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ADSORBENT ANALYSIS OF ANNISTON CHEMICAL AGENT DISPOSAL FACILITY MUNITION DEMILITARIZATION BUILDING (MDB) BANKS 1 AND 2 FILTER SAMPLES FOLLOWING COMPLETION OF THE GB AGENT AND VX ROCKET CAMPAIGNS

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14. ABSTRACT Carbon samples from the Munition Demilitarization Building (MDB) Banks 1 and 2 ventilation filters from the Anniston Chemical Agent Disposal Facility were analyzed for the level of GB and VX contamination following the completion of the GB agent and VX rocket campaigns. The results of this investigation, using either thermal desorption, headspace, or NMR analysis, showed no GB or VX above the minimum detectable level on either of these filter samples. The use of NMR analysis resulted in the discovery of a significant amount of hydrolysis products from these agents on the MDB Filter Bank 1 carbon, but none on the MDB Filter Bank 2 carbon. Evaluation of adsorbent capacity studies found that the MDB Filter Bank 2 carbon had the same filtering capacity as a new filter, whereas the MDB Filter Bank 1 carbon showed signs of chemical loading and 12% of its original adsorption capacity remained active.					
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PREFACE

The work described in this report was authorized under project no. 7RJL11. The work was started in March 2007 and completed in July 2007.

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**ADSORBENT ANALYSIS OF ANNISTON CHEMICAL AGENT DISPOSAL FACILITY
MUNITION DEMILITARIZATION BUILDING (MDB) BANKS 1 AND 2 FILTER
SAMPLES FOLLOWING COMPLETION
OF THE GB AGENT AND VX ROCKET CAMPAIGNS**

1. INTRODUCTION

Carbon samples from the Anniston Chemical Agent Disposal Facility (ANCDF) were submitted to the U.S. Army Edgewood Chemical Biological Center (ECBC) in Edgewood, MD to quantify the amount of GB or VX agent and their degradation products on the adsorbent and to assess the remaining filtration capacity of the Munition Demilitarization Building (MDB) Banks 1 and 2 Type II adsorbent filters. The effort to determine the agent concentration on the adsorbent employed three different analytical techniques: (1) headspace analysis, (2) solid-phase phosphorus (^{31}P) NMR, and (3) thermal desorption followed by flame photometric detection–gas chromatography–mass spectroscopy (FPD/GC/MS). The filter capacity evaluations were performed using dimethyl methylphosphonate (DMMP) breakthrough data and fundamental adsorption relationships to determine the residual life of these filters.

The ANCDF design included a MDB air-ventilation system, which consisted of nine carbon filtration units. Each of the nine MDB filter units contained a roughing filter, a high-efficiency particulate air (HEPA) prefilter, six carbon filter beds, and a HEPA post-filter to remove any airborne contaminants from this complex. The MDB carbon filter units were placed into service in December 2002. The units remained in service during the surrogate trial burns, the GB agent campaign, and during most of the VX rocket campaign, and accumulated at least 650 days of agent-processing activity. The ANCDF utilizes sodium hydroxide as the decontamination solution for GB and VX in the contaminated areas of the MDB. All of the air exiting the MDB is processed through these filter units or the furnaces.

VX is monitored as the G-analog of VX utilizing a silver fluoride conversion pad at the sample inlet of a depot area air-monitoring system (DAAMS). The 12 h worker population limit (WPL) for VX is $6.0 \times 10^{-7} \text{ mg/m}^3$. On 1 December 2006, filter unit MDB-FILT-102 was taken offline due to intermittent G-analog of VX readings that were below the WPL level, but were high enough to be recorded by the DAAMS. To further study the chemical characteristics of the carbon in filter unit MDB-FILT-102, a sample of the carbon was collected from the first and second carbon beds. For safety purposes, the carbon samples were handled, packaged, and transported as would be expected for agent surety samples. The onsite ANCDF laboratory was not authorized to receive and/or analyze surety samples. Arrangements were made with ECBC for the transportation and subsequent analysis of the carbon samples in a facility with surety capabilities.

Two different carbon reference materials were also made available to aid in the examination of the MDB Banks 1 and 2 filter samples. The first material was a sample of new carbon that was used in the manufacture of these filter subunits and served as the control carbon. The second material was a composite sample of carbon from the pollution abatement system filtration systems (PFSs) from all of the furnaces and from the backup PFS carbon filter. Because

ANCDF had not experienced any operational or upset conditions in the furnace and PAS during agent processing, this sample was considered free of GB and VX and served as an air-aged carbon sample for comparison purposes only. The sample of the PFS carbon was collected from the sample canisters in November 2006.

2. FILTER HOUSING DESIGN

Each of the nine main filtration housing units employed in the MDB were identical, and each housing contained 288 Class A Type II adsorbents that were stacked 12 high by 4 wide by 6 deep banks, hereafter called the *filters*. The design maximum airflow rate to each housing was 16,000 cfm. The average operational flow rate to each housing was measured at 14,500 cfm. Thus, there were 48 filters oriented in parallel relative to the flow direction. This was equivalent to six Type II filters in a series to treat 302 cfm of feed air. Each Class A Type II filter contained approximately 48.2 lb of granular, activated, coconut shell-based carbon. A given filter bank (effective layer) of each housing processed 14,500 cfm of air using 48 filters \times 48.2 lb of carbon per filter = 2318 lb of carbon.

3. AGENT CONCENTRATION ANALYSES

The effort to determine the agent concentration on the adsorbent employed the use of three different analytical techniques: ^{31}P NMR, thermal desorption followed by FPD/GC/MS, and headspace analysis.

