Evaluation of Long-Term Storage Stability and Operational Efficiency of Rapid Cycle Amine Adsorbents

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With the recent incorporation of Mars Extravehicular Activity (EVA) into the 2025 NASA roadmap, Rapid Cycle Amine (RCA) technology advancement within the Exploration Extravehicular Mobility Unit (xEMU) applies to both the upcoming Lunar Artemis missions and future human exploration of Mars. The incorporation of commercial spacesuit vendors to service NASA's crewed-space programs since 2021 has increased the demand for regenerable, RCA-based carbon dioxide (CO_2) and humidity control adsorbents. The regenerable RCA subunit is the most advanced, long-term solution for CO_2 removal and humidity control, enabling both lunar and Martian EVAs. The adsorbent selected for use within the RCA unit must exhibit sufficient storage stability and operational efficiency for prolonged missions. As XploSafe worked to simultaneously develop both a recirculating sub-atmospheric test rig and adsorbents for the RCA system within the xEMU, several novel adsorbents were evaluated for long-term storage stability in support of future extended-duration missions. The chosen materials were periodically evaluated by nuclear magnetic resonance (NMR) spectroscopy, thermal desorption-coupled with gas chromatography/mass spectrometry (TD-GC/MS), and CO_2 adsorption to assess long-term storage efficacy across various environmental storage conditions. NMR spectroscopy was utilized by extracting the active CO_2 adsorbing chemical from the solid support with deuterated solvent and comparing the spectra over time for degradation and change. The solid adsorbents were also analyzed via TD-GC/MS to reveal any potential off-gassing chemicals over time. Additionally, XploSafe's breakthrough test rig was utilized to dose the solid adsorbents with a 585 BTU/h metabolic rate flow-equivalent CO_2 stream and monitored for 0–99% CO_2 breakthrough. The performance metrics from the breakthrough analysis were compared over the storage study duration for CO_2 removal and humidity control. Xplo-SA9T was evaluated for 24 months, whereas two additional adsorbent variants, MMPA-Sorbent and LPEI-Sorbent, were each evaluated for 12 months.

Acronyms and Nomenclature

BTEX	=	benzene toluene ethylbenzene xylenes
CO_2	=	carbon dioxide
ESD	=	estimated standard deviation, of a sample
EVA	=	Extravehicular Activity
FTIR	=	Fourier-transform infrared
h	=	hour
JSC	=	Johnson Space Center

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LPEI	=	linear polyethylene imine
MMPA	=	methyl methacrylate tetraethylenepentamine
mmHg	=	millimeters of mercury, unit of pressure
NASA	=	National Aeronautics and Space Administration
N_2	=	nitrogen gas
NH_3	=	ammonia
NMR	=	nuclear magnetic resonance
O_2	=	oxygen gas
PMMA	=	poly(methyl methacrylate)
PLSS	=	Portable Life Support System
ppm	=	parts per million, unit of concentration
RCA	=	Rapid Cycle Amine
RH	=	relative humidity
SA9T	=	solid amine adsorbent (proprietary adsorbent)
SBIR	=	Small Business Innovation Research
TCC	=	Trace Contaminant Control
TEPAN	=	acrylonitrile modified tetraethylenepentaamine
TD-GC/MS	=	thermal desorption gas-chromatography mass-spectrometry
TD	=	thermal desorption
UHP	=	ultra-high purity
VOC	=	Volatile Organic Contaminant
xEMU	=	Exploration Extravehicular Mobility Unit
Xplo-SA9T	=	XploSafe's proprietary solid amine adsorbent (SA9T variant)

I. Introduction

Rapid Cycle Amine (RCA) technology is considered as a prominent solution for carbon dioxide (CO_2) and humidity control within both the lunar and future proposed Mars spacesuits in NASA's 2025 roadmap [1]. With the benefits of RCA technology for regenerable scrubbing of the spacesuit breathing air stream comes the drawbacks of off-gassed volatile organic contaminant (VOC) species associated with the chosen adsorbent material. The current RCA unit within the Portable Life Support System (PLSS) uses SA9T, and is responsible for, among others, a measured source rate of 30 mg/day of ammonia, a VOC that must be removed or reduced for human survival [2]. Within the current spacesuit designs, VOCs are removed by the Trace Contaminant Control (TCC) System and all species, not just ammonia, that could be present must be identified to determine their removal efficiency[3–5]. Acrylonitrile modified tetraethylenepentamine (TEPAN), the active CO_2 adsorber of SA9T, and both TEPAN-coated and uncoated poly(methyl methacrylate) (PMMA) beads have previously been explored for amine decomposition and oxidation using thermal-desorption gas-chromatography mass-spectrometry (TD-GC/MS) [6]. At 100˚C, the amine TEPAN provided no evidence of immediate decomposition; however, at 150˚C the resin support began to release complex ring structures, and the amine was starting to extract from the resin support. At 200˚C, TEPAN and the resin support started to fail, providing evidence of amine decomposition. This amine decomposition is well known in the literature, as thermal degradation of amines is prominent[7–9]. Traditional SA9T, developed by Hamilton Sundstrand, was tested by the White Sands Test Facility in 2003 concluding that 370 mg of ammonia (NH_3) was generated per gram of adsorbent after heating to 49˚C for 72 h [10]. This ammonia generation was further quantified by Monje and co-workers using calibrated Fourier transform infrared (FTIR) spectroscopy and suggested NH_3 off-gassing rates can be overestimated based on residual NH_3 trapped within interstitial spaces. Beyond ammonia, acetonitrile was detected when storing SA9T for several days (~12 ppm) but concentrations were not confirmed with FTIR spectroscopy due to interferences with pentane in the gas stream. These results, along with the later Human In The Loop RCA testing, indicate that when an amine, such as SA9T, is used for CO_2 scrubbing and humidity control within the Extravehicular Mobility Unit (xEMU), it should be vacuum regenerated and vented prior to use after sitting stagnant [11]. Over time, NASA has utilized methods such as EPA TO-15 (GC/MS) and GC/Gerstel Thermal Desorption System, to determine off-gassed VOCs within simulated and ground level space cabins that can be applied to xEMU components [12]. Expanding upon those, nuclear magnetic resonance (NMR) spectroscopy can be used to further analyze the state of materials and elucidate avoidable pathways to off-gassing [13], [14]. Utilizing TD-GC/MS and NMR spectroscopy, a storage study was developed herein for three CO_2 adsorbents assessing the effects of environmental storage conditions on off-gassing, material stability, and overall performance across multiple time durations from 48 to 96 weeks.

