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Feasibility Study for Reuse of Activated Carbon for Capture of Methyl Bromide



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Feasibility Study for Reuse of Activated Carbon for the Capture of Methyl Bromide Used for Decontamination

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Disclaimer

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Executive Summary

Methyl bromide (MeBr) fumigation has been shown to be effective in decontaminating buildings contaminated with *Bacillus anthracis* (Ba) spores. Previous laboratory and field tests have shown that activated carbon (AC) is effective in capturing the MeBr following such fumigation, to prevent its release to the atmosphere. In the event of a large urban Ba spore release, large quantities of MeBr would be needed and hence potentially large quantities of AC as well. The purpose of this study was to evaluate the feasibility of processing the AC to allow it to be reused for further capture of MeBr.

In the present study, we quantified how well an AC sample maintained its adsorption capacity for MeBr over several adsorption/desorption cycles, using three different gas conditions. During the adsorption phase, the AC was exposed to a feed gas of 5.3% MeBr until saturation of the AC sample was achieved. Subsequently, the MeBr was desorbed from the saturated AC by exposing the carbon bed to dry or ambient air heated to 100 °C.

Overall, the results for the adsorption tests showed relatively high levels of adsorption and ranged from approximately 0.43 to 0.58 g MeBr per gram AC. These higher-than-expected adsorption capacities may be due to the preconditioned AC samples we used, as well as the low relative humidity (RH) levels in the challenge gases (applicable to the first two test series).

The differences in adsorption capacity as a function of challenge gas and/or desorption gas characteristics were generally minor, although in some cases the differences were statistically significant. Tests to determine adsorption of moisture at high RH (75%), without the presence of MeBr, suggest that the adsorption capacity for moisture was approximately 10% of the AC capacity for MeBr.

The adsorption capacity of the AC was not affected (did not diminish) through the five adsorption/desorption cycle series that each AC sample was subjected to. The process of desorbing the MeBr using a 100 °C temperature gas was effective in maintaining relatively high and stable adsorption levels of the AC samples for at least five cycles; the adsorption capacity did not diminish over the course of the five cycles but remained rather stable. However, we caveat that the tests used only five cycles and may not yield sufficient data to assess the effect of numerous repeated adsorption/desorption cycles.

While we have demonstrated in this study the ability to efficiently remove MeBr from AC and in the process, allow the AC to be reused (i.e., regenerate the AC without losing its adsorption capacity for MeBr over several cycles), further research is recommended related to the reuse of MeBr on a wide scale following a Ba incident, including development of methods to allow reuse of the MeBr desorbed from AC.

Table of Contents

Dis	sclaime	9r	ii	
Ex	ecutive	e Summary	iv	
Lis	t of Fig	gures	vi	
Lis	t of Ta	bles	vi	
Ac	ronyms	s and Abbreviations	viii	
1	Introd	luction	1	
2 Materials and Methods			2	
	2.1	Test Matrix and Study Description	2	
	2.2	Activated Carbon and MeBr	3	
	2.3	Test facility	4	
	2.4	AC Adsorption/Desorption Test Apparatus	4	
	2.5	Gas Flow Rate	8	
	2.6	Relative Humidity and Temperature	8	
	2.7	Sample Preparation and Conditioning	8	
	2.8	AC Moisture Content	9	
	2.9	Methyl Bromide Concentration		
	2.10	Adsorption Tests		
	2.11	Desorption Tests	12	
	2.12 Gravimetric Method to Determine Adsorption Capacity			
	2.13 Ir	ntegration Method to Determine Adsorption Capacity	13	
2.14 Adsorption Capacity Characterization		Adsorption Capacity Characterization	15	
	2.15 C	Control Test with Elevated RH	15	
	2.16 S	Statistical Analysis	15	
3	Qualit	ty Assurance/Quality Control	16	
	3.1	Sampling, Monitoring, and Equipment Calibration		
		3.1.1. VIG FID Model 20 Concentration Measurement		
		3.1.2. Temperature and RH Measurements		
		3.1.3. Mass Flow Rate	17	
		3.1.4. Mass Measurements		
		3.1.5. Equipment Calibrations		
	3.2	Acceptance Criteria for Critical Measurements		
4	Results and Discussion			
	4.1 Stability of AC Moisture Content and Related Measures			
	4.2. A	Activated Carbon Regeneration Tests	24	
		4.2.1 Adsorption and Desorption Results for Each Test Cycle		

	4.2.2 Effect of Challenge Gas Conditions on Adsorption Capacity	
	4.2.3 The Effect of Reuse on Adsorption Capacity	
	4.3. Control Tests with Elevated RH Only	
5	Summary and Conclusions	
6	References	35
6 Apj	References pendix A: Test Conditions	35 1
6 Apj Apj	References pendix A: Test Conditions pendix B: Carbon tube mass stability preliminary tests	35 1 1

List of Figures

Figure 2-2. Sample column prepared for installation	9
Figure 2-3. Sealed sample tube	9
Figure 2-4. Typical Adsorption Curve	11
Figure 2-5. Typical Desorption Curve	12
Figure 4-1. Comparison of MeBr desorbed vs MeBr adsorbed using gravimetric analysis	28
Figure 4-2. Comparison of MeBr desorbed vs MeBr adsorbed using the integration method FID	29
Figure 4-3. Average adsorption capacity for each test series (±SD)	30
Figure 4-4. Average adsorption capacities for Test 1 cycles (±SD)	31
Figure 4-5. Average adsorption capacities for Test 2 cycles (±SD)	32
Figure 4-6. Average adsorption capacities for Test 3 cycles (±SD)	32
Figure 4-7. Adsorbed and desorbed moisture with an exposure stream of 75% RH in ambient air	33

List of Tables

Table 2-1. Test Matrix	2
Table 2-2. AC Manufacturer Specifications	3
Table 3-1. FID Operating Specifications	16
Table 3-2. Relative Humidity Sensor and Temperature Probe Operating Specifications	17
Table 3-3. Mass Flow Controller Specifications	17
Table 3-4. Flow Calibrator Specifications	18
Table 3-5. Balance Operating Specifications	18
Table 3-6. Summary Sampling and Monitoring Equipment QA/QC Checks	19

Table 3-7. Critical Measurement Acceptance Criteria	20
Table 3-8. Accuracy (% Error) of Critical Measurements	21
Table 3-9. Data Precision (SD) of Critical Measurements	21
Table 3-10. FID Drift for Each Test Duration	22
Table 4-1. Moisture Content (%) of Bulk Carbon During Evaluation Period	23
Table 4-2. Amount of Moisture Removed from Fresh Carbon Bed (g/g carbon)	24
Table 4-3. Adsorbed and Desorbed MeBr Using Gravimetric and Integration Analysis	26
Methods 26	
Table 4-4. Adsorption Capacity Comparison for Each Test Series	30
Table A-1. Adsorption Phase Test Conditions	A-2
Table A-2. Desorption Phase Test Conditions	A-4
Table A-3. RH only Test Conditions	A-6

Acronyms and Abbreviations

AC	activated carbon
ACS	activated carbon system
ASTM	American Society for Testing and Materials
ANOVA	analysis of variance
Ba	Bacillus anthracis
сс	cubic centimeter
CCM	cubic centimeters per minute
CCl ₄	carbon tetrachloride
CMAD	Consequence Management Advisory Division (EPA)
DAS	data acquisition system
DCMD	Decontamination and Consequence Management Division (EPA)
EPA	U.S. Environmental Protection Agency
ft	feet
FID	flame ionization detector/detection
g	gram(s)
GC	gas chromatograph/chromatography
KOH	potassium hydroxide
L	liter
Lpm	liter per minute
MeBr	methyl bromide
MFC	mass flow controller
mg	milligram(s)
min	minute(s)
NA	not applicable, not available
N ₂	nitrogen
NHSRC	National Homeland Security Research Center (EPA)
NIST	National Institute of Standards and Technology
OLEM	Office of Land and Emergency Management (EPA)
ORD	EPA Office of Research and Development
PDAQ	personal data acquisition
ppm	part(s) per million
psi	pound(s) per square inch
QA	quality assurance
QC	quality control
RH	relative humidity
SD	Standard deviation
slpm	standard liter(s) per minute
UHP	ultra high purity
WACOR	work assignment contracting officer's representative

1 Introduction

Methyl bromide (MeBr) has been demonstrated in the laboratory (Wood et al., 2016; Juergensmeyer et al., 2007) as well as in full-scale field testing (Serre et al., 2016) to be an effective decontaminant for the inactivation of *Bacillus anthracis* (Ba) spores on a wide range of materials. Other advantages of using MeBr as a decontaminant include many personnel trained in its use (as an agricultural/commodity fumigant), ease of penetration of materials, and relative compatibility with most materials.

To prevent release of MeBr to the atmosphere to avoid human exposure (MeBr is toxic, with a Permissible Exposure Limit of 20 parts per million; The National Institute for Occupational Safety and Health, 2018), air quality impact, and depletion of stratospheric ozone, laboratory studies have demonstrated the capture of MeBr onto activated carbon (AC) (Leesch et al., 2000; Snyder and Leesch, 2001; Gan et al., 2001). Additionally, a full-scale study was conducted to evaluate an activated carbon system (ACS) employed for the capture of MeBr under the conditions that would be used for decontaminating a building structure contaminated with Ba spores (Wood et al., 2015).

In the event of a large-scale Ba spore release, large quantities of MeBr would potentially be needed for decontamination and ideally, the AC used to capture the MeBr could be regenerated and deployed for reuse. (The reuse of the captured MeBr is also desired, but that is a topic for future research.) Indeed, once the MeBr is adsorbed onto the AC ("adsorption" refers to when a gas such as MeBr adheres to the microscopic surfaces within the pores of the carbon granules), there are processes that can be used to remove it from the AC and render the MeBr into a less hazardous chemical (Yang et al., 2015; Joyce and Bielski, 2010). Further, in the temperature swing adsorption process, hot air is used to desorb (remove) the MeBr from the AC, and in the process, the hot air also regenerates the AC so that it can be reused (Value Recovery, 2018). This technology is used at a few quarantine and pre-shipment locations in the U.S, where MeBr is used to fumigate agricultural products.

In the present study, we evaluated a similar temperature swing adsorption process, utilizing gas streams with different temperatures and relative humidity levels for adsorption and desorption of the AC. More specifically, we quantified how well an AC sample maintained its adsorption capacity for MeBr over several adsorption/desorption cycles, using three different adsorption/purge gas conditions. Additionally, a few tests were also conducted to determine adsorption of water vapor from air without MeBr. Lastly, preliminary scoping test results are provided in Appendix C that demonstrate the effect of various operational parameters (e.g., gas temperature, MeBr concentration, relative humidity) on the adsorption capacity of AC.

2 Materials and Methods

2.1 Test Matrix and Study Description

Three tests were conducted in triplicate, with each test replicate consisting of a series of five complete cycles of adsorption and desorption phases. Each test replicate began with a fresh 1 g sample of AC. During the adsorption phase of testing, 53,000 parts per million (ppm) MeBr (5.3%) in nitrogen gas (N₂) was used as the challenge gas at a flow rate of 0.5 liters per minute (Lpm) at ambient temperature (uncontrolled but averaged 22 °C throughout the study). (Note, although chloropicrin is sometimes added to cylinders of MeBr as an odorant to detect leaks, none was used in these tests.) The RH of the MeBr gas stream in Tests 1 and 2 was relatively low (~ 3%), and the MeBr gas was at the moisture content of the gas cylinder. The RH was elevated to 75% for the Test 3 evaluations. The desorption gas stream was heated to the target temperature prior to entering the column. Dry compressed air was used as the desorption gas for Test 1 and ambient air was used for Tests 2 and 3. Table 2-1 details the test parameters evaluated for this study.