3.1 NMR Introduction

The solid-state, magic-angle spinning (MAS) NMR has previously enabled the nondestructive, *in situ* detection of simulants¹ and agents HD,² GB³, and VX³ directly on activated carbon without the need for extraction. Additionally, decomposition products for agents and simulants were also observable using this technique. For example, ^{31}P MAS NMR was used to easily distinguish isopropyl methylphosphonate (IMPA) and ethyl methylphosphonate (EMPA), the hydrolysis products of GB and VX, respectively, from the agents themselves.³ Although MAS NMR enables the resolution of a single agent from its typical product peak, as in the case where VX and GB are both present, extraction is needed to adequately resolve their product peaks. Therefore, MAS NMR was still useful in this study to detect the total amount of agent and/or product present, but not to determine the relative amounts of each.

Figure 1 shows the ^{31}P MAS NMR spectra obtained over time for 10 wt% GB on wet carbon (13 wt% water).³ In the initial spectrum, only the “doublet” for GB was primarily observed (chemical shift at 27.5 and 18.8 ppm), which was due to splitting by the attached fluorine (coupling constant, $J_{\text{PF}} = 1046$ Hz). Yet, later spectra (at time, $t = 6, 13,$ and 16 days) showed a decrease in the GB doublet and the emergence of the singlet for IMPA at a chemical shift of 20.5 ppm (underneath one of the GB doublet peaks) as the P–F bond of GB was hydrolyzed to yield the latter. In the final spectrum at $t = 16$ days, only a small shoulder was

evident for the minor amount of GB still present. Note that the half-life of GB on this particular wet carbon was about 1 week at room temperature.

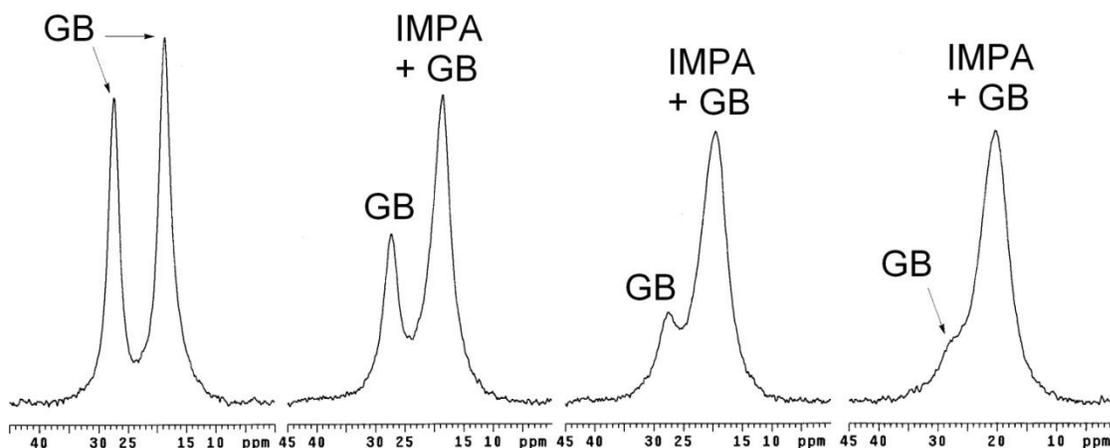


Figure 1. ^{31}P MAS NMR spectra obtained for 10 wt% GB adsorbed on wet carbon (13 wt% water). Left to right: initial and $t = 6, 13,$ and 16 days.

Figure 2 shows ^{31}P MAS NMR for 10 wt% VX on wet carbon (13 wt% water).³ The initial spectrum reveals that considerable decomposition occurred because, in addition to the broad peak detected for VX at a chemical shift of 49.4 ppm, intense product peaks are present: a rather sharp product peak at a chemical shift of 16.4 ppm astride a broader second peak at about 20 ppm, which are assignable to VX-pyro and EMPA, respectively, based on the known reaction mechanism of VX in the presence of water.⁴ Note that in the second spectrum, obtained at $t = 24$ days, VX has vanished; thus, the half-life of VX must be less than several days at room temperature. Therefore, once adsorbed, both GB and VX were not expected to be persistent on wet carbon for extended periods of time. In this study, carbon samples from ANCDF MDB Filter Banks 1 and 2, which were used to process GB and (to a lesser extent) VX, were examined using an MAS NMR to determine whether these agents and/or their byproducts were present.

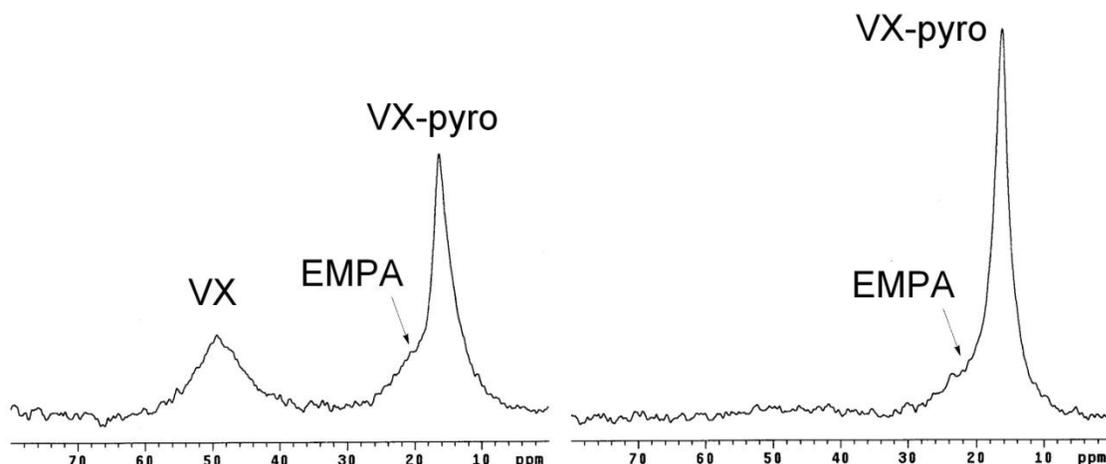


Figure 2. ^{31}P MAS NMR spectra obtained for 10 wt% VX adsorbed on wet carbon (13 wt% water). Left to right: initial and $t = 24$ days.

