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ARSENIC TRICHLORIDE FILTRATION PERFORMANCE WITH THE IMPREGNATED CARBON ASZMT

John J. Mahle

RESEARCH AND TECHNOLOGY DIRECTORATE

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14. ABSTRACT

The vapor filtration of $AsCl_3$ by the adsorbent ASZMT is examined in this report. Microscale testing is performed, with analysis of the concentration by FTIR. The effect of humidity on $AsCl_3$ stability and filtration performance is considered. Large adsorption capacity is determined, approximately 4 mol/kg, by calculating a mass balance from the measured breakthrough results. Hydrochloric acid breaks through prior to $AsCl_3$ under humid conditions.

15. SUBJECT TERMS

Arsenic trichloride	Hydrogen chloride	ASZMT
Filtration	Adsorption	Chemical Agent Filtration System (CAFS)

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PREFACE

This work was started in November 2010 and completed in March 2011.

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ARSENIC TRICHLORIDE FILTRATION PERFORMANCE WITH THE IMPREGNATED CARBON ASZMT

1. INTRODUCTION

In an earlier report, an engineering analysis of arsenic trichloride ($AsCl_3$) filtration at the Spring Valley site was presented,[1] where it was proposed that adequate protection is offered by the Chemical Agent Filtration System (CAFS). A more definitive resolution to this question would be provided by measurement of the vapor filtration of $AsCl_3$, a commercially available material. This report describes these measurements. The adsorbent used in CAFS is the military adsorbent, ASZMT (Calgon Corp., Pittsburgh, PA), which provides broad spectrum vapor filtration protection. ASZMT is an activated carbon treated with a metal-salt formulation that reacts with acid gases; $AsCl_3$ is known to hydrolyze forming hydrochloric acid (HCl). It is also reported that $AsCl_3$ is soluble in water to a ratio of 1:9.[2] At low dilution, $AsCl_3$ hydrolyzes to form the non-volatile precipitate As_2O_3. The hydrolysis intermediate arsenous acid ($As(OH)_3$) has been identified in solution but never isolated. To measure adsorption filtration of $AsCl_3$, two issues must be resolved. First, a detection technique must be developed; and then, the vapor phase stability of $AsCl_3$ must be determined. Earlier work had shown that HCl is effectively filtered by ASZMT so by analogy, $AsCl_3$ filtration is anticipated.

The adsorption filtration performance of toxic industrial chemicals is usually performed by challenging a fixed concentration to a glass tube packed with adsorbent using the same velocity and bed depth conditions as the actual filter. The eluting stream concentration is monitored until an endpoint concentration is recorded, which usually corresponds to a toxic threshold concentration. The results are reported in terms of the challenge dose that is delivered at a given set of conditions.

The possible paths for $AsCl_3$ and water interaction are listed in the schematic (Figure 1). In the top scheme, no water interaction occurs. In the center scheme, $AsCl_3$ and water coalesce to create fumes where high $AsCl_3$ and water concentrations can lead to condensation of one or both species. In the bottom scheme, $AsCl_3$ is shown to go into a liquid water phase where it either exists in a soluble or hydrolyzed form. Starting with dry conditions, FTIR spectra will be compared at different relative humidity (RH) levels. If during testing in the presence of humidity, the vapor phase $AsCl_3$ spectra change, or quantity of $AsCl_3$ changes with RH, then aerosols are likely being formed. If aerosol formation is suspected, it could be examined by a particle counter to quantify the aerosol content.

The adsorption of $AsCl_3$ on activated carbon at dry conditions is expected to be favorable because of its high boiling point 130 °C, see Table 1. In the presence of humidity, significant adsorbed water is also present. For high volatility vapors, this adsorbed water can have complex effects of competitive adsorption and chemical reaction. However, for moderate volatility vapors such as $AsCl_3$, the adsorber vapor generally displaces water. If hydrolysis of $AsCl_3$ occurs with adsorbed water, the HCl formed in the adsorbed solution should readily react with the impregnants, for which a large adsorption capacity of ASZMT for HCl has previously been quantified. No HCl would be expected to be generated from the adsorbent.

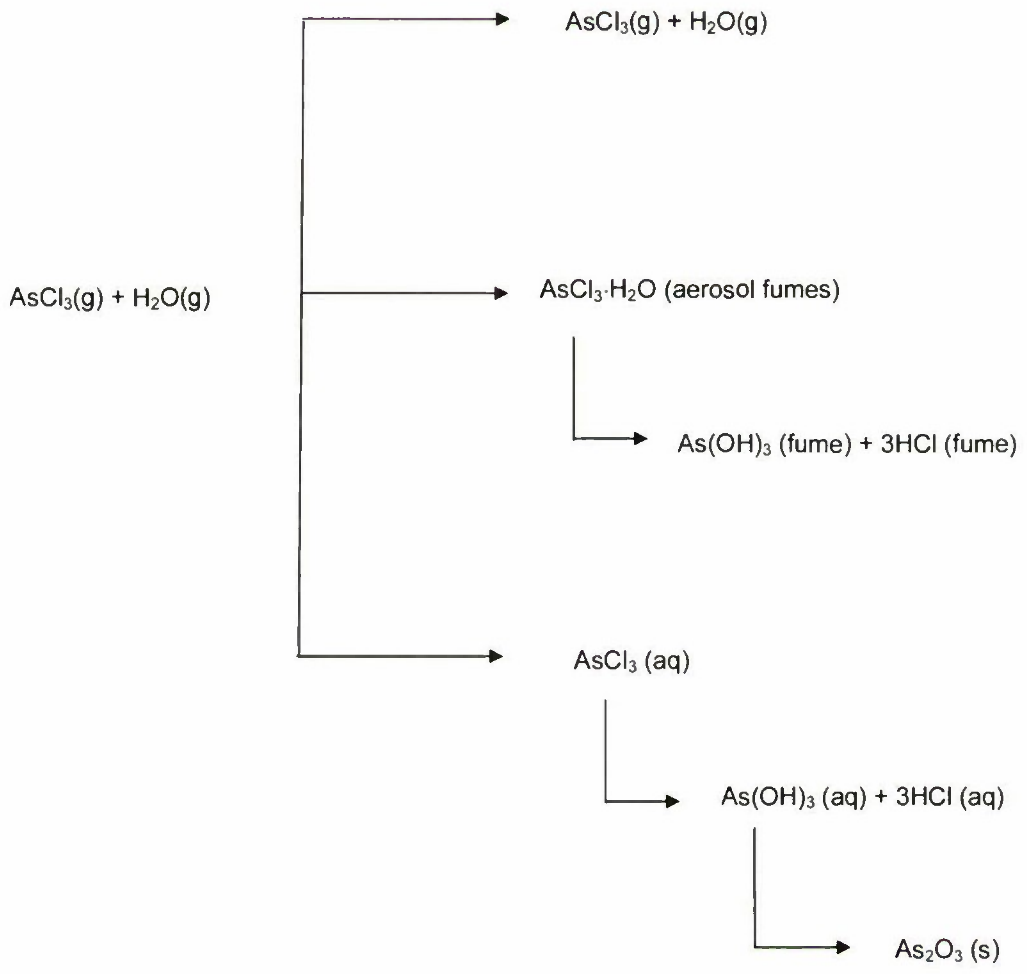


Figure 1. $AsCl_3$ Hydrolysis Scheme.