Test ID	Cycle Phase	Challenge Gas	Gas Temperature (°C)	RH (%)
	Adsorption	5.3% MeBr in N₂	Ambient	As received (typically 3%)
1	Desorption	Dry air from the laboratory air compressor system ("house air")	100	Typically, 1.0% @ 100°C
0	Adsorption 5.3% MeBr in N ₂		Ambient	As received (typically 3%)
2	Desorption	Ambient air	100	Ambient (typically 5%)
3	Adsorption	5.3% MeBr in N ₂ , with moisture added to raise RH	Ambient	75
	Desorption	Ambient air	100	Ambient (typically 5%)
Control test with	Adsorption	Ambient air with moisture added to raise RH – no MeBr	Ambient	75
air and elevated RH – no MeBr	Desorption	Ambient air	100	Ambient (typically 5%)

Table	2-1.	Test	Matrix

Ancillary tests were also conducted outside the primary test matrix as follows:

- Tests to determine mass adsorption of water vapor only. (Control test listed in Table 2-1.) This test was done to compare the mass of water adsorbed to the total mass adsorbed in Test 3 (mass gain on AC attributed to both MeBr and water vapor).
- A mass stability analysis of the carbon tube over an observation period representative of a regeneration test series, to ensure that variations in the mass of the tube did not affect the measurements of the mass of carbon.
- Temporal evaluations of the bulk AC moisture content.
- Scoping tests to assess the effect of operational parameters such as gas temperature, MeBr concentration, relative humidity, and AC moisture content on the adsorption capacity of the AC.

2.2 Activated Carbon and MeBr

Premium coconut shell-derived granular AC (General Carbon Corp., Paterson, N.J., part number (p/n) 30100) was used for this study because of its absorptivity for MeBr compared to other ACs (Snyder and Leesch, 2001). The manufacturer's specifications for the AC are detailed in Table 2-2.

Parameter	Value
Mesh Size – 4 x 8, %	90
Less than No. 4, %	5
Greater than No. 8, %	5
CCl ₄ ^a Activity, %	70
lodine No., milligrams (mg)/gram (g)	1200
Hardness No., %	98
Ash Content, %	5
Moisture Content, % (as packaged)	5
Typical Density, g/cubic centimeter (cc)	0.47 – 0.50
pH	6 - 8

Table 2-2. AC Manufacturer Specifications

^aCarbon tetrachloride. CCl₄ activity is used as a relative measure of pore volume.

The AC was stored indoors throughout the duration of the study in double-bagged vinyl plastic, to maintain dryness.

The challenge gas used for this study was 53,000 ppm (209 mg/liter (L)) MeBr gas mixed in nitrogen (N_2) (Custom Gas Solutions; Durham, NC). A comparable concentration was previously used in a full-scale study to evaluate an ACS for the capture of MeBr at conditions that would be used for decontaminating a building structure contaminated with Ba spores (Wood et al., 2015).

2.3 Test facility

All work for this effort was conducted in the Air and Energy Management Division's test facility located at the U.S. EPA, Research Triangle Park High Bay Building room 226. Because of the hazardous nature of MeBr, the test facility was designated as chemical safety level 4. The MeBr gases were stored in an external gas closet located approximately 20 feet from the facility and piped into the test facility using connected 1/4-inch stainless steel tubing. A fixed gas regulator located in the test facility served as the supply point for the gases located in the gas closet. A portable gas cabinet located in the facility housed the dilution N₂ and hydrogen/helium (H₂/He) fuel for the MeBr analyzer. A flexible duct connected the internal gas cabinet to the central exhaust system of the building, effectively isolating the gas cabinet from the work area in the event of a gas leak.

A bench top oven (1300U, VWR, Radnor, PA) used for drying the AC (for moisture content measurement) was maintained at 150 °C (302 °F) using an Omega CSC32-K bench top temperature controller (Omega Engineering, Inc., Stamford, CT). A bench top desiccator (model 1340; Boekel Scientific; Philadelphia, PA) containing silica was also used for moisture content evaluations. A HOBO® temperature and humidity logger (UX100, Onset Computer Corp., Cape Cod, Massachusetts) placed inside the desiccator indicated that the internal RH was 15% throughout the duration of testing. An ENTIRS 124-1S top loading balance (Sartorius, Göttingen, Germany) with a range of 120 g and resolution of 0.0001 g was used for all mass measurements. A custom plexiglass enclosure was used as a secondary barrier against moving air that could adversely affect the accuracy of the mass readings.

2.4 AC Adsorption/Desorption Test Apparatus

The MeBr experiments were carried out in a bench-scale system custom-built to maintain and/or monitor the prescribed test conditions. The AC sample was contained in a custom borosilicate glass AC tube. The bench-scale system was assembled under a chemical hood located in the test facility as a safety precaution in the event of an unplanned MeBr gas release. The system consisted of:

- Approximately 36 feet (ft) of 316 stainless steel tubing (McMaster Carr, Elmhurst, IL)
- Flame ionization detector (FID) (VIG Industries, Anaheim, CA)
- 4 Sierra Smart-Trak mass flow controllers (MFCs) (Sierra Instruments, Monterey, CA)
- 1 Vaisala HMP50 temperature and relative humidity probe (Vaisala, Helsinki, Finland)
- 3 Omega K-Type thermocouples (Omega Engineering, Stamford, CT)
- Gas humidity bottle (Fuel Cell Technologies, Inc., Albuquerque, New Mexico)
- MeBr gases: 500 ppm (2 mg/L) MeBr, 13,000 ppm (51 mg/L) MeBr, and 53,000 ppm (209 mg/L) (Custom Gas Solutions, Durham, NC)
- Ultra-high purity (UHP) nitrogen (Airgas, Durham, NC)
- FID fuel: 40% hydrogen/60% helium UHP gas mixture (Airgas, Durham, NC)
- Dry compressed air (Airgas, Durham, NC)



• Pump for ambient air desorption (Cole-Parmer L-792000-30)

Figure 2-1. Flow diagram of test apparatus

Fig. 2-1 I.D.	Equipment	Description
ACT	Ambient collection tube	Open to the atmosphere; under constant vacuum. Prevents significant spikes and drops in system pressure.
AF	Sample filter	Protects FID by filtering particles from sample gas.
СТ	Carbon trap	Removes MeBr from bypass streams before being vented into the hood
C1	Coiled heating tube	Increases resonance time of the exposure gas stream to allow adequate heating and mixing ahead of the carbon tube.
C2	Coiled mixing tube	Mixes dilution nitrogen with the exposure gas ahead of the FID
DAQ	Data acquisition system	Digitally records MeBr concentration, RH, temperatures and flow rates
FID	Flame ionizing detector	VIG Industries Model 20 total hydrocarbon analyzer
FM	Flow meter	20 Lpm rotameter.
G1	Nitrogen gas cylinder	Zero gas used for FID calibrations
G2	0.05% MeBr cylinder	Span gas used for FID calibrations
G3	1.3% MeBr cylinder	Span gas used for FID calibrations
G4	5.3% MeBr cylinder	Exposure gas used for adsorption
G5	Nitrogen gas cylinder	Dilution gas for sample
G6	H ₂ in He gas cylinder	40% hydrogen in helium. Used to fuel FID
HB	Gas humidity bottle	Adds water vapor to exposure gas stream
HT	Humidity transmitter	Vaisala, used to measure the relative humidity of the exposure gas stream
M1	Mass Flow Controller	10 Lpm, used to regulate zero and span gases during FID calibration
M2	Mass Flow Controller	1 Lpm, used to regulate 5.3% MeBr gas flow during adsorption phase
M3	Mass Flow Controller	5 Lpm, used to regulate ambient air flow during desorption phase
M4	Mass Flow Controller	15 Lpm, used to regulate nitrogen dilution flow
OV	GC oven	Heats coiled tubing to 100°C
P1	Thomas pump	Generates ambient air flow during desorption phase

Table 2-3.	Identification	of Test	Equipment
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P2	Chemical pump	Moves contents of ambient collection tube through the carbon trap
ST	Carbon tube	Borosilicate glass chamber, 3" effective length, 5/8" I.D. to 5/16" tube studs (Contains the AC.)
TC1	Thermocouple probe	Located at inlet port to measure the temperature of inlet gas stream
TC2	Surface thermocouple	Affixed to the outer surface of the carbon tube adjacent to the carbon sample to monitor temperature changes during testing
ТС3	Thermocouple probe	Located at outlet port to measure the temperature of outlet gas stream
V1-4	On/Off Valve	Starts and stops gas flow of respective calibration gases. Located on gas manifold in the H-240 gas cabinet
V5	Regulator Valve	Dilution nitrogen regulator
V6	Regulator Valve	FID fuel cylinder regulator
V7	Regulator Valve	Gas regulator located in H-226 connected to H-240 gas manifold
V8	Flow adjustment valve	Located between the inlet and outlet of the ambient air pump. Used to set the gas pressure for the air MFC (M3)
V10-12	On/Off Valve	Starts and stops gas flow through manifold in the H-226 chemical hood
V13	Directional Valve	Directs exposure gas through the test stand or bypasses the test stand and sends gas to the ambient collection tube
V14	Flow adjustment valve	Used in conjunction with V15 to direct a portion of the exposure gas through the gas humidity bottle
V15	On/Off Valve	Opened to allow flow through gas humidity bottle, closed to bypass the gas humidity bottle
V16	Directional Valve	Directs flow through or around the GC oven or around it
V17	Directional Valve	Directs flow through or around the sample port inlet
V18	Directional Valve	Directs flow from the outlet sample port or the bypass to the mixing coil (C2)
V19	On/Off Valve	Opens/closes access to the ambient collection tube
V20	Directional Valve	Directs flow from either the hood (ambient air) or the sample lines
V21	Flow adjustment valve	Located between the inlet and outlet of the chemical pump. Allows the flow rate to be reduced to 10 Lpm without deadheading the 20 Lpm pump

2.5 Gas Flow Rate

Velocity measurements of each gas stream (exposure, dilution, and bulk) were controlled using Sierra Smart-Trak MFCs (Sierra Instruments; Monterey, CA). During flow rate verifications, each gas was introduced to the system in the same manner and location as during a test scenario. MeBr and desorption gases entered the system at a gas manifold located in the test facility and were measured at a point located immediately in front of the FID. Nitrogen gas was used to dilute the MeBr gas stream leaving the carbon tube prior to being measured by the FID. Concentrations of MeBr that exceeded 1.3% were diluted with N₂ to maintain the accuracy of the FID (Section 2.9). A series of five flow rate measurements was collected before and after each phase (adsorption and desorption) using a calibrated Gilibrator-2 Standard Air Flow Calibrator (Sensidyne LP, St. Petersburg, FL). The average of the series was used as the measurement.

2.6 Relative Humidity and Temperature

The RH of the challenge gas stream during both the adsorption and desorption phases was measured at the inlet of the carbon bed using a temperature and RH transmitter that had been calibrated within seven days of the test dates. This "HOBO" was calibrated prior to each test by comparing its RH data with known RH values that were generated in the sealed headspace above the individual saturated solutions of various salt compounds. The transmitter sensors were replaced if the calibration criteria could not be met.

