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COMPARISON OF BUBBLER VERSUS SORBENT TUBE SAMPLING FOR THE ANALYSIS OF GB (SARIN) VAPOR FOR INHALATION TOXICOLOGY

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Previous GB (sarin) inhalation studies have typically used solvent bubblers to determine vapor concentrations, particularly at lethal exposure levels. However, investigations for future low-level GB exposures necessitate the need for a sampling system more sensitive than bubblers. To meet this requirement, an automated sorbent tube/thermal desorption system was tested and validated against sample bubblers. Data was obtained during an existing GB inhalation exposure study with vapor concentrations ranging from 2 to 7 mg/m^3 GB. Samples from both techniques were drawn from the same inhalation chamber and quantitatively analyzed by gas chromatography for GB vapor. Concentrations derived from each sampling method were compared against each other and statistically evaluated. A paired t-test of the data showed no statistical difference between the two methods at the 95% confidence interval. Future applications of the sorbent tube sampler would include monitoring GB levels approaching the TLV-TWA of 0.0001 mg/m^3.

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PREFACE

The work described in this report was authorized under Project No. 201500, Low Level Toxicology. This work was started in February 1999 and completed in December 1999. The experimental data are recorded in laboratory notebooks 99-0021 and 99-0102. The storage location for all the raw data and final report are in the Toxicology Archives, Building E-3150.

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QUALITY ASSURANCE

This study, conducted as described in the report titled "Comparison of Bubbler Versus Sorbent Tube Sampling for the Analysis of GB (Sarin) Vapor for Inhalation Toxicology", was examined for compliance with Good Laboratory Practices as published by the U. S. Environmental Protection Agency in 40 CFR Part 792 (effective 17 Aug 1989). The dates of all inspections and the dates the results of those inspections were reported to the Study Director and management were as follows:

Phase Inspected	Date	Date Reported
Data and Final Report	25 Jun 01	25 Jun 01

To the best of my knowledge, the methods described were the methods followed during the study. The report was determined to be an accurate reflection of the raw data obtained.

DENNIS W. JOHNSON 25 Jun 01
Quality Assurance Coordinator
Research and Technology Directorate

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COMPARISON OF BUBBLER VERSUS SORBENT TUBE SAMPLING FOR THE ANALYSIS OF GB (SARIN) VAPOR FOR INHALATION TOXICOLOGY

1. INTRODUCTION

Sampling for organic vapors in air has traditionally been performed using solvent bubblers. In this methodology, organic vapors are typically drawn through a glass collection tube or "bubbler" containing an appropriate solvent.[1] The dissolution of the organic vapor with the solvent traps the vapor within the bubbler. Once sampling is completed, the solvent containing the absorbed organic is diluted to a known volume and quantitated, typically through gas chromatographic analysis. Problems with bubbler usage include handling, dilution of analyte, time consumption, and sample flow rate correction due to solvent evaporation.

Using a solid sorbent tube sampler followed by thermal desorption has become a more recently accepted methodology for analyzing organic vapors in air. This technology has provided near real-time monitoring for occupational exposure to chemical warfare agents since 1992.[2] A solid absorbent, such as Tenax TA, is packed into a small glass sampling tube. As the test atmosphere is sampled through the tube, organic vapors are adsorbed onto the resin. At the completion of sampling, the trapped organics are thermally desorbed directly onto a gas chromatograph (GC) for quantitation. Advantages of this method over bubblers include higher sampling flow, easy use, automation, no solvent dilution, and increased sensitivity.

Previous inhalation studies (Cullumbine et al.,[3] Barrett,[4] and Callaway and Blackburn[5]) have traditionally used bubblers to quantitate for GB vapor to establish lethality (LCt_{50}) on different animal species. A recent study by Mioduszewski et al.[6] has repeated some of these previous GB vapor concentrations but varied exposure time to determine whether Haber's Rule (Concentration x Time = Constant) applies in predicting GB lethality. To compare previous GB toxicity studies with the Mioduszewksi study,[6] bubbler samples were drawn to determine the chamber concentration. At the same time, an automated solid-sorbent tube system sampled the chamber concurrently with the bubblers. A statistical comparison of the data from the two sampling methods was conducted. A favorable comparison between the two sampling techniques would place increased confidence on the sorbent tube methodology, particularly when conducting future GB vapor toxicity studies below the practical limits for bubbler sampling.

2. MATERIALS AND METHODS

2.1 Chemicals.

Chemical agent standard analytical reagent material (CASARM)-grade sarin (GB) (lot # GB-U-6814-CTF-N (GB2035) was verified as 97.2 $\pm$ 0.2 wt % (as determined by quantitative NMR ^{31}P) in samples obtained from the U.S. Army Edgewood Chemical Biological Center and stored in sealed ampules containing nitrogen. Ampules were opened as needed either

to prepare external standards or to be used as neat agent for vapor dissemination. All external standards for GB vapor quantitation were prepared on a daily basis. Triethylphosphate (99.9% purity), obtained from Aldrich Chemicals (Milwaukee, WI) was used as the internal standard for the GB purity assay via NMR.[7] Hexane (purity > 85% n-hexane and 99.9% n-hexane and isomers), purchased from Burdick & Jackson (Muskegon, MI) was used for standard preparation and bubbler collection procedures.

