Detection of the chemical warfare agents bis-(2-chloroethyl)ethylamine (HN-1) and tris-(2-chloroethyl)amine (HN-3) in air

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Abstract

This paper describes the method development and validation for detection of the chemical warfare agents HN-1 and HN-3 in air using C_8 solid-phase extraction disks followed by liquid desorption and analysis by gas chromatography. The method is contrasted to the standard approach which uses solid sorbent tubes followed by thermal desorption and analysis by gas chromatography. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Currently, the USA is engaged in several programs to demilitarize chemical warfare (CW) agents. Several factors are driving this program including direction from the US Congress [1], agreements with the former Soviet Union [1], and the Chemical Weapons Convention [2]. The scope of the demilitarization programs encompasses all types of CW materials including stockpiled chemical agents, binary chemical weapons, buried CW material, recovered CW material from range clearing operations and from research and development testing. For non-stockpiled CW materials and for some stockpiled materials, incineration may not be economically or politically feasible. Alternatives to incineration are being considered for these sites.

One specific type of non-stockpiled material is Chemical Agent Identification Sets (CAIS). The US Army used CAIS from 1928 to 1969 to train soldiers and sailors in the safe handling, identification, and decontamination of chemical warfare agents. Identification sets were produced in large quantities and various configurations, and were widely distributed to military and civilian groups. They are periodically recovered at a variety of locations throughout the USA. The sets consist of chemical agents placed in glass ampoules, vials, and bottles, then packed in metal shipping containers or wooden boxes [3].

Sulfur mustard [bis-(2-chloroethyl)sulfide, HD], nitrogen mustards [bis-(2-chloroethyl)ethylamine, HN-1 and tris-(2-chloroethyl)amine, HN-3], and lewisite [dichloro-(2-chlorovinyl)arsine, L] are the chemical agents found in these sets. Once these agents are treated with appropriate decontaminants, the remaining neutralants will be transported to a

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commercial waste treatment facility for disposal. These materials will be handled using a mobile destruction facility. Chemical operations, to include identification, repackaging and neutralization, will take place inside a glovebox housed in an operations trailer [3].

In order to ensure operations within the trailer are safe for workers, near real time air monitoring for the chemical agents is required. Near real time monitoring is accomplished using a continuous environment monitoring system (Model FM-2000, OI Analytical, College Station, TX, USA). The FM-2000 consists of a vacuum pump which is used to draw air over a solid sorbent tube containing Tenax. Compounds adsorbed onto the Tenax are thermally desorbed onto a short packed chromatographic column and detected by either a halogen-specific detector (OI Analytical, College Station, TX, USA) or a flame photometric detector. The solid sorbent tube is desorbed and conditioned with each cycle. The instrument is calibrated with agent standards and alarmed at a level equivalent to one time weighted average (TWA) exposure limit. If an alarm sounds, operations are ceased and the alarm is confirmed with a secondary technique.

The secondary techniques for HD and L are solid sorbent-based techniques. Air samples are drawn through a 'depot area air monitoring system' (DAAMS) tube. The DAAMS tube is a fritted glass tube packed with Tenax. Tenax has been used as an effective sorbent material for several types of chemical warfare agents [4–6]. The tubes are thermally desorbed into a capillary gas chromatograph and detected using flame photometric detection. Alarms are confirmed by comparison of retention time with a known standard. The secondary, confirmation, techniques are run on a fully outfitted capillary GC system which provides better resolution of the target analytes from possible interferents than the FM-2000 system.

This study looks at method development and validation of secondary techniques using solid sorbent or solid-phase extraction-based technology for the analysis of HN-1 and HN-3 in air samples. Two types of methods are needed for the operations trailer. The first method is used for confirmation of the primary system when an alarm is sounded. This method will have flow-rates and sampling times similar to the primary analysis system. A second method, known as historical monitoring, uses lower flow-rates and longer sampling times to record agent concentration in the trailer over an extended period of time. Previous studies used bubblers filled with diethyl phthalate to trap nitrogen mustards from air. The samples were analyzed using colorimetric methods. These methods are laborious and are subject to interferences [7,8].

2. Experimental

All experiments were performed on a Hewlett-Packard 5890 Series II gas chromatograph with a 5972 mass-selective detector or nitrogen–phosphorus detection (NPD) system. The instrumental conditions for the GC–MS analyses were as follows: The carrier gas was helium at a flow-rate of 1.0 ml/min. The inlet temperature was 250°C. The column used was a Hewlett-Packard HP-5MS or a Restek RTX-5 amine, 30 m×0.25 mm, with a 0.25-μm film thickness. The GC oven program was 50°C (1 min hold), 15°C/min to 280°C (0.67 min hold). The detector temperature was 280°C. The mass spectrometer was run in the selected ion mode, HN-1 (ions 92, 120), HN-3 (ions 154, 156, 158).

The instrumental conditions for the GC–NPD analyses were as follows: the carrier gas was helium at a flow-rate of 1.2 ml/min. The column used was a Restek RTX-5 amine, 30 m×0.25 mm, with a 0.25-μm film thickness. The GC oven program was 55°C (1 min hold), 35°C/min to 250°C (3.0 min hold). The detector temperature was 210°C. The bead power was variable with a signal between 10 and 20 pA.