Table 1. $AsCl_3$ Physical Properties.

Property	Value
Boiling Point (°C)	130.2
Vapor Pressure (kPa 20 °C)	1.17
Molecular Weight	181.2
Liquid Density (g/cm^3)	2.1

Using a small scale adsorbent test system, the use of the FTIR will be assessed first at dry conditions and then as a function of humidity. Details of this method have been reported.[3] Most likely at some humidity, $AsCl_3$ and HCl will coalesce with water to form droplets that are retained on the walls of the system and no HCl product is observed in the FTIR. A capacity test will be performed for ASZMT with $AsCl_3$ at any feasible conditions.

Two types of microtesting were considered. In the first, a closed loop apparatus was used to monitor the vapor composition of $AsCl_3$ and water mixtures. If the results of Phase 1 identify some conditions where $AsCl_3$ is stable as a vapor, then breakthrough testing will be conducted using standard carbon breakthrough methods.[4] $AsCl_3$ will be examined first by feeding a bed of glass beads and then a filter tube with ASZMT, see Table 2. The glass beads can be used as control to determine the stability of $AsCl_3$ in humid air. The $AsCl_3$ detection would be conducted using either an FTIR, photo-acoustic, or electrochemical cell to simultaneously monitor for HCl.

Table 2. Conditions for Breakthrough Testing.

Chemical	Conc (ppm)	RH (%)	Bed Depth (cm)	Temp (°C)	Adsorbent
$AsCl_3$	2000	0	-	25	Glass Beads
	2000	50	-	25	Glass Beads
	2000	0	2	25	ASZMT
	2000	50	2	25	ASZMT

2. EXPERIMENTAL METHODS

Published data by Mathews et al.[5] of the vapor pressure of $AsCl_3$ was used to correlate an Antoine fit. The data, correlation fit and parameters are shown in Figure 2.

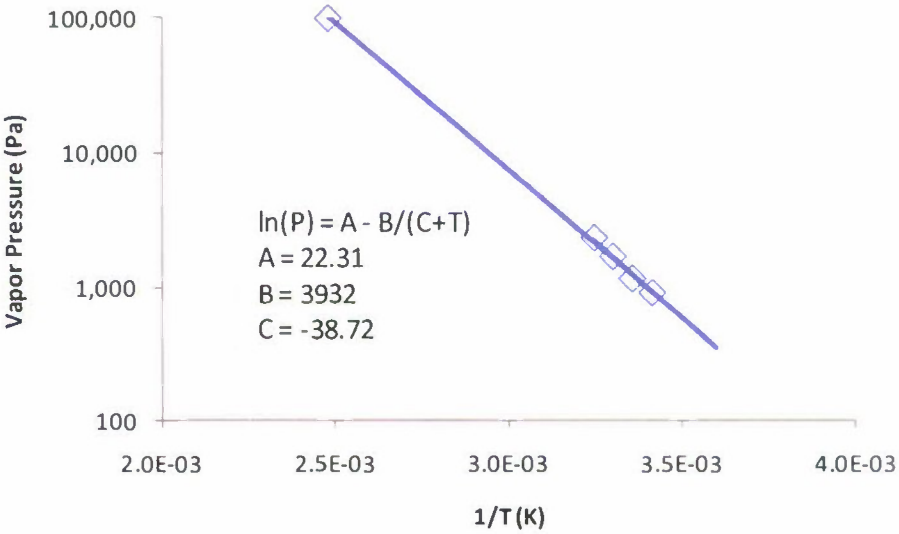


Figure 2. Vapor Pressure and Antoine Correlation of $AsCl_3$.

The adsorbent used in this study is the military impregnated carbon ASZMT, Calgon Corp., 12x30 mesh, lot number N06A01CD. The adsorbent samples were found to have

3% water loading as received and were used as received because high temperature drying is known to affect the impregnant composition.

The two apparatuses used to assess adsorption were a closed loop volumetric system and a continuous flow micro-breakthrough system. Schematic diagrams of both systems are provided in Figures 3 and 4, respectively. The size and conditions for each system are shown in Tables 3 and 4. The closed loop circulating apparatus was used to determine the adsorbent capacity for $AsCl_3$. The system consists of a circulating pump and FTIR. A four-way selector valve is used to challenge or bypass the adsorbent sample. Operation consists of a series of steps. Purging of the system is accomplished with dry, carbon dioxide (CO_2)-free air. The FTIR is calibrated by introducing measured liquid volumes of $AsCl_3$ into the system with a known volume. The loop is first purged, then the adsorbent samples are loaded. Chemical vapor injections were made to the closed loop for either $AsCl_3$ or water. A mass balance is used to determine the uptake of vapor on the adsorbent. The micro-breakthrough system is operated by establishing flow rates through the $AsCl_3$ contactor with the addition of a dilution flow. For the humid micro-breakthrough tests, an additional water sparger flow is included where the adsorbent is first equilibrated at humidity prior to addition of chemical vapor.

Table 3. Closed Loop Adsorption System Parameters.

Bed Bypass Volume (cm^3)	269
Bed Volume (cm^3)	24
Temperature (°C)	25
Adsorbent Mass (mg)	21
Liquid Injection volume (μL)	~2

Table 4. Micro-Breakthrough System Parameters.