The temperature was measured with Omega K-type thermocouples in three locations: (1) at the inlet of the column, (2) on the external surface of the column at the carbon bed, and (3) at the outlet of the column. The glass tube would not accommodate the direct insertion of a thermocouple probe into the carbon bed; therefore, a K-Type surface thermocouple was affixed to the outer surface of the AC tube at the carbon bed to monitor the progression of the exothermic reaction driven by the MeBr adsorption onto the AC. The thermocouples were calibrated annually by comparisons to the temperature sourced by a Fluke 744 Documenting Process Calibrator. The temperature and RH measurements data were logged continuously using a personal data acquisition (PDAQ) system (Measurement Computing Corporation; Norton, MA.

2.7 Sample Preparation and Conditioning

The AC sample was housed in a custom borosilicate glass AC tube with an inside diameter of 5/8 inch (in) and a length of 3 in that reduced to 1/4 in tube ports on both ends. An approximate 1 g sample was collected from the center of the bulk container of the AC and transferred to the glass AC tube. Leco® fine quartz wool (Saint Joseph, MI) was packed into the column on both sides of the carbon bed to hold the sample in the approximate center of the column. The initial weight of the tube assembly with AC was measured gravimetrically using the procedure detailed in Section 2.12. Figure 2-1 shows the column containing the AC sample prepared for installation into the test stand.



Figure 2-2. Sample column prepared for installation

Prior to starting the series of five cycles of adsorption/desorption, the carbon bed was conditioned to ensure that the physical state of the AC sample prior to initiating the first cycle was consistent with the physical state of the sample for each subsequent cycle. During the conditioning phase, the carbon bed was exposed to an air (dry compressed or ambient) flow of 1 liter per minute (Lpm) at 100 °C. These conditions were maintained overnight for approximately 18 hours. Upon completion, the sample column was removed from the test stand, the tube ends were sealed with silicone rubber plugs (McMaster-Carr, Atlanta, GA; p/n 9277K37), and the column then was transferred to a desiccator that was maintained at 15% RH and room temperature to cool for 1 hour. The sample mass was subsequently analyzed gravimetrically (Section 2.12). Figure 2-2 shows a sample column with both tube ends plugged, which is the typical sample column configuration when it is not installed in the test stand.



Figure 2-3. Sealed sample tube

2.8 AC Moisture Content

The moisture content of the bulk AC was monitored over the duration of the project. A daily calibration check was performed on the balance prior to use. (Briefly, the initial weight of each of three empty Pyrex dishes was measured. A sample of fresh AC (approximately 10 g) was collected from the bulk container and transferred to each dish. The initial mass for each sample replicate was measured and recorded (AC + dish). The samples were placed in the oven (150 °C) for 6 hours (\pm 15 min), then allowed to cool in a desiccator containing silica indicating desiccant

(p/n S162-500, Fisher Scientific, Hampton, NH) for 1 hour. The samples (AC + dish) were weighed individually for the final mass measurement. The moisture content of each AC sample was calculated as follows:

Moisture content (%) =
$$\frac{B-C}{B-A} \times 100$$

where:

A was the weight of the dish, g B was the weight of fresh AC + dish, g C was the weight of dry AC + dish, g

2.9 Methyl Bromide Concentration

A dual-channel VIG Industries (Anaheim, CA) model 20/2 flame ionization detector (FID) was used to continuously and simultaneously monitor MeBr levels at two of the three sample locations. Hydrogen gas was supplied to the instrument from a pressurized gas cylinder for the flame source. MeBr data were collected, logged, and stored using a data acquisition system (lotech Corporation). The FID calibration and the MeBr dilution were checked before and after each cycle using a bias span (calibration gases traveled through the sample line prior to detection). Calibration gases were obtained from Custom Gas Solutions (Durham, NC), and included 0.05% MeBr in N₂, 1.3% MeBr in N₂, and 5.3% MeBr in N₂, to span the range of MeBr concentrations that would be expected during adsorption and desorption tests. The FID was zeroed using ultra-high-purity N₂ (Airgas, Inc., Fort Lauderdale, FL). The channel 1 detector of the FID served as the high-level MeBr monitor and was calibrated using the 1.3% MeBr gas, while channel 2 was the lower level detector and was calibrated using the 0.05% gas.

Previous method development work identified issues with the FID response factor at concentrations exceeding 1.3%. Therefore, a dilution system consisting of ultra-zero N_2 and an MFC was used to dilute the gas exiting the carbon tube prior to analysis by the FID.

The total mass of MeBr adsorbed onto the AC was determined using two methods, gravimetric analysis and integration using the gas measurements of MeBr.

2.10 Adsorption Tests

The FID instrument was used during the adsorption tests to continuously measure the MeBr concentration in the gas at the outlet of the AC bed. Immediately before and after each adsorption test, the MeBr concentration in the bulk stream was confirmed via bypassing the carbon tube and sending the gas directly to the FID as follows. A nitrogen dilution system was used to adjust the bulk flow rate to 4 liters per minute (Lpm), approximately twice the required flow for the FID analyzer. The FID continuously sampled the bulk gas while the excess portion or the overflow stream was directed to the ambient carbon trap to scrub the MeBr before being released into the chemical hood. During Test 3, the RH of the MeBr exposure stream was controlled using a gas humidity bottle (model LF-HBA, Fuel Cell Technologies, Inc., Albuquerque, NM) and two inlet feed streams as shown in Figure B-1. Valves V14 and V15

were adjusted to achieve the desired prescribed RH condition. The flow rate of the 5.3% MeBr challenge gas was controlled at 0.5 Lpm using a calibrated 0-1 Lpm MFC. The flow rates of all streams were verified with a calibrated Gilian Gilibrator-2 (Sensidyne, LP, St. Petersburg, FL) calibration system before and after each test.

After verifying MeBr concentration, flow rates and the target RH were reached, the challenge gas was directed through the carbon bed, initiating the MeBr adsorption cycle. See Figure 2-4 for a typical adsorption breakthrough curve. (The curve below shows the MeBr concentrations after dilution with N₂. The initial portion of the curve is the verification of the MeBr concentration, which was approximately 7,200 ppm after dilution, and remained steady for 5 minutes. Following the verification, the MeBr gas enters the carbon tube, with breakthrough occurring rapidly.) The adsorption phase continued until the bulk sample concentration at the outlet of the AC tubes was stable, indicating that the carbon bed was saturated. A stable concentration of adsorption, the MeBr gas bypassed the carbon tube, and the sample column was removed from the test stand, the carbon tube ends were plugged, and the column allowed to cool for 1 hour. The mass of MeBr adsorbed onto the carbon sample was analyzed gravimetrically (Section 2-12). Adsorption capacity was assessed by the mass of MeBr adsorbed per gram of conditioned AC. After the AC tube was weighed, it was placed back into the test stand, and the desorption cycle commenced as discussed below.



Figure 2-4. Typical Adsorption Curve

2.11 Desorption Tests

The FID was used during the desorption cycles to continuously measure the MeBr concentration in the gas at the outlet of the sorbent bed. Immediately before and after each desorption test, a bump test was performed on the FID with 1.3% MeBr certified gas. A nitrogen dilution system was used to adjust the bulk flow rate to 4 Lpm, approximately twice the required flow for the FID analyzer. The FID sampled the bulk sample stream continuously while the excess portion or the overflow stream was directed to the ambient carbon trap to scrub the MeBr before the flowing gas was released into the chemical hood. The flow rate of the air (zero and ambient) gas was controlled at 1 Lpm using a calibrated 0-5 Lpm MFC. The flow rates of all streams were verified with a calibrated Gilian Gilibrator-2 (Sensidyne, LP, St. Petersburg, FL) calibration system before and after each test.

After verifying flow rates, the desorption gas was directed through the saturated carbon bed, initiating the desorption phase. The desorption phase continued until the bulk sample outlet concentration was stable, indicating the end of the desorption cycle. A stable concentration was marked when the FID reading showed less than 1% change within 2 minutes (min), which typically occurred within two hours, although desorption was allowed to proceed overnight. Refer to Figure 2-5 for a typical desorption curve. Upon completion, 1.3% MeBr gas was directed through the bypass, and the sample column was removed from the test stand, the carbon tube ends were then plugged, and the column was cooled for 1 hour. The mass of MeBr adsorbed onto the carbon sample was analyzed gravimetrically. Desorption efficiency was assessed by the mass of MeBr desorbed per mass adsorbed. After the AC tube was weighed, it was placed back into the test stand to conduct another adsorption cycle. Five adsorption/desorption cycles were conducted for each AC sample.



Figure 2-5. Typical Desorption Curve

2.12 Gravimetric Method to Determine Adsorption Capacity

At the start of each sampling day, the balance was verified with Class-S calibration weights. Calibration data were recorded in the laboratory record book associated with the balance. Gravimetric analyses of the carbon samples were performed with the AC in the tube assembly, which included borosilicate glass tube, quartz wool (model 502-177; Leco; St. Joseph, MI), Keck® joint clamp (Cole Parmer; Chicago, IL), and two plugs, on a custom weighing stand. When weighing the carbon tube, the balance reading was allowed 20 min to stabilize before recording the reading. This procedural step was based on preliminary test findings that are detailed in Appendix C.

Each fresh AC sample was weighed in a tared weigh boat (model YBW 01L; Göttingen, Germany) before transferring to the tube assembly, henceforth carbon tube.

The mass of MeBr adsorbed by the AC sample during a cycle was determined as the difference of the masses of the carbon tube with conditioned (or desorbed) AC and the mass of the carbon tube with saturated AC from the subsequent adsorption cycle. The adsorption capacity of the AC sample was determined by dividing the mass of the adsorbed MeBr by the mass of the conditioned AC sample.

The amount of desorbed MeBr was determined by the difference in the masses of the carbon tube with saturated AC from the adsorption phase and the mass of the carbon tube with desorbed AC from the following desorption cycle. The amount of MeBr desorbed was normalized by dividing by the mass of the conditioned AC.

All gravimetric measurements were recorded to the fourth decimal place.

2.13 Integration Method to Determine Adsorption Capacity

Real-time gas flowrates (Lpm), gas temperatures (°C), and MeBr concentration (ppm) data were used for the integration method to determine mass of MeBr mass adsorbed and desorbed and were digitally recorded (ten-second averages) during testing for post-test processing. For the integration method, the total mass of MeBr adsorbed onto the AC was calculated based on the difference between the carbon tube challenge concentration (target of 53,000 ppm) and outlet concentration of MeBr in the gas stream, and then converted to mass (as described below), for each time step, for the duration of the adsorption phase.

Inlet MeBr Mass (adsorption)

Prior to the start of adsorption testing, the inlet (challenge) MeBr gas concentration was measured by bypassing the carbon tube. Avogadro's Law was used to determine the number of moles detected for the time interval (moles (mol)/min) (using the recorded gas temperature and assuming the pressure was close to atmospheric).

$$\frac{N_{inlet}}{t} = \frac{PV}{RT} = \frac{(1 \text{ atm})(\dot{V})}{\left(0.082057 \frac{L \text{ atm}}{mol \text{ K}}\right)(T)}$$

where N_{inlet} is the total number of moles of gas at the inlet, t is a unit of time (e.g., minutes), \dot{V} is the volumetric flow rate of the inlet gas (L/minute), P is pressure (1 atmosphere), R is the ideal gas law constant, and T is the temperature (K) of the inlet gas.