For thermal desorption, the GC system was interfaced to a Dynatherm ACEM 900 Thermal Desorption Unit (Kelton, PA, USA). The Dynatherm conditions were as follows: the tube dry temperature was 60°C for 1.0 min. The tube desorb temperature was set to 210°C for 3.0 min. The tube cool was set to 60°C for 1.0 min. The trap desorb was set to 300°C for 3.0 min. The valve compartment was set to 250°C. The transfer line was set to 250°C and the tube purge flow set to 30 ml/min.

A GC–NPD system configured for thermal desorption was used for all DAAMS work. A GC–MS

system configured for liquid injections was for C_8 disk work. Method development and validation activities were run concurrently for both approaches.

Empore Octyl solid-phase extraction (SPE) disks (3 ml) were obtained from Varian (Walnut Creek, CA, USA).

A 12-port vacuum manifold was constructed using Tygon tubing and needle valves for individual flow control. An Air Cadet Vacuum/Pressure Station from Cole-Parmer (Vernon Hills, IL, USA) was used to supply a vacuum.

HN-1 and HN-3 standards were obtained from the Chemical Agent Standard Analytical Reference Material (CASARM) Program at Edgewood Research, Development, and Engineering Center (Aberdeen Proving Ground, MD, USA). Ethyl acetate, anhydrous, 98%, was purchased from Aldrich (Milwaukee, WI, USA).

3. Results and discussion

3.1. DAAMS method development

The first approach was to examine the use of conventional DAAMS technology for the analysis of HN-1 and HN-3 in air samples. The variables considered were sample collection time, sampling flow-rate, and collection volume.

The effects of sampling time were investigated first. Sixteen tubes were preconditioned at 270°C for 15 min. Twelve of the 16 tubes were spiked with 36 ng of each agent, four were used as blanks. Nine spiked tubes and three blanks were attached to the vacuum manifold and sampled at 50 ml/min. The other three spiked tubes and blank were run immediately. The other tubes were analyzed after 60, 120 and 180 min. A blank tube was analyzed with each set. The tubes were analyzed by thermal desorption–gas chromatography–NPD. The recoveries were calculated versus a five-point calibration curve for each agent. The results, Table 1, show a loss of approximately 50% for both agents after 3 h of sampling.

With the most significant decrease in agent recovery occurring within the first hour, a second time study was performed. Tubes were prepared as before with sampling times of 2, 5, 15 and 30 min. The

Table 1
Percent recoveries for HN-1 and HN-3 at 50 ml/min

Agent	Recovery (%)			
	0 min	60 min	120 min	180 min
HN-1	100±5	61±1	50±2	42±3
HN-3	100±6	62±2	59±2	55±4

results, Table 2, show significant losses of both agents within the first 30 min.

Two flow-rates were tested to examine the effects of sampling flow-rate on the recoveries of the two agents. A low flow-rate of 50 ml/min and a relatively high flow-rate of 500 ml/min were considered. Sample tubes were spiked with 36 ng of HN-1 and HN-3 and sampled for 30 min. Three replicates were run at each flow-rate. The average recovery for HN-1 at 50 ml/min was 67±2%. At 500 ml/min, the average recovery was 74±3%. The average recovery for HN-3 at 50 ml/min was 66±1%. At 500 ml/min the average recovery was 78±2%. The results show better recoveries at higher flow-rates. If the loss of agent was due to breakthrough on the tube, one would expect lower recoveries at higher flow-rates. The mechanism of agent loss is most likely due to hydrolysis of the agent on the tube.

A study was performed where the total sample volume was constant at 6.0 l. The sample flow-rate and collection time were changed for three trials with the total sample volume equal to 6.0 l for each trial. The three trials were 200 ml/min for 30 min, 100 ml/min for 60 min, and 50 ml/min for 120 min. Each sample tube was spiked with 18 ng of HN-1 and HN-3 before being sampled. Little difference was observed between the three trials. The average recovery ($n=3$) for HN-1 at 200 ml/min sampled at 30 min was 66±4%. The HN-1 recovery at 100 ml/min for 60 min was 65±3% and at 50 ml/min for 120 min was 64±5%. Similar behavior was seen for the HN-3 recoveries. The HN-3 recovery at 200

Table 2
Recoveries for HN-1 and HN-3 at 50 ml/min, 0–30 min

Agent	Recovery (%)				
	0 min	2 min	5 min	15 min	30 min
HN-1	100±4	81±1	75±2	70±3	71±1
HN-3	100±6	80±1	74±3	71±4	72±2

ml/min for 30 min was 74±6%, at 100 ml/min for 60 min was 73±3%, and at 50 ml/min for 120 min was 74±4%. This shows, given a fixed sample volume, the recoveries for each agent are the same.

During the course of this study, humidity was measured using a Thermohygro recorder (VWR Scientific Products, Bridgeport, NJ, USA). The humidity was measured because agent hydrolysis was considered a potential problem. The recovery of HN-1 was generally lower on days when humidity in the laboratory was higher. The recovery of HN-3 was affected less by changes in humidity. No attempts were made to control humidity in the laboratory.