II. Background

The development of new adsorbents and their operational use within the RCA system is dependent upon storage stability (shelf-life), ensuring the material remains safe, functional, and reduces future process risks [15], [16]. XploSafe has previously published two adsorbents, Xplo-SA9T and MMPA-Sorbent, that were each synthesized to the multi-kilogram batch scale for commercialization [17]. These materials were tested toward realistic xEMU conditions at the sub-scale(≤ 128 mL) and Xplo-SA9T was tested at the xEMU scale [18]. Beyond these two materials, LPEI-Sorbent (an unpublished polyethyleneimine variant synthesized by XploSafe) was evaluated, as it is composed of a different resin support. LPEI-Sorbent was designed to eliminate acrylonitrile from the adsorbent and minimize pathways that would potentially support the formation of ammonia. The use of a different resin support within the study will further reveal insight into amine vs support off-gassed VOCs. Each storage environment was chosen to evaluate two different aspects of material longevity. First, storage post-synthesis, prior to commercial procurement (for either direct use or long-term stowage), ultimately led to evaluation of a test plan to determine which environment lends to the best adsorbent state upon use. Second, test parameters were developed to determine how the usable life of the adsorbents may be affected if each material is loaded within a subunit (e.g., an RCA assembly), used, stored sub-optimally, or utilized in a non-traditional manner [19]. The desiccant was chosen specifically to target synthetic artifacts (chemical residue that remains from the material generation) by removing or reducing these volatile organic compounds. Additionally, it can be hypothesized that since the adsorbents were designed for CO_2 removal and humidity control, they can and will adsorb other unwanted volatile chemicals that are present within the environment surrounding the material. A vacuum bag was chosen for oxygen and humidity removal while utilizing a simple and common storage method for potential commercial implementation. A control is defined as a standard of comparison for all environments and minimization of variables associated with material production and handling. In this study, a control was made by taking the freshly synthesized material and placing it directly into a glass 20 mL vial sealed with a Teflon lined cap. The humidity was noted within the room at the time of packing to be between 20–45%. An evacuated glass vial was utilized to remove oxygen/humidity; however, glass was chosen to determine if the vacuum bag chosen previously was reacting with the material. An inert atmosphere (argon) was also evaluated to examine the effect of storage in an environment devoid of oxygen. When the RCA is shut down for storage post-EVA, it could be flushed with argon if proven to be a desirable storage method. Two temperatures (beyond the control of ~ 23˚C) were selected to determine if cold or hot storage affects the material over time (5 and 40˚C, respectively). Last, an amber glass vial was chosen to determine if the materials were light sensitive and would benefit from storage in the dark prior to use. Within these environmental conditions, long-term adsorbent viability will be discussed and performance will be ascertained.

III. Equipment Design

All storage environments consisted of a ~2 grams of material loaded within either glass vials or vacuum bags. In this study, one month is defined as four weeks (28 days) due to the variation in days per month. Analyses were performed for each storage environment of Xplo-SA9T at 1, 4, 12, 24, 48, 60, 72, and 96 weeks (unless the storage environment was halted early due to degradation/reactivity). For both MMPA-Sorbent and LPEI-Sorbent, an analysis interval of 4, 24, and 48 weeks was used after insight was gained from the initial Xplo-SA9T storage study. With all materials, the length of the synthesis, preparation, and validation process indicates that by 48 weeks of the actual storage timeline, a full year will have surpassed since initial amine/adsorbent formation. The 20 mL glass vials (Kimble F574515-20 with Polyseal) were used as supplied. For the desiccant environment, an open 1 Dram vial was loaded with material and placed within a 20 mL glass vial. Surrounding the internal glass vial was ~2 g of Drierite (23005, chosen desiccant for this study) and then only the 20 mL glass vial was sealed. The analytical balance used for measuring sample mass was an externally calibrated Ohaus Pioneer PA224C. The 1 Dram amber glass vials (Pacific Vial VA131545G) were used as supplied. The polycarbonate vacuum bags (Impak Corp. SS02510N35 Special Surface 2.5" × 10" 3.5 mil embossed vacuum food sealer bag) were used as received and sealed with a vacuum sealer with inert gas purge (AmeriVacs AVN-20). For the 5 and 40˚C storage, a separate calibrated (± 0.1˚C) incubator was used (TriTech Research DigiTherm Incubator ICELESS-40) and the temperature was further verified by an external NIST calibrated temperature probe. Inert atmosphere storage samples were purged with argon (99.998%), capped with Teflon seal, and then wrapped with 3M electrical tape as a secondary seal. At the start of each storage study, the synthesized material was loaded into the corresponding environment within 1-week to 1-month post-synthesis (time due to staggering of studies for equipment availability). All eight storage environments were explored for Xplo-SA9T until 15 months whereas the five best were chosen for MMPA-Sorbent and LPEI-Sorbent storage evaluation. Three environments were eliminated after the 15-month Xplo-SA9T storage time (prior to the start of

MMPA-Sorbent or LPEI-Sorbent storage testing) due to either environment-based leaching/contamination or for manufacturer defects in the storage device. Over 150 samples were prepared for this storage study as two backup samples per storage environment and material were set aside as to account for human or instrumental error (breakage or equipment failure).

A. TD-GC/MS Equipment and Analysis Methods

Storage samples were packed within glass TD tubes, and subsequently analyzed by thermal desorption-coupled gas chromatography mass spectroscopy (TD-GC/MS) using a Markes TD-100 thermal desorber attached to an Agilent 6890 gas chromatograph/5973N mass spectrometer. A Markes TD-100 instrument was used to thermally desorb analytes from the tubes, ~90–100 mg of adsorbent packed within glass ¼" diameter TD tubes from CAMSCO. Each tube was desorbed at 38°C with a helium flow rate of 20 mL/min for 10 min. After the desorption, the utilized cold trap (U-T15ATA-2S) was flushed with helium over one minute at a rate of 20 mL/min and temperature of –10°C. The trap was than ramped to 280˚C over several seconds at a flow rate of 10 mL/min and held at the final temperature for 3 min. A split flow of 10 mL/min was used to further dilute the output of the cold trap. The desorbed analytes were directed to the GC column with a column flow computed to be at 2 mL/min. At the start of the cold trap temperature ramp, a GC equipped with a 60 m × 0.25 mm × 1.4 µm DB-624UI MS column and a mass spectrometer were used to record chromatograms in a mode combining single-ion monitoring (m/z = 17) mode for ammonia (from a retention time of ~4.860 min to ~6.008 min) and a broad scan (m/z = 35–550) for the remaining spectrum. Each GC/MS spectrum was recorded at an initial temperature of 30°C, initial holding time of 3 min, temperature ramp rate of 10°C/min, final temperature of 200°C, and a final holding time of 10 min.

To test if a bias was introduced by this method of material thermal desorption testing, a secondary experiment was conducted on the 72-week stored Xplo-SA9T adsorbent. A glass TD tube with Xplo-SA9T was placed before a Carbopack X thermal desorption tube and a calibrated total of 200 mL of ultra-high purity (UHP) N_2 at ~21°C was passed across the material through the TD tube. Any species that would off-gas within the Spacesuit would occur similarly, thus the Carbopack X tube was analyzed for collected species. Nitrogen was chosen over oxygen to prevent the loss of any reactive species. This method was repeated four-fold, and compared to the above method utilized for the storage study. In both experiments, the thermal desorption of the adsorbent itself as opposed to the collection of off-gassed species followed by subsequent Carbopack X thermal desorption did not yield a different set of species. The chromatogram magnitude of each was compared by using a calibrated external benzene, toluene, ethylbenzene, and xylenes (BTEX) calibrated check standard and there was no observable change in off-gassing species concentrations.