Adsorbent Column Dia (cm)	0.9
Adsorbent Bed Depth (cm)	2.0
Adsorbent Mass (g)	0.99
Flow rate (sccm)	452
Temperature (°C)	25
Residence Time (s)	0.17

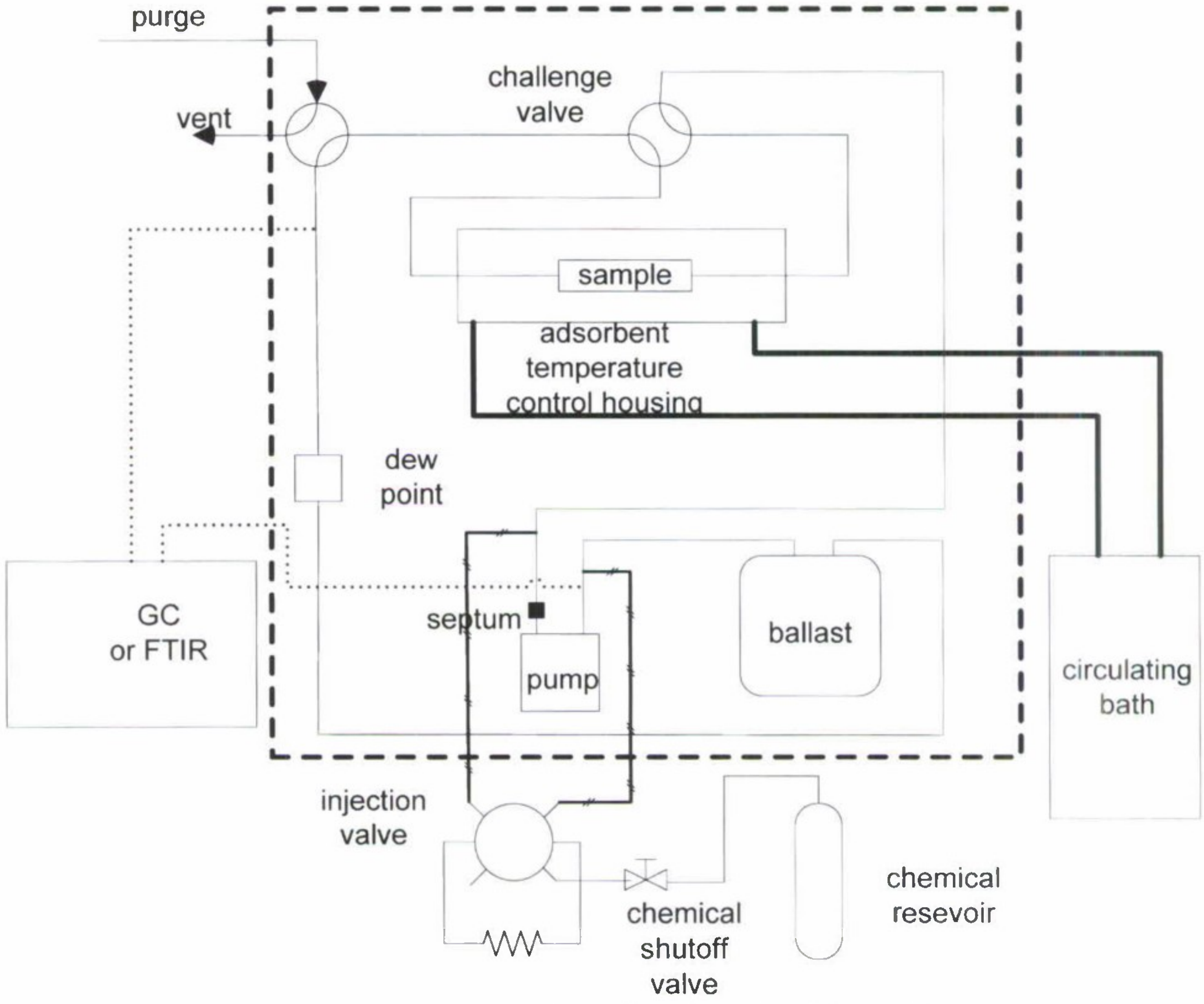


Figure 3. Volumetric Adsorption Apparatus Schematic.

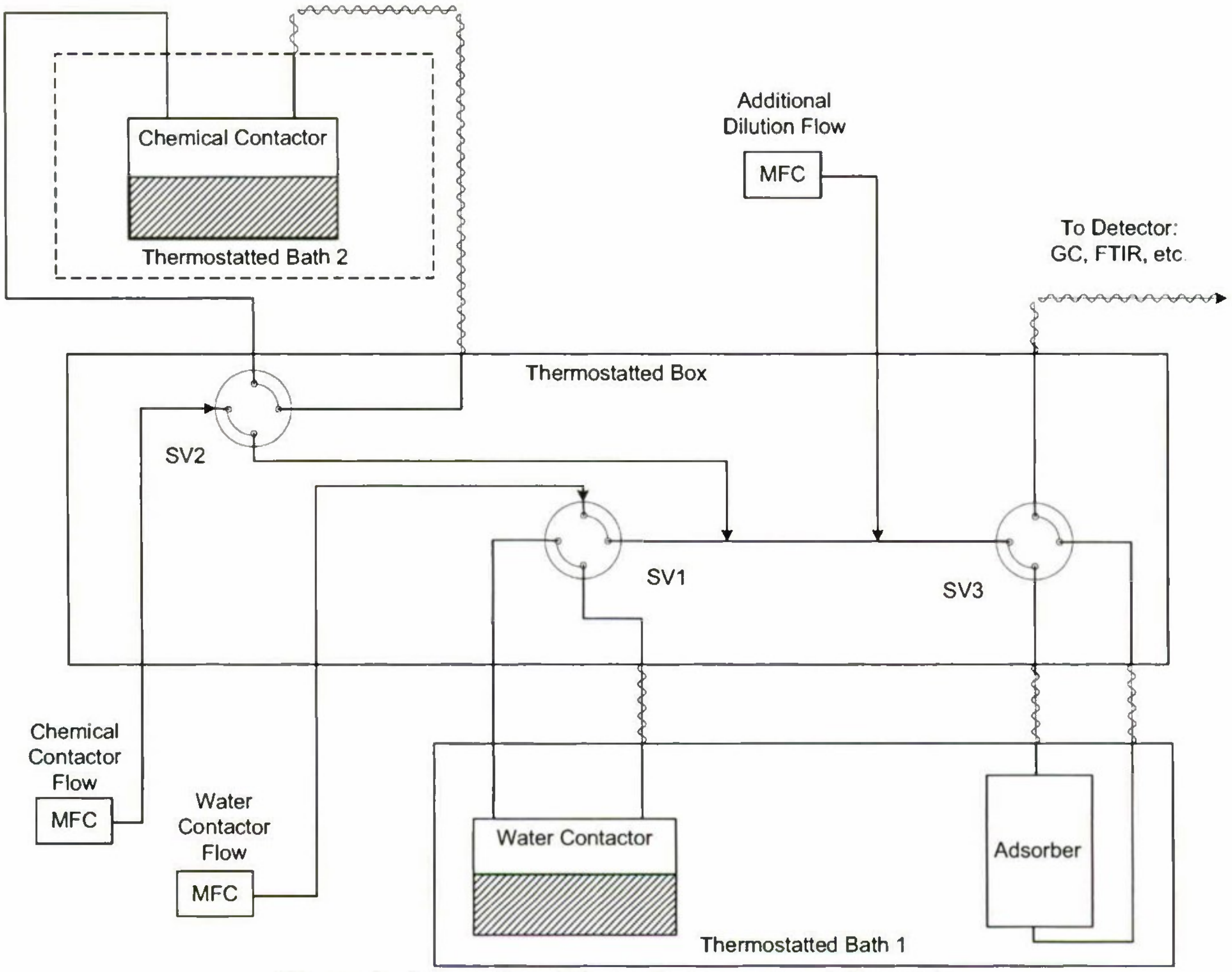


Figure 4. Micro-Breakthrough Apparatus Schematic.