3.2. DAAMS method validation

The requirements for validation of the two types of methods required for air sampling of HN-1 and HN-3, historical and near real time confirmation, have been well defined. [9]

The near real time confirmation method must be subjected to what is defined as a 'Class 2' precision and accuracy study. In this type of study, DAAMS tubes are spiked at 0.5, 0.7, 1.0 and 1.25 times the defined action level. The action level (Z) is determined by multiplying the time weighted average exposure limit for these agents (3 ng/l for HN-1 and HN-3) by the sampling rate (0.3 l/min, the same rate as the primary system) and the sampling time (3 min, the same time as the primary system). The result, 2.7 ng, is the action level for the method. This amount is post-spiked onto the solid sorbent tubes. The amount of time in which air is drawn through the tubes is optimized such that the two agents can still be detected amongst the background collected on the tube. In practical terms, the longer the time in which the agents can still be detected, the less frequently the tubes will need to be replaced in the 'field'.

Experimentally, four tubes are spiked at the 0.5 level, two tubes at the 0.7 level, four tubes at the 1.0 level, and two tubes at the 1.25 level. This spiking regime is carried out for two consecutive days. The tubes are analyzed by thermal desorption–GC–NPD and the recovered amount calculated from a five-point calibration curve. To evaluate the results, the amount of agent found is plotted versus the amount of agent spiked. A best fit line is then drawn through the 24 points. A target action level (TAL) has been defined as 0.7 times the action level. The found action level (FAL) is determined by inserting the value for the TAL into the linear regression data. The acceptance criteria states that 100% of the 1.0 and 1.25 spike levels must be above the FAL for each of the 2 days. For the 0.5 spike levels, 75% of the points must be below the FAL [9].

The described experiment was carried out for the DAAMS tubes. The DAAMS tubes were sampled at 300 ml/min for 240 min. The resulting trendlines are plotted in Figs. 1 and 2, for HN-1 and HN-3, respectively. The FAL for HN-1 was found to be 0.65 and the FAL for HN-3 was 0.69. A complete pass/fail examination of the HN-1 and HN-3 data is shown in Table 3. The DAAMS method meets the criteria for the Class 2 validation for the near real time confirmation method.

The historical method is subjected to a different set of criteria to validate the method. The spiking regime consists of 12 tubes, duplicates spiked at six different levels. The spiking levels are 0.0, 0.2, 0.5, 0.8, 1.0 and 1.5 times the action level set for the method. The action level is determined by multiplying the time-weighted average exposure limit (3 ng/l for HN-1 and HN-3) by the sampling rate (0.05 l/min) and the sampling time (240 min). The result, 36 ng, is the action level for the method. This amount is pre-spiked onto the solid sorbent tubes before the sampling takes place. The experiment is repeated for 4 days. The results are evaluated as a Class 1 precision and accuracy study using Government developed 'Certify' software [15]. The Certify software performs a weighted least-squares regression analysis of the found concentration versus the target concentration. Confidence bounds are calculated for each target concentration. The output is a found action limit (FAL), limit of quantitation (LOQ), overall recovery and uncertainty in found mass (UIFM). The criteria that has been established for this type of study are: the FAL must be greater than the LOQ, the overall recovery must be greater than 75%, and the UIFM with 95% confidence must be less than 25% [10].

The DAAMS historical method was subjected to a four day Class 1 precision and accuracy study. Typical chromatograms for this analysis is shown in Fig. 3. The data were analyzed using the Certify
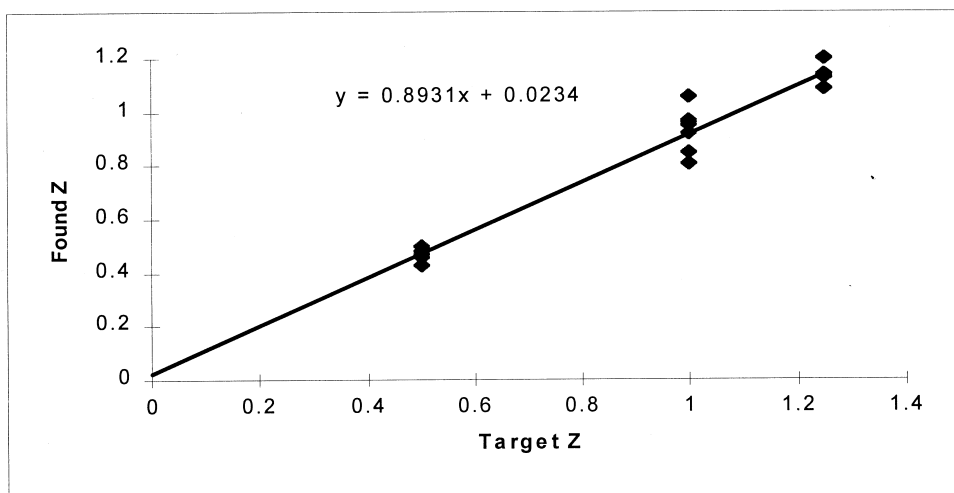
Fig. 1. Trendline plot of found Z vs. target Z for HN-1, DAAMS tube, class 2 P&A. Z=level at which the CW agent was spiked. Z=2.70 ng (1 TWA) for near real time confirmation method.

software. These results are shown in Table 4. The data meets the first criteria in that the FAL is greater than the LOQ. However, the overall recovery for both HN-1 and HN-3 fails to meet the required 75%. Likewise, the UIFM is greater than 25% for both analytes.