An acetonitrile calibration curve was generated using a NIST certified 1033 ppm (+/– 21 ppm) gas cylinder standard procured from an ISO-certified third-party gas supplier. The calibrated acetonitrile source was dosed onto eight thermal desorption sampling tubes containing dual bed 70:30 OSU-6 (nanoporous-silica based sorbent):Carbograph 5 using a set of calibrated mass flow controllers at 0.5 to 1.0 mL/min flow rates[20]. The times and flow rates were chosen to deliver pre-calculated concentrations that would be predicted across the storage study timeframe (86.7–2.60 × 10^4 nanograms). All of these tubes were evaluated by TD-GC/MS using the same equipment as above. Each tube was desorbed at 300°C with a helium flow rate of 20 mL/min for 5 min. After desorption, the utilized cold trap was flushed with helium over one minute at a rate of 20 mL/min and temperature of –10°C. The trap was then ramped to 280˚C over several seconds at a flow rate of 10 mL/min and held at the final temperature for 3 min. A split flow of 10 mL/min was used to further dilute the output of the cold trap. The desorbed analytes were directed to the GC column with a column flow computed to be at 2 mL/min. At the start of the cold trap temperature ramp, the gas chromatograph and a mass spectrometer were used to record chromatograms in a broad scan (m/z = 35–550) for each calibration sample. The raw intensity data from each calibration tube was plotted within Excel using a LINEST function to perform a linear regression through zero to find the best-fit line for the data set [21–24]. The corresponding sample data concentration (nanograms) from the storage study was then calculated from the slope of the calibration curve. All values reported within the Xplo-SA9T two-year storage study are within the upper bounds of the calibration curve. Acetonitrile was chosen for calibration, to expand upon the published literature for an SA9T-variant material [10]. The raw intensity values for the remaining observed species were utilized without calibration curves as generation vs stored synthesis artifacts were the primary focus of this study.

B. NMR Spectroscopy Equipment and Analysis Methods

Nuclear magnetic resonance (NMR) spectroscopy was utilized to track the condition of the active amine on the resin support for each material. At each storage interval, deuterated chloroform ($CDCl_3$) purchased from Thermo Fisher

Scientific (166251000) was used as received to extract the amine off the resin support for spectroscopic evaluation. All ^{1}H NMR spectra were recorded on a Bruker AVANCE 400 with 16 scans per sample. Initial as-synthesized NMR spectra were reported by XploSafe in 2023 for Xplo-SA9T and MMPA-Sorbent [17]. LPEI is a polymer based on a linear polyethyleneimine and does not provide a well-defined NMR spectrum. The resin support was not soluble in any material evaluated using $CDCl_3$ solvent.

C. Carbon Dioxide Adsorption Equipment and Analysis Methods

Carbon dioxide adsorption was measured by a pre-established 0–99% breakthrough analysis performed in triplicate for each sample [17]. A quarterly calibration check was performed on the breakthrough rig, during which the volumetric flow rates of the calibrated Dakota Mass Flow Controllers were verified. For each sample, the breakthrough rig was turned on, the software was set to start logging, and the rig was left to equilibrate for a minimum of one hour before proceeding. During this time the samples to be analyzed that day were prepared. Once the breakthrough rig was adequately equilibrated, a triplicate set of CO_2 dosing source tests (2.128 mmHg CO_2) was confirmed daily to be within acceptable operating parameters in order to ensure accuracy. Once this system check was completed, the first sample was then placed on the rig and the gas flow (100 mL/min) was immediately (as to not allow positive flow to flush away any adsorbed specices generated from storage environment or residual CO_2) switched to begin dosing the material with the CO_2 stream. During dosing, the system records the CO_2 concentration, using a Telaire T6615-50KF sensor, in the gas stream exiting the adsorbent bed, along with the temperature and RH. After 1 hour (full breakthrough of CO_2 occurs) the CO_2 flow was switched off, the sample was replaced by a blank tube and the system was left to return to baseline. Once baseline was achieved, the process was repeated for the remaining triplicate samples. After all three samples were collected, the data was plotted against time to generate 0–99% CO_2 breakthrough plots and the corresponding 0–99% CO_2 capacity in mmol/g (CO_2/adsorbent) [17].

IV. Results and Discussion

A. TD-GC/MS Off-gassing Study

Each adsorbent was screened for potential off-gassing species to determine direct integration viability into current RCA systems[19]. Xplo-SA9T TD-GC/MS analysis (Figures 1 and 2) suggests the desiccant removed or reduced the formation of volatile species that may off-gas during storage or use. All of the remaining storage environments showed a steady increase in off-gassing concentrations over time with the 40˚C environment having the most accelerated increase. Three storage environments (vacuum bag, evacuated glass, and amber glass) were ended early (at 15 months) for independent reasons. First, the vacuum bag samples began to show numerous (>10) new small peaks over time, either hypothetically caused by a chemical reaction between the amine and the inside of the poly-bag or leaching occurred. Next, the evacuated vial did not show a major difference from the inert atmosphere and was deemed more likely to leak. Lastly, the amber vial did not show any clear changes and over time the manufacturer supplied cap seals began to leak and caused new peak formation. Two separate graphs were plotted based on what species were believed to be controllable (Figure 1) either by synthetic procedure, work-up methods, or storage environments and which were inherent artifacts from synthesis (Figure 2). The synthetic artifacts in Figure 1 are all components within the resin support manufacturing, lab glassware cleaning (acetone), or the amine synthesis procedures. In both the 40˚C and desiccant storage environments, methacrylic acid was completely removed or reacted. Acrylonitrile, used in the synthesis of TEPAN, remains statistically similar in concentration in all environments except for the vacuum bag. The first major peak in Figure 1 was most likely attributed to water, supported by the hydrophilic nature of the adsorbent and its considerable capacity for water storage. While water is undistinguishable from ammonia and ammonium with the utilized column, a secondary test was conducted to support if ammonia is present in large concentrations (near 10,000 ppm). Agilent, the manufacturer of the utilized GC/MS, states in an application note that low concentration ammonia gas chromatogram peaks (<100 ppm) are broad, unfortunately water also appears broad from peak tailing [25]. A TD tube with a dual bed (70:30 OSU-6: Carbograph 5) was loaded with 2 mL/min of calibrated 9.5 ppm ammonia gas for one minute (13 ng). A broad peak between 4.871 to 5.985 mins was observed with a peak width of 1.114 mins. A second dual tube was loaded at 20 mL/min for 15 min with the same calibrated ammonia gas (2000 ng). The peak shape sharpened with a signal from 4.934 to 5.602 mins and a peak width of 0.669 mins. With this information, all peaks labeled as “water” within the chromatograms could contain low levels of ammonia; however, no sharp peak was observed, indicating the unlikely nature of large ammonia concentrations. Ammonia generation by SA9T has been well documented, and accordingly, its detection and quantification by electrochemical sensor will be discussed in the Carbon Dioxide Adsorption Study section [10].