Chemical vapor detection was performed using a Thermo-Nicolet FTIR Model 380 equipped with a Gemini 2 m gas cell. Calibration of water and $AsCl_3$ was performed by generating a stream of known composition of single component vapors. The gas-liquid contactor illustrated in Figure 5 is used to establish a saturated vapor at the temperature of the bath using published vapor pressure correlation for water and the correlated $AsCl_3$ results from Figure 2. The FTIR sample spectra, Figure 5, and calibration curves, Figure 6 and 7, are presented. The absorbance of $AsCl_3$ is not particularly strong; therefore, the lowest calibration point was 250 ppm. The region at 760 cm-1 was chosen for $AsCl_3$.

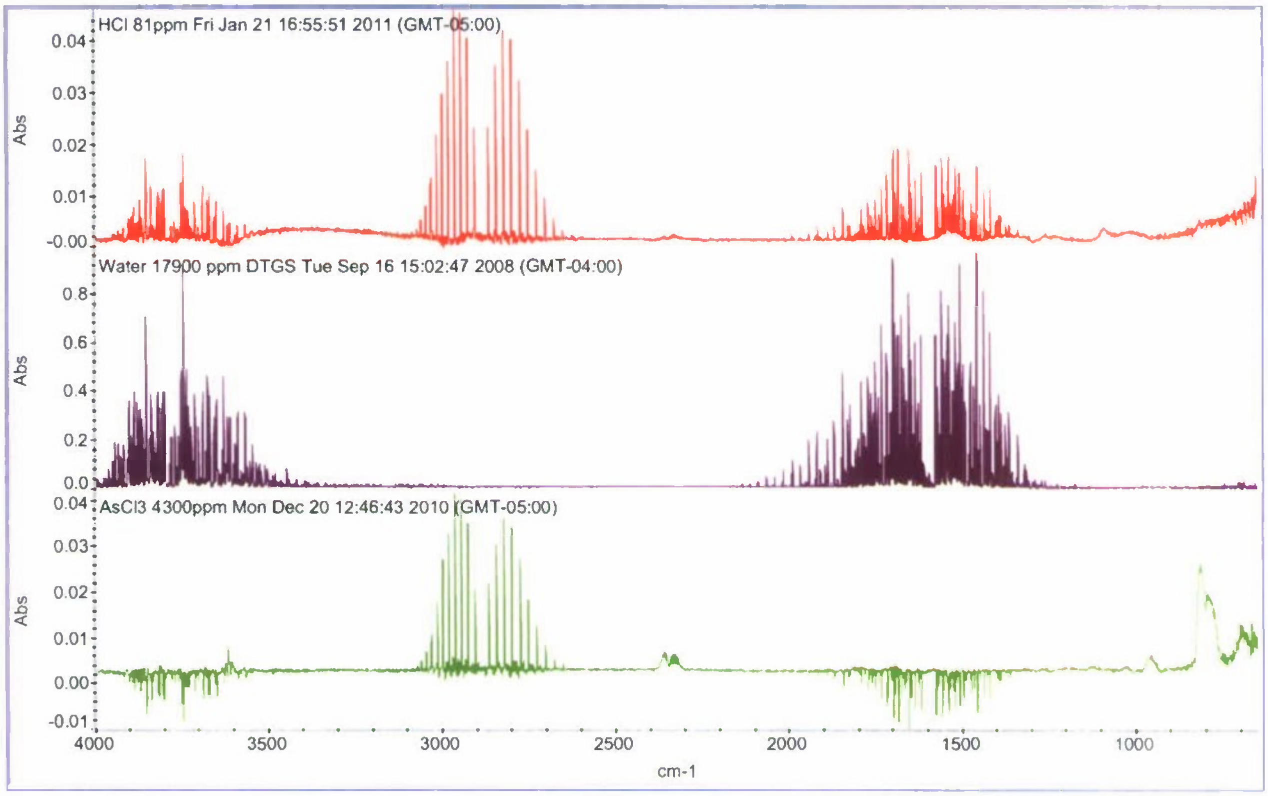
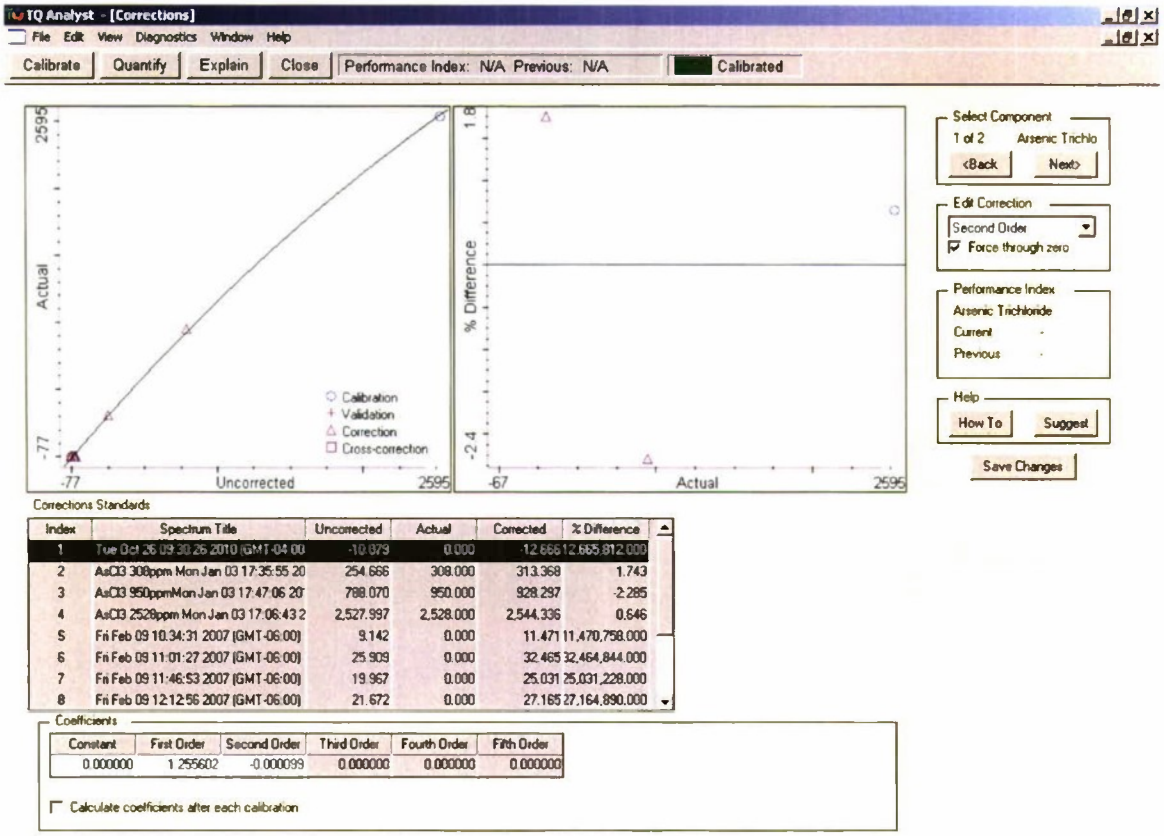


Figure 5. FTIR Spectra of $AsCl_3$, HCl and Water.