3.1.1 NMR Experimental Procedure

Materials: Four samples were received for analysis: clean carbon, PFS carbon, and one carbon sample each from MDB Filter Banks 1 and 2. EMPA, methylphosphonic acid (MPA), deuterated chloroform (CDCl_3) and deuterated acetonitrile (CD_3CN) were all obtained from Sigma-Aldrich Company LLC (St. Louis, MO).

NMR: NMR spectra were run on a Varian (Palo Alto, CA) Unityplus 300WB equipped with a Doty Scientific (Columbia, SC) 7 mm CP-MAS probe. Solid-state ^1H and ^{31}P MAS NMR spectra were obtained for carbon samples contained in 7 mm macor rotors (Doty Scientific) sealed with o-ring caps. Solution ^1H and ^{31}P NMR spectra of extracts from some of the carbon samples were obtained using the standard 5 mm solution NMR probe (Varian). Spectra were referenced in terms of the size of the chemical shift in parts per million by frequency to either external tetramethylsilane (TMS, ^1H , 0 ppm) with 85% H_3PO_4 (^{31}P , 0 ppm) or internal solvent peaks for ^1H solution spectra (CDCl_3 , 7.30 ppm; CD_3CN , 1.93 ppm).

Solvent Extraction of Carbon for Liquid-Phase NMR Analysis of Adsorbate Species: About 200 mg of carbon was added to a 3 mL glass vial. A volume of 1 mL of solvent was added and the vial was capped, shaken briefly, and allowed to stand for 10 min. A 0.75 mL aliquot was then removed and placed in a 5 mm NMR tube. Extracts were spiked with EMPA and MPA to verify the assignment and detection of these analytes.

Solid-Phase NMR Calibration Curve for Quantitation of P-Compound(s) Adsorbed on Carbon: Using a 10 μL syringe, small volumes of EMPA were added to 100 mg of the clean carbon contained in a macor 7 mm MAS NMR rotor. The rotor was sealed with an o-ring cap and weighed to accurately determine the amount of EMPA added. ^{31}P MAS NMR spectra were obtained after each addition and the peak area of the adsorbed EMPA was determined. A calibration curve was constructed by plotting ^{31}P NMR area vs μmol EMPA.

3.1.2 NMR Results

Clean Carbon: No P-compounds (minimum detectable quantity ca. 0.15 wt%, see Figure 3) were detected using the ^{31}P MAS NMR. A small broad peak at a chemical shift of 5.0 ppm for surface-sorbed water and a larger broad peak at -1.5 ppm for microporous water were detected using ^1H NMR .

PFS Carbon: No P-compounds (minimum detectable quantity ca. 0.15 wt%, see Figure 3) were detected using the ^{31}P MAS NMR. An intense, rather sharp peak at a chemical shift of 4.7 ppm for surface-sorbed water and an intense peak at -0.65 ppm for microporous water were detected using ^1H NMR.

MDB Filter Bank 1 Carbon: A rather large, broad peak at a chemical shift of 18.6 ppm (Figure 3) was detected using ^{31}P MAS NMR. This peak was quite similar to that previously observed for GB on carbon⁵ (Figure 1 at 16 days), where only a single, broad-product peak was observed. Note that the intensity of the peak in Figure 3 is far above the minimum detectable quantity (estimated to be ca. 0.15 wt%; see below). Furthermore, no small shoulder is present; thus, the “doublet” for GB was not detected. Similarly, no broad peak near 49 ppm is evident, which indicates that detectable amounts of VX were not present either. In the ^1H MAS NMR spectrum, only a single, intense, broad peak at -6.5 ppm was detected for the micropore-sorbed organic protons of the P-compound(s).

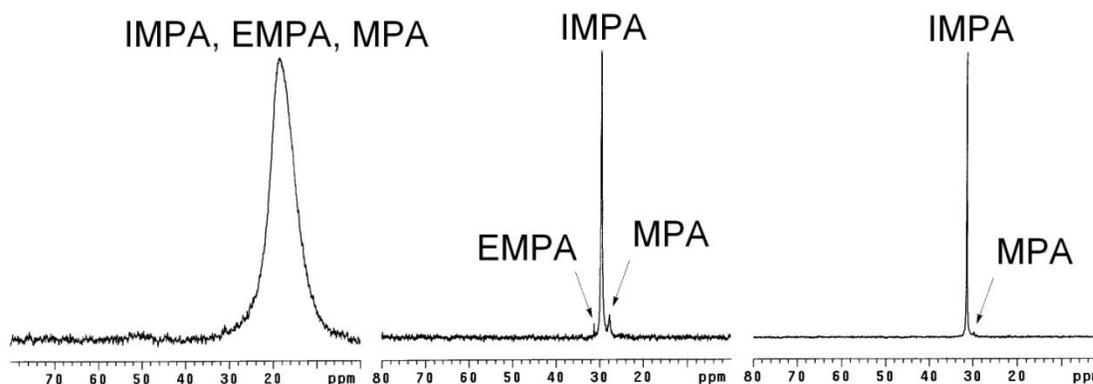


Figure 3. ^{31}P MAS NMR spectra obtained for the MDB Filter Bank 1 carbon (left), ^{31}P NMR spectra obtained for the CD_3CN (middle), and CDCl_3 (right).

Because GB and VX products were both anticipated to be found on the carbon, extractions were performed to identify the detected product and to determine if more than one product contributed to the single, broad-product peak detected using the ^{31}P MAS NMR. The ^{31}P NMR spectra obtained for the solvent extracts are also shown in Figure 3, and the results are given in Table 1. The CDCl_3 extract showed two ^{31}P NMR peaks at chemical shifts of 31.4 (major) and 29.8 ppm (minor). ^1H NMR spectra showed the major P-compound to be IMPA. The CD_3CN extract revealed three ^{31}P NMR peaks at chemical shifts of 31.23 ppm (small, sharp), 29.57 ppm (major, sharp), and 27.71 ppm (minor, broad). Results obtained from EMPA-spiking

enabled assignment of the 31.23 ppm peak to this compound. Spiking with MPA enabled assignment of this species to the 27.71 ppm peak and to the minor species in the CDCl_3 extract.