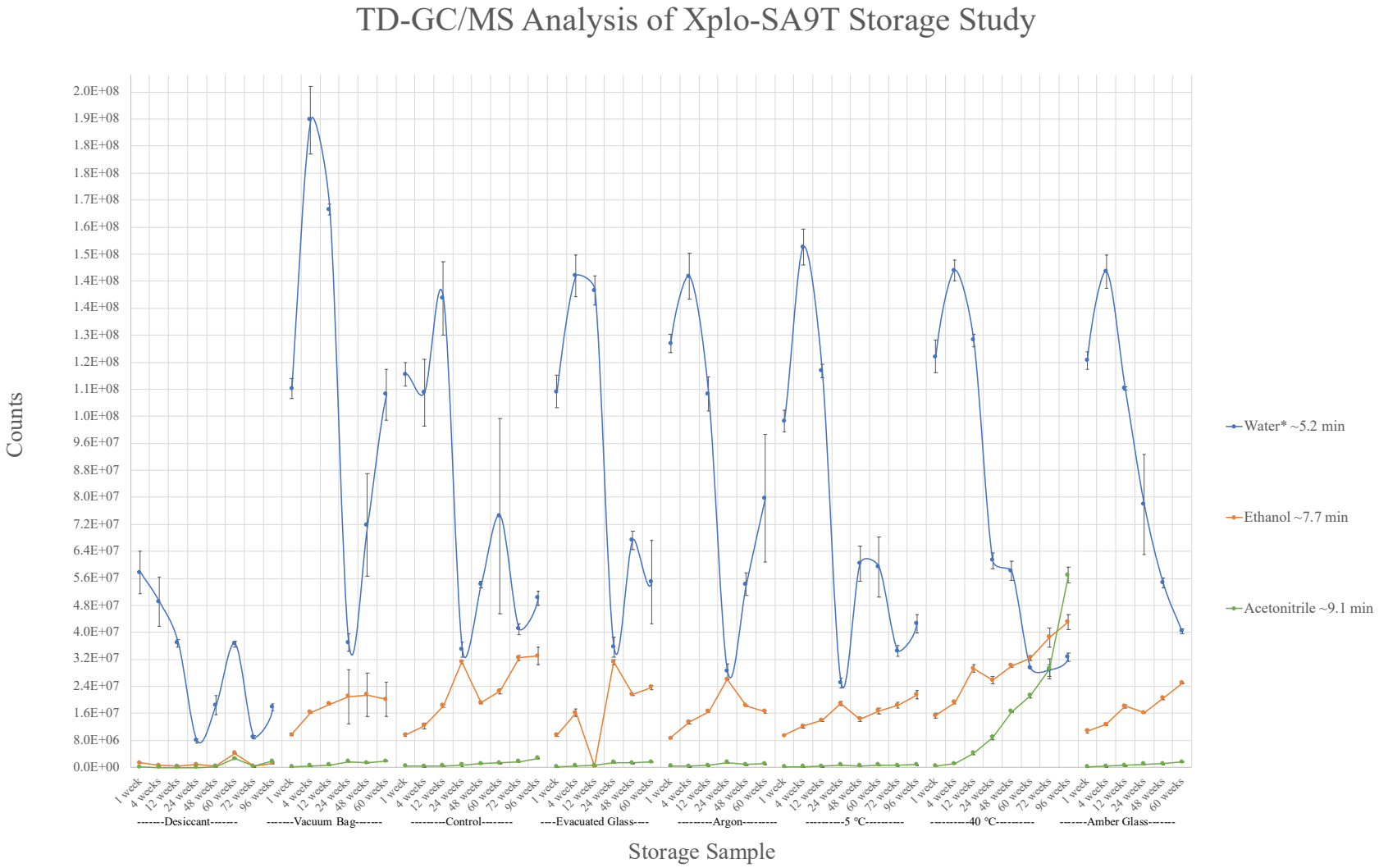

Figure 1. Time dependent off-gassing of presumed controllable species from eight environmental conditions for Xplo-SA9T. Each component's average retention time is specified in the legend. * = peak location could be a mixture of water, ammonia, and ammonium; a detailed explanation is provided within the main text.

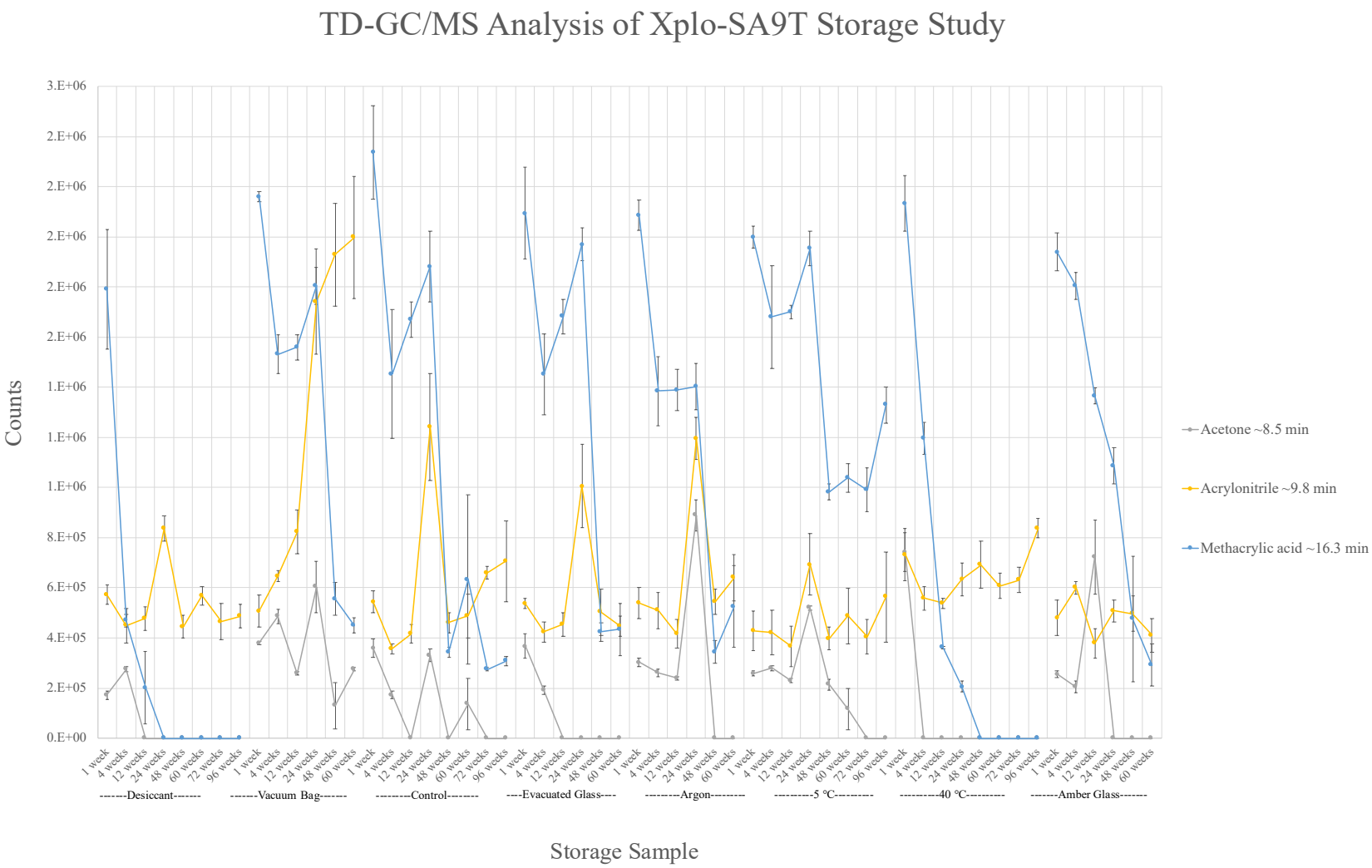

Figure 2. Time dependent off-gassing of presumed inherent synthetic artifacts from Xplo-SA9T under eight environmental storage conditions. Each component's average retention time is specified in the legend.

The second major peak, ethanol, was due to the amine synthesis process; this contaminant was currently unavoidable; however, it could be further reduced with theoretically extended evacuation during the work-up period. The final controllable peak, acetonitrile, has been deemed a direct byproduct of poor storage environments and/or material decomposition over time. Acetonitrile was further confirmed by building a calibration curve with a known calibrated acetonitrile source (described in the experimental section). With the proper long-term storage, this peak could be reduced, as proven by this storage study (Figure 3). In agreeance with the literature, thermal degradation of amines is well known and is hypothesized as the major component for this acetonitrile production over time (further indicated by the lowest concentration detected when stored at 5˚C) [13], [26], [27].