Performance Index: N/A Previous: N/A

Select Component
1 of 2 Arsenic Trichlo

Edit Correction
Second Order
☑ Force through zero

Performance Index
Arsenic Trichloride
Current -
Previous -

Corrections Standards

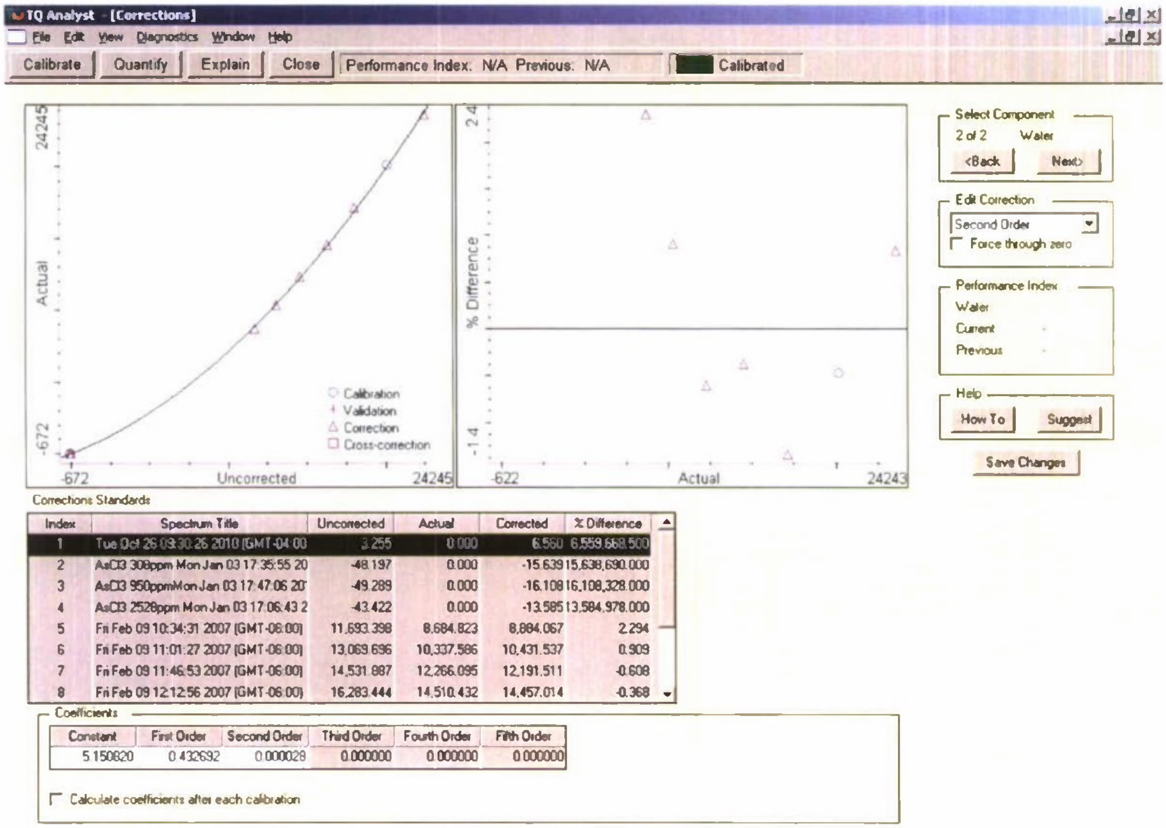
Index	Spectrum Title	Uncorrected	Actual	Corrected	% Difference
1	Tue Oct 26 09:30:26 2010 (GMT-04:00	-10.079	0.000	-12.666	12,665,812.000
2	AsCl3 308ppm Mon Jan 03 17:35:55 20	254.666	308.000	313.368	1.743
3	AsCl3 950ppmMon Jan 03 17:47:06 20	788.070	950.000	928.297	-2.285
4	AsCl3 2528ppm Mon Jan 03 17:06:43 2	2,527.997	2,528.000	2,544.336	0.646
5	Fri Feb 09 10:34:31 2007 (GMT-06:00)	9.142	0.000	11.471	11,470,758.000
6	Fri Feb 09 11:01:27 2007 (GMT-06:00)	25.909	0.000	32.465	32,464,844.000
7	Fri Feb 09 11:46:53 2007 (GMT-06:00)	19.967	0.000	25.031	25,031,228.000
8	Fri Feb 09 12:12:56 2007 (GMT-06:00)	21.672	0.000	27.165	27,164,890.000

Coefficients

Constant	First Order	Second Order	Third Order	Fourth Order	Fifth Order
0.000000	1.255602	-0.000099	0.000000	0.000000	0.000000

☐ Calculate coefficients after each calibration

Figure 6. FTIR Calibration Curve for $AsCl_3$.



Performance Index: N/A Previous: N/A

Select Component: 2 of 2 Water

Edit Correction: Second Order

☐ Force through zero

Performance Index: Water
Current -
Previous -

Corrections Standards

Index	Spectrum Title	Uncorrected	Actual	Corrected	% Difference
1	Tue Oct 26 09:30:26 2010 (GMT-04:00	3.255	0.000	6.560	6,559,668.500
2	AsCl3 308ppm Mon Jan 03 17:35:55 20	-48.197	0.000	-15.639	15,638,690.000
3	AsCl3 950ppmMon Jan 03 17:47:06 20	-49.289	0.000	-16.108	16,108,328.000
4	AsCl3 2528ppm Mon Jan 03 17:06:43 2	-43.422	0.000	-13.585	13,584,978.000
5	Fri Feb 09 10:34:31 2007 (GMT-06:00)	11,693.398	8,684.823	8,884.067	2.294
6	Fri Feb 09 11:01:27 2007 (GMT-06:00)	13,069.696	10,337.586	10,431.537	0.909
7	Fri Feb 09 11:46:53 2007 (GMT-06:00)	14,531.887	12,266.095	12,191.511	-0.608
8	Fri Feb 09 12:12:56 2007 (GMT-06:00)	16,283.444	14,510.432	14,457.014	-0.368

Coefficients

Constant	First Order	Second Order	Third Order	Fourth Order	Fifth Order
5.150820	0.432692	0.000028	0.000000	0.000000	0.000000

☐ Calculate coefficients after each calibration

Figure 7. FTIR Calibration Curve for Water.