Table 1. NMR Solvent Extract Results of MDB Filter Bank 1 Carbon

Solvent	IMPA (mol %)	MPA (mol %)	EMPA (mol %)
CDCl_3	98	2	Not detected
CD_3CN	92	7	1

Note: Results expressed as the molar percentage of total P-compounds detected.

MDB Filter Bank 2 Carbon. ^{31}P MAS NMR did not detect any P-compounds (minimum detectable quantity ca. 0.15 wt%, see Table 2). A small, sharp peak at a chemical shift of 4.75 ppm for surface-sorbed water, and an intense, rather sharp peak at -2.3 ppm for microporous water were detected using ^1H NMR. No P-compounds were detected with the CDCl_3 extract.

Solid-Phase ^{31}P MAS NMR Calibration Curve. A calibration curve was constructed to allow determination of the total weight percentage of the product, primarily IMPA (GB-acid), residing on the MDB Filter Bank 1 carbon from the detected ^{31}P MAS NMR peak intensity. A 7 mm macor rotor was loaded with 0.1056 g clean carbon then incremental amounts of EMPA (molecular weight = 124.08, density $d = 1.172$ g/mL) were added, and successive ^{31}P MAS NMR spectra were obtained to determine the ^{31}P MAS NMR peak area afforded by each EMPA addition. The results are shown in Table 2. Note that the amount of EMPA added was determined from the weight increase of the rotor (not the nominal volume of EMPA). A plot of ^{31}P MAS NMR peak area versus micromoles of EMPA (total) is shown in Figure 4. The relationship was linear up to ca. 15 wt% EMPA. Because the ^{31}P MAS NMR spectra obtained for the first 0.94 wt% EMPA calibration point exhibited a signal-to-noise ratio (S/N) of 19, the estimated minimum-detectable quantity of agent and/or product was on the order of 0.15 wt% (i.e., one-sixth of the 0.94 wt% concentration [0.15 wt%] is assumed to provide one-sixth of the S/N [3]).

Table 2. Solid-Phase NMR Results of EMPA Addition to 0.1056 g Clean Carbon

Volume Added		Weight Added		EMPA (wt%)	Total EMPA (μmols)	^{31}P MAS NMR Area (ppm)
Nominal (μL)	Total (μL)	Nominal (mg)	Total (mg)			
1.0	1.0	1.0	1.0	0.94	8.1	11
1.0	2.0	1.3	2.3	2.1	19	26
3.0	5.0	3.9	6.2	5.5	50	59
5	10.0	5.9	12.1	10.3	98	105
5	15.0	6.1	18.2	14.7	145	160

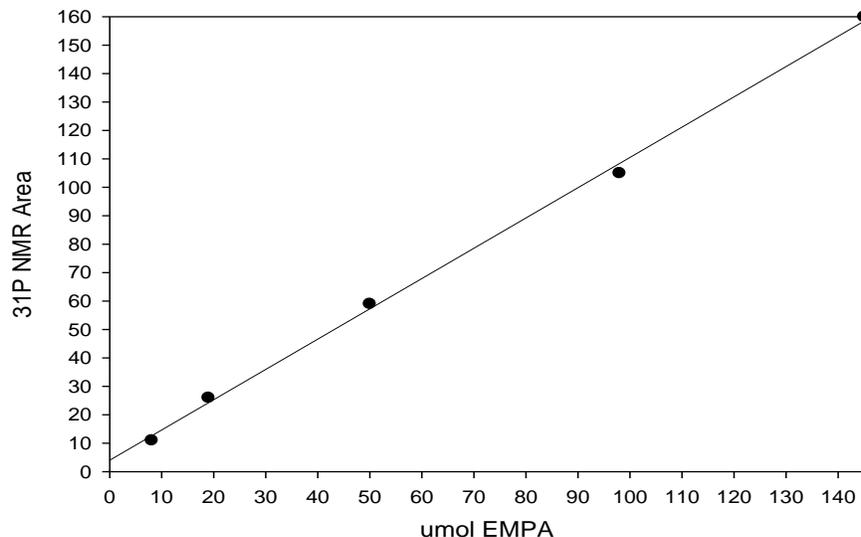


Figure 4. Plot of solid-phase ³¹P MAS NMR peak area vs micromoles of EMPA (total). The slope of the line is 1.1 area/ μ mol with an intercept of 4.0 area.

3.1.3 NMR Discussion

No P-compounds were detected on the clean control carbon, MDB Filter Bank 2 carbon or PFS carbon (minimum detectable quantity ca. 0.15 wt%, see previous page). A relatively small amount of water was present on the clean carbon, and much larger amounts of water were present on the MDB Filter Bank 2 and PFS carbons. Similarly, extraction of the MDB Filter Bank 2 carbon using CDCl₃ did not result in the detection of any P-compounds.

However, analysis of MDB Filter Bank 1 carbon yielded an intense ³¹P MAS NMR peak. Solvent extraction was used to show that the major P-compound was IMPA, with CDCl₃ extraction findings of 98% IMPA and 2% MPA. Whereas, extraction with CD₃CN yielded 92% IMPA, 7% MPA, and 1% EMPA. Note that MPA is known to readily form from the secondary hydrolysis of EMPA,⁵ which was the likely source of this product.

The ³¹P MAS NMR peak area of the MDB Filter Bank 1 carbon peak was 153, which indicates that this area corresponds to 140 μ mol when compared with the EMPA calibration curve. Because the major species is IMPA, its molecular weight of 138.11 g/mol can be used to calculate the weight of the P-compounds: 140 μ mol \times 138.11 g/mol = 19 mg. The weight of the MDB Filter Bank 1 sample was 146.3 mg; thus, the weight percent loading was 19 mg/146.3 mg = 13%.