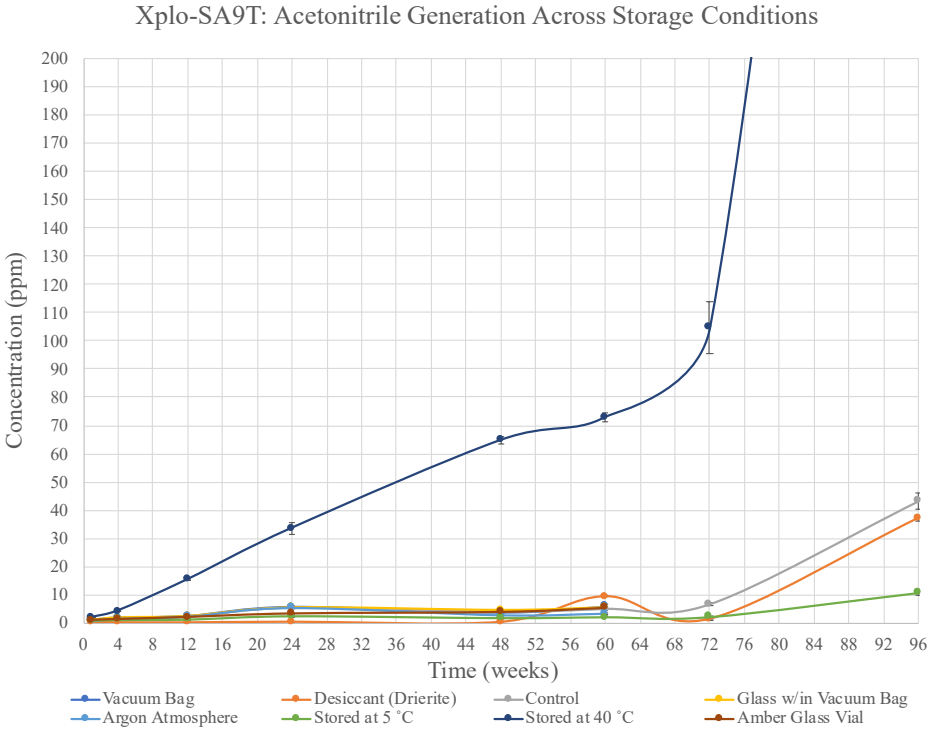

Figure 3. Time dependent concentration of acetonitrile per storage environment. Values were calculated using a calibration curve and the raw integrated intensities from the gas chromatograms. At 96-weeks the triplicate acetonitrile concentration for the 40˚C storage environment was 679 ± 39 ppm.

Similar to Xplo-SA9T, MMPA-Sorbent was evaluated for 48 weeks with only the five most applicable storage environments (Figure 4). Additionally, the same large ethanol and presumably water peaks were forefront in the chromatograms across all environments; however, MMPA-Sorbent also displayed large concentrations of methyl methacrylate which is attributed to its use in the synthesis process.

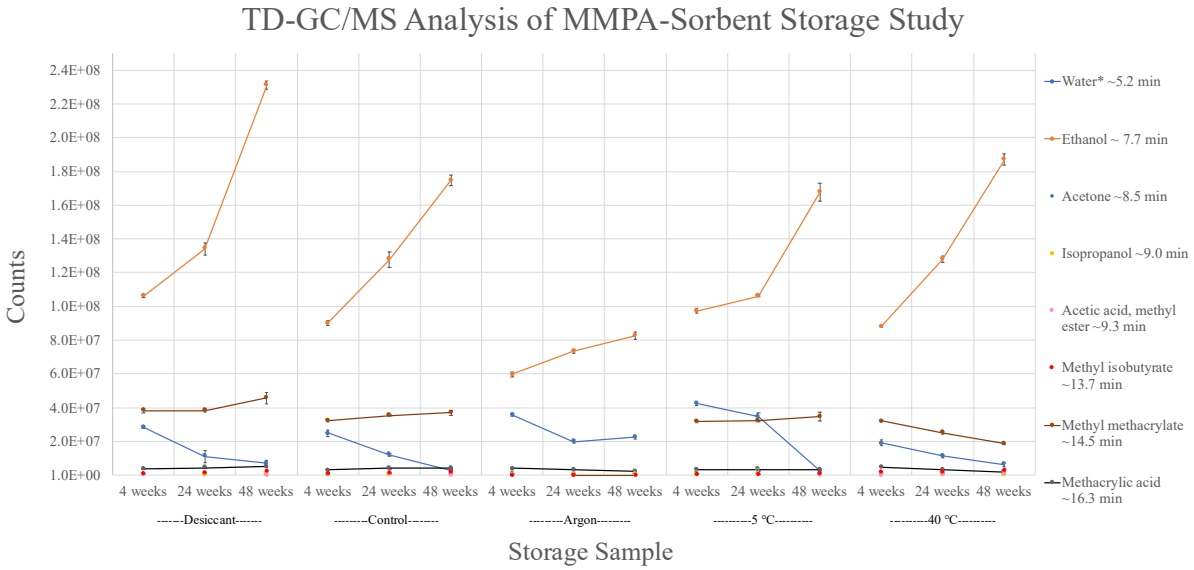

Figure 4. Time dependent off-gassing of all detected species from MMPA-Sorbent under five environmental conditions. Each component's average retention time is specified in the legend. * = peak location can be a mixture of water, ammonia, and ammonium; a detailed explanation is provided within the main text.

Three of the species found in low concentrations (Figure 5) are attributed to lab cleaning and the resin support (acetone, isopropanol, and methacrylic acid, respectively). Acetic acid, methyl ester and methyl isobutyrate may generate if the active amine is reacting or decomposing over time with either oxygen or water [28]. This theory is supported by the absence of acetic acid, methyl ester, and methyl isobutyrate within the inert atmosphere across the full 48-week study.

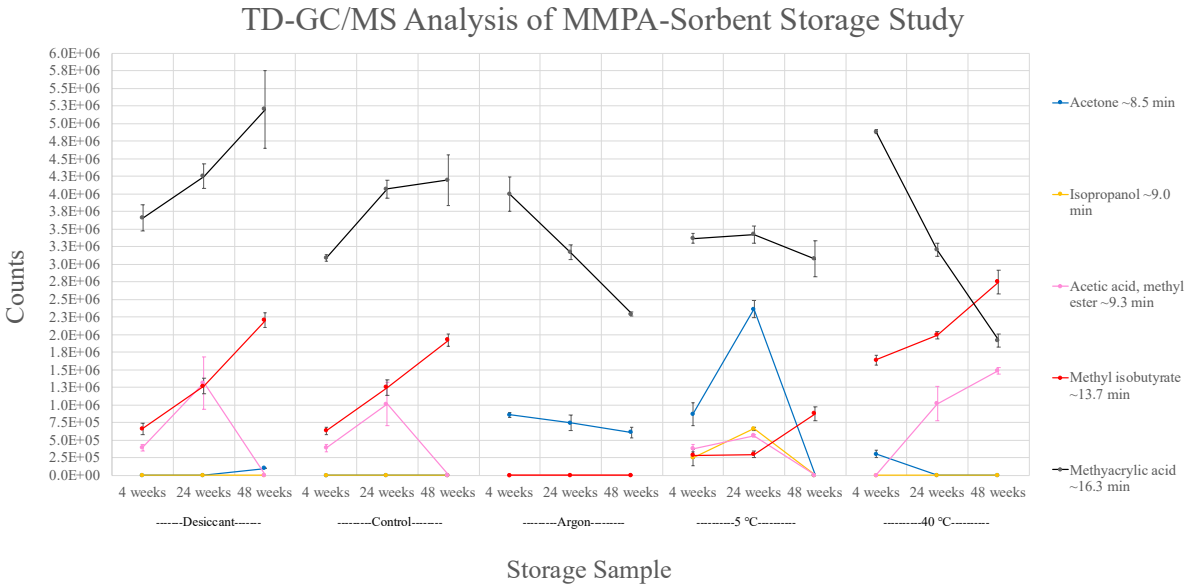

Figure 5. Time dependent off-gassing of all detected species from MMPA-Sorbent under five environmental conditions excluding water* and ethanol. Each component's average retention time is specified in the legend.