The majority of impurities in the CASARM GB consisted of 0.2% o,o'-diisopropyl methylphosphonate (DIMP), 0.2 % methylphosphonic difluoride (DF), 0.3% methylphosphonofluoridic acid (Fluor Acid), and 0.3% excess HF/F ion. Impurity percentages were based on mole ratios from acid-base titration.

Chemical and Physical Properties.

Among the traditional nerve agents (G-agents), GB has the highest volatility and vapor pressure. Hence, it poses the greatest inhalation hazard. Pertinent physical and chemical data for vapor exposures of GB are listed in Table 1.

Table 1. Physical and Chemical Data for GB.[8]

Chemical Name	Isopropyl methyl phosphono fluoridate
Molecular Formula	$C_4H_{10}FO_2P$
Vapor Density Relative to Air	4.8
Volatility @ 25 °C	2.2×10^4 mg/m^3
Vapor Pressure @ 25 °C	2.9 mm Hg
Boiling Point	158 °C

2.2 GB Test Atmosphere System, Overview.

GB test atmospheres were generated by dispensing liquid GB into a vapor generation system, which in turn was connected to the inlet of a dynamic flow inhalation chamber. The GB vapor was monitored in the chamber with a variety of sampling techniques, including bubbler, sorbent tube, and a continuous phosphorus analyzer (Figure 1). Concentrations derived from the bubbler and sorbent tube were compared against each other and statistically evaluated. The phosphorus analyzer was used primarily to monitor the chamber vapor profile (i.e., the rise, equilibration, and fall) of the GB vapor concentration during a chamber run. Testing and evaluation concentrations ranged from 2 to 7 mg/m^3 of GB to compare the bubbler versus the sorbent tube.

2.3 Generation System.

The generation system consisted of a syringe drive and spray atomization system located on top of the inhalation chamber (chamber inlet). The system was confined within a stainless steel generator box (23 in. long by 14 in. wide by 18 in. high), which was maintained

under negative pressure (-0.25 in. H_2O). A Plexiglas door at the front of the box allowed for syringe loading and syringe drive adjustments during set-up operations.

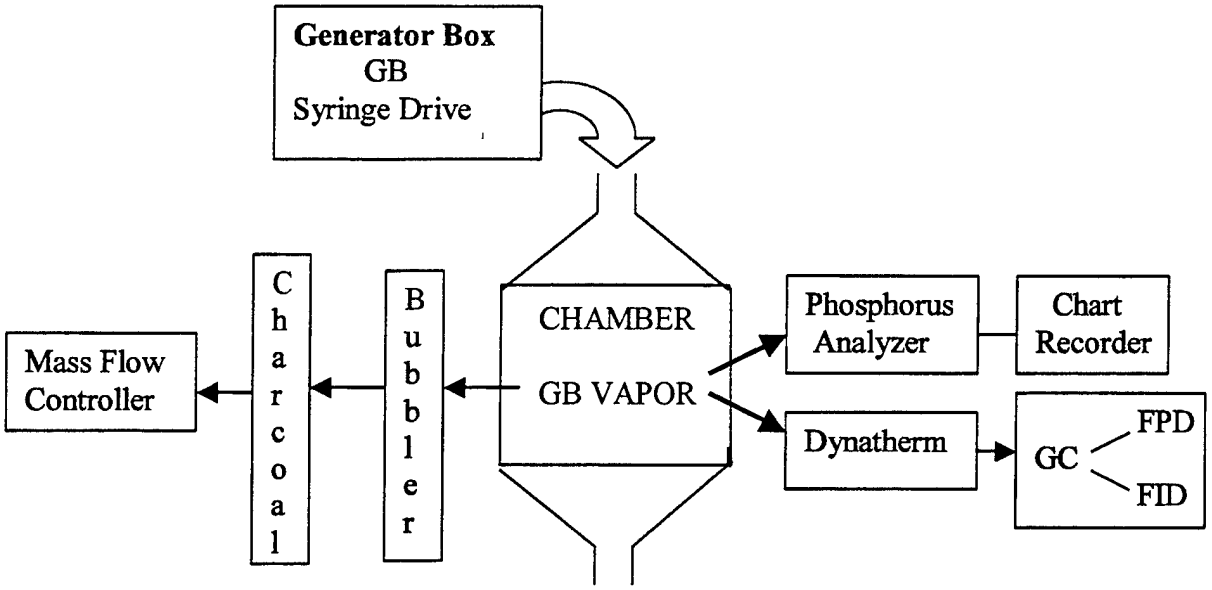

Figure 1. GB Inhalation Chamber and Monitoring Systems.

Syringe Drive/Spray Atomization System.