3.3. C_8 SPE disk method development

As an alternative method to DAAMS tubes, SPE disks were considered as trapping media for HN-1 and HN-3 from air. SPE is commonly used in sample preparation for sample cleanup or analyte concen-
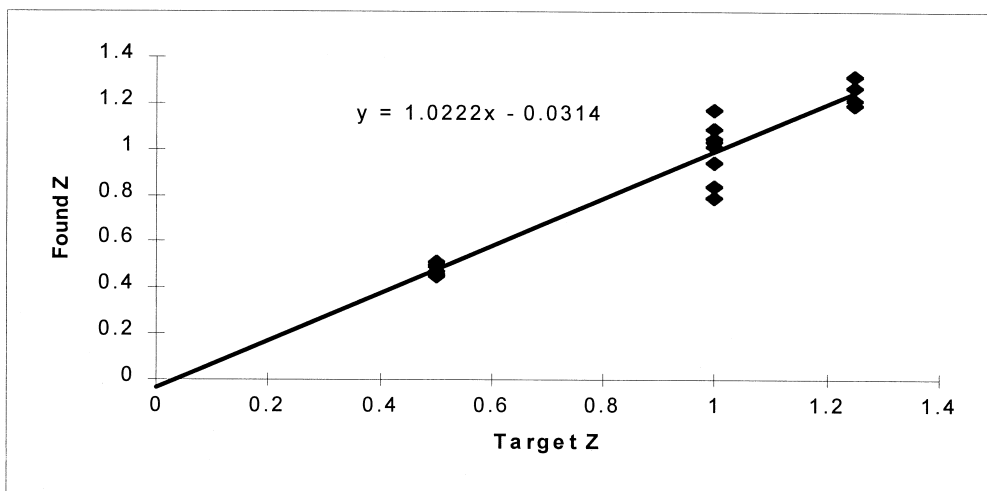

Fig. 2. Trendline plot of found Z vs. target Z for HN-3, DAAMS tube, class 2 P&A. Z=level at which the CW agent was spiked. Z=2.70 ng (1 TWA) for near real time confirmation method.

Table 3
Pass/fail results for HN-1 and HN-3 in class 2 P&A test

Target 2	HN-1				HN-3			
	Day 1		Day 2		Day 1		Day 2	
	Found Z[a]	P/F[b]	Found Z	P/F	Found Z	P/F	Found Z	P/F
0.5	0.46	P	0.43	P	0.49	P	0.47	P
0.5	0.50	P	0.46	P	0.50	P	0.46	P
0.5	0.47	P	0.48	P	0.51	P	0.47	P
0.5	0.50	P	0.46	P	0.49	P	0.45	P
1.0	0.97	P	0.92	P	1.09	P	1.01	P
1.0	0.85	P	0.96	P	0.94	P	1.03	P
1.0	0.95	P	1.06	P	1.05	P	1.17	P
1.0	0.81	P	0.81	P	0.79	P	0.84	P
1.25	1.13	P	1.20	P	1.21	P	1.19	P
1.25	1.14	P	1.09	P	1.32	P	1.27	P

[a] Z=Level at which the CW agent was spiked. Z=2.70 ng (1 TWA) for near real time confirmation method.
[b] P/F=pass or fails criteria for class 2 P&A.

tration. SPE has also been used in air sampling applications [11–13]. Disks were chosen over columns to accommodate the high air flows, reduce the amount of eluant needed, and avoid degradation of the agents from adsorbed water. C_8 was chosen as an intermediate nonpolar phase. SPE disks have been used for the analysis of the chemical agent lewisite in air [14].

Five micrograms of agent were used initially to demonstrate the feasibility of this approach. This amount was lowered in later experiments to meet the method requirements. Four C_8 disks were spiked with 5 µg of each agent. Air was pulled through the disks at 300 ml/min for several time intervals. The disks were then eluted with 1 ml of ethyl acetate. The recoveries for the agents were measured by GC–MS versus a five-point calibration curve. The results are shown in Table 5. Excellent recoveries for both of the agents were seen, indicating good extraction efficiency from the disk, little or no breakthrough of the agents, and little or no hydrolysis.

The next set of experiments looked at spiking three disks at a significantly lower level. One was prespiked with 30 ng of both agents and air drawn through it at 300 ml/min for 60 min. A second disk had air drawn through it at 300 ml/min for 60 min and then was postspiked with 30 ng of both agents. A third disk had no air drawn through it and was spiked with 30 ng of both agents. All three disks

were extracted with 1 ml of ethyl acetate and analyzed by GC–MS in selected ion mode. The results were recoveries of 86, 94 and 97% for HN-1 at 0 and 60 min prespike, and 60 min postspike, respectively. For HN-3, the recoveries were 105, 118 and 115% at 0 and 60 min prespike, and 60 min postspike, respectively. Even at a lower spike level, excellent recoveries are seen for both agents for all disks indicating no loss due to breakthrough, hydrolysis or poor extraction efficiency.