LPEI-Sorbent produced the least number of volatile species compared to Xplo-SA9T and MMPA-Sorbent. Similar to both, ethanol and water are the major off-gassed components (Figure 6). Both, species can be reduced by using the desiccant; alternatively, extended vacuum time will further purify the material.

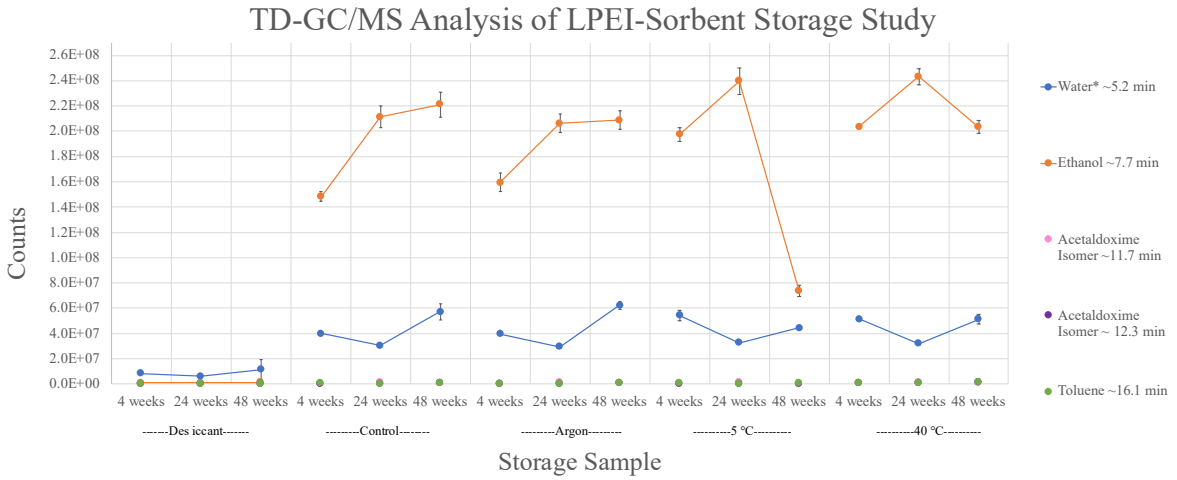

Figure 6. Time dependent off-gassing of all detected species from LPEI-Sorbent under five environmental conditions. Each component's average retention time is specified in the legend. * = peak location could be a mixture of water, ammonia, and ammonium; a detailed explanation is provided within the main text.

Three low concentration species were observed for all storage environments (Figure 7). Both acetaldoxime isomers were present within the study and are theorized to be possible as polyethyleneimine can undergo oxidative degradation into oximes. Toluene was found and may be releasing from either component of the adsorbent as LPEI-Sorbent uses a different resin support than that for Xplo-SA9T and MMPA-Sorbent.

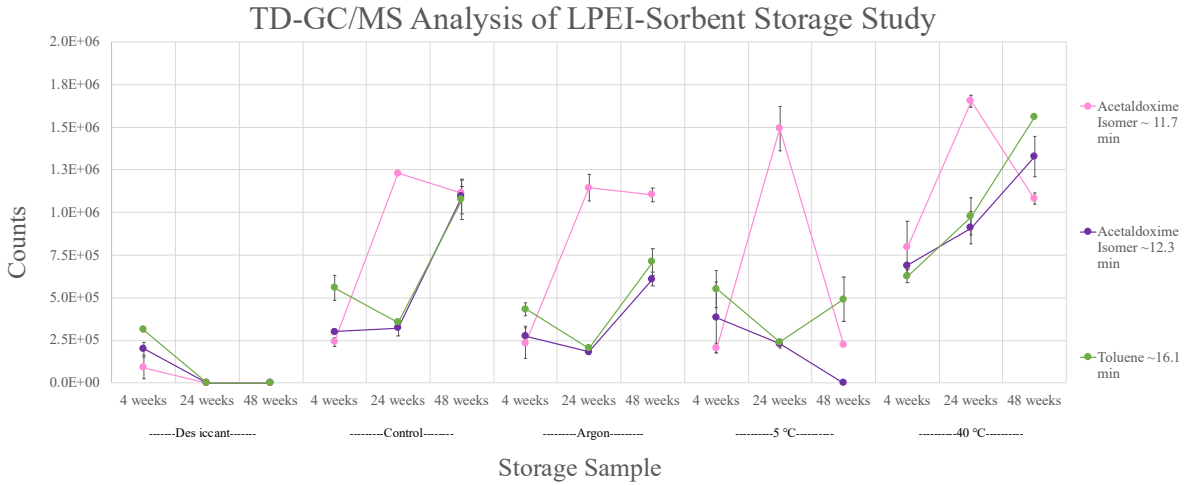

Figure 7. Time dependent off-gassing of all detected species from LPEI-Sorbent under five environmental conditions excluding water* and ethanol. Each component's average retention time is specified in the legend.

B. NMR Spectroscopy Study

The amine component of the synthesized adsorbents is the CO_2 adsorbing modifier and accordingly should be tracked for specific degradation/reactivity over the course of storage studies. In addition, extensive research into amines designed for CO_2 capture and their corresponding thermal decomposition points exist [13]. By employing nuclear magnetic resonance (NMR) spectroscopy, one can elucidate the chemical structure, monitor relative concentration, and purity of a desired sample of interest over time. With Xplo-SA9T and MMPA-Sorbent, both were reproducibly evaluated for as-synthesized ^{1}H NMR spectra. LPEI-Sorbent, is synthesized with a complex polymer and the proton NMR spectrum is not well defined/visible. With the initial clean material spectrum in hand, each storage environment and time point were explored to determine if and how the amine may be changing over time. While each data time interval/condition resulted in its own spectrum, only key spectra are shown. For Xplo-SA9T at the 96-week timepoint, the 5˚C, control, and desiccant samples remained the most in-tact from the as-synthesized TEPAN (Figure 8). The 5 protons corresponding to the secondary amines (R_2-N-H) may broaden and shift due to hydrogen bonding,

solvent effects, and temperature dependance [29], [30]. The individual timepoint spectra revealed the same trends over time as observed in Figure 8; however, the trends are more pronounced in the 96-week timepoint and accordingly were presented.