Prior to chamber operation, the liquid GB was drawn into a gas-tight syringe (Hamilton, Reno, NV), transported to the generator box, then mounted onto a variable rate syringe drive (Model 22, Harvard Apparatus, Incorporated, South Natick, MA). Once activated, the syringe drive delivered a constant flowrate of GB microliters per minute through a flexible plastic line (~ 8 in.) into a spray atomization system (Spray Atomization Nozzle 1/4 J SS, Spraying Systems Company, Wheaton IL) (Figure 2). The atomizer was modified by inserting a syringe needle (SS 25 gauge 3 in.) into the top of the sprayer to decrease the orifice size. As liquid GB entered through the top of the atomizer, compressed air (30-40 psi) entered through the side to atomize the liquid into fine droplets. Due to the volatility of GB, these droplets quickly evaporated into GB vapor, which was then drawn down through the chamber.

2.4 Inhalation Chamber.

The GB vapor was monitored in a 750-L dynamic airflow inhalation chamber located within a 20,000-L containment chamber. The Rochester style chamber was constructed of stainless steel with Plexiglas windows on each of the six sides. The chamber's negative pressure (-0.25 in. H_2O) was monitored with a calibrated magnehelix (Dwyer, Michigan City, IN). Chamber airflow (500 - 650 L/min) was measured at the chamber outlet with a thermo-anemometer (Model 8565, Alnor, Skokie, IL). Monitored environmental parameters included temperature and relative humidity.

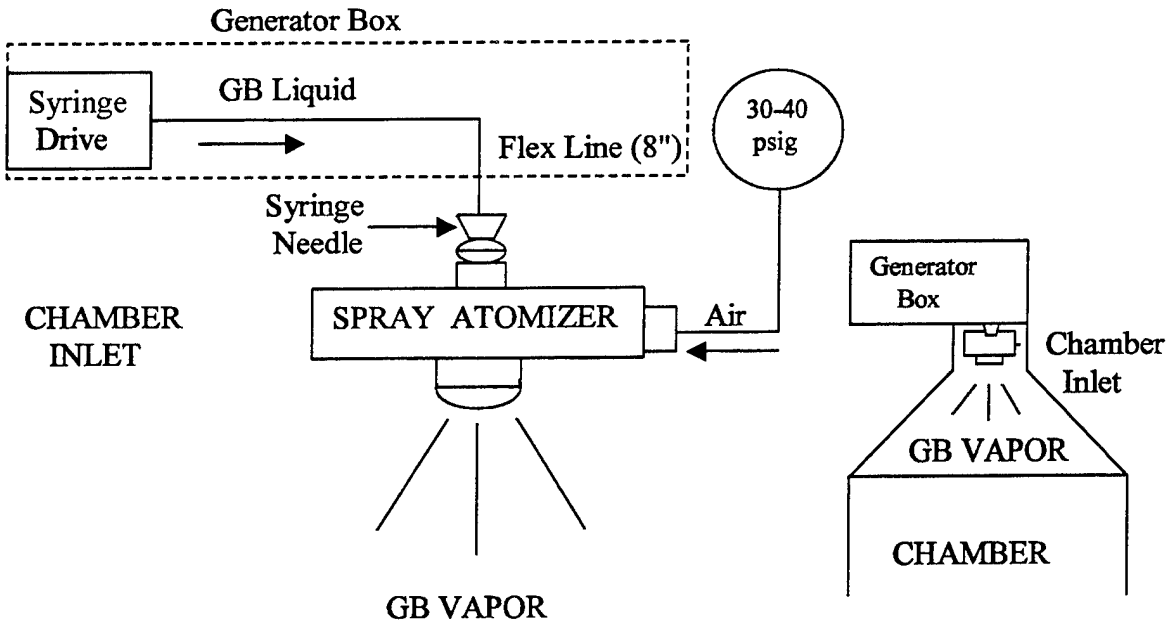

Figure 2. Spray Atomization System.

2.5 Sampling System.

A variety of sampling systems were used to monitor GB vapor in the chamber. The bubbler and sorbent tube systems were quantitative measures of GB, while the phosphorus analyzer was used primarily to follow the chamber profile.

All sample flowrates for the bubbler and sorbent tube systems were controlled with calibrated mass flow controllers (Matheson Gas Products, Montgomeryville, PA). Typical flowrates were 0.9 - 1.0 L/min for the bubblers and 100 sccm for the sorbent tubes. Due to solvent (hexane) evaporation during sampling, an in-line charcoal filter was installed between the bubbler and mass flow controller to prevent the cooling effect of the solvent from affecting the mass flow sensor. Flowrates from both systems were verified before and after sampling by temporarily connecting a calibrated flowmeter ("DryCal," Bios International, Pompton Plains, NJ) in-line to the sample stream.

2.5.1 Bubbler Sampling.

The concentration of GB in the chamber was determined by collecting chamber air samples into "Edgewood" bubblers containing hexane.[9] During sampling, chamber air was drawn through glass sample lines (0.25 in. o.d.) into paired bubblers (front and rear) at the rate of 0.9 - 1.0 L/min. The collected solvent was diluted to a known volume and injected into a GC with flame photometric detection (GC-FPD) phosphorus mode. External standards (GB/hexane) were injected into the GC-FPD to generate a calibration curve. A linear regression fit ($R^2 = 0.999$) of the standard data was used to compute for GB concentration in the chamber. Instrumental parameters for GB analysis by the GC-FPD are listed in Appendix A.