3.1.4 NMR Conclusions

No P-compounds were detected using NMR on the clean control carbon, MDB Filter Bank 2 carbon, or PFS carbon (minimum detectable quantity ca. 0.15 wt%, see previous page).

Using ^{31}P MAS NMR to analyze the MDB Filter Bank 1 carbon, and using ^{31}P NMR to analyze its solvent extracts resulted in the detection of P-compounds, which were assigned to IMPA (major, >90%), MPA (minor, >10%), and EMPA (trace, ca. 1%). The total weight percent loading of P-compounds was 13%.

3.2 Thermal Desorption Analysis of Carbon Samples

In this study, carbon samples from MDB Filter Banks 1 and 2 were thermally heated, and their effluent vapors were collected to determine whether GB and VX could be off-gassed from these materials. Neither chemical was found in either of these samples.

3.2.1 Thermal Desorption Experimental Procedure

A Dynatherm ACEM 900 thermal desorption unit, equipped with a fast-flow 10 mm collection tube (CDS Analytical, Oxford, PA), was used to collect, concentrate, and thermally desorb the vapors from each of the carbon samples into an integrated GC/MS system for chemical agent screening. The Dynatherm was modified slightly to eliminate the sample-saver feature by replacing the 1/16 in. tee fitting with a union inside the heated valve box and by attaching an external low-flow helium mass flow controller (MFC) with a small, inline carbon trap to the rear or “swing-arm side” of the fast-flow tube. Removal of the sample-saver pathway reduced ghost peaks between successive injections that were caused by chemical entrapment in this tubing. The connection between the end of the collection tube and the carbon trap was easily made with a short length of thick-walled, 1/16 in. polytetrafluoroethylene (PTFE) tubing; a reducing union; and the thumbwheel-and-ferrule assembly borrowed from the now-abandoned swing arm.

The carbon sample to be studied (approximately 0.5 g) was placed inside an empty collection tube and supported against the glass frit with a plug of deactivated glass wool. The helium flow through the MFC was fixed at 25 mL/min, and the following conditions were programmed into the Dynatherm. In this configuration, only the tube heat step transferred the effluent vapors to the focusing trap for collection.

Temperatures (°C):	Tube Idle	30
	Tube Heat	60, 80, or 100, depending on test
	Valve Box	150
	Transfer Line	175
	Trap Idle	30
	Trap Heat	300

Times (min):	Sample	0
	Dry	0
	Heat	40
	Cool	0
	Trap	5
	Recycle	55

Cycle counter:	10
Carrier gas:	Helium 2 mL/min total; split FPD/mass selective detector (MSD) 1.2:0.8 mL/min
Oven parameters:	40 °C for 2 min, ramp 2.5 °C/min to 200 °C, hold 2 min
Focusing trap:	80–100 mesh Tenax-TA (Buchem B.V., Apeldoorn, NL)

The column interface connecting the Dynatherm to the GC was a 30 m, 0.25 mm i.d. HP5-MS with a 1.0 µm film thickness, connected in an open-split configuration within the GC oven using a Y-type press-fit connector. A short length of 0.53 mm i.d. deactivated capillary column was used to connect to the GC's FPD detector, which was equipped for simultaneous phosphorus and sulfur monitoring using dual photomultiplier tubes and electrometers. A suitable length of 0.25 mm, deactivated capillary tubing was chosen as a restrictor to limit the flow to 0.8 mL/min from the remaining end of the Y-connector to an attached Agilent 5973 MSD. The flow rates for the FPD were set according to the manufacturer's specifications: column plus makeup at 20 mL/min, H₂ at 75 mL/min, and air at 100 mL/min.

The configuration of the Dynatherm and FPD-GC/MS instruments allows for a user-defined number of cycles to be run on a given sample when an MS sequence is set up to capture the data. This is particularly important when testing the equilibration of chemicals with a given adsorbent or the strength of their bonds. Repeated processing of the same adsorbent sample can also be useful when evaluating the mass transport of low-volatility chemicals through the equipment. Observing the same type of elution profile between successive cycles provides confidence that sample retention between the adsorbent effluent and the equipment was not significant. In this case, the effluent chemicals should either decrease in concentration, if they are depleted, or stay relatively the same, if they are equilibrated. Chemical compounds should not show a gradual increase in concentration over successive runs unless surface passivation has occurred with repeated injections.

3.2.2 Thermal Desorption Results

No GB or VX vapors were detected in any of the MDB Filters Bank 1 or 2 carbon samples processed by thermal desorption at a detection limit of 1e-4 mg/m³, established for the phosphorus channel of the FPD. Thermal desorption temperatures as high as 100 °C were explored with each carbon sample in a process volume of 1.0 L.

3.3 Headspace Analyses

Samples of carbon from MDB Filter Banks 1 and 2 were evaluated using standard headspace analysis. The detailed results are given in the appendix. The results may be summarized as follows: both analyses showed that no agent (GB or VX) was present on either carbon sample above the monitoring limits of 1.5×10^{-5} mg/m³ for GB or $5.1E-7$ mg/m³ for

VX. In other words, all of the agent that adsorbed on MDB Filter Bank 1 was converted to degradation products of either GB or VX.

4. FILTER PERFORMANCE AND CAPACITY MEASUREMENTS

The purpose of this study is to determine the level of contamination, based on loss of adsorption capacity of MDB Filter Banks 1 and 2 and the PFS Filter. Representative samples were obtained of the activated carbon media from each filter. The standard approach used to assess the capacity of a carbon filter for strongly adsorbed chemicals such as GB and VX is to conduct breakthrough testing with the simulant DMMP. This test is conducted by introducing a vapor contaminant to a flowing stream, which then passes through a packed column of adsorbent. The retention of the contaminant on the adsorbent is determined by monitoring the effluent contaminant concentration profile. The effects of both adsorption capacity and adsorption rate contribute to the shape of the effluent profile. The adsorbent capacity for DMMP can be compared to that of the exposed samples to estimate the sample's residual adsorption capacity. In this study, carbon samples were examined from MDB Filter Banks 1 and 2 and the PFS Filter, along with a control carbon sample that was made up of the carbon adsorbent found in new filters.