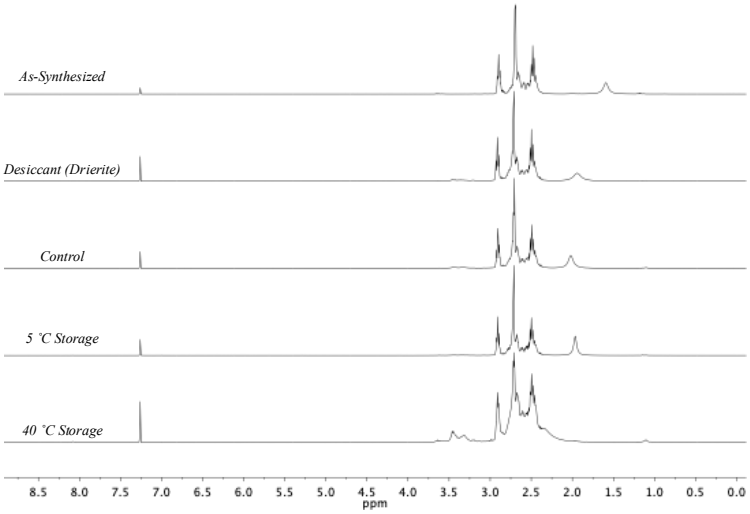

Figure 8. Proton NMR spectra of TEPAN (active amine stripped from Xplo-SA9T) samples stored for 96 weeks compared to as-synthesized material. The peak at 7.26 ppm corresponds to deuterated chloroform.

The control and desiccant also display minimal amine reactivity or decomposition due to the environmental storage method. The 40˚C sample, on the other hand, shows clear relative concentration change by a chemical shift indicative of a new species. This generated component is presumed to be the thermal decomposition product directly, as trace quantities exist in the control and desiccant samples which were stored at ~23˚C.

When comparing all samples collected for Xplo-SA9T stored at 40˚C for 96 weeks, a clear and evident trend appears with the multiplet located within 3.51–3.25 ppm. At 24 weeks, the chemical shifts are defined enough to integrate with respect to the multiplet previously assigned to TEPAN. Without quantitative NMR, the exact concentration is not defined; however, all ratios are representative of material conversion. At 24 weeks, the new multiplet integrates to 3% of that of the initial TEPAN (Figure 9). As the material is further analyzed at 48, 60, 72,
and 96 weeks the corresponding new multiplet ratio integrations are 6, 9, 7, and 10%. This implies that at 96 weeks ~90% of TEPAN is still intact (due to material solubility, the two species may not be equally soluble in $CDCl_3$). A key takeaway is that even at the attributed most non-conducive long-term storage method, the amine still remains ~90% pure even while being held at 40˚C for 672 days.

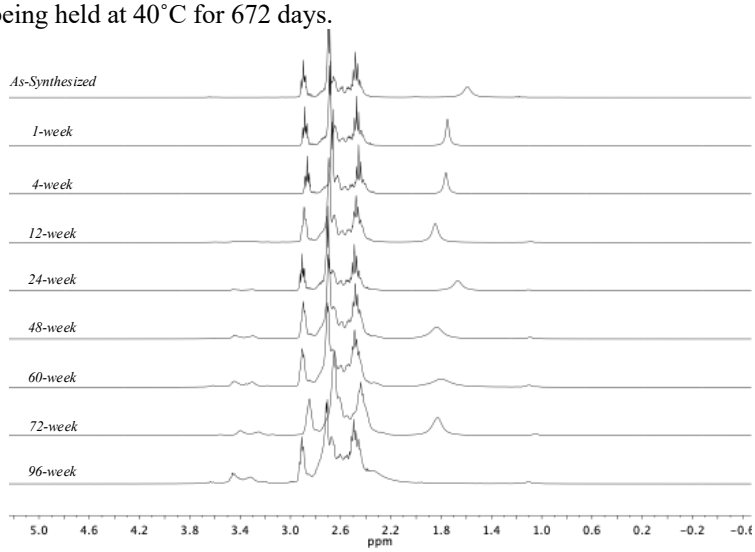

Figure 9. Proton NMR spectra of TEPAN (active amine stripped from Xplo-SA9T) thermally degrading over time at 40˚C.

MMPA-Sorbent in Figure 10 revealed a chemical shift (new peaks at ~3.64, ~3.38, and ~1.08 ppm) for all storage environments. The most resolved is the inert atmosphere spectrum (suggesting that MMPA-Sorbent is air sensitive, therefore slowly reacting with oxygen), further supported by the additional spectra (peak exchange between ~3.64 and ~3.38 ppm) possibly exhibiting a paramagnetic effect of dissolved molecular oxygen. The remaining spectra, can also be associated with restricted rotation causing formerly equivalent functional groups to become magnetically non-equivalent. This diastereotopic phenomenon results in peak doubling at lower temperatures that can coalesce at higher temperatures (note the 40˚C storage spectrum, peak ~3.38 ppm) [31].

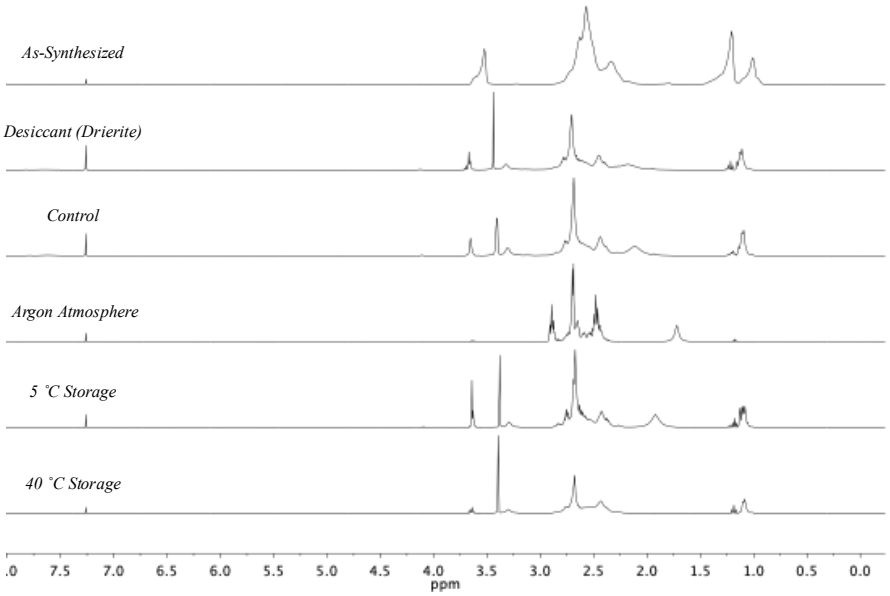

Figure 10. Proton NMR spectra of MMPA (active amine stripped from MMPA-Sorbent) samples stored for 48 weeks. The peak at 7.26 ppm corresponds to deuterated chloroform.

C. Carbon Dioxide Adsorption Study

1. 0–99% CO_2 Breakthrough Studies

During any long-term storage study the main concern for any material with a dedicated life-support task is minimum performance. Previously, Xplo-SA9T and MMPA-Sorbent were evaluated using an identical specialized breakthrough rig that delivers calibrated humidity and CO_2 at a specific rate [17]. For all comparisons below, a relative humidity of 52% and a CO_2 concentration of 2.128 mmHg was delivered at 100 mL/min. Each sample was run in triplicate, and the sensor accuracy and dosing source were verified daily. The adsorbent bed size, packed within a glass TD tube, was 4 mm x 14 mm (~ 90–100 mg), and each sample was dosed from 0–99% CO_2 breakthrough. Previously, Xplo-SA9T was published at 1.037 ± 0.005 mmol/g and MMPA-Sorbent at 0.97 ± 0.07 mmol/g for as-synthesized material [17]. Over the course of 48 weeks, Xplo-SA9T and MMPA-Sorbent remained at or above the previously reported values. At 48 weeks LPEI-Sorbent remained at or above the as-synthesized material (1.04 ± 0.05 mmol/g) for only the 40˚C storage environment. With remaining environments, all capacities were within three estimated standard deviations (ESD) and are therefore statistically similar. At 96 weeks Xplo-SA9T, continued to perform at or above the minimum CO_2 capacity published in 2024 [17].