2.5.2 Sorbent Tube System.

The automated sorbent tube sampling system (Figure 3) was comprised of four parts: (1) a heated sample transfer line, (2) heated external switching valve, (3) thermal desorption unit, and (4) GC. A stainless steel sample line (1/16 in. o.d. by 0.004 in. i.d. by 6 ft length) extended from the middle of the chamber to an external sample valve. The sample line was commercially treated with a silica coating (Silicosteel® Restek, Bellefonte, PA) and covered with a heated (60 °C) sample transfer line (CMS, Birmingham, AL). The combination line coating and heating was to minimize GB adsorption onto sample surfaces. From the transfer line, the sample entered a heated (125 °C) 6-port gas-switching valve (UWP, Valco Instruments, Houston, TX). In the by-pass mode, chamber air was continuously drawn through the sample line onto a charcoal vent filter. In the sample mode, the gas sample valve would redirect the chamber air to a 10 mm Tenax TA sorbent tube located in the thermal desorption unit (ACEM-900, Dynatherm Analytical Instruments, Kelton, PA). Temperature and flow programming within the Dynatherm desorbed GB from the sorbent tube and injected the vapor directly onto the GC for quantitation. Either flame ionization detection (FID) or FPD could be used, depending upon the level of sensitivity required. Instrument parameters for the GC and the Dynatherm are listed in Appendix A. Valving positions for the switching valve and Dynaterm during various stages of sampling and transfer are illustrated in Appendix B.

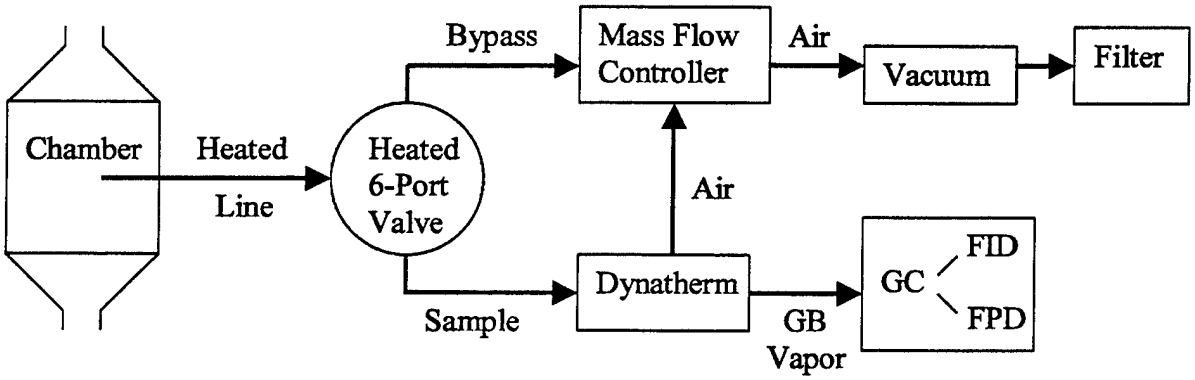

Figure 3. Automated Sorbent Sampling of GB Vapor from the Chamber.

Calibration of the sampling and analysis system was conducted by starting the Dynatherm program and injecting external standards (GB/hexane) directly into the inlet of the heated sample line. In this way, injected GB standards were put through the same sampling and analysis stream as were the chamber samples. Standards injected through the sample line as well as directly onto the sorbent tube showed comparable data and demonstrated the integrity of the sample line system. A linear regression fit ($R^2 = 0.999$) of the standard data was used to compute for GB concentration from the chamber samples.

2.5.3 Phosphorus Monitor (HYFED).

The GB levels in the chamber were continuously monitored with a phosphorus analyzer (HYFED, Model PH262, Columbia Scientific, Austin, TX). The analyzer output was recorded on a strip chart recorder, which showed the rise, equilibrium, and decay of the chamber vapor concentration during each experimental run. In addition, it gave a close approximation of the amount of GB milligram per cubic meter in the chamber based on data (bubbler and sorbent tube quantitation with HYFED response) from previous chamber runs.

2.6 Chamber Runs for Bubbler and Sorbent Tube Comparison.

Ten separate chamber runs were conducted to make the bubbler and sorbent tube comparison. Samples were drawn at different chamber concentrations ranging from 2 to 7 mg/m^3 of GB. All samples were drawn from the middle of the chamber. Bubbler and sorbent tube samples were drawn after the chamber attained equilibration (t_{99}), while the HYFED monitored the entire run. Two separate sets of bubblers ran concurrently during each sample collection period, while each sorbent tube represented a single measurement. Frequency of sampling for the bubblers was approximately every 20 min for each 60 min run, every 60 min for each 240 min run, and every 90 min for each 360 min run. Each bubbler sampling collection period lasted from 8-12 min. Sorbent tube samples were drawn from the chamber approximately every 10-15 min with each sample draw lasting 2-3 min. Appendix C illustrates an experimental 1-hr chamber run monitored via the HYFED with sampling intervals indicated for the bubblers and sorbent tubes.

3. RESULTS

Bubbler and Sorbent Tube Comparison.