The final postspiking experiment looked at eluting disks spiked at the TWA level with a smaller amount of ethyl acetate. Seven disks were sampled for 360 min at 300 ml/min. Three of the disks were then spiked with 2.7 ng (1.0 TWA) of both agents. Another three disks were spiked with 8.1 ng (3.0 TWA) of both agents. The final disk was left unspiked and used as a blank. All seven disks were eluted with 0.250 ml of ethyl acetate and analyzed by GC–MS in the selected ion mode. The results were average recoveries of 108 ± 20 and $91\pm3\%$ for HN-1 at the 1.0 and 3.0 TWA levels, respectively. For HN-3, the recoveries were 141 ± 20 and $102\pm6\%$. This showed that the lower amount of ethyl acetate is sufficient for eluting the agents from the disk.

At this point, a new column (HP-5MS) was substituted for the RTX-5 amine column. Solvent blanks were showing column bleed which was interfering with the detection of the analytes and
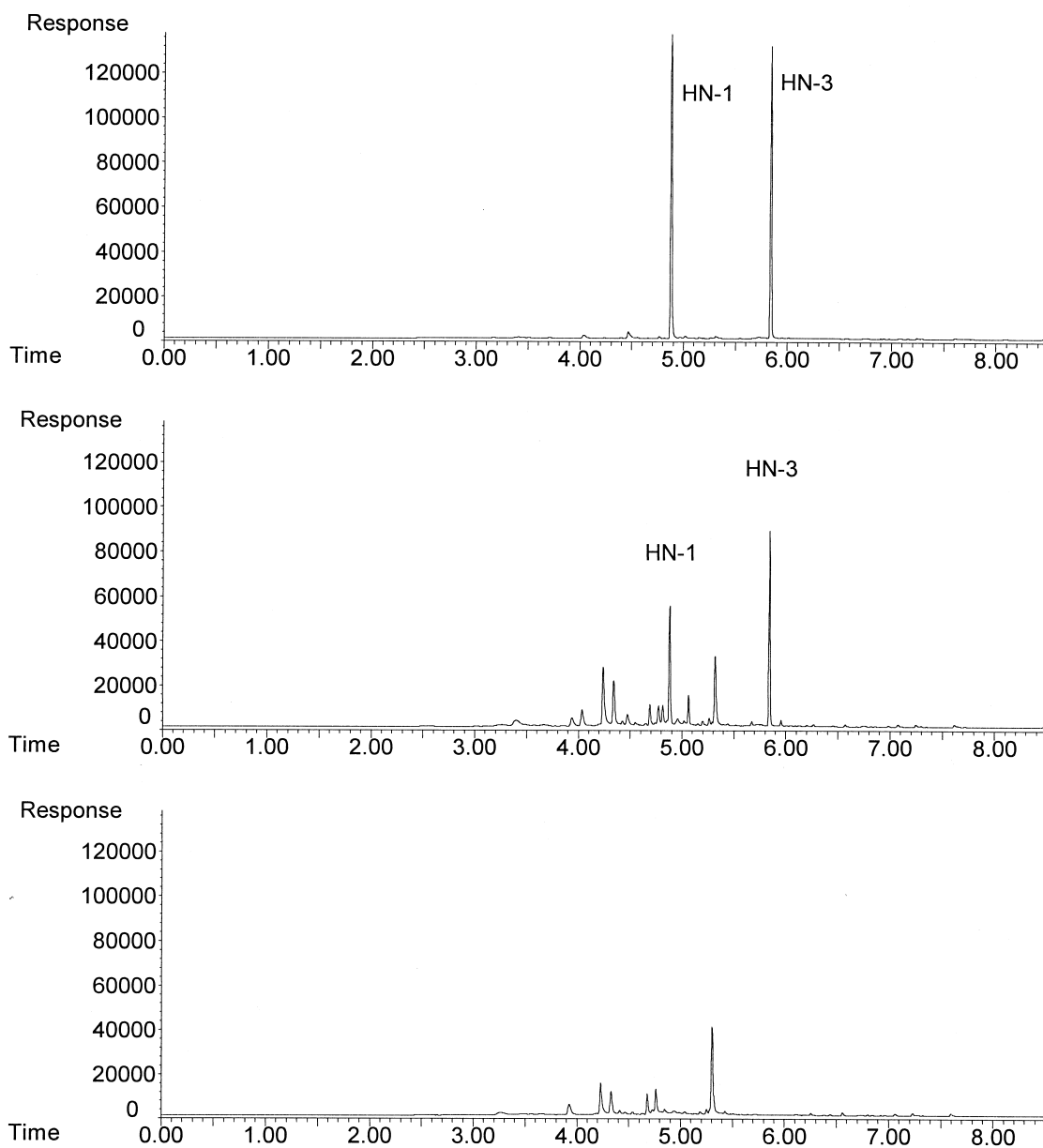
Fig. 3. Chromatogram of HN mix standard at 1.0 TWA (top), air sample pre-spiked at 1.0 TWA (middle), and air sample blank (bottom) by GC–NPD with thermal desorption. Time scales in min.

causing some of the high recoveries and lack of precision at the lower spike levels.

Time and flow experiments were done on pre-spiked C_8 disks in order to optimize the conditions. To test the effect of sampling time, four disks were set up at intervals of 2, 4 and 6 h. Two of the four disks of each time set were spiked at 0.2 TWA and the other two spiked at 1.0 TWA. The C_8 disks were sampled at 50 ml/min then eluted with 0.250 ml of ethyl acetate. The average recoveries for each set of duplicate disks were calculated for HN-1 and HN-3 (Table 6).