3. RESULTS

3.1 Close Loop

An experiment was conducted with the closed loop apparatus described in Section 2. The resulting transient profile is presented in Figure 8. Starting at 1490 min, three injections of 2 μL liquid water are delivered in the bypass loop. The vapor concentration rises to approximately 23000 ppm, 75% RH. At 1520, the vapor adsorbent loop is opened and the adsorbent sample becomes equilibrated with humidity. At 1533 min, the system is put back into bypass mode and 2 μL of $AsCl_3$ is injected. The $AsCl_3$ concentration is seen to rise, and the water concentration simultaneously falls as a result of water condensation. At 1545, this mixture is exposed to the adsorbent and the vapor concentration of $AsCl_3$ is seen to drop to the baseline. A second $AsCl_3$ injection and equilibration station is then conducted. At the end of this step, the concentration does not drop completely to baseline but to an equilibrium vapor concentration of approximately 700 ppm. By a material balance, the adsorbed amount is determined be 4.2 mol/kg.

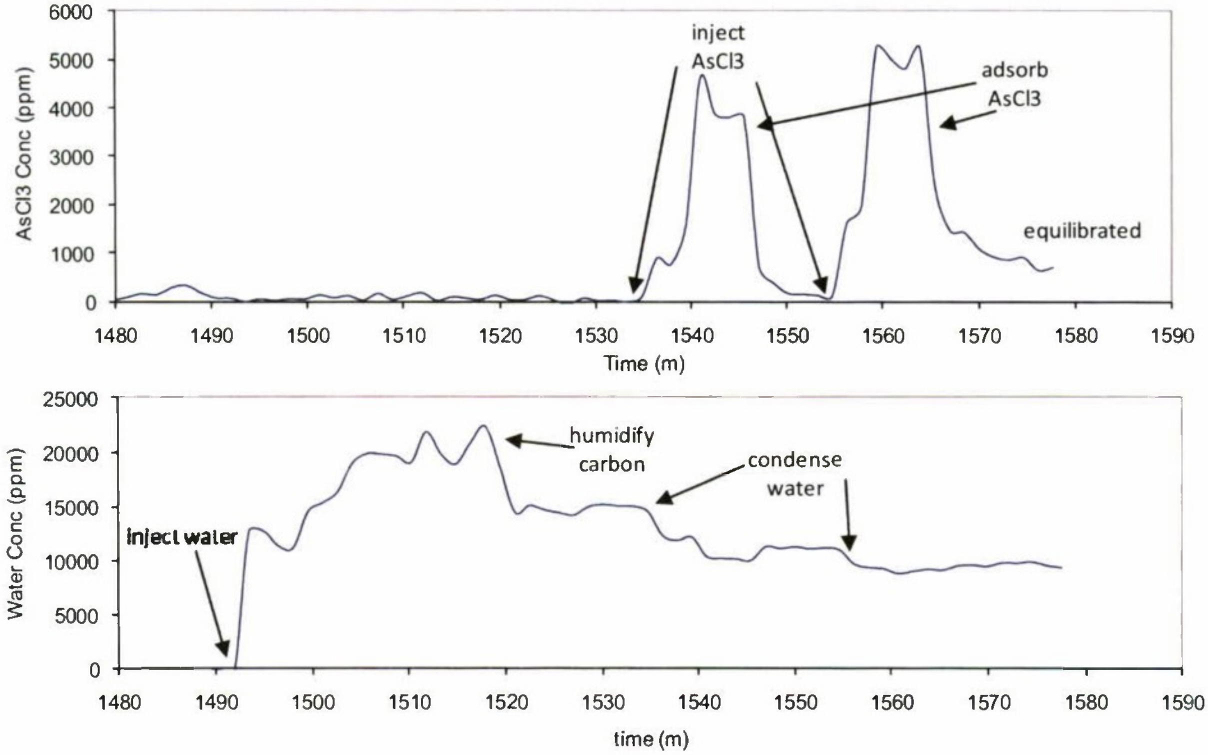


Figure 8. Transient Profile of Water and $AsCl_3$ Injections in Closed Loop Volumetric Adsorption Apparatus.

3.2 Micro-Breakthrough Tests

Three micro-breakthrough tests were conducted with $AsCl_3$ using the procedure described in Section 2. Using an adsorption bed packed with 2 cm depth of 0.4 mm diameter glass beads at dry conditions, immediate breakthrough was observed at 1200 ppm for a feed concentration of 2543 ppm. The experiment was stopped after 1 min. This confirmed that there was negligible adsorption in the system.

Next, the 9 mm ID adsorber column was packed with 2 cm depth of 1 mm diameter ASZMT yielding nine particle diameters of adsorbent. Again, dry conditions were used. The transient breakthrough profile was monitored using the FTIR, Figure 9. It is seen that no $AsCl_3$ is detected in the product until 25 min. The $AsCl_3$ feed was stopped when the product concentration reached 100 ppm to limit the contact of $AsCl_3$ with the FTIR cell and the formation of non-volatile arsenous acid. The low concentration end of the breakthrough concentration versus time relationship can be described by an exponential relationship (Wheeler equation) as discussed by Tien.[6] Figure 9 also presents an exponential fit to the data, demonstrating reasonable agreement.

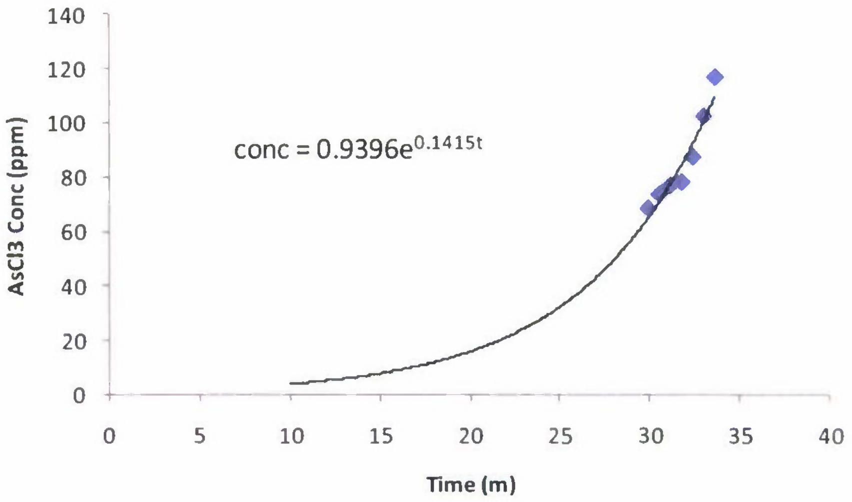


Figure 9. Micro-Breakthrough Profile of $AsCl_3$ to 2 cm Depth of ASZMT at 9.6 cm/s, Dry, 25 °C. Data are symbols, line is exponential fit.