The DMMP challenge concentration for these tests was 3000 mg/m^3 . This value was much greater than the actual challenge concentration to in-use filters and was close to the saturation concentration of DMMP at ambient temperature. This high concentration allowed for a reduced test time, but also permitted a valid determination of adsorption capacity when compared with that of a lower concentration chemical challenge. All other test conditions were chosen as scaled design specifications of the MDB filters. The bed depth used for all tube tests reported here was 2 in., and all carbon samples were used as-received. The superficial linear velocity was fixed at 40 ft/min, and the filter tube diameter was 4.1 cm. A summary of test conditions is shown in Table 3. Duplicate breakthrough runs were performed on all samples.

The concentrations versus time breakthrough results of this investigation are shown in Figure 5. The effluent concentration is plotted on a logarithm scale to emphasize the low-concentration breakthrough behavior. Greater adsorption capacity results in breakthrough at later times. The data clearly show that the capacity of the carbon in MDB Filter Bank 1 was greatly reduced versus the control carbon. The near immediate breakthrough on the MDB Filter Bank 1 sample also suggests that this sample was loaded almost to saturation. In addition, these data show that the carbon in MDB Filter Bank 2 and in the PFS Filter did not change relative to the control carbon. Therefore, the amount of agent or contaminant chemical adsorbed on MDB Filter Bank 2 was negligible. The breakthrough was logarithmic for almost 5 orders of magnitude for these samples. It follows that the filtration performance of MDB Filter Bank 2 and the PFS Filter would be close to that of a new filter bank.

The data are plotted on a linear concentration scale in Figure 6. The adsorption capacity can be calculated by integrating the difference between the challenge and effluent concentrations with respect to time. This integral can be estimated if the curve is assumed to be symmetric by noting the elapsed time when the concentration corresponding to 50% of the feed

concentration appears in the effluent. The product of this time, the flow rate, and the feed concentration yields the mass adsorbed. For the control carbon, the equilibrium capacity for DMMP was 0.455 g DMMP per gram of carbon at a concentration of 3000 mg/m³ and a temperature of 25 °C.

$$\text{Equilibrium Capacity} = \frac{\text{Feed Concentration} \times \text{Flow rate} \times \text{Time to 50\% of Feed Concentration}}{\text{Mass Dry Carbon}}$$

(assumes symmetric breakthrough curve)

Table 3. Breakthrough Test Conditions of Control Carbon

Parameter	Condition
Feed concentration	3000 mg/m ³
Flow rate	0.016 m ³ /min
Time to 50% feed concentration	328 min
Mass of dry carbon	34.56 g

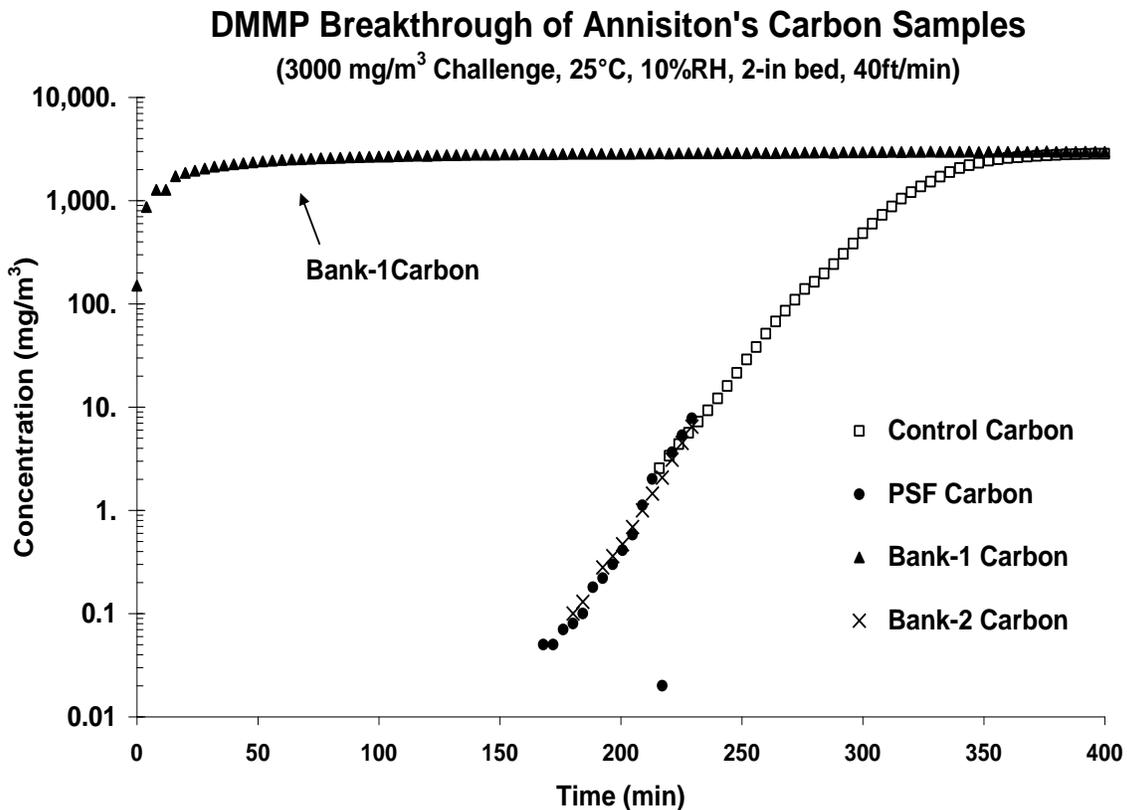


Figure 5. DMMP adsorption capacity results for new, PFS, MDB Filter Banks 1 and 2 carbon samples from ANCDF filters with a 3000 mg/m³ challenge at 25 °C and 10% RH using a 2 in. bed at a rate of 40 ft/min.