Table 4
Certify results

Agent	Found action level (TWA[a])	Limit of quantitation (TWA)	Overall recovery (%)	Uncertainty in found mass (%)
HN-1	0.322	0.0732	47.1	28.1
HN-3	0.410	0.0644	62.8	28.3

[a] TWA, Level at which the CW agent was spiked; 1 TWA=36.0 ng for historical method.

Table 5
Prespike experiments for C_8 disks

Time (min)	Recoveries (%) ($n=1$)	
	HN-1	HN-3
60	87	94
120	97	120
180	84	122
240	63	93

While the initial rate of loss for HN-1 is quick, the rate seems to level off after the first 2 h at both 0.2 and 1.0 TWA yielding good recoveries at both time points. For HN-3 the initial loss is a little slower, but again the rate seems to level off between 2 and 4 h for both 0.2 and 1.0 TWA yielding good recoveries.

For the purpose of the sampling event, a longer sampling time is more practical in labor terms. Since the recoveries did not fall off much after the initial drop, 6 h was chosen as the sampling time.

Next the flow-rate through the prespiked C_8 disks was investigated as to its effect on the recoveries of HN-1 and HN-3. At flow-rates varying from 50 to 400 ml/min, eight C_8 disks (duplicates at each flow-rate) were each spiked with 108 ng and sampled for 6 h. The disks were then extracted and the average recoveries calculated for each set of duplicates. For HN-1, the recoveries were 67±6% (50 ml/min), 66±2% (100 ml/min), 69±2% (200 ml/min), and 69% (400 ml/min, $n=1$). For HN-3, the average recoveries were 76±8, 73±3, 70±1 and 66% ($n=1$) for the same four flow-rates. The results suggest that the flow-rate at which the disks are sampled has little to no effect on the recoveries.

With the sampling time optimized at 6 h (360 min) and using 3 ng/l (the TWA exposure limit), a sampling flow-rate of 100 ml/min was chosen to minimize the amount (ng) loaded onto the disk.

An experiment was set up using a 108 ng spike as 1.0 TWA. Duplicate spikes were done on C_8 disks at 0.0, 0.2, 0.5, 0.8, 1.0 and 1.5 TWA. The disks were extracted with 0.250 ml and the recoveries calculated. However, two problems were apparent. The recoveries were low and the duplicate spikes in some cases were not comparable.

Since in going from a postspike (2.7 ng) for the near real time confirmation method, to a prespike (108 ng) for the historical method, the amount of HN-1 and HN-3 loaded onto the C_8 disk increased significantly, elution volume studies were performed. The spiked C_8 disks that were already eluted with 0.250 ml of ethyl acetate were eluted with another

Table 6
Effect of sampling time on recoveries from prespiked C_8 disks

Sampling time (h)	Spike (ng)	TWA level	Average recovery for HN-1 (%) ($n=2$)	Average recovery for HN-3 (%) ($n=2$)
0	30.0	0.8	86 ($n=1$)	105 ($n=1$)
2	3.6	0.2	75±1	103±1
2	18.0	1.0	69±4	85±6
4	7.2	0.2	62±3	72±4
4	36.0	1.0	62±1	73±2
6	10.8	0.2	66±3	77±5
6	54.0	1.0	60±3	68±1

0.250 ml of ethyl acetate two more times each (total of 0.750 ml). The percent recoveries were calculated for each 0.250-ml extract. For HN-1, the average recoveries were 69, 11 and 3% for the three extractions. The recoveries for HN-3 were 75, 12 and 3% for the three successive extractions. The results show that the elution volume needed to be increased.

For all spike and recovery studies conducted, recoveries were calculated from a calibration curve with a minimum of five points and a correlation coefficient of 0.99 or greater. The concentration of standards was chosen such that the response of all the samples fell into the range of concentrations covered by the standards.

Pre- and post-spike experiments indicate that C_8 disks are effective for trapping of HN-1 and HN-3 from air samples. The method is unaffected by humidity and flow-rate. Validation of the method is accomplished by Class 1 and 2 precision and accuracy studies.

3.4. C_8 SPE disk method validation

For the Class 2 precision and accuracy study, duplicate C_8 disks were spiked at each level for two consecutive days. The disks were extracted with 250 μl of ethyl acetate and analyzed. The resulting trendlines are plotted in Figs. 4 and 5 for HN-1 and

HN-3, respectively. The FAL for HN-1 was found to be 0.69 and the FAL for HN-3 was 0.69. A complete pass/fail examination of the HN-1 and HN-3 data is shown in Table 7. The C_8 disk method meets the criteria for the Class 2 validation for the near real time confirmation method.

