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Savannah River Site/K Area Complex Getter Life Extension Report

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Abstract

The K Area Complex (KAC) at the Savannah River Site (SRS) has been utilizing HiTop hydrogen getter material in 9975 Shipping Containers to prevent the development of flammable environments during storage of moisture-containing plutonium oxides. Previous testing and subsequent reports have been performed and produced by Sandia National Laboratories (SNL) to demonstrate the suitability and longevity of the getter during storage at bounding thermal conditions. To date, results have shown that after 18 months of continuous storage at 70°C, the getter is able to both recombine gaseous hydrogen and oxygen into water when oxygen is available, and irreversibly getter (i.e. scavenge) hydrogen from the vapor space when oxygen is not available, both under a CO₂ environment. [Refs. 1-5] Both of these reactions are catalytically enhanced and thermodynamically favorable. The purpose of this paper is to establish the justification that maintaining the current efforts of biannual testing is no longer necessary due to the robust performance of the getter material, the very unlikely potential that the recombination reaction will fail during storage conditions in KAC, and the insignificant aging effects that have been seen in the testing to date.

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Acronyms

3013	DOE-STD-3013 Standard
DE	destructive examination
DOE	Department of Energy
ISSC	Interim Safe Storage Criteria Program
KAC	K Area Complex
LANL	Los Alamos National Laboratory
LLNL	Lawrence Livermore National Laboratory
NDE	non-destructive examination
NMR	nuclear magnetic resonance spectroscopy
PCV	Primary Containment Vessel
RFETS	Rocky Flats Environmental Technology Site
SNL	Sandia National Laboratories
SRNL	Savannah River National Laboratory
SRS	Savannah River Site

KAC/SRS Getter Life Extension Report

Background

The US Department of Energy (DOE) issued a Standard by which its various Sites are to package excess plutonium-bearing (and later also some uranium-bearing) metals and oxides. This standard, known as DOE-STD-3013, or the 3013 Standard, provides requirements in the stabilization, packaging, and surveillance of this material. Compliance with the 3013 Standard is assumed to provide a long-term safe storage capability for approximately 50 years, and each of the production Sites (e.g. SRS, RFETS, Hanford, LANL, LLNL) has either produced or is producing containers of material that are compliant with the Standard. The ongoing surveillance portion of this program includes both destructive examination (DE) and non-destructive examination (NDE) of a statistical sampling of 3013 containers. SRS is leading the DOE Complex in both DE and NDE of 3013 containers, but only the DE process is germane to this discussion.

During DE, a 3013 container of oxide contents is brought into a glovebox, punctured, cut open, and cut apart, and the material contained within is sampled for detailed analysis. Containers of metal contents are not yet a part of the DE process. After oxide samples are obtained, the bulk of the original oxide quantity remains in the DE glovebox. The glovebox environment has no credited environmental controls, and since many of the oxides contain salt impurities, they can absorb moisture from the relatively humid air. This absorbed moisture can be radiolyzed (i.e. split apart) during storage due to the continual bombardment of alpha radiation from the oxide. In theory, such a process can quickly produce a flammable environment inside a sealed storage container, and the Interim Safe Storage Criteria Program (ISSC) at KAC prohibits the formation of flammable environments during storage. [Ref. 6] As KAC does not have the capability to recreate a 3013-compliant container, it is necessary to provide for alternate storage of moist oxide after DE is complete.

KAC personnel learned of polymeric hydrogen getter technology from scientists at the Savannah River National Laboratory (SRNL) from previous work with waste storage and shipping containers. Polymeric hydrogen getters, developed at SNL, have been deployed under a variety of environments, for a range of consumer, industrial, and government applications, over 10 million times per year. Contacts were made with SNL and a suitability report was generated by KAC. [Ref. 7] SNL recommended the use of the HiTop family of hydrogen getters for this purpose but had not performed testing of these getters in the type of environment that would be used in KAC. This environment included inerting the vapor space with carbon dioxide (CO₂), which meant that the getter must perform its hydrogen removal function in the presence of CO₂ and residual air. Once the initial test concluded that HiTop would work for this application [Ref. 1], KAC set about to ensure the storage packaging would facilitate vapor space interaction of the hydrogen and the getter. This was accomplished by instituting the use of filter-vented inner cans, filter-vented glovebox bag-out bags, and filter-vented outer cans that could be handled as radiologically clean items. The getter was procured from Vacuum Energy, Inc. in gas permeable bags fitted inside perforated metal cans. A bag of zeolite desiccant was also placed inside each can to provide a collection location for any water generated by the recombination reaction (see discussion below). The multi-filter-vented can assembly is placed underneath the getter can assembly inside a 9975 Shipping Container's Primary Containment Vessel (PCV). See

Figure 1 for a picture showing the inner can, outer can, and perforated metal can, and Figure 2 showing the cans in their deployed assembly formation.



Figure 1. Representative inner filter-vented can with filter-vented bag (left), outer filter-vented can (center), and perforated metal can (right).