Seventy-five bubbler samples and 145 sorbent tube samples were collected throughout the 10 chamber runs. The mean GB vapor concentration from each sampling method was determined for each run (Table 2). The mean values from each set of runs (60 min, 240 min, and 360 min) were computed and compared against each other using a paired t-test (Table 3). Results showed that the difference of the means between the two techniques was well within the computed 95% confidence interval. Thus, there were no significant differences between the means for the two sampling methods.

Table 2. Mean and Variance of GB Vapor Concentrations (mg/m^3) from Bubbler and Sorbent Tubes Obtained During Chamber Runs.

60 Min Chamber Runs	(N)	Bubbler	Sorbent Tube	(N)
1	(4)	5.91 ± 0.23	6.00 ± 0.12	(5)
2	(4)	6.95 ± 0.29	6.98 ± 0.23	(5)
3	(4)	6.55 ± 0.34	6.37 ± 0.16	(5)
240 Min Chamber Runs	**(N)**	**Bubbler**	**Sorbent Tube**	**(N)**
4	(8)	2.12 ± 0.08	2.04 ± 0.04	(12)
5	(8)	3.28 ± 0.09	3.26 ± 0.05	(16)
6	(8)	4.79 ± 0.13	4.87 ± 0.08	(15)
7	(7)	2.64 ± 0.08	2.81 ± 0.10	(15)
360 Min Chamber Runs	**(N)**	**Bubbler**	**Sorbent Tube**	**(N)**
8	(8)	2.99 ± 0.10	2.99 ± 0.09	(25)
9	(8)	2.76 ± 0.19	2.66 ± 0.08	(24)
10	(8)	2.78 ± 0.10	2.77 ± 0.09	(23)

N = number of samples

Table 3. Paired T-Test* of Mean GB Concentrations (mg/m^3) Obtained from each Set of Chamber Runs (Bubbler Versus Sorbent Tube Samples).

Chamber Run Time	(N)	Bubbler	Sorbent Tube	Difference of Means	95% Confidence Interval
60 Min	3	6.47 ± 0.50	6.45 ± 0.53	-0.02	(-0.37 - 0.33)
240 Min	4	3.21 ± 1.16	3.25 ± 1.20	-0.04	(-0.14 - 0.21)
360 Min	3	2.84 ± 0.13	2.81 ± 0.17	0.03	(-0.37 - 0.33)

*All data was normally distributed with no statistically significant difference between the two sampling methods. Ho = 0.

N = Number of chamber runs per chamber run time (60, 240, and 360 min).

4. DISCUSSION

4.1 Sampling Systems.

Traditionally, discrete sampling for GB vapor has been accomplished using bubblers. Herd *et al.*[9] and Bartram *et al.*[10] have evaluated the sampling efficiency of bubblers and impingers to monitor GB vapors. Although labor intensive, bubblers have provided a reliable method for the quantitation of GB vapor. Unfortunately, as the GB vapor concentration decreases, the length of sampling time significantly increases. Drawbacks to extended sampling times include increased risk of analyte loss due to evaporation, hydrolysis, and breakthrough. In addition, the number of samples drawn during an exposure are significantly reduced. An

automated solid sorbent system was introduced to offset these drawbacks, especially for use at lower (< 2.0 mg/m^3) GB concentrations. A comparison of GB concentrations between the bubblers and the sorbent tubes confirmed the performance of the automated approach. A table summary of the advantages and disadvantages of each of the two sampling systems is listed in Appendix D.

Bubblers were sampled at their maximum flowrate (0.9 - 1 L/min) to decrease sampling time (typically 12 min for a GB concentration of 2.0 mg/m^3). The drawback to this flowrate was an increased amount of hexane evaporation during sampling. Consequently, this resulted in an increased amount of sample breakthrough from the front to the rear bubbler.

Although bubblers can be drawn almost indefinitely, the lower practical limit for bubblers sampling GB in the chamber would probably fall within the range of 0.5 to 2.0 mg/m^3. Below that range, problems associated with extended sampling times (hydrolysis, breakthrough, sample throughput, solvent evaporation, and flow rate adjustments) would occur, which might increase error.

Although solid sample tube collection is not a new technology, difficulties may arise when (1) attempting to provide a continuous deactivated sampling system, and (2) quantitating a sample from an automated system. Samples such as GB have a tendency to adsorb onto active metal surfaces. For example, Trurnit *et al.*[11] reported on the adsorption of GB on the chamber walls. For this reason, a combination of sample line deactivation (silicosteel®) and uniform heating (heated transfer line) were essential to ensure the recovery of the vapor. In addition, the transference of vapor from a chamber atmosphere to an analytical instrument must follow the ideal gas law ($PV = nrt$). In other words, for gas sample loop operation, the effects of pressure and temperature that the vapor undergoes during transference must be considered for proper quantitation. In this technique, the flow of GB vapor through the continuous flow sample line was simply diverted to the sorbent tube. Thus, integration of a switching valve with the controlled mass flow meter eliminated potential gas sample loop problems and provided an accurate sample volume.