For the Class 1 precision and accuracy study, duplicate C_8 disks were spiked at each level for four consecutive days. The disks were extracted with 750 μl ethyl acetate and analyzed. The results of the Certify analysis of the data are shown in Table 8. Typical chromatograms for this analysis is shown in Fig. 6. All three criteria, FAL>LOQ, UIFM <25%, and overall recovery>75%, were met for both HN-1 and HN-3 indicating a successful completion of a Class 1 P&A study. Although solid-phase extraction disks have not been utilized in the past for air monitoring of CW materials, this method does have advantages over conventional DAAMS technology for the detection of HN-1 and HN-3 from air. This method is not affected by changes in humidity as is the DAAMS method. The final sample analyzed is a liquid, therefore multiple or repeat injections can be made if an instrumental problem arises. DAAMS tubes can only be desorbed once. The use of GC–MS in the selected ion mode for analysis also adds an extra level of confidence as ion ratios can be compared to standard values for the two agents.
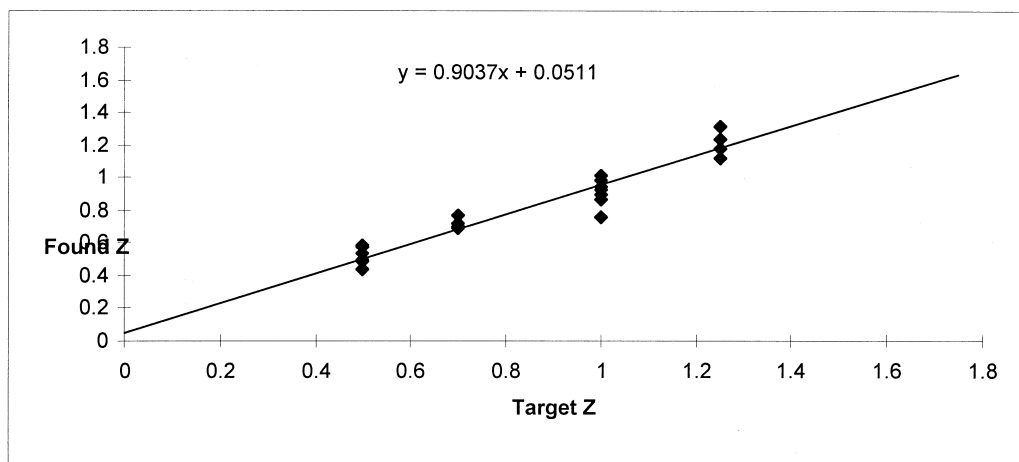

Fig. 4. Trendline plot of found Z vs. target Z for HN-1, C_8 disk, class 2 P&A. Z=level at which the CW agent was spiked. Z=2.70 ng (1 TWA) for near real time confirmation method.
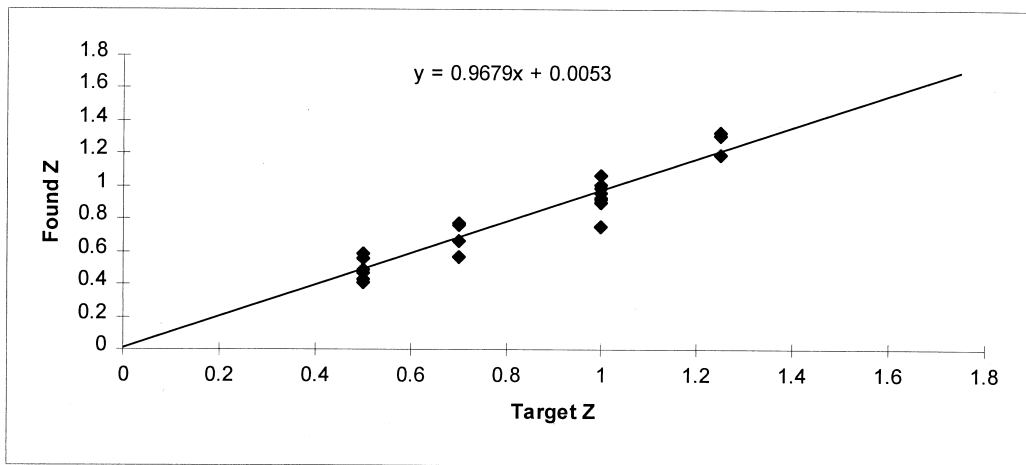
Fig. 5. Trendline plot of found Z vs. target Z for HN-3, C_8 disk, class 2 P&A. Z=level at which the CW agent was spiked. Z=2.70 ng (1 TWA) for near real time confirmation method.

Table 7
Pass/fail results for HN-1 and HN-3 in class 2 P&A test

Target Z	HN-1				HN-3			
	Day 1		Day 2		Day 1		Day 2	
	Found Z[a]	P/F[b]	Found Z	P/F	Found Z	P/F	Found Z	P/F
0.5	0.44	P	0.49	P	0.43	P	0.49	P
0.5	0.54	P	0.44	P	0.56	P	0.43	P
0.5	0.50	P	0.57	P	0.47	P	0.59	P
0.5	0.44	P	0.58	P	0.41	P	0.59	P
1.0	0.90	P	0.92	P	0.92	P	0.96	P
1.0	0.98	P	0.87	P	0.99	P	0.90	P
1.0	1.01	P	0.76	P	1.01	P	0.75	P
1.0	0.94	P	1.01	P	0.93	P	1.07	P
1.25	1.31	P	1.24	P	1.33	P	1.31	P
1.25	1.12	P	1.18	P	1.19	P	1.19	P