In Table 1, each storage environment was coined conducive, acceptable, or non-conducive for long-term stowage based on interpretations of all three analysis methods discussed herein. Conducive implies this storage environment lends to low decomposition/reactivity yielding the best material for long-term applications. The term “Acceptable” refers to an acknowldgement that adverse effects are occurring with the selected storage method; however, the material remains functional. Non-conducive environments are negatively impacting the material and not-advisable for long-term stowage. Specific long-term effects from the generation of new species (such as the thermal decomposition product of TEPAN) could react inadvertently with exposed VOCs, or increase the kinetic decomposition rate of the remaining TEPAN.

Table 1. Performance characterization of all adsorbents with respect to 0–99% CO_2 breakthrough capacity.

Storage Environment/Material and Study Duration	Capacity (mmol/g)*	ESD (mmol/g)	Long-Term Storage
Xplo-SA9T (48-week Storage)			
Desiccant (Drierite) Glass Vial	1.32	0.01	Conducive
Evacuated Vacuum Bag Filled with Adsorbent	1.24	0.01	Acceptable
Glass Vial (Control)	1.27	0.02	Acceptable
Closed Vial Evacuated	1.22	0.03	Acceptable
Glass Vial with Argon Atmosphere	1.28	0.04	Acceptable
Sealed Glass Vial Stored at 5 ˚C	1.23	0.02	Acceptable
Sealed Glass Vial Stored at 40 ˚C	1.16	0.04	Non-Conducive
Amber Glass Vial	1.18	0.04	Non-Conducive
Xplo-SA9T (96-week Storage)			
Desiccant (Drierite) Glass Vial	1.38	0.01	Conducive
Glass Vial (Control)	1.32	0.02	Acceptable
Sealed Glass Vial Stored at 5 ˚C	1.31	0.04	Acceptable
Sealed Glass Vial Stored at 40 ˚C	1.15	0.03	Non-Conducive
MMPA-Sorbent (48-week Storage)			
Desiccant (Drierite) Glass Vial	1.37	0.10	Conducive
Glass Vial (Control)	1.32	0.06	Acceptable
Glass Vial with Argon Atmosphere	1.40	0.05	Conducive
Sealed Glass Vial Stored at 5 ˚C	1.46	0.07	Conducive
Sealed Glass Vial Stored at 40 ˚C	1.11	0.08	Non-Conducive
LPEI-Sorbent (48-week Storage)			
Desiccant (Drierite) Glass Vial	0.77	0.05	Non-Conducive
Glass Vial (Control)	0.87	0.07	Acceptable
Glass Vial with Argon Atmosphere	0.90	0.02	Acceptable
Sealed Glass Vial Stored at 5 ˚C	0.79	0.04	Acceptable
Sealed Glass Vial Stored at 40 ˚C	1.14	0.04	Conducive

*** All capacities given are determined with the 0–99% carbon dioxide breakthrough. CO_2 dosed at 2.128 mmHg and 52% RH for 1-hour. Adosrbent beds were ~90–100 mg (4 × 14 mm). As-synthesized capacities for Xplo-SA9T, MMPA-Sorbent, and LPEI-Sorbent are 1.12 ± 0.02, 1.45 ± 0.07, and 1.04 ± 0.05 mmol/g, respectively.**

2. Ammonia Detection

During the CO_2 adsorption study, an electrochemcial ammonia sensor (DF Robot SEN0469) was located directly on the output of the CO_2 sensor [17]. The sensor possesses a detection range of 1–100 ppm NH_3, a response time of <150 seconds, a maximum measurment error of 5 ppm, and a resolution of 1 ppm. When each sample was loaded onto the test rig, there was an immediate signal for ammonia at some storage conditions when flowing through the adsorbent bed. Each value given consists of the highest peak (if any) detected during each triplicate sample set. Xplo-SA9T did not display any ammonia when stored with the desiccant or with the inert atmosphere. The desiccant can adsorb off-gassed ammonia whereas the argon atmosphere indicates oxygen/water may facilitate ammonia production. All other environments display varying amounts of ammonia over time with the highest concentrations resulting at and after 24-weeks of stowage. Xplo-SA9T further revealed accumulated ammonia above the sensor's upper bounds (>100 ppm) by 60 weeks for the 40˚C storage and the amber glass (for both storage conditions, onset of ammonia detection

occurred at 24 weeks). A possible explanation for both would be water and oxygen-based leaching when the seals are heated or failing over time. Alternatively, the 40˚C storage samples are thermally decomposing as seen by the above NMR spectroscopy studies. The Xplo-SA9T control only displayed 2 ppm ammonia at the 72-week time interval. The 5˚C Xplo-SA9T samples revealed 4 ppm ammonia at 12 weeks; however, no other accumulated ammonia was detected across the time intervals. Both the evacuated bag, and evacuated glass displayed low levels of ammonia at the 60-week storage interval (7 and 26 ppm NH_3, respectively). For all samples of Xplo-SA9T, if accumulated NH_3 was detected, often it would trend in an increasing manner across the storage time intervals. MMPA-Sorbent displays ammonia throughout all storage environments; albeit, in lower concentrations than Xplo-SA9T (no detected peak > 24 ppm NH_3). For MMPA-Sorbent storage samples, a 6 ppm NH_3 reading was detected on the as-synthesized material. No trend was observed over time for a statistical increase or decrease in MMPA-Sorbent accumulated NH_3 levels, rather just low concentrations (< 24 ppm NH_3) being detected each time. For the inert atmosphere, MMPA-Sorbent did not reveal any accumulated NH_3 after the as-synthesized material. These observations support the ongoing theory of MMPA-Sorbent minor oxygen/water reactivity over time. LPEI-Sorbent did not release ammonia in a concentration that the sensor could detect anytime during the storage study.

V. Conclusion

Three adsorbents were evaluated for potential off-gassing, amine/imine decomposition, and CO_2 adsorption performance over a two-year period. TD-GC/MS was utilized to elucidate what species can off-gas from Xplo-SA9T, MMPA-Sorbent, and LPEI-Sorbent at various environmental conditions. A quantitative concentration for acetonitrile generation over time from Xplo-SA9T is reported with eight different storage environments over 60 to 96 weeks. NMR spectroscopy was utilized to determine the best storage methods for Xplo-SA9T and MMPA-Sorbent. Xplo-SA9T was shown to slowly thermally degrade by ~10% over 96-weeks during long-term storage in the 40 ˚C storage environment. MMPA-Sorbent likely interacted with, presumably, oxygen and exhibited a diastereotopic phenomenon during storage at 5–40˚C storage. Ammonia was detected over time for Xplo-SA9T and MMPA-Sorbent; furthermore, the observed ammonia accumulation rates can be attributed to specific storage environments. The LPEI-Sorbent did not exhibit detectable ammonia release during the storage study, indicating a potential reduction in the ammonia generation relative to the current solution. The carbon dioxide adsorption abilities of all materials were evaluated over time, and, although certain storage conditions caused undesirable reactivity or decomposition, the materials performed near identically to fresh material and successfully scrubbed a simulated air stream of CO_2.

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