Micro-breakthrough testing at humid conditions was considered next. An RH of 20% was established, and the adsorbent column equilibrated to those conditions. The $AsCl_3$ feed concentration of 2528 ppm was then mixed with the humid air. In the Teflon tubing downstream of the mixing point and upstream of the adsorber, condensation was readily apparent. In addition, the vapor phase water concentration recorded downstream of the adsorber dropped from 8000 to 6000 ppm. The breakthrough profile for $AsCl_3$ is shown in Figure 10. Again breakthrough occurs at approximately 25 min, and an exponential fit is seen to describe the data well. If it is of interest to project backward to find a time when a lower concentration would elute, then the correlations can be presented on a logarithmic plot, Figure 11.

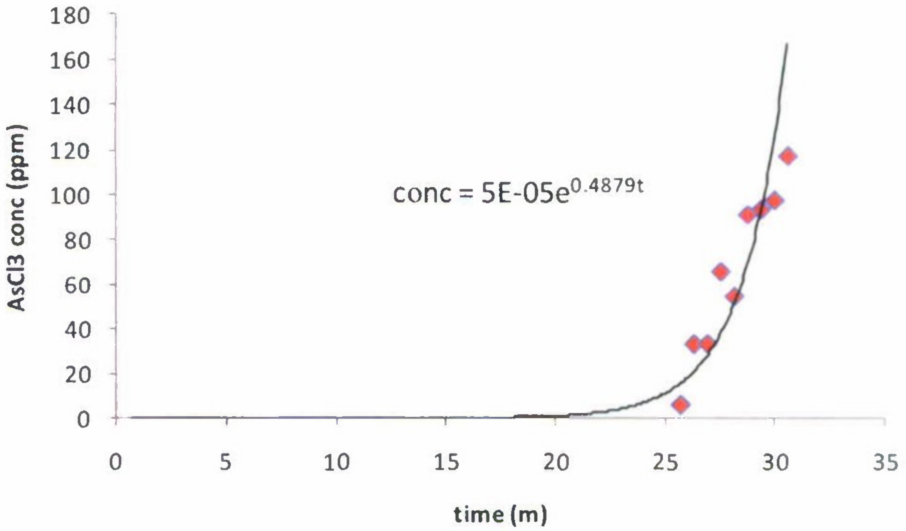


Figure 10. Micro-Breakthrough Profile of $AsCl_3$ to 2 cm Depth of ASZMT at 9.6 cm/s, 20% RH, 25 °C. Data are symbols, line is exponential fit.

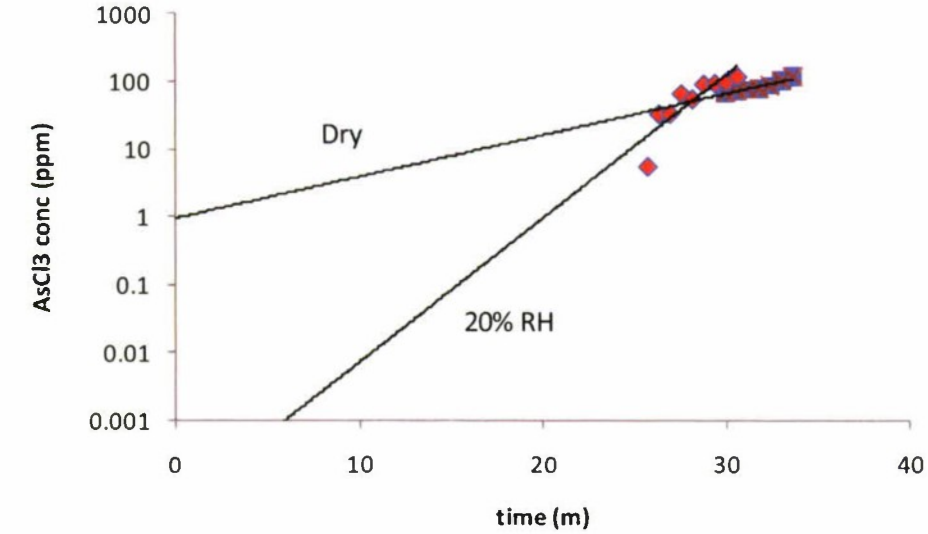


Figure 11. Micro-Breakthrough Profile Logarithmic Scale of $AsCl_3$ to 2 cm Depth of ASZMT at 9.6 cm/s, Dry 20% RH, 25 °C. Data are symbols, line is exponential fit.

These results indicate that the capacity at dry conditions is greater than at humid conditions, but that the breakthrough curve is sharper for humid conditions. The capacity measured in the volumetric system of 4.2 mol/kg corresponds to approximately 107 min until saturation at the feed condition at 80% RH and 2528 ppm $AsCl_3$.

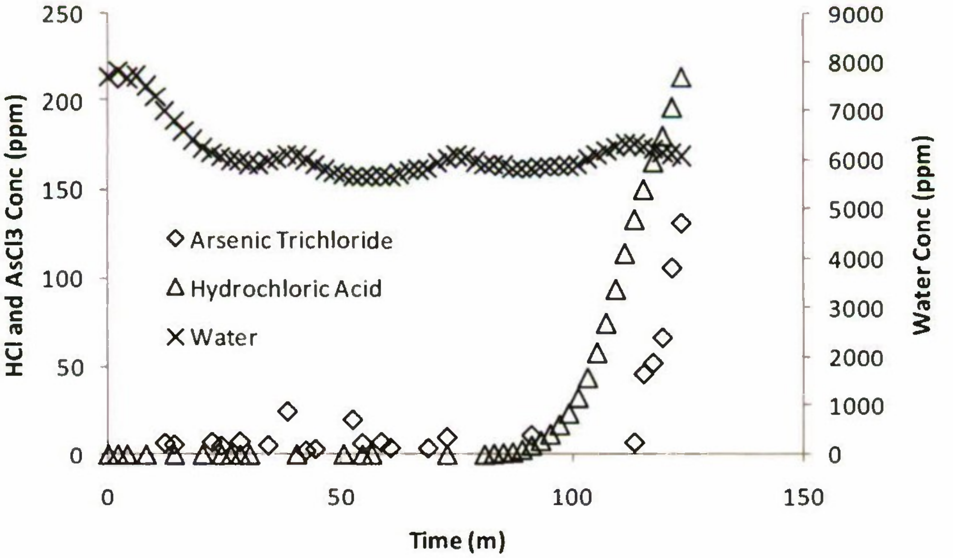


Figure 12. Breakthrough 4 cm Bed Depth of ASZMT Monitoring for $AsCl_3$, HCl and Water.