The moles of gas at the inlet for each time interval were multiplied by the elapsed time for number of moles.

$$N_{inlet} = \frac{N_{inlet}}{t} \times \Delta t$$

where N_{inlet} is the number of moles of gas at the inlet, t is a unit of time, and Δt is the time interval.

The moles of MeBr were calculated using the concentration of MeBr measured by the FID (C_{MeBr} [ppm]) at the time interval:

$$N_{MeBr} = \frac{C_{MeBr}(ppm)}{1,000,000} \times N_{inlet}$$

where N_{MeBr} is the number moles of MeBr at the inlet.

The molecular weight of methyl bromide (94.94 g/mol) was used to determine the mass (g) adsorbed at the time interval:

$$m_{MeBr\ inlet} = MW_{MeBr} \times N_{MeBr}$$

where $m_{MeBr inlet}$ is the mass of MeBr entering the AC tube for a specific time step, and MW_{MeBr} is the molecular weight of MeBr

Outlet MeBr mass (desorption)

A similar method was used to calculate the mass of MeBr desorbed at the outlet of the carbon tube. Instead of using the MeBr concentration measurement at the inlet, real-time MeBr measurements at the outlet were used to calculate the MeBr mass exiting the carbon tube.

The total mass of MeBr desorbed was determined by subtracting the calculated MeBr mass at the outlet from the inlet mass (FID reading when sampling the desorption air adjusted by the baseline reading) for each time interval, then adding the amounts over the duration of the desorption cycle. The point at which the system reached steady state marked the time the test cycle was complete.

$$M = \sum_{i=1}^{n} \left(\frac{C_i}{1,000,000} \times Q \times \Delta t \times 1/V_M \times MW \right)$$

where M is the total mass of MeBr (g), C_i is the concentration of MeBr (ppm) at time interval I (minute), Q is the volumetric flow rate of gas (liters/minute), Δt is the time interval (minutes), V_m is the molar volume of ideal gas at the temperature of the gas (liters), and MW is the molecular weight of MeBr (94.94 g/mol).

2.14 Adsorption Capacity Characterization

Each adsorption cycle was conducted for approximately 33 minutes to ensure that the concentration of MeBr at the outlet of the carbon tube had stabilized (indicating saturation or maximum adsorption capacity of the AC). The outlet level was considered stable when the difference between each successive 10-min block average of MeBr concentration was less than 0.3%.

The mass of MeBr adsorbed and desorbed for each cycle was determined using the two methods: a gravimetric approach and an integration approach.

For the integration method (Section 2.13), the total mass of MeBr adsorbed onto the AC was calculated based on the difference between the carbon tube challenge concentration (target of 53,000 ppm) and outlet concentration of MeBr in the gas stream, and then converted to mass (as discussed in Section 2.13), for each time step. Initially, the mass adsorbed was calculated using a time step of six seconds, but for the last two tests (3.2 and 3.3), a time step of one second was used to identify the moment of breakthrough more accurately. The total mass adsorbed was then accumulated for the total time the adsorption cycle took place, i.e., until the stable MeBr level was reached. This approach to determining mass adsorbed is like the method used by Li et al. (2003).

The adsorption capacity was also determined gravimetrically as the mass of MeBr adsorbed divided by the conditioned mass of AC tested. AC samples were weighed with a gravimetric balance before the adsorption and desorption phases of each regeneration cycle (Section 2.12).

2.15 Control Test with Elevated RH

Control tests were conducted using a challenge gas with elevated RH (75%) but no MeBr, to assess the mass of moisture adsorbed onto the AC bed compared to the total mass gain when exposed to a challenge gas with an RH of 75% and MeBr (Test 3). These control tests were carried out in the same manner as Test 3 except ambient air at 75% RH was used as the challenge gas instead of 5.3% MeBr in N₂, at 75% RH.

2.16 Statistical Analysis

Adsorption capacities as well as other measurements associated with the study parameters were compared using one-way analysis of variance (ANOVA) in MS Excel. The p-value from two-sided (non-directional) tests was used to test for significance ($\alpha = 0.05$).

3 Quality Assurance/Quality Control

Quality assurance (QA)/quality control (QC) procedures and results are summarized below.

3.1 Sampling, Monitoring, and Equipment Calibration

3.1.1. VIG FID Model 20 Concentration Measurement

The Model 20 is a microprocessor-based oven-heated total hydrocarbon gas analyzer designed for high accuracy, sensitivity, and stability. The Model 20 uses an FID for continuous measurement. All components that contact the sample throughout analysis are maintained in a temperature-controlled oven to prevent condensation and to provide repeatable, reliable performance in the analysis. Ultra-zero N₂ was used for zero calibrations. Certified concentrations of 0.05% and 1.3% MeBr (balanced in nitrogen) were used for span calibrations. The specifications for the instrument are listed in Table 3-1.

Parameter	Specifications		
Zero and Span Noise	Less than 0.2% of full scale		
Zero and Span Drift	±1% full scale per 24 hours		
Range ^a	0-100, 0-1000, 0-10000, 0-100000 ppm		
Linearity	Within 1% of full scale through all ranges		
Repeatability	Within 1% of full scale through all ranges		
Stability	Within 1% of full scale through all ranges		
Sample Flow Rate	4 L/min		
Avg. Accuracy (0.05% MeBr) ^b	13.3% (± 12.5% RSD)		
Avg. Accuracy (1.3% MeBr) ^b	1.5% (± 1.8% RSD)		
Precision as Calibrated (%RSD) ^c	± 1.818%		
^a Four ranges per amplifier			
$^{\rm b}$ Expressed as percent error. Assessed in-situ with certified MeBr (0.0500% ± 0.001% or 1.3% ±			

Table 3-1. FID Operating Specifications

0.0026%) prior to each test over the duration of the study

 $^{\rm c}$ Assessed with certified MeBr (1.3% \pm 0.0026%) over the duration of the study

3.1.2. Temperature and RH Measurements

The real-time temperature and RH measurements were collected using a K-type thermocouple and Vaisala (Vantaa, Finland) HMD53 temperature and humidity probe, respectively. The specifications for each device are shown in Table 3-2.

Parameter	K-Type Thermocouple	Vaisala		
RH range	NA ^a	0 to 98%		
RH accuracy: 0–90 %	NA	± 3%		
RH accuracy: 90–98 %	NA	± 5%		
RH resolution	NA	0.001% ^b		
Temperature range	-200 to 1200 °C	-10 to 60 °C		
Temperature accuracy	± 1.2 °C @ 25 °C	±0.6 °C @ 20 °C		
Temperature resolution	0.01 °C	0.001 °C ^b		
Uncertainty as Calibrated ^c	± 0.15 °C	1.5%		
Precision as Calibrated ^d (%RSD)	N/A	± 1.7%		
^a Not applicable. ^b Vaisala resolution				

Table 3-2. Relative Humidity Sensor and Temperature Probe Operating Specifications

^dAssessed in-situ with Vaisala NaCl calibration cell periodically over the duration of the study

3.1.3. Mass Flow Rate

SmartTrak® 100 (Sierra Instruments, Inc., Monterey, CA) mass flow controllers were used to control and collect real-time measurements of each gas introduced to the system. Table 3-3 shows the specifications of each MFC used in this investigation.

Table 3-3. Mass Flow Controller Specifications

Parameter			
Range	0 – 1 slpm	0 – 5 slpm	0 – 15 slpm
Accuracy ^a	±1.0% full scale	±1.0% full scale	±1.0% full scale
Linearity	± 0.05% full scale	± 0.05% full scale	± 0.05% full scale
Repeatability	± 0.2% full scale	± 0.2% full scale	± 0.2% full scale
Uncertainty as Calibrated ^b	± 2.9 SCCM	± 0.07 % of corrected reading and ± 0.01 LPM	± 0.03 % of corrected reading and ± 0.10 LPM
Precision as Calibrated ^c (%RSD)	± 1.19%	± 0.692%	± 1.27%
^a As received from the manufacturer ^b Assessed by the Metrology Laboratory prior to testing ^c Assessed in-situ at test conditions with the Gilian flow calibrator over the duration of the study			

Prior to each test, flow rates were verified using the Gilian Gilibrator-2 Flow Calibrator (Sensidyne, LP, St. Petersburg, FL). An average of five readings was used as the accepted measurement. For each sequence of readings, no individual reading varied more than 10 standard cubic centimeters per minute (CCM) from the average. The specifications of the flow calibrator are shown in Table 3-4.

Parameter	Specification		
Flow Cell Type	Standard		
Flow range	20 CCM to 6 Lpm		
Accuracy ^a (wet cell)	Better than 1%		
Uncertainty as Calibrated ^b	± 0.04% of corrected reading and ± 25 SCCM		
^a As received from the manufacturer			
^b Assessed by the Metrology Laboratory prior to testing			

Table 3-4. Flow Calibrator Specifications

3.1.4. Mass Measurements

Mass measurements of the carbon and associated tube/column apparatus were performed using an Entris 124-1S analytical balance (Sartorius, LLC, Columbus, OH). The weighing range was up to 210 g with a readability of 0.0001 g. Prior to each use, the calibration was verified using Troemner-certified class 2 weights (ASTM International (ASTM) Certification 782762A). Table 3-5 shows the balance specifications.

Parameter	Specification	
Capacity	120 g	
Readability	0.0001 g	
Repeatability	0.0001 g	
Linearity	0.0002 g	
Accuracy as Calibrated ^{a,b}	± 0.0010 g	
Precision ^{b,c} (%RSD)	± 0.0002%	
Display Drift⁵	± 0.0005 g	
^a Assessed by the Metrology Labo	ratory prior to testing	
^b Tolerance		
^c Assessed in-situ with Class S check weights over the duration of the		
study		

Table 3-5. Balance Operating Specifications

3.1.5. Equipment Calibrations

Approved operating procedures were used for the maintenance and calibration of all laboratory equipment. All equipment was certified calibrated or underwent calibration validated by EPA's Metrology Laboratory prior to use. Standard laboratory equipment such as balances, RH meters, and MFCs were routinely monitored for proper performance. Calibration of measurement devices was done at the frequency shown in Table 3-6. All deficiencies were noted, and instrumentation was adjusted to meet calibration tolerances and recalibrated within 24 hours. If tolerances were not met after recalibration, additional corrective action was taken, including recalibration or/and replacement of the equipment.

Equipment	Matrix	Measurement	Calibration	Calibration Method	Acceptance Criteria	Corrective
RH probe	Challenge gas	Inlet RH	Weekly	Saturated salt cells	± 5%	Replace Vaisala sensor.
FID	Outlet gas	MeBr in outlet stream	Before each test	Zero and certified span gases	± 5% target	Leak check system and repeat calibration.
Thermocouple	Challenge gas	Inlet temperature	Annually	Compared to NIST*- traceable thermometer	± 1.1 °C	Replace thermocouple.
Balance	Activated carbon sample	MeBr gained/ lost	Before each use	Comparison to class 2 weights	± 0.1% target	Recalibrate balance.
MFC	Feed gases	Gas flow rate	Annually	Comparison to a Gilibrator calibration system	± 1% of full scale	Check line for leaks. Recalibrate MFC, if necessary.
NIST ^a - traceable timer	Exposure duration	Time	Annually	Compared to NIST- calibrated timer	± 1 minute per hour	Return to manufacturer for recalibration.