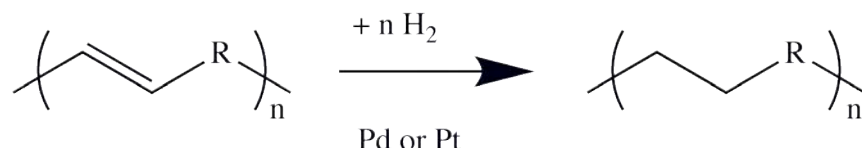


Figure 2. Representative installation of multi-filter-vented can and getter can assemblies, shown in cutaway.

Requirement for Storage

Fundamentally, a vapor space rich in hydrogen but without free oxygen is not flammable. Removing any residual oxygen from the PCV is therefore the minimum requirement for meeting the intention of the KAC ISSC Program. To this end, the PCV vapor space is inerted with CO₂ prior to closure and leak testing. However, the method used to inert the PCV is a simple gravity fill and may not remove 100% of oxygen. Moisture radiolysis may also produce additional oxygen during storage. Therefore, the getter is essential to ensure that a flammable environment inside the PCV is prevented.

The underlying basis of hydrogen getter operation is a chemical reaction that uses hydrogen gas to reduce carbon-carbon double or triple bonds. Hydrogenation of unsaturated compounds (carbon-carbon multiple bonds) requires a precious metal such as palladium or platinum to catalyze the reaction at modest temperatures and pressures such as will exist in KAC's application. A representative reaction proceeds as follows:



In the presence of both hydrogen and oxygen, a precious metal will preferentially catalyze the formation of water in a reaction known as recombination. Under conditions where water can be tolerated, this is often a desired effect because the reaction removes both hydrogen and oxygen, thus more quickly reducing the potential for flammability-related accidents; it is this recombination reaction that is able to maintain compliance with the ISSC Program. Once oxygen is depleted, the gettering reaction simply removes hydrogen and serves to reduce the hydrogen partial pressure inside the PCV atmosphere. The relative rates of hydrogenation and recombination vary with the concentration of the reactants, but at low hydrogen concentrations (e.g., <1 %) recombination proceeds at a much faster rate and is observed almost exclusively until the oxygen concentration is below a few percent. The getter has no trouble switching from one reaction the other (depending solely on whether or not oxygen is available), and continues to recombine even if the theoretical gettering capacity had been reached. Theoretical gettering capacity refers to the total amount of hydrogen that could be gettered by the hydrogenation of the carbon-carbon double bonds in the polymer. Recombination does not consume the capacity of the getter.

The quantity of getter per assembly was determined assuming that a bounding quantity of moisture was radiolyzed, and the resulting volume of hydrogen gas was to be removed from the vapor space solely by gettering. This is conservative from the standpoint that the first quantities of hydrogen to be generated encounter oxygen and are recombined. It is also very conservative in that the highest measured oxide moisture to date (0.6 wt%) has been much less than the bounding moisture assumed in the getter procurement specification (3 wt%). [Ref. 8] However, even if the moisture were to somehow be in excess of the assumed bounding value, and it was to be completely radiolyzed and provide more hydrogen than the getter could remove via the gettering/hydrogenation reaction, the getter would still recombine all free oxygen and keep the vapor space non-flammable.

Summary of Testing to Date

Periodic testing of the getter has been performed by SNL and is documented in Refs. 1-5. This testing continuously exposed getter material at the highest bounding thermal condition of 70°C (assumed to be the most potentially damaging environmental condition) for a period of time. The material was then removed from the oven, a portion of the aged material was irradiated by a bounding radiation field, and both the irradiated and non-irradiated samples were tested under recombination (CO₂/Air with 5% H₂) and gettering (CO₂/N₂ with 5% H₂) conditions. The pressure drop data obtained was then compared to the gettering and recombination performance of unaged getter from the same manufacturing lot. These tests are conservative because in the SNL tests, the getter is exposed to a flammable quantity of H₂ instantly, saturating many of the reaction sites on the getter. In KAC's application, however, the H₂ concentration is initially zero. As minute quantities of H₂ are produced and exposed to the getter, more of the getter surface area is available for reaction.

¹H NMR spectra of the materials were also collected to monitor any degradation of the material and confirm the occurrence of the gettering reaction under the appropriate conditions. The ¹H NMR spectra are plotted on a scale of 0-10 ppm. If gettering occurs, the carbon-carbon multiple bonds of the getter (appearing as multiple peaks around 7 ppm) are reduced to saturated moieties, with the saturated peaks appearing around 1-2.5 ppm. Olefin peaks resulting from the partial reduction appear at 5-6 ppm. The sharp peak at 5.98 ppm is the residual proton signal in the 99+% deuterated solvent 1,1-2,2 tetrachloroethane-d₂. The peak around 1.5-1.7 ppm (appearing either broad or sharp) is residual water that is always seen unless samples and NMR tubes are handled in a dry glove box.

This periodic testing revealed that essentially no degradation has occurred in the getter's ability to recombine hydrogen and oxygen, which as discussed above is its crucial function. As described earlier, it is the precious metal that catalyzes the recombination reaction. Even with a theoretical degradation of the polymer portion of the getter, the recombination reaction would remain unaffected. Recombination results from the last four series of tests, at aging times of 3, 6, 13, and 18 months at the bounding thermal condition of 70°C, are summarized in Figure 3. The initial pressure drop represents the opening of the sample chamber to the rest of the testing system; the subsequent gradual pressure drop represents the removal of hydrogen from the system due to recombination.