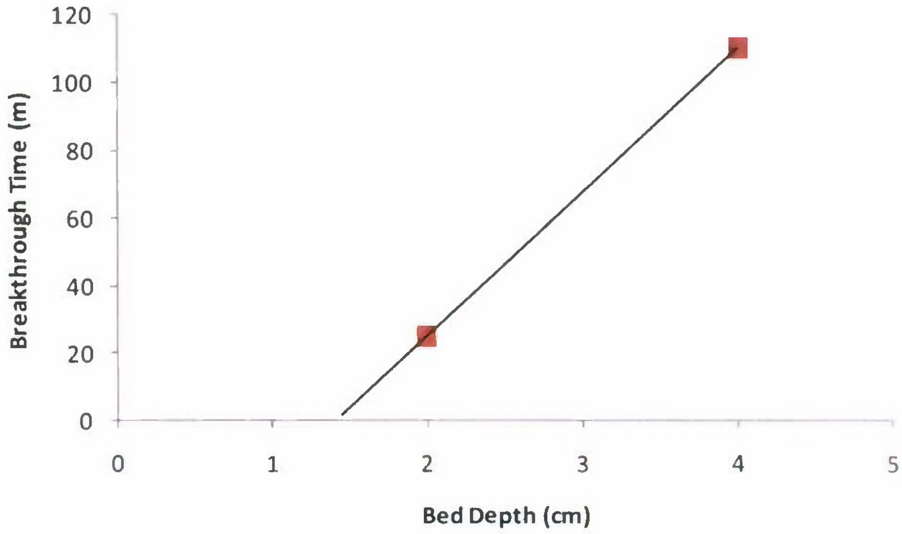


Figure 13. Critical Bed Plot for $AsCl_3$ Breakthrough to ASZMT.

To further characterize the filtration, another breakthrough run was performed using a deeper bed while monitoring for HCl and $AsCl_3$. The transient profile (Figure 12) shows that the initial challenge of chemical causes a drop in water vapor concentration of 8000 to 7000 ppm, as seen earlier. The breakthrough of HCl is seen to occur approximately 30 min prior to $AsCl_3$. Also, the product concentration of $AsCl_3$ breaks through at 110 versus 25 min for the 4 versus 2 cm bed depth. Figure 13, a critical bed plot, can be used to estimate the depth of the mass transfer zone, 1.5 cm.

3.3 Predicted CAFS Filter Performance

It is of interest to establish the filter performance requirement for $AsCl_3$. The shelter concentration can be determined from the maximum credible event calculated by assuming 1 L of $AsCl_3$ released in 1 min into 2500 scfm, which corresponds to 3800 ppm for 1 min (personal communication, Dan Noble, U.S. Army Corp of Engineers (USACE), 2011). From the Parson's Filter Study* and consolidated Response to AU Comments data August 27, 2010,** it appears that Temporary Emergency Exposure Limit (TEEL)-2 levels are appropriate for $AsCl_3$, which as seen in Table 5 is 1.35 ppm.[7]

Table 5. TEEL Values for $AsCl_3$ (ppm).

	TEEL-0	TEEL-1	TEEL-2	TEEL-3
$AsCl_3$	0.024	0.2	1.35	12.1

*TEEL represents a 15 min average concentration

---

* Paul Rich P.E., *Worker and Public Protection Analysis for $AsCl_3$ Find.* Parson Inc.: Fairfax, VA, unpublished data, May 2010.

** *TAPP Comments on the Site Wide Work Plan, Site-Specific Work Plan for High Probability Investigations at 4825 Glenbrook Rd, and the Three Supporting Memoranda* (May 2010) *and Associated Responses*; unpublished data, May 2010.

The correlation result for the concentration profile can be used to calculate the dose, concentration multiplied by time (Ct) of the tested filter tube. Using the exponential correlation fit for the 20%RH case the breakthrough time for 1.35 ppm is 20.9 min. The filter Ct is then the feed concentration multiplied by breakthrough time at TEEL-2 or 53000 ppm*m. From this value, the breakthrough time for the CAFS filter can be estimated using the ratio of residence time between the CAFS, see the Appendix, and the tube, which is 2.9, and the concentration of the 1 min $AsCl_3$ event versus the tube test. From these results, the CAFS filter is thus estimated to retain approximately 41 $AsCl_3$ releases; whereas at dry conditions, the CAFS would only retain 5 $AsCl_3$ releases.

4. CONCLUSIONS

An experimental investigation is reported for the adsorption of $AsCl_3$ vapor on the activated carbon ASZMT. At humid conditions, condensation was observed. Both volumetric closed loop data and micro-breakthrough testing demonstrate significant capacity at dry and humid conditions. Application of these results to the case of the Chemical Agent Filtration System filter indicates that conditions identified for the maximum at the U.S. Army Corp of Engineer's Spring Valley credible event are well within the design space.

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APPENDIX: CAFS FILTER SYSTEM LAYOUT AND SIZING

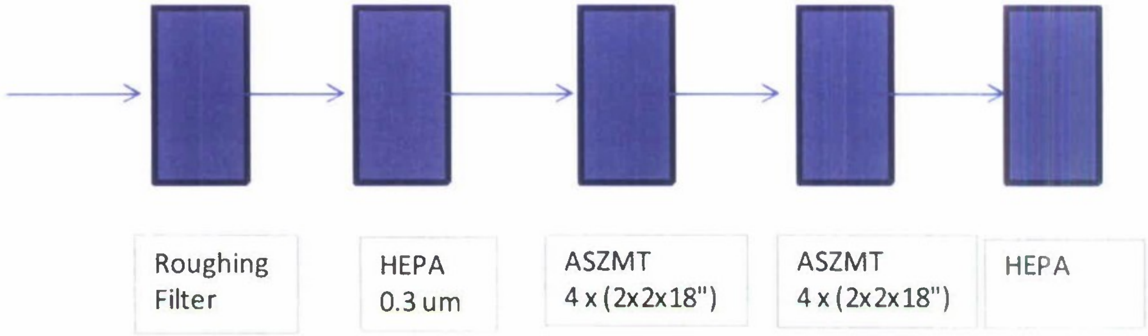

Figure. Schematic of CAFS.

Table. Operating Parameters of CAFS Carbon Filters.

CAFS nominal flow rate	2500 cfm
CAFS actual flow rate	2080 cfm
Number of carbon banks	2
Carbon cells per bank	4
Number of V beds per cell	3
Number of sections per V bed	2
Residence time per bank	0.25 s
Nominal size of V carbon cell element	2ft x 2ft x 18in.
Effective size of a V half face	18 in. x 18 in.
Velocity per bank	19.5 cm/s

*A carbon bank is called a HEGA (High Efficiency Gas Adsorber)