Table 3-6. Summary Sampling and Monitoring Equipment QA/QC Checks

^aNational Institute of Standards and Technology

3.2 Acceptance Criteria for Critical Measurements

Equipment detection limit values were provided by the manufacturer in the product literature. Failure to provide a measurement method or device that meets these goals resulted in a rejection of results derived from the critical measurement. For instance, some data points can be missing for the real-time test MeBr concentration, but the concentration can be calculated for whatever time interval data are available. Failure to collect the sorbent weight before the test, however, completely invalidated the test, and the test was repeated. Table 3-7 lists the quantitative acceptance criteria for critical measurements. Table 3-8 lists the critical measurements, their target values and, the accuracy of the actual values with respect to the target values (expressed as percent error) for each test. Table 3-9 lists the precision (as assessed by standard deviation) of the critical measurements.

Critical Measurement	Measurement Device	Accuracy	Precision	Detection Limit	Target	Corrective Action
MeBr test concentration	FID	Unknown	± 5%	250 ppm	NA	Check sample lines for leaks. Recalibrate FID.
MeBr challenge concentration	FID	± 5% of calibration gas	± 5%	250 ppm	13,000 ppm ± 1%	Check sample lines for leaks. Recalibrate FID.
RH of MeBr challenge stream	Vaisala	± 5%	± 5%	NA	75%ª	Replace Vaisala sensor.
Temperature of air stream (desorption)	K-type thermocouple	± 1.2 °C @ 100 °C	NA	0.01 °C	100 ± 1 °C	Adjust GC oven set point.
MeBr flow rate (adsorption)	Gilibrator	± 5%	± 5%	.02 Lpm	0.47 Lpm	Check sample lines for leaks.
Air flow rate (desorption)	Gilibrator	± 5%	± 5%	.02 Lpm	1.1 Lpm	Check sample lines for leaks.
Carbon bed mass	Sartorius Entris 124-1S	± 1%	± 0.001 g	0.001 g	1.0 ± 0.01 g	Add/remove sample (virgin only).
NA = not applicable. GC = Gas chromatograph. ^a Test 3 series only						

Table 3-7. Critical Measurement Ac	ceptance Criteria
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Test ID	AC Sample Mass	MeBr Challenge Gas Flow Rate	RHª	Desorption Air Flow Rate	Inlet Temperature ^ь
			Target Valu	e	
	1 g	0.5 LPM	75%	1 LPM	100°C
1.1°	3.4	28.5	-	-	-
1.2	0.4	20.7	-	12.6	1.4
1.3	3.5	26.0	-	11.9	0.9
1.4	1.9	26.0	-	11.9	1.4
2.1	4.8	26.0	-	9.6	0.8
2.2	4.9	26.0	-	9.0	0.4
2.3	2.5	26.0	-	9.7	0.6
3.1°	2.8	-	-	-	-
3.1b	3.2	4.0	3.4	10.3	0.6
3.2	4.4	0.86	1.8	9.4	1.2
3.3	5.8	0.87	2.0	8.3	2.1

Table 3-8. Accuracy (% Error) of Critical Measurements

Values in unshaded cells are in units of % error, i.e., the % difference between the target value and the actual value

^aRH was a critical measurement only for the Test 3 series.

^bTemperature was monitored during adsorption and controlled during desorption.

^cTest 3.1 was aborted due to a technical issue, incomplete data. A new test was run which is referred to as 3.1b

Table 3-9. Data Precision (SD) of Critical Measurements

Test ID	MeBr Flow Rate	RH ^a	Air Flow Rate	Inlet Temp ^b
	(Lpm)	(%)	(Lpm)	(°C)
1.1°	-	-	-	-
1.2	0.058581	0.6	0.00447	2.4
1.3	0.000015	0.7	0.00028	1.8
1.4	0.000022	0.7	0.00028	1.7
2.1	0.000082	0.52	0.00038	1.42
2.2	0.000010	0.50	0.0051	0.84
2.3	0.000038	0.61	0.0087	1.84
3.1°	-	-	-	-
3.1b	0.044721	2.06	0.0074	1.04
3.2	0.000034	1.7	0.0047	1.2
3.3	0.000020	1.4	0.015	1.4
^a RH was a critical measurement only for the Test 3 series.				

^bTemperature was a critical measurement only for the desorption phase.

°Test aborted; incomplete data. A new Test 3.1b was conducted in place of Test 3.1

While the MeBr concentration was a critical measurement, the accuracy of the FID could not be assessed because it is not specific to MeBr. That is, there was the small possibility that trace amounts of hydrocarbons or gases capable of producing a signal on the FID (other than MeBr) were present in the gas stream, especially from the desorption cycle. Nevertheless, the FID was zeroed and spanned on certified MeBr calibration gases before and after each test.

A post-test span bias check on the FID was performed with 1.3% MeBr after each test, repeating the procedure performed for the pre-test span. Both points were used to assess the analyzer drift over the test duration (5 cycles) of five to seven days. The FID maintained less than 5% drift for each test. Table 3-10 shows the FID drift (calculated as the percent difference in instrument readings taken before and after each test, when using the 1.3% MeBr calibration gas).

	Pre-test 1.3% MeBr	Post-test 1.3% MeBr	MeBr Analyzer	
Test ID	Span	Span	Drift	
	(ppm)	(ppm)	(%)	
1.1ª	-	-	-	
1.2	13004	13174	1.31	
1.3	12808	12694	-0.89	
1.4	12551	13116	4.50	
2.1	13072	13459	2.97	
2.2	13256	13517	1.97	
2.3	12677	12939	2.07	
3.1ª	-	-	-	
3.1b	13090	13658	4.34	
3.2	13019	12643	-2.89	
3.3	12824	12653	-1.34	
^a Test aborted; incomplete data. A new Test 3.1b was conducted in the place of				
Test 3.1				

Table 3-10. FID Drift for Each Test Duration

4 Results and Discussion

The results from the test matrix (see Table 2-1) and some additional ancillary/preliminary tests are presented in this section. Test results to assess the stability of the carbon tube mass measurements over time are presented in Appendix B, and scoping results related to operational factors affecting adsorption capacity are presented in Appendix C.

4.1 Stability of AC Moisture Content and Related Measures

Each AC sample was collected from the bulk container stored in the test facility (indoors in the laboratory). Upon arrival, the bulk container contained approximately 50 pounds (lb) of AC. The moisture content of the AC was monitored over the duration of the investigation, since moisture levels of the AC could potentially impact adsorption capacity.

The moisture content observation period totaled 693 days during which the measurements ranged from the minimum (2.46% [± 0.03 SD]) to maximum (3.53% [± 0.03 SD]). Table 4-1 shows that the moisture content of the bulk AC under storage conditions was generally stable.

Date	Time Under Observation (Days)	Ave. Moisture Content ^a (%, ±SD)
1/12/16	0	2.46 ±0.03
5/11/16	120	2.55 ±0.03
2/1/17	386	2.70 ±0.0
9/22/17	619	3.38 ±0.05
10/17/17	644	3.53 ±0.03
11/9/17	667	3.50 ±0.17
11/24/17	682	3.38 ±0.12
12/5/17	693	3.44 ±0.07

 Table 4-1. Moisture Content (%) of Bulk Carbon During Evaluation Period

^a average of 3 samples

On average, 0.02 g (±0.005 SD) of moisture were removed from AC samples during the conditioning phase portion of testing. Conditioned AC samples ranged from 1.0267 g (Test 2.1) and 1.1237 g (Test 3.2); the precision within the group of AC test samples (Test Series 1-3) was 0.0335 (SD). Table 4-2 details the amount of moisture removed from fresh AC samples at completion of the conditioning phase, adjusted per gram of carbon.

Test ID	Unconditioned Carbon (g)	Conditioned Carbon	Moisture Removed (g
		(g)	water/g carbon)*
1.2	1.0959	1.0647	0.0284
1.3	1.0616	1.0267	0.0329
1.4	1.0787	1.0516	0.0251
2.1	1.0471	1.0276	0.0186
2.2	1.0466	1.0276	0.0181
2.3	1.0730	1.0560	0.0158
3.1b	1.0653	1.0418	0.0220
3.2	1.1480	1.1237	0.0211
3.3	1.0360	1.0133	0.0220

Table 4-2. Amount of Moisture Removed from Fresh Carbon Bed (g/g carbon)

*calculated by dividing the difference in mass by the unconditioned carbon mass

4.2. Activated Carbon Regeneration Tests

Actual measured test conditions for regeneration (adsorption/desorption) tests are detailed in Appendix A. The prescribed challenge gas conditions for each test series were as follows:

- Test 1
 - Adsorption (challenge) gas: dry 5.3% MeBr in N₂ at ambient temperature (22 ± 0.03 °C)
 - Desorption: dry, laboratory air at 100 °C
- Test 2
 - Adsorption (challenge) gas: dry 5.3% MeBr in N₂ at ambient temperature (22 ± 0.03 °C)
 - Desorption: ambient air at 100 °C
- Test 3
 - Adsorption (challenge) gas: 5.3% MeBr in N₂ at 75% RH at ambient temperature (22 ± 0.03 °C)
 - Desorption: ambient air at 100 °C

4.2.1 Adsorption and Desorption Results for Each Test Cycle

Table 4-3 shows the MeBr adsorption and desorption results, determined using both the gravimetric and integration methods, for every test cycle (n=45 for total of these tests). Note: the MeBr scrubber system with potassium hydroxide (KOH) solution was replaced with an MeBr scrubbing system containing carbon (see Appendix A) between Tests 2.2 and Test 2.3. This

was done because during Test 2.2, KOH scrubber solution inadvertently back-flowed into the FID due to a change in pressure in the line. The FID had to be repaired, and to prevent potential recurrence of having KOH back-flow into the FID again, the KOH scrubber was replaced with a dry carbon trap.

We note also that about a third of the test replicate results from the "integration" method showed that the mass desorbed was somewhat greater than the mass adsorbed. We believe this is an artifact of the method, and indicative of the inherent variability in such measurements using the FID; we do not believe more mass is being desorbed than adsorbed in these cases. We note also that when we average the replicate results for each test, there was always less mass being desorbed than adsorbed.