Figure 6 also shows the results for the control and MDB Filter Bank 1 carbon samples. Integration of this data shows that the remaining capacity of the MDB Filter Bank 1 carbon was only 12% of the control carbon or about 0.06 g/g. Thus, the usage capacity from MDB Filter Bank 1 carbon was 0.395 g/g.

Since MDB Filter Bank 2 carbon had no measurable capacity change, MDB Filter Bank 1 had removed all the adsorbable contaminants during the demilitarization operation. This removal was done at a high efficiency. The concentration front was sharp, which was consistent with the shape of the breakthrough profile shown in Figures 5 and 6. The time between low to feed concentration in the breakthrough profile was short relative to the first appearance of the low concentration. In the MDB Filter Bank application, this result provided evidence that with appropriate monitoring between filter banks, only MDB Filter Bank 1 would need to be replaced when breakthrough was noted between MDB Filter Banks 1 and 2.

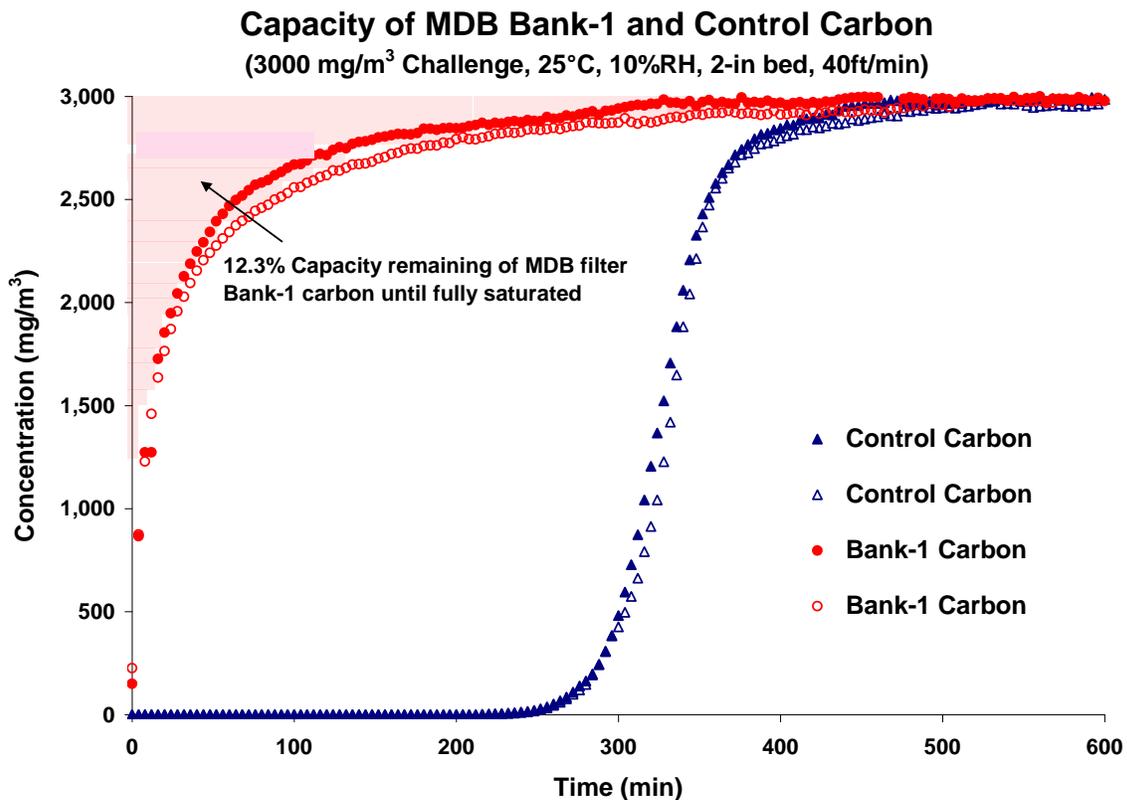


Figure 6. DMMP breakthrough results for new and MDB Filter Bank 1 carbon, tested with a 3000 mg/m³ challenge at 25 °C and 10% RH using a 2 in. bed at a rate of 40 ft/min.

5. CONCLUSIONS

Carbon samples from the ANCDF were submitted to ECBC in Edgewood, MD to quantify the amount of GB or VX agent on the adsorbent and to determine the remaining filtration capacity of the MDB Filter Banks 1 and 2 Type II adsorbent filters.

Analysis of the carbon samples by solid-phase P NMR, thermal desorption followed by FPD/GC/MS, and headspace analysis techniques detected no GB or VX agent on these carbon samples, but did detect agent hydrolysis products on the MDB Filter Bank 1 carbon.

The filter capacity evaluations used DMMP breakthrough data and fundamental adsorption relationships to determine the residual life of these filters. MDB Filter Bank 1 carbon was measured to have only 12% residual life remaining while the MDB Filter Bank 2 carbon had no measurable capacity reduction when compared with the new control carbon.

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LITERATURE CITED

1. Wagner, G.W.; MacIver, B.K.; Yang, Y.-C. *Langmuir* **1995**, *11*, 1439–1442.
2. Karwacki, C.J.; Buchanan, J.H.; Mahle, J.J.; Buettner, L.C.; Wagner, G.W. *Langmuir* **1999**, *15*, 8645–8650.
3. Wagner, G.W.; Buchanan, J.H.; Karwacki, C.J., unpublished results.
4. Yang, Y.-C.; Szafraniec, L.L.; Beaudry, W.T.; Rohrbaugh, D.K.; Procell, L.R.; Samuel, J.B. *J. Org. Chem.* **1996**, *61*, 8407–8413.
5. Wagner, G.W.; Procell, L.R.; O'Connor, R.J.; Munavalli, S.; Carnes, C.L.; Kapoor, P.N.; Klabunde, K.J. *J. Am. Chem. Soc.* **2001**, *123*, 1636–1644.