Future work to detect "low level" GB (< 0.1 - 0.0001 mg/m^3) would include sampling at significantly higher flow rates (2 L/min) and sampling times to increase loading on the Tenax TA. In addition, connection to a GC-FPD detector would increase sensitivity by 2 - 3 orders of magnitude compared to the FID.

4.2 Bubbler and Sorbent Tube Statistical Comparison.

The paired t-test was used to compare the two sampling methods conducted on one sample (GB vapor). In this case, the paired t-test compared the difference between the means of each of the two sampling methods for chamber runs conducted at 60, 240, and 360 min. The null hypothesis (Ho) was that the difference between the two methods equaled zero. Results of the paired t-test failed to reject Ho and concluded that there was no significant difference between the two methods, $p>0.05$.

5. CONCLUSIONS

The automated sorbent tube approach provided a rapid, sensitive methodology for the sampling and quantitation of GB vapor. The system demonstrated an inert sample pathway for continuous sampling from the chamber. A statistical comparison of the bubbler and sorbent tube methods showed that no significant difference existed between the two methods. This study verifies the performance of the Dynatherm-gas chromatograph sampling and analysis system for future "low-level" GB studies.

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LITERATURE CITED

1. Levaggi, D.A., "Sampling and Storage of Gases and Vapors," In *Methods of Air Sampling and Analysis,* 3rd ed., Lodge, J.P., Ed.; Lewis Publishers, Incorporated, Chelsea, MI, 1989.

2. Abrams, W.C., and Albro, T.G., "Chemical Warfare Agents – Breakdown Products and Precursor Analysis," UNCLASSIFIED Conference Paper, In *Proceedings of the ERDEC Scientific Conference on Chemical Defense Research*, ERDEC SP-024, pp 203-209, U.S. Army Edgewood Research, Development and Engineering Center, Aberdeen Proving Ground, MD, November 1993, UNCLASSIFIED Report (AD-E479 749).

3. Cullumbine, H., and Callaway, S., *The Inhalation Toxicity of GB to Rats, Sheep, Monkeys and Guinea Pigs*, Porton Technical Paper No. 495, Chemical Defence Experimental Establishment, Porton Down, England, July 1955, UNCLASSIFIED Paper (AD-072 014).

4. Barrett, H.M., *Studies on the LCt_{50} of Nerve Gas Vapour in the Rat and the Mouse*, Porton Technical Paper No. 2756, Porton Down, England, 1951, UNCLASSIFIED Paper.

5. Callaway, S., and Blackburn, J.W., *A Comparative Assessment of the Vapour Toxicities of GB, GD, GF, T.2132, T.2137 and T.2146 to Male and Female Rats*, Porton Technical Paper No. 404, Chemical Defence Experimental Establishment, Porton Down, England, February 1954, UNCLASSIFIED Paper (AD-031 119).

6. Mioduszewski, R.J., Manthei, J., Way, R., Burnett, D, Gaviola, B., Muse, W., Anthony, J., Durst, H., Thomson, S., Crouse, C., Crouse, L., Sommerville, D., and Crosier, R., *Estimating Probability of Sarin (GB) Vapor Toxicity in Rats as a Function of Exposure Concentration and Duration,* Presented at the 2000 International Chemical Weapons Demilitarisation Conference, May 22-24, The Hague, Netherlands, 2000.

7. Brickhouse, M.D., Rees, M.S., O'Connor, R.J., and Durst, H.D., *Nuclear Magnetic Resonance (NMR) Analysis of Chemical Agents and Reaction Masses Produced by their Chemical Neutralization*, ERDEC-TR-449, U.S. Army Edgewood Research, Development and Engineering Center, Aberdeen Proving Ground, MD, December 1997, UNCLASSIFIED Report (AD-A339 308).

8. *Chemical Agent Data Sheets*, Vol. 1, EA-SR 74001, Edgewood Arsenal, Aberdeen Proving Ground, MD, December 1974, UNCLASSIFIED Data Sheets (AD-B028 222).

9. Herd, R.E., Bouck, J., Kolakowski, J.E., Miskelly, P.R., and Norris, G. *Evaluation of the Sampling Efficiency of Beaded Glass Bubblers for Monitoring Isopropylmethyl Phosphonofluoridate (GB) Emissions in Air*, ARCSL-TR-82027, U.S. Army Chemical Systems Laboratory, Aberdeen Proving Ground, MD, May 1983, UNCLASSIFIED Report, (AD-B074 693).

10. Bartram, P.W., and Meyers, M.B., *The Efficiency of Scrubbing CW (Chemical Warfare) Agent Vapors in Impingers*, CRDEC-TR-88162, U.S. Army Chemical Research, Development and Engineering Center, Aberdeen Proving Ground, MD, August 1988, UNCLASSIFIED Report (AD-B126 273).

11. Trurnit, H.J., Bales, P.D., Esposito, E.J., and Horowitz, P., *Comparative Study of GB Inhalation Toxicity on Mice, Rats, Guinea Pigs, Cats, Dogs and Monkeys with Exposure Times Between One Second and Several Minutes*, MLRR-205, U.S. Army Chemical Center, Edgewood Arsenal, MD, August 1953, UNCLASSIFIED Report (AD-026 592).