		Gravimetric		Integ	ration
Test ID	Cycle	MeBr	MeBr	MeBr	MeBr
	-	Adsorbed,	Desorbed,	Adsorbed,	Desorbed,
		g/g AC	g/g AC	g/g AC	g/g AC
	1	0.5132	0.5079	0.4399	0.475
	2	0.5003	0.4999	0.3396	0.445
1.2	3	0.5026	0.5013	0.4189	0.492
	4	0.5028	0.5043	0.5061	0.446
	5	0.5065	0.5052	0.4480	0.534
	1	0.4884	0.4874	0.3876	0.484
	2	0.4744	0.4738	0.5551	0.494
1.3	3	0.4716	0.4722	0.5499	0.470
	4	0.4805	0.4788	0.5982	0.480
	5	0.4856	0.4853	0.6100	0.508
	1	0.4520	0.4505	0.4959	0.471
	2	0.4507	0.4499	0.5517	0.459
1.4	3	0.4618	0.4611	0.3558	0.412
	4	0.4421	0.4416	0.4998	0.384
	5	0.4487	0.4482	0.3663	0.425
Average ± SD		0.4787±0.023	0.4778±0.023	0.4749±0.089	0.4653±0.038
	1	0.4612	0.4591	0.6138	0.500
	2	0.4742	0.4752	0.7378	0.540
2.1	3	0.4754	0.4747	0.4670	0.519
	4	0.4746	0.4741	0.6706	0.539
	5	0.4813	0.4802	0.6577	0.519
	1	0.4709	0.4711	0.6283	0.503
	2	0.4628	0.4609	0.6123	0.521
2.2	3	0.4643	0.4649	0.6088	0.501
	4	0.4665	0.4637	0.5788	0.521
	5	0.4592	0.4585	0.6595	0.493
	1	0.4310	0.4283	0.5613	0.489
	2	0.4382	0.4392	0.4695	0.495
2.3	3	0.4294	0.4284	0.4924	0.496
	4	0.4362	0.4360	0.5242	0.478
	5	0.4326	0.4309	0.5454	0.497
Average ± SD		0.45719±0.018	0.45634±0.019	0.5885±0.079	0.5074±0.018
<u>_</u>					

Table 4-3. Adsorbed and Desorbed MeBr Using Gravimetric and Integration AnalysisMethods

		Gravi	metric	Integration		
	Cycle	MeBr	MeBr	MeBr	MeBr	
Test ID	Cycle	Adsorbed,	Desorbed,	Adsorbed,	Desorbed,	
		g/g AC	g/g AC	g/g AC	g/g AC	
	1	0.4515	0.4459	0.4631	0.470	
	2	0.4504	0.4476	0.4971	0.457	
^a 3.1b	3	0.4474	0.4490	0.4244	0.457	
	4	0.4564	0.4533	0.4966	0.488	
	5	0.4532	0.4590	0.4501	0.487	
	1	0.4598	0.4580	0.4466	0.507	
	2	0.4553	0.4552	0.4831	0.468	
3.2	3	0.4602	0.4581	0.4786	0.467	
	4	0.4571	0.4543	0.4921	0.473	
	5	0.4646	0.4637	0.4301	0.477	
	1	0.4457	0.4494	0.4284	0.488	
	2	0.4590	0.4543	0.4916	0.473	
3.3	3	0.4467	0.4467	0.4993	0.471	
	4	0.4532	0.4576	0.4766	0.510	
	5	0.4599	0.4574	0.5401	0.484	
Average ± SD		0.4547±0.006	0.4540±0.005	0.4732±0.03	0.478±0.016	

^a Due to a technical issue, Test 3.1 was not completed, and so a new Test 3.1b was conducted in its place.

As Table 4-3 shows, the results for the adsorption and desorption tests range from approximately 0.43 to 0.58 g MeBr per gram AC. The results were generally similar for the two methods used to determine adsorption capacity, except in Test 2. In Test 2, results determined via the "integration" method were ~ 25% higher compared to the gravimetric method. It is unclear why the difference in the results, but the difference may be related to having the FID repaired during the Test 2 series, as discussed above. No other changes in methods or equipment occurred.

The correlation between the adsorption and desorption cycles (mass of MeBr) is further discussed below; the effects of the challenge gas characteristics and the number of reuse cycles on adsorption capacity are also discussed below.

Figure 4-1 shows good correlation between the adsorbed and desorbed MeBr gravimetric measurements, for all 45 cycles conducted in the study. The high linear correlation between the two phases indicates low variability in the MeBr mass data as well as effective desorption of the MeBr.



Figure 4-1. Comparison of MeBr desorbed vs MeBr adsorbed using gravimetric analysis

The adsorption versus desorption measurements that were performed using the integration method show more variability ($R^2 = 0.3037$) than the mass measurements. This is most likely due to the additional variability that may be associated with the gas measurement (basis of integration method). Additionally, the correlation between the two phases (based on linear fit data) suggests that the FID response was not proportional between the two phases. Figure 4-2 shows a comparison of the MeBr (g /g AC) adsorption versus the desorption on the AC bed using the integration method.



Figure 4-2. Comparison of MeBr desorbed vs MeBr adsorbed using the integration method FID

4.2.2 Effect of Challenge Gas Conditions on Adsorption Capacity

Figure 4-3 shows the average adsorption capacities for each test (using the gravimetric method), and Table 4-4 details the adsorption capacities, RH levels of adsorption and desorption gases, and ANOVA analysis results.

For Test 1, while the average (based on 15 cycles; 5 cycles per each of the three test replicates) adsorption capacity (0.4787 g/g [\pm 0.0236 SD]) significantly exceeded the other two test conditions based on a single factor ANOVA (MS Excel) analysis (p-value 0.00016), the difference was minor (< 0.025 g MeBr/g AC). With the dry challenge gas, MeBr was free to adhere to the AC active sites virtually unchallenged by moisture. Additionally, desorbing MeBr from the saturated AC with heated air at an RH of 1% was likely effective for priming the AC sample for optimal MeBr adsorption for the subsequent adsorption event.

The Test 2 series AC samples were exposed to adsorption conditions comparable to those of Test 1, although the desorption gas for Test 2 had somewhat higher average RH levels (4.6%) than the desorption gas for Test 1 (1%). The resulting average adsorption capacity for the Test 2 conditions (n = 15) was 0.4572 g/g (\pm 0.0184 SD). An ANOVA analysis showed that the Test 2 results were not significantly different from the other two conditions (p-value = 0.14).

The Test 3 challenge gas RH was elevated to 75% and the desorption gas (ambient air with an initial RH of 25.6% [\pm 9.7 SD]) had an RH of 0.9% (\pm 2.0 SD) at 100 °C. The average adsorption capacity for the Test 3 series (n = 15) was 0.4547 g/g (\pm 0.0056 SD). The ANOVA analysis showed that the elevated RH test conditions had a significant (albeit minor) effect on the adsorption capacity (p-value 0.04).

Overall, the results show comparable adsorption capacities for the three test conditions, regardless of the RH of the adsorption gas. Table 4-4 provides a comparison of the adsorption capacity (gravimetric method) for each of the three tests.

The adsorption capacity results obtained in this study (average of approximately 0.45 g MeBr/g AC) are much higher than adsorption capacity results that were obtained in a field study (0.05 g MeBr/g AC; Wood et al., 2015). This difference may be because in the field study, the challenge concentration diminished over time as the fumigated building was aerated. The adsorption capacity results for the present study are also somewhat higher than what was obtained in method development tests (~ 0.30 g MeBr/g AC; refer to Appendix D). This difference in results may be due to the lower RH of the present study compared to what was used in method development (~40%) tests; the present study also incorporated preconditioning (essentially drying) of the AC, whereas the method development tests did not.



Figure 4-3. Average adsorption capacity for each test series (±SD)

Test Series	Ave. Carbon Bed Inlet RH (%, ±SD)	Ave. Desorption Air RH @100°C (%, ±SD)	Ave. MeBr Adsorption Capacity (g/g AC) (±SD)	P-Value (α = 0.05)
T1	3.8 ±0.6	1.0 ±0.2	0.4787 ±0.0236	0.00016
T2	3.1 ±2.6	4.6 ±0.3	0.4572 ±0.0184	0.14
Т3	74.4 ±2.1	0.9 ±0.2	0.4547 ±0.0056	0.04

Table 4-4. Adsor	ption Capacity	y Comparison [·]	for Each	Test Series
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4.2.3 The Effect of Reuse on Adsorption Capacity

The results show stable adsorption capacities over the course of the five adsorption/desorption cycles, for each of the three conditions (with each test having three replicates) tested. As seen in Figures 4-4 through 4-6, average adsorption capacity (gravimetric method) is essentially unchanged after the fifth cycle.



Figure 4-4. Average adsorption capacities for Test 1 cycles (±SD)



Figure 4-5. Average adsorption capacities for Test 2 cycles (±SD)



Figure 4-6. Average adsorption capacities for Test 3 cycles (±SD)

4.3. Control Tests with Elevated RH Only

The purpose of these control tests using air only (no MeBr) with elevated RH was to gauge the amount of water vapor that could be adsorbed onto the AC and compare this value to the mass adsorbed for the Test 3 evaluations that used the same elevated RH but with MeBr.

The average moisture adsorption capacity was 0.0442 g/g AC (± 0.0003 SD), which was less than 10% of the average adsorption capacity determined for Test 3 (0.45 g/g AC). Figure 4-7 shows the moisture loaded versus the moisture removed on the AC sample. The desorption portion for Test 1 was inadvertently not completed.



Figure 4-7. Adsorbed and desorbed moisture with an exposure stream of 75% RH in ambient air

5 Summary and Conclusions

Overall, the results for the adsorption tests showed relatively high levels of MeBr adsorption and ranged from approximately 0.43 to 0.58 g MeBr per gram AC. These high adsorption capacity levels may be due to the preconditioned (dried) AC samples we used, as well as the low RH levels in the challenge gases (applicable to the first two test series).

The differences in adsorption capacity as a function of challenge gas and/or desorption gas humidity levels were generally minor, although in some cases the differences were statistically significant. Tests to determine adsorption of moisture at high RH (75%), without the presence of MeBr, suggest that the adsorption capacity for moisture was approximately 10% of the AC capacity for MeBr.

The adsorption capacity of the AC samples was not affected (did not diminish) in the five adsorption/desorption cycle series to which each AC sample was subjected. That is, the process of desorbing the MeBr using a 100 °C temperature gas was effective in maintaining relatively high adsorption levels of the AC samples for at least five cycles; the adsorption capacity did not diminish over the course of the five cycles but remained rather stable. However, we caveat that using only five cycles may not yield sufficient data to assess the effect of numerous repeated adsorption/desorption cycles.

While we have demonstrated in this study the ability of AC to be reused (i.e., regenerated) without losing its adsorption capacity for MeBr over several cycles, further research remains related to the use of MeBr on a wide scale following a *B. anthracis* incident. Specifically, research related to the reuse of the MeBr desorbed from AC is recommended. Anecdotal evidence suggests that the MeBr gas desorbed from AC may contain impurities (i.e., other chemical species produced from the chemical interactions between the MeBr and AC during the adsorption/desorption process) that could make the gas unsuitable for reuse as a decontaminant. Further investigation into this potential is recommended.

