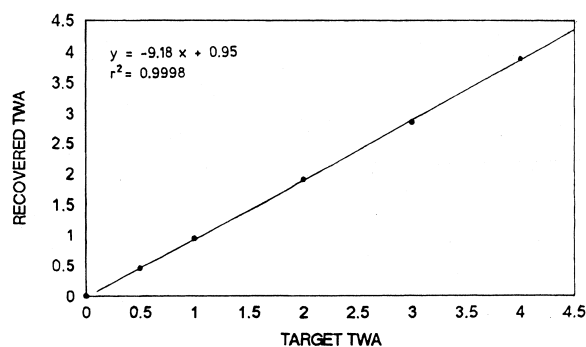

Fig. 1. Trend line plot of recovered concentration vs. spiked concentration (TWA=720 ng HD).

Table 3
Percent recoveries of HD from XAD-2 sorbent tubes in air-flow experiments at 500 ml/min

Sampling time (h)	Average recovery (%±SD) ($n=3$)				
	Spiking level				
	0.5 TWA	1 TWA	2 TWA	4 TWA	10 TWA
8	96±6	98±2	100±2	99±4	99±4
16	95±7	97±3	101±3	100±5	100±6

and desorbed reliably at the entire linear dynamic range of the analytical system, we sampled and determined HD vapour in the output stream from the dynamic diffusion/purging system under various sets of humidity (20–99%) conditions.

Sampling was done by the sample train by sucking measured gas volumes through the sorbent tube filled approximately with 230 mg of XAD-2 from the gas generation system. The amount of HD sampled by sorbent tubes at 500 ml/min of air was 0.72 μg–2.4 mg. In these studies, similar to air flow experiments a second sorbent tube was also placed at the rear side of the first tube for breakthrough check-up, which was also desorbed and analysed similar to the first tube using SIM. Results are given in Table 4. No breakthrough was observed either in active sampling or in air-flow experiments even at a challenge concentration of 10 mg/m^3 proving the high adsorption capacity of the sorbent, which was more than sufficient to allow sampling for a maximum time of 8 h. However, as the analyses of the tubes are done immediately after 8 h of sampling, breakthrough beyond 8 h has not been attempted.

3.7. Storage experiment study with spiked sorbent tubes

The stability of HD on XAD-2 tubes was studied using 10 tubes spiked with 720 ng (1 TWA) of HD. The sorbent tubes were placed in glass-stoppered tubes and sealed. Five tubes were stored at room temperature (temperature 25–30°C, relative humidity 45–55%) and five tubes in a refrigerator (temperature < +5°C). All sorbent tubes were in sealed glass stoppered tubes protected from ambient light for 48 h prior to analysis. Five additional tubes were used as control samples and analysed immediately. All sor-

bent tubes were extracted and analysed in the same way as the tubes for the desorption efficiency study. The loss from the tube loaded with 720 ng of HD during 48 h storage at room temperature was 4.2% and in the refrigerator the loss was 1.3%. However, as the requirement warrants analysis of the tubes immediately after sampling for 8 h no further storage stability studies were carried out.

As far as the influence of humidity on the sampling and analysis procedures was concerned, it was evident from the results, that the effect was least on the sampling efficiency as shown by negligible reduction in the recovery. The negligible influence of water on the sampling efficiency of XAD-2 can be ascribed to the highly hydrophobic nature of the XAD-2 polymer [9].

3.8. Application

In order to evaluate the applicability of the procedure, the proposed method was used to monitor HD vapour concentrations both in our laboratory and destruction sites. The analysis showed that during synthesis, weighing, or charging operations, the air level of HD near the breathing zone was 0.005 mg/m^3. This was the maximum concentration observed occasionally and at other places it was much below this level (data not shown). During this operation, the workers donned the impermeable protective gear. However, when unprotected workers enter areas after the operations, exposure to HD from contaminated surfaces, as a ''pick up'' is possible. Therefore it is important to identify all contaminated areas including corridors, donned protective gear and ensure that the level is below TWA level. In these situations the proposed method is the most reliable method in the absence of any standard detector.

Table 4
Percent recoveries of HD from XAD-2 sorbent tubes in active sampling experiments at 500 ml/min

Amount of sulfur mustard sampled (μg)	Recovery (%) (n=4)	RSD (%)	Note
0.72	94.5	3.1	No breakthrough
7.20	98.4	2.4	No breakthrough
24.0	101.0	3.3	No breakthrough
240.0	99.4	4.5	No breakthrough
2400.0	100.5	3.4	No breakthrough

4. Conclusion

It is evident from the results of the method development and validation, the proposed monitoring method meets the requirements for an ideal historical method for monitoring of HD. It is satisfying the criterion that has been imposed for this type of method development like the overall recovery must be greater than 75% and standard deviation with 95% confidence must be less than 25% [6,14]. Hence it can be concluded that HD vapour present in the work place can be monitored effectively with high sensitivity and with adequate accuracy and precision. This method is now presently adopted in our destruction site.

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