APPENDIX A

GC PARAMETERS FOR GB ANALYSIS

GC/FPD Operation for Bubblers

Gas chromatograph	Hewlett Packard 6890
Capillary column	DB-5, 30 m x 0.53 mm i.d., x 1.5 mm film thickness
Injection volume	2 μL
Column flow (He)	13.1 mL/min (velocity 84 cm/s) (head pres = 9.0 psi)
Septum purge (He)	15 mL/min (9.0 psi)
Detector flow (FPD)	110 mL/min (air); 150 mL/min (hydrogen)
Detector temp (FPD)	250 °C
Injector temp	200 °C
Injection mode	Splitless, Single taper liner (HP part no. 5181-3316)
Inlet Purge	Off Time: 0.00 min; On Time: 0.50 min
Col temperature program	60 °C (hold 1 min) to 100 °C @ 25 °/min (run time: 4 min)

GC/FID Operation for Dynatherm

Same Chromatographic Parameters as above except:

Detector flow (FID)	400 mL/min (air); 30 mL/min (hydrogen)
Detector temp (FID)	250 °C

Instrumental Parameters for Thermal Desorption

Model: Dynatherm (ACEM 900)

Temperature/Flow Program:

Tube Desorb	275 °C	Tube Heat	3 min
Transfer Line	150 °C	Trap Heat	1 min
Trap Desorb	300 °C	Tube Dry	1 min
		Tube Cool	1 min
Purge Flow	5 mL/min (He)		
Solid Sorbent	Tenax TA (11.5 cm x 6 mm o.d.)		

Sample Time:

External Sample	External Standard Calibration through sample line	5-7 min
	External Standard Calibration directly on sorbent tube	0 min
	Chamber Sample	2-3 min

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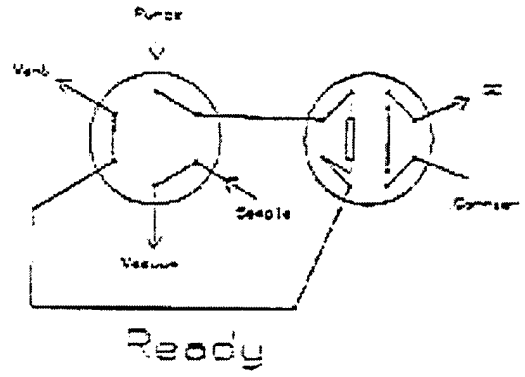
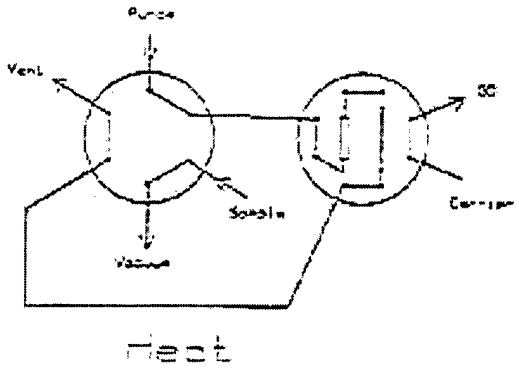
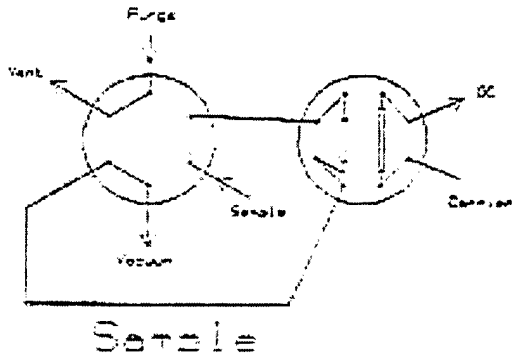
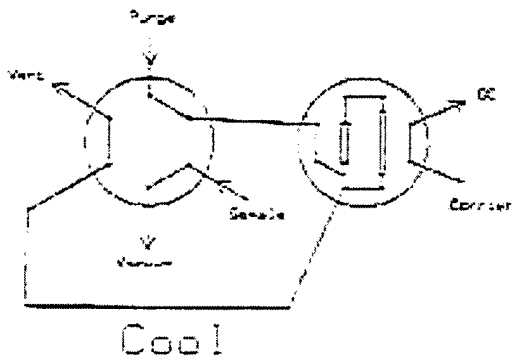
APPENDIX B