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Appendix A: Test Conditions

Test ID	Cycle	Ave. MeBr Flow Rate	Ave. Dilution N ₂ Flow Rate	Ave. Inlet RH % (+ SD)	Ave. Inlet Temp °C (+ SD)	Ave. Outlet Temp °C (+ SD)	Cycle Duration minutes
				// (± 0D)	0 (1 00)	0 (1 00)	
1.2	1	0.5 ± 0.0001	3.56 ±0.0010	4.4 ±0.4	20.3 ±0.1	21.7 ±0.9	31.8
	2	0.37 ± 0.00008	3.07 ±0.0006	3.2 ±0.3	20.7 ±0.2	23.0 ±0.4	31.2
	3	0.37 ± 0.00008	3.58 ±0.0007	4.1 ±0.4	21.6 ±0.4	23.0 ±0.4	30.8
	4	0.37 ± 0.00008	3.48 ±0.0007	3.0 ±0.3	20.9 ±0.1	22.5 ±0.4	29.8
	5	0.37 ± 0.00008	3.53 ±0.0008	3.6 ±0.4	22.6 ±0.2	22.1 ±0.5	29.3
1.3	1	0.37 ± 0.000077	3.12 ±0.0007	2.8 ±0.3	20.0 ±0.1	21.4 ±0.8	30.7
	2	0.37 ± 0.000069	3.53 ±0.0008	4.1 ±0.4	21.1 ±0.2	21.9 ±0.4	30.8
	3	0.37 ± 0.000068	3.46 ±0.0008	3.5 ±0.3	20.6 ±0.2	22.2 ±0.4	32.8
	4	0.37 ± 0.000076	3.55 ±0.0007	4.3 ±0.4	22.2 ±0.5	21.8 ±0.4	36.3
	5	0.37 ± 0.000068	3.55 ±0.0019	4.3 ±0.4	20.5 ±0.3	21.1 ±0.1	36.5
1.4	1	0.37 ± 0.000073	3.55 ±0.0008	3.3 ±0.4	21.1 ±0.1	23.0 ±0.1	32.7
	2	0.37 ± 0.000070	3.55 ±0.0008	4.4 ±0.4	23.2 ±0.4	22.8 ±0.3	32.3
	3	0.37 ± 0.000069	3.55 ±0.0007	4.6 ±0.4	21.0 ±0.2	21.8 ±0.1	34.8
	4	0.37 ± 0.000078	3.55 ±0.0021	4.6 ±0.3	24.6 ±0.7	24.1 ±0.3	36.0
	5	0.37 ± 0.000078	3.48 ±0.0006	3.5 ±0.3	20.8 ±0.1	23.1 ±0.2	32.7
2.1	1	0.37 ± 0.000096	3.48 ±0.0006	4.8 ±0.4	22.5 ±0.4	25.2 ±1.02	33.0
	2	0.37 ± 0.000071	3.55 ±0.0007	4.7 ±0.3	21.7 ±0.1	23.0 ±0.1	33.2
	3	0.37 ± 0.000072	3.53 ±0.0015	4.5 ±0.4	21.3 ±0.2	23.2 ±0.2	33.5
	4	0.37 ± 0.000075	3.56 ±0.0007	5.5 ±0.3	20.7 ±0.04	22.7 ±0.1	33.0
	5	0.37 ± 0.000075	3.56 ±0.0008	4.6 ±0.5	21.0 ±0.2	22.9 ±0.03	33.7
2.2	1	0.37 ± 0.000070	3.56 ±0.0012	5.2 ±0.2	21.1 ±0.3	22.8 ±0.1	33.5
	2	0.37 ± 0.000067	3.46 ±0.0007	5.2 ±0.2	20.7 ±0.04	23.2 ±0.3	33.5
	3	0.37 ± 0.000065	3.53 ±0.0020	4.6 ±0.4	20.9 ±0.1	23.1 ±0.3	33.4
	4	0.37 ± 0.000082	3.5 ±0.00080	4.4 ±0.5	20.8 ±0.04	22.8 ±0.04	33.5

Table A-1. Adsorption Phase Test Conditions

	5	0.37 ± 0.000075	3.52 ±0.0007	4.5 ±0.4	20.9 ±0.1	23.5 ±0.4	33.0
Test ID	Cycle	Ave. MeBr	Ave. Dilution N ₂	Ave. Inlet	Ave. Inlet	Ave. Outlet	Cycle
		Flow Rate	Flow Rate	RH	Temp	Temp	Duration minutes
		Lpm (± SD)	Lpm (± SD)	% (± SD)	°C (± SD)	°C (± SD)	
2.3	1	0.37 ± 0.000079	3.32 ±0.0009	0.3 ±0.1	21.8 ±0.3	25.3 ±0.4	34.2
	2	0.37 ± 0.000072	3.47 ±0.0007	0.3 ±0.3	21.5 ±0.2	24.1 ±0.4	34.0
	3	0.37 ± 0.000069	3.5 ±0.00080	-0.8 ±0.2	22.4 ±0.3	25.3 ±0.5	33.3
	4	0.37 ± 0.000074	3.5 ±0.00070	-0.9 ±0.3	22.0 ±0.2	24.2 ±0.3	33.3
	5	0.37 ± 0.000078	3.5 ±0.00080	-0.8 ±0.1	22.2 ±0.3	24.5 ±0.4	32.2
3.1b	1	0.40 ± 5.8E-15	3.45 ±0.0026	71.8 ±0.9	21.0 ±0.2	23.6 ±0.3	33.6
	2	0.5 ± 0.00026	3.51 ±0.0026	72.2 ±1.3	21.0 ±0.1	23.4 ±0.4	33.4
	3	0.50 ± 0.00026	3.51 ±0.0026	71.4 ±0.8	21.3 ±0.1	23.7 ±0.4	33.3
	4	0.50 ± 0.000081	3.49 ±0.0008	72.9 ±8.0	20.3 ±0.1	22.9 ±0.1	33.2
	5	0.50 ± 0.00026	3.48 ±0.0026	74.4 ±0.9	21.3 ±0.2	23.2 ±0.2	34.0
3.2	1	0.50 ± 0.00026	3.50 ±0.00250	75.3 ±1.9	21.1 ±0.1	23.8 ±0.2	33.7
	2	0.50 ± 0.00026	3.51 ±0.0026	73.8 ±0.6	21.1 ±0.1	23.5 ±0.6	33.9
	3	0.50 ± 0.00027	3.51 ±0.0028	73.3 ±1	20.6 ±0.1	22.8 ±0.3	33.7
	4	0.50 ± 0.00026	3.49 ±0.0027	71.9 ±0.7	21.0 ±0.2	23.1 ±0.1	33.6
	5	0.50 ± 0.00009	3.5 ±0.00090	76.5 ±1.1	20.5 ±0.1	22.9 ±0.1	33.5
3.3	1	0.50 ± 0.00027	3.51 ±0.0026	77.6 ±1.6	21.3 ±0.2	23.6 ±0.6	33.5
	2	0.50 ± 0.00023	3.53 ±0.0026	75.6 ±1.3	21.0 ±0.2	23.4 ±0.3	33.8
	3	0.50 ± 0.00026	3.45 ±0.0026	75.7 ±0.3	21.6 ±0.1	24.2 ±0.4	33.4
	4	0.50 ± 0.00026	3.43 ±0.0026	77.1 ±1.1	21.3 ±0.1	23.4 ±0.2	33.6
	5	0.50 ± 0.000083	3.50 ±0.0015	76.3 ±0.9	21.8 ±0.2	23.6 ±0.2	33.7

Note: the MeBr scrubber system with potassium hydroxide (KOH) solution was replaced with an MeBr scrubbing system containing carbon between Tests 2.2 and Test 2.3.

Test ID	Cycle	Ave. MeBr Flow Rate Lpm (± SD)	Ave. Dilution N₂ Flow Rate Lpm (± SD)	Ave. Inlet RH % (± SD)	Ave. Inlet Temp °C (± SD)	Ave. Outlet Temp °C (± SD)	Cycle Duration min
1.2	1	0.87 ±0.00026	3.07 ±0.0018	1.3 ±0.08	100.3 ±2.3	20.3 ±0.1	998.9
	2	0.87 ±0.00025	3.07 ±0.0008	1.3 ±0.10	100.0 ±0.9	20.7 ±0.2	1105.8
	3	0.87 ±0.00026	3.07 ±0.0016	1.2 ±0.08	103.2 ±1.3	21.6 ±0.04	1058.9
	4	0.87 ±0.00027	3.07 ±0.0006	1.3 ±0.09	104.0 ±2.4	20.9 ±0.1	1105.7
	5	0.88 ±0.00028	3.12 ±0.0016	1.2 ±0.08	100.1 ±0.6	22.6 ±0.2	1120.9
1.3	1	0.88 ±0.00026	3.11 ±0.0009	0.9 ±0.13	99.4 ±1.9	22.9 ±1.4	1040.2
	2	0.88 ±0.00027	3.11 ±0.0009	0.9 ±0.12	101.7 ±1.2	24.0 ±1.3	1145.8
	3	0.88 ±0.00027	3.11 ±0.0008	0.9 ±0.13	100.4 ±0.7	23.1 ±1.3	1157.7
	4	0.88 ±0.00026	3.11 ±0.0008	1.0 ±0.16	100.0 ±0.8	23.0 ±1.0	1102.0
	5	0.88 ±0.00027	3.11 ±0.0017	0.9 ±0.15	102.9 ±1.6	22.8 ±1.1	1061.2
1.4	1	0.88 ±0.00026	3.11 ±0.0008	0.9 ±0.10	100.2 ±0.9	24.1 ±0.9	1119.4
	2	0.88 ±0.00027	3.11 ±0.0008	0.9 ±0.15	102.3 ±1.3	24.1 ±0.9	1152.8
	3	0.88 ±0.00027	3.11 ±0.0008	0.8 ±0.14	101.8 ±2.3	24.0 ±0.7	1130.5
	4	0.88 ±0.00026	3.11 ±0.0008	0.9 ±0.17	101.9 ±1.7	24.0 ±0.7	1234.4
	5	0.88 ±0.00027	3.07 ±0.0007	0.9 ±0.15	100.8 ±0.6	24.2 ±0.7	1135.6
2.1	1	1.10 ±0.00037	2.97 ±0.0007	4.5 ±0.61	102.9 ±1.3	24.2 ±0.7	1154.4
	2	1.10 ±0.00037	3.07 ±0.0009	4.6 ±0.41	100.4 ±1.2	25.0 ±0.9	1079.2
	3	1.10 ±0.00037	3.07 ±0.0016	4.4 ±0.52	100.0 ±0.9	24.1 ±0.4	1142.6
	4	1.10 ±0.00037	3.07 ±0.0012	4.9 ±0.53	100.3 ±0.4	24.4 ±0.6	1091.3
	5	1.10 ±0.00039	3.07 ±0.0008	4.4 ±0.33	100.5 ±0.8	24.6 ±0.8	1086.5
2.2	1	1.10 ±0.00039	3.56 ±0.0012	4.4 ±0.47	100.6 ±0.9	24.8 ±0.6	555.2
	2	1.10 ±0.0004	3.03 ±0.0008	4.7 ±0.49	100.2 ±0.5	23.8 ±0.9	1154.7
	3	1.09 ±0.00038	3.05 ±0.0019	4.9 ±0.46	100.6 ±1.3	24.5 ±0.7	1280.9
	4	1.09 ±0.00037	3.04 ±0.0018	5.0 ±0.49	100.2 ±0.5	24.1 ±0.7	988.2
	5	1.09 ±0.0004	3.05 ±0.0007	4.8 ±0.64	100.6 ±0.7	24.6 ±0.6	1087.7