[a] Z=Level at which the CW agent was spiked. Z=2.70 ng (1 TWA) for near real time confirmation method.
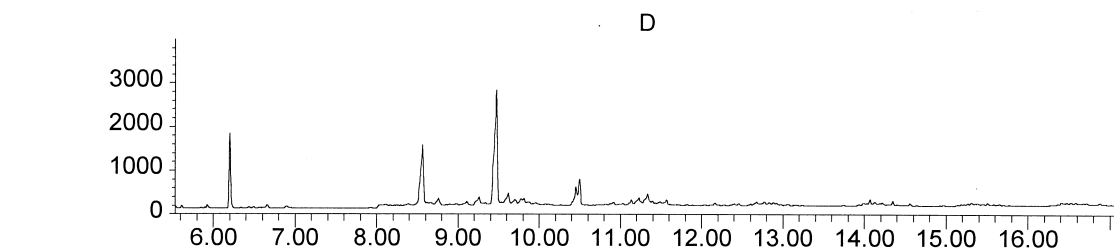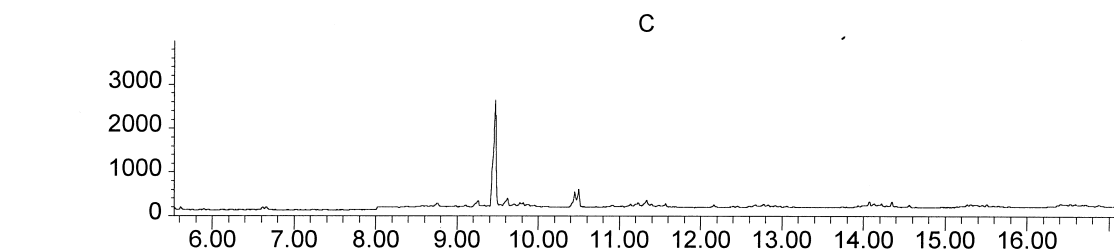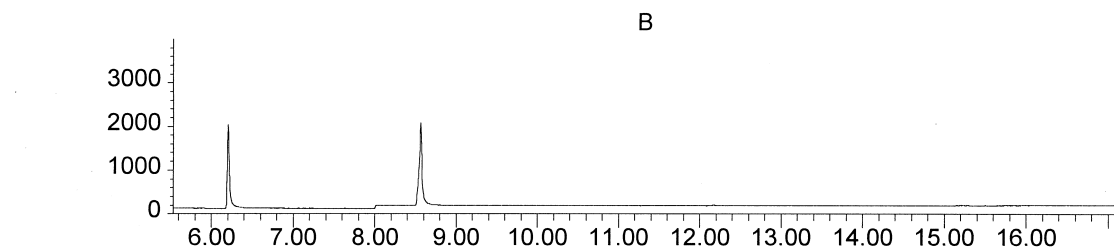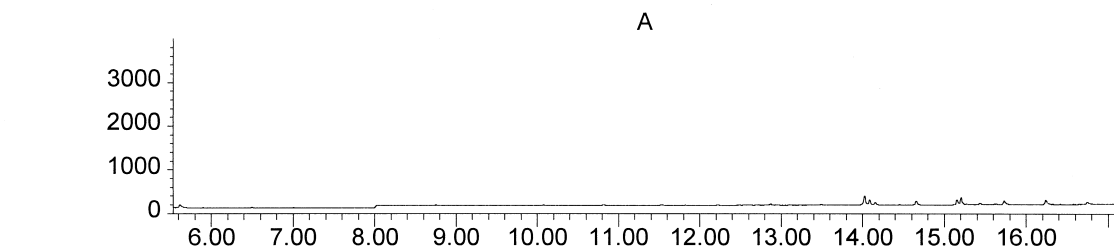[b] P/F=pass or fails criteria for class 2 P&A.

Table 8
Certify results

Agent	Found action level (TWA[a])	Limit of quantification (TWA)	Overall recovery (%)	Uncertainty in found mass (%)
HN-1	0.589	0.0538	85.3	24.4
HN-3	0.638	0.0266	89.9	23.4

[a] TWA, Level at which the CW agent was spiked. 1 TWA=108 ng for historical method.

Fig. 6. GC–MS electron-impact selected-ion mode chromatograms of (A) ethyl acetate blank, (B) 100 ng/ml standard of HN-1 and HN-3, (C) ethyl acetate extract of an unspiked C_8 disk and (D) ethyl acetate extract of a C_8 disk prespiked with 50 ng of HN-1 and HN-3 ($\approx$70 ng/ml). Tubes run at 100 ml/min for 6 h. HN-1, t_R=6.2 min; HN-3, t_R=8.55 min. Time scales in min.

4. Conclusions

This study shows the results of method development and validation for two separate methods for the analysis of the chemical agents HN-1 and HN-3 in air samples. The DAAMS tube and C_8 disk methods both meet the requirements for near real time confirmation methods for air monitoring. The DAAMS method uses well-established methodology for this type of analysis and requires no sample preparation. The C_8 disk method requires elution of the C_8 disk prior to analysis, but offers the advantage of repeat analysis. For longer term historical monitoring, the DAAMS method fails to meet the requisite criteria. This is most likely due to hydrolysis of the agents on the tube. The C_8 disk method meets the criteria for historical monitoring and appears not to be affected by humidity.

Acknowledgements

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