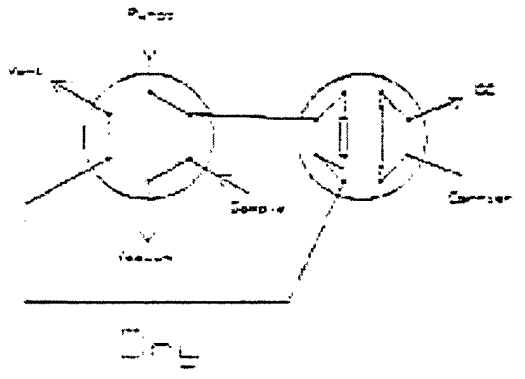
VALVING POSITIONS FOR SAMPLE SWITCHING VALVE AND DYNATHERM

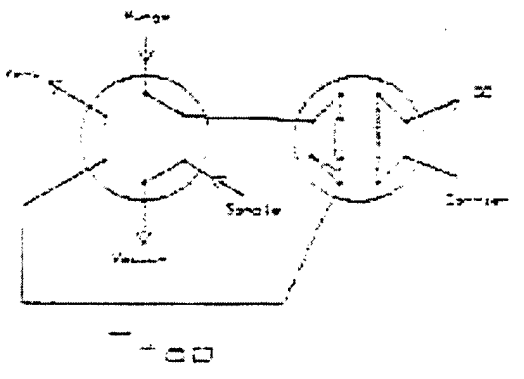












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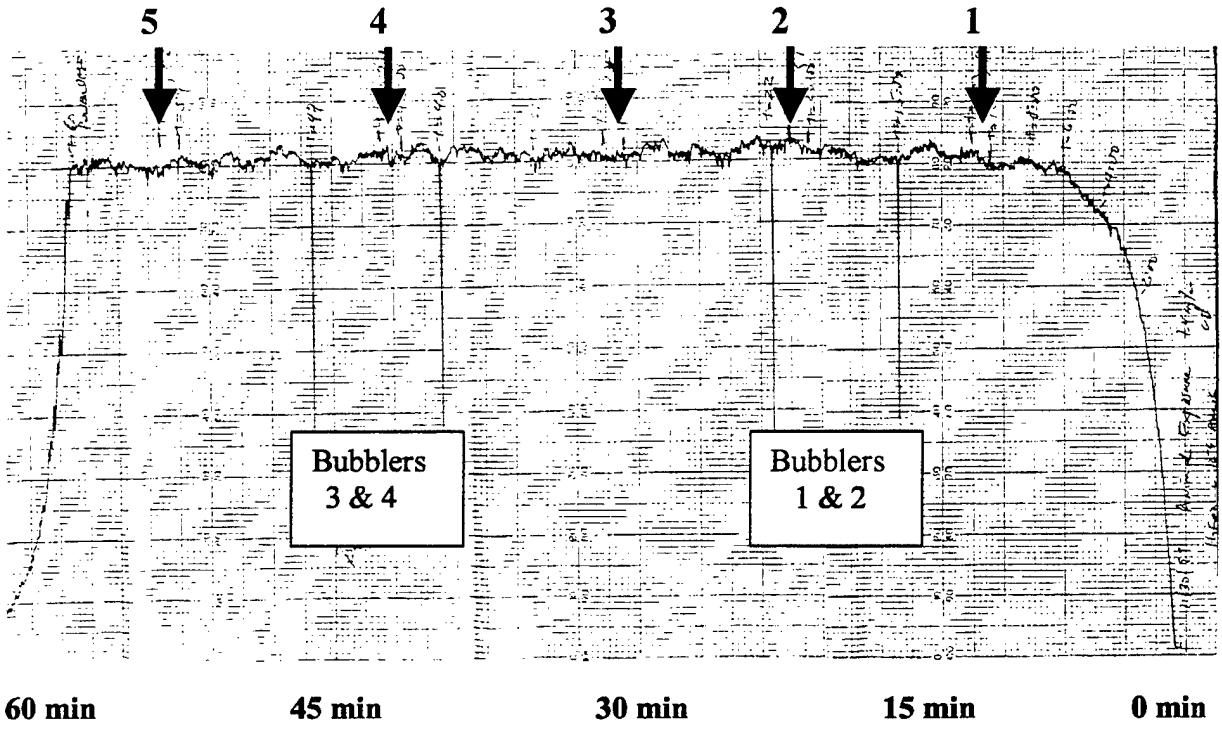
APPENDIX C

HYFED PROFILE FOR GB VAPOR IN AN INHALATION CHAMBER WITH CONCURRENT DYNATHERM AND BUBBLER SAMPLES

Dynatherm Samples (1 – 5)



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APPENDIX D

ADVANTAGES AND DISADVANTAGES OF BUBBLER VERSUS SORBENT TUBE SAMPLING

BUBBLERS

Advantages	Disadvantages
1. Reliable method.	1. Labor intensive (set-up, sample manipulation connections, and leak check.
2. Many previous studies have used bubblers, therefore, providing a basis for comparison studies.	2. Requires front and back bubblers to prevent significant analyte (GB) breakthrough.
	3. Extended sampling draws water into the bubbler solution, which may affect the analyte over time.
	4. Cannot automate.
	5. Lower GB concentrations require extended sampling times (iced), which limits the number of samples taken during a run.

SORBENT SAMPLING

Advantages	Disadvantages
1. Continuous sample line from the chamber to the GC. Less chance for leaks or errors.	1. Dust particles in sample line may act as absorption sites. May require sample line deactivation (inject dilute GB) prior to calibration.
2. Not labor intensive (same sorbent tube can be reused, no reconnections or sample manipulations).	
3. System can be easily automated.	
4. Samples can be drawn frequently.	
5. Water vapor does not collect in the sorbent tube.	
6. Larger dynamic range and more sensitive.	
7. Amount of Tenax TA in one tube prevents GB breakthrough.	