Table A-2. Desorption Phase Test Conditions

Test ID	Cycle	Ave. MeBr Flow Rate	Ave. Dilution N ₂ Flow Rate	Ave. Inlet RH	Ave. Inlet Temp	Ave. Outlet Temp	Cycle Duration
		Lpm (± SD)	Lpm (± SD)	% (± SD)	°C (± SD)	°C (± SD)	min
2.3	1	1.09 ±0.00038	2.93 ±0.0017	5.1 ±0.47	101.1 ±0.9	27.1 ±1.3	1036.0
	2	1.09 ±0.00039	2.96 ±0.0007	4.4 ±0.77	103.0 ±2.5	26.6 ±1.2	1085.0
	3	1.11 ±0.0004	3.01 ±0.0008	4.3 ±0.32	99.9 ±0.9	26.5 ±0.9	1088.5
	4	1.11 ±0.00043	2.97 ±0.0008	4.1 ±0.38	100.2 ±1.0	26.5 ±1.0	1137.8
	5 ^a	1.10 ±0.0004	2.45 ±0.5105	5.0 ±0.54	99.7 ±1.0	26.4 ±0.5	1048.5
3.1b	1 ^a	1.11 ±0.0004	2.29 ±0.7647	0.0 ±0.18	100.1 ±1.0	27.0 ±1.5	1073.4
	2ª	1.11 ±0.00041	2.59 ±0.6730	-0.5 ±0.17	100.5 ±0.7	26.3 ±1.4	1094.7
	3	1.11 ±0.00041	2.93 ±0.2493	-0.2 ±0.17	100.7 ±0.4	27.1 ±1.4	1178.8
	4 a	1.11 ±0.00041	2.03 ±0.7412	2.4 ±0.13	100.1 ±0.6	26.5 ±1.2	1045.3
	5ª	1.09 ±0.00043	2.43 ±0.7352	-0.2 ±0.22	102.2 ±0.8	27.3 ±1.5	1135.4
3.2	1 ^a	1.09 ±0.0004	2.75 ±0.5718	0.5 ±0.20	100.4 ±0.9	26.2 ±1.8	1089.2
	2	1.09 ±0.00053	3.00 ±0.0026	-0.4 ±0.10	100.8 ±0.8	24.6 ±0.7	1172.1
	3	1.09 ±0.00048	3.00 ±0.0023	0.2 ±0.09	101.1 ±0.7	24.8 ±1.3	1207.6
	4	1.10 ±0.0005	2.99 ±0.0025	1.7 ±0.14	102.1 ±1.3	25.2 ±1.5	1512.8
	5	1.10 ±0.00052	2.90 ±0.4444	1.5 ±0.22	100.9 ±1.3	25.2 ±1.3	1031.5
3.3	1	1.10 ±0.00051	3.02 ±0.0025	-0.4 ±0.10	101.2 ±0.9	25.3 ±1.1	1196.8
	2	1.10 ±0.00056	3.02 ±0.0027	-2.8 ±0.09	103.4 ±1.8	25.1 ±1.1	1087.7
	3	1.09 ±0.00056	2.99 ±0.0026	4.6 ±0.19	102.3 ±1.1	26.0 ±1.4	1179.4
	4	1.06 ±0.00048	2.94 ±0.0028	4.6 ±0.16	101.6 ±1.4	25.2 ±0.8	1079.1
	5	1.07 ±0.00052	2.99 ±0.0067	2.5 ±0.09	102.1 ±0.7	26.3 ±1.1	1196.6

^aThe dilution flow setting was reduced to conserve gas after the FID reading was less than 100 ppm.

Note: the MeBr scrubber system with potassium hydroxide (KOH) solution was replaced with an MeBr scrubbing system containing carbon between Tests 2.2 and Test 2.3.

Test ID	Phase	Challenge Gas ^a Ave. Flow Rate Lom (±SD)	Ave. Inlet RH % (±SD)	Ave. Inlet Temp °C (±SD)	Ave. Outlet Temp °C (±SD)	Cycle Duration min		
1 ^b	Adsorption	0.47 ±0.025	75.8 ±0.4	22.3 ±0.1	24.8 ±0.3	33.2		
	Desorption	-	-	-	-	-		
2	Adsorption	0.48 ±0.0001	75 ±0.3	22.6 ±0.2	24.9 ±0.5	33.1		
	Desorption	1.08 ±0.0004	4.1 ±0.4	101 ±0.5	28.1 ±0.6	1067.0		
^a Ultra-high-purity nitrogen was used for the adsorption gas and ambient air for the desorption gas.								
^b Desorption	n phase was n	ot completed for Test	1.					

Table A-3. RH only Test Conditions

Appendix B: Carbon tube mass stability preliminary tests

Mass Stability Observations

The following three reactor tube configurations were used:

- 1. Empty tube: The mass of an empty reactor tube with ends sealed with Parafilm was monitored to assess the stability of the materials and balance at ambient temperature and RH over a period of three days.
- 2. Two identical tubes, A and B, were empty and secured with a Keck® joint clamp. Tube A was sealed with Parafilm while Tube B remained open on both ends. The masses of both tubes were monitored over 20 minutes (measurements taken at 1-minute intervals) each day, for a period of five days.
- 3. Two identical tubes, A and B, were assembled with 1 g of carbon, quartz wool, and a Keck® joint clamp. This configuration was consistent with the test configuration. The tube ends of tube A were plugged with chemical resistant stoppers while Tube B remained open on both ends. The masses of both tubes were monitored at 20 min over a duration of 20 minutes (measurements taken at 1-minute intervals) each day, over a period of four days.

The agreement in the measurements was assessed as standard deviation. An ANOVA analysis was performed to assess the statistical significance of the variability in the data.

Empty - Sealed Tube

Mass measurements were recorded every second for a 15-minute duration using a calibrated balance. This procedure was performed for three consecutive days. The data showed excellent agreement within each set of readings, suggesting the reactor tube was not a likely source of measurement variability. Although the data were precise, there was a period of time lasting approximately 10 minutes when the mass appeared to be stabilizing. As a result, the procedural step was taken during the AC regeneration tests to allow the tube 20 minutes (double the observed time) to stabilize prior to recording the mass reading.

A comparative analysis performed on the data over the three-day periods suggests a significant change occurred (p-value =1.67516E-56). The change was likely the result of temperature and RH fluctuations in the facility which were also likely present during AC regeneration testing. A subsequent test was performed to determine if the fluctuations were caused or exacerbated by sealing the tube ends. The SD in the data collected over the 3-day period was 0.002719. Figure 4-1 shows the mass reading for the reactor tube over the 15-minute observation period. Table 4-1 provides descriptive statistics for each of the data sets.



Figure 1. Mass stability of an empty tube with sealed ends over 15 min interval

∆ Time (Days)	Min	Мах	Average	SD (each day)	SD (3-day)	P-value (α=0.05)
1	111.8644	111.8651	111.8649	0.0002566	0.002719	< 0.0001
2	111.8699	111.8703	111.8702	0.0001412		
3	111.8709	111.8710	111.8710	4.4722E-05		

Table 1. Descriptive Statistics for Mass Stability Observation of an Empty Tube

Sealed vs. Unsealed Tube - Empty

As previously mentioned, this observation was conducted to determine the effect of sealing the tube ends on the mass stability of the reactor tube. As before, the data for the sealed tube showed excellent agreement within each set of measurements. The period of time required for the mass to stabilize lasted for nearly 20 min at times (Day 4 and Day 5).

As before, comparative analysis performed on the data over the three-day periods suggests a significant change occurred (p-value = 2.2552E-116). The change may be a result of temperature and RH fluctuations in the facility which were also likely present during AC regeneration testing. The SD in the data collected over the three-day period was 0.002220. Figure 4-2 shows the mass reading for the reactor tube over the 15-minute observation period. Table 4-2 provides descriptive statistics for each of the data sets.



Figure 2. Mass readings empty, sealed tube over 20 min intervals for 5 days

∆ Time (Days)	Min	Мах	Average	SD (each day)	SD (5-day)	P-value (α=0.05)
1	119.4586	119.4594	119.4591	0.0002598	0.002220	< 0.0001
2	119.4546	119.4547	119.4546	0.00002182		
3	119.4538	119.4542	119.4539	0.00008536		
4	119.4563	119.4564	119.4563	0.00002182		
5	119.4525	119.4531	119.4528	0.0001989		

Table 2. Descriptive Statistics for Mass Stability Observation of an Empty, Sealed TubeOver 5 Days

The unsealed tube mass measurements showed improved correlation as demonstrated by the significantly lower standard deviations. Additionally, the open tube ends appear to eliminate the need to wait for the tube to stabilize; the readings were stable from the onset of the observation period. Although there is excellent correlation in each set of data, there is considerably more variation in the data over the entire observation period compared to the sealed tube data (standard deviations are 0.01082 and 0.002220, respectively). ANOVA analysis indicates that there is a significant change in the data during the observation period (p-value < 0.0001). These findings show that while an unsealed tube has superior correlation in the data for individual days and does not require time for stabilization, there was significantly higher variation in the collective data for the five-day period. Again, this is likely due to temperature and RH changes. However, a follow-up test was performed to determine if preparing the reactor tube in the same manner as a regeneration test (i.e., with AC and packed with quartz wool) will affect these

findings. Figure 4-3 shows the mass reading for the reactor tube over the 20-minute observation period. Table 4-3 provides descriptive statistics for each of the data sets.



Figure 3. Mass reading for empty, unsealed tube (Tube B) 20 min intervals for five days

Table 3. Descriptive statistics for mass stability measurements of an empty, unsealedtube (Tube B) over five Days

∆ Time (Days)	Min	Мах	Average	SD (each day)	SD (5-day)	P-value (α=0.05)
1	117.5269	117.5272	117.5271	0.0001044	0.01082	< 0.0001
2	117.5186	117.5187	117.5187	0.00002182		
3	117.5136	117.514	117.5136	0.00009258		
4	117.5132	117.5133	117.5132	0.00004976		
5	117.4942	117.4944	117.4943	0.00006796		

Sealed vs. Unsealed Tube with AC

As previously mentioned, this observation was conducted to determine if preparing a reactor containing AC and quartz wool and AC (i.e., no air pocket) would yield results like those discussed in Section 4.2.2. As before, the data for the sealed tube showed excellent agreement within each set of measurements.

Compared with the sealed empty tube, variability in the data over the four-day evaluation was comparable (SD values are 0.001017 and 0.002220, respectively).

As before, comparative analysis performed on the data over the five-day periods suggests a significant change occurred (p-value < 0.0001). The change may be a result of temperature and RH fluctuations in the facility, which were also likely present during AC regeneration testing. The

SD in the data collected over the three-day period was 0.002220. Figure 4-4 shows the mass reading for the reactor tube over the 15-minute observation period. Table 4-4 provides descriptive statistics for each of the data sets.



Figure 4. Mass readings for tube prepared with plugged ends (Tube A) over 20 min intervals for four days

Table 4. Descriptive statistics for mass stability observation of sealed prepared tube
(Tube A) over four days

Δ Time (Days)	Min	Мах	Average	SD (each day)	SD (5-day)	P-value (α=0.05)
1	96.3454	96.346	96.3457	0.00021657	0.001017	< 0.0001
2	96.3428	96.3429	96.3429	0.00004976		
3	96.3444	96.3445	96.3444	0.00002182		
4	96.3446	96.3447	96.3447	0.00005071		

The unsealed tube mass measurements showed comparable correlation with the sealed counterpart. Although there is excellent correlation in each set of data, there is slightly more variation in the data over the four-day observation period compared to the sealed tube data (standard deviations are 0.001017 and 0.002514, respectively). An ANOVA analysis indicates there was a significant change in the data at a point during the four-day observation period (p-value < 0.0001). Figure 4-5 shows the mass reading for an unsealed tube over the 20-minute observation period, and Table 4-5 provides descriptive statistics for each of the data sets.





Table 5. Descriptive statistics for mass stability measurements of an empty, unsealed
tube (Tube B) over four days

∆ Time (Days)	Min	Мах	Average	SD (each day)	SD (5-day)	P-value (α=0.05)
1	95.992	95.9921	95.9921	0.00004024	0.002514	< 0.0001
2	95.9861	95.9862	95.9862	0.00002182		
3	95.9862	95.9863	95.9863	0.00004830		
4	95.9865	95.9866	95.9866	0.00004364		

The findings in this section were used to develop the procedures implemented for preparing and weighing the reactor tubes during AC regeneration testing. While in this orientation, the sample tube proved stable during the weighing process. Additionally, an acceptable level of variation over the test cycle was observed. The tube ends were plugged during the weighing procedure and for sample storage between regeneration cycles.

Appendix C: Preliminary Activated Carbon Adsorption Tests











Figure C-3: Adsorption capacity of MeBr as a function of carbon moisture content



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