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BIBLIOGRAPHY

Internal Operating Procedure Operations Directorate Environmental Monitoring Laboratory, *Analysis of Chemical Warfare Agents and Degradation products on DAAMS Tubes using Gas Chromatography System Coupled with Flame Photometric Detector (GC/FPD)*; ECBC IOP MT-19; Revision 4; U.S. Army Edgewood Chemical Biological Center: Aberdeen Proving Ground, MD, October 2005.

Internal Operating Procedure Operations Directorate Environmental Monitoring Laboratory, *Analysis of Chemical Warfare Agents in Extracts using a Gas Chromatograph /Mass Spectrometer System*, ECBC IOP MT-8; Revision 4; U.S. Army Edgewood Chemical Biological Center: Aberdeen Proving Ground, MD, June 2006.

Internal Operating Procedure Operations Directorate Environmental Monitoring Laboratory, *Analysis of Chemical Warfare Agents on DAAMS using a Gas Chromatography System Coupled with a Mass Spectrometer Detector*, ECBC IOP MT-13; Revision 11; U.S. Army Edgewood Chemical Biological Center: Aberdeen Proving Ground, MD, February 2006.

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ACRONYMS AND ABBREVIATIONS

^{31}P NMR	solid-phase phosphorus nuclear magnetic resonance
ANCDF	Anniston Chemical Agent Disposal Facility
CDCl_3	deuterated chloroform
CD_3CN	deuterated acetonitrile
DAAMS	depot area air-monitoring system
DMMP	dimethyl methylphosphonate
ECBC	U.S. Army Edgewood Chemical Biological Center
EMPA	ethyl methylphosphonate
FPD	flame photometric detection
GC	gas chromatography
GB	sarin, a nerve agent, isopropyl methylphosphonofluoridate
HEPA	high-efficiency particulate air (filter)
IMPA	isopropyl methylphosphonate
MAS	magic-angle spinning (NMR)
MDB	Munition Demilitarization Building
MFC	mass flow controller
MPA	methylphosphonic acid
MS	mass spectroscopy
MSD	mass selective detector
PFS	pollution abatement system filtration system
PTFE	polytetrafluoroethylene

S/N	signal-to-noise ratio
TMS	tetramethylsilane
VX	methylphosphonothioic acid, persistent nerve agent
WPL	worker population limit

**APPENDIX
HEADSPACE ANALYSIS RESULTS
FOR MDB FILTER BANKS 1 AND 2 CARBON SAMPLES**

DATE:03/07/2007

RE Monitoring Results for MDB FILTER BANK 1

LOCATION: 3832
PROGRAM: STEL XXX MONITORING
SAMPLE DATE: 03/06/07

ITEM #	LAB ID	RESULTS	RESULTS	
			mg/m3 Q	STEL ST ON/OFF
70306003	0703060120-M01 GB	<1.5E-5	U	<STEL ND 1320-1420
70306004	0703060121-M01 GB	<1.5E-5	U	<STEL ND 1320-1420

If result is greater than the action level (WPL or STEL), or sample status - CD, E, or IN, please conduct appropriate corrective action(s) and request resampling of item(s) for the failed analyte(s), by using the online Monitoring Request Form (MRF). The EML Sample Team will reschedule to resample item(s) for analyte(s) with sample status of LF, PF or RJ.

For questions concerning the above results, contact the ECBC Environmental Monitoring Laboratory.

ST - STATUS LEGEND:
 ND - No detection at/above reporting level
 CB - Clear, detection below the action level (WPL or STEL)
 CD - Confirmed detection above the action level (WPL or STEL)
 E - Estimated quantitation; result above calibration curve
 IN - Interference
 LF - QL (Quality Lab) failure
 PF - QP (Quality Point) failure
 RJ - Rejected sample (broken tube, pump failure, wet sample)

Q - QUALIFIERS LEGEND:
 U - No detection at/above reporting level
 J - Estimated; result between MDL (method detection limit) and RL (reporting limit)
 E - Estimated result above calibration curve

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DATE:03/07/2007

RE Monitoring Results for MDB FILTER BANK 2

LOCATION: 3832
PROGRAM: STEL XXX MONITORING
SAMPLE DATE: 03/06/07

ITEM #	LAB ID	RESULTS	RESULTS		
			mg/m ³ Q	STEL	ST ON/OFF
70306003	0703060122-M01	VX	<5.1E-7	U	<STEL ND 1320-1420
70306004	0703060123-M01	VX	<5.1E-7	U	<STEL ND 1320-1420

If result is greater than the action level (WPL or STEL), or sample status - CD, E, or IN, please conduct appropriate corrective action(s) and request resampling of item(s) for the failed analyte(s), by using the online Monitoring Request Form (MRF). The EML Sample Team will reschedule to resample item(s) for analyte(s) with sample status of LF, PF or RJ.

For questions concerning the above results, contact the ECBC Environmental Monitoring Laboratory.

ST - STATUS LEGEND:

- ND - No detection at/above reporting level
- CB - Clear, detection below the action level (WPL or STEL)
- CD - Confirmed detection above the action level (WPL or STEL)
- E - Estimated quantitation; result above calibration curve
- IN - Interference
- LF - QL (Quality Lab) failure
- PF - QP (Quality Point) failure
- RJ - Rejected sample (broken tube, pump failure, wet sample)

Q - QUALIFIERS LEGEND:

- U - No detection at/above reporting level
- J - Estimated; result between MDL (method detection limit) and RL (reporting limit)
- E - Estimated result above calibration curve

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