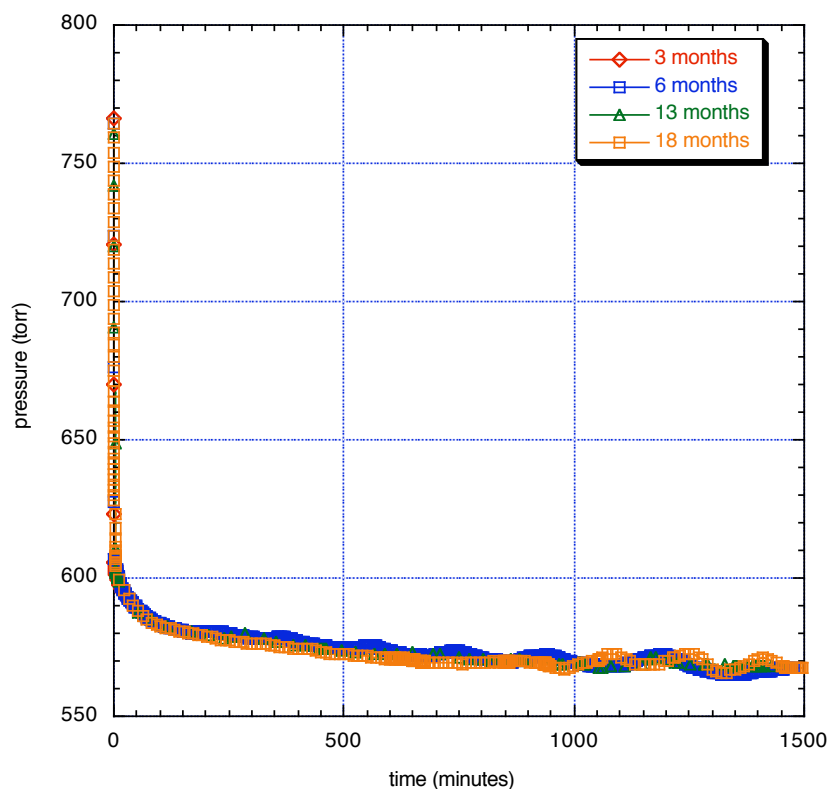


Figure 3. Pressure change over time for HiTop material, aged for 3 months, 6 months, 13 months, and 18 months at 70°C, under recombination conditions (CO₂/Air with 5% H₂) at 20°C. Minor pressure fluctuations reflect changes in ambient laboratory temperature over the multi-hour experiment.

The ¹H NMR spectra collected in the latest test after 18 months of aging at 70°C [Ref. 5] show extremely minor changes in the aged material, which can be possibly attributed to slight decomposition of the HiTop material or absorption of contaminants during the aging process. Appendix A includes NMR spectra for unaged HiTop, HiTop after 18 month of aging, and HiTop after 18 month aging and recombination/gettering (Spectra 1-3). The latest test also revealed some unknown reduction in gettering rate, but it was inconclusive whether the getter had been thermally degraded, a contaminant had entered the testing apparatus and rendered an anomalous reading, or the quantitative ability of the apparatus was at its limit to detect a change.

As a comparison to the small amount of gettering achieved by this sample as shown in Spectrum 3, a ¹H NMR spectrum from the initial set of tests (Appendix A, Spectrum 4, see also Ref. 1) shows HiTop with 72% of its rated gettering capacity consumed. The appearance of significant peaks in the 4-5 ppm and 1-2.5 ppm ranges for the 72% sample indicate the occurrence of the gettering reaction; these peaks are barely visible for the 18 month aging sample. However, pressure change data under gettering conditions showed that the gettering reaction did proceed for the aged sample, though at a rate incalculable from the NMR data alone. Recombination and gettering rates calculated from the pressure change data (see Figure 3 for an example of this type of data) are summarized in Table 1.

Table 1. Summary of approximate H₂ removal rates for the 575 g getter assembly under various experimental conditions.

Material	Recombination rate (std. cc. H₂/h)	Gettering rate (std. cc. H₂/h)
HiTop, 18 months at 70°C	114	11
HiTop, 13 months at 70°C	112	32
HiTop, 6 months at 70°C	131	29

Even with the conservative assumption that gettering stops at some point between 13 and 18 months of storage, the recombination reaction still occurs at a sufficiently fast rate (i.e. much faster than any calculated bounding generation rate, see Refs. 5 and 6) to maintain a non-flammable environment. Another conservatism is that the bounding thermal conditions has not likely ever been reached in any actual shipping container. The bounding temperature was based on a bounding constant ambient temperature in the storage vault and bounding heat-generating capability of the oxide contents. [Ref. 9] Therefore, current documented testing supports the judgment of getter subject matter experts that the recombination reaction and the rates thereof will not be adversely affected by indefinite time in the storage conditions established by KAC.

Recommended Surveillance

In order to further confirm the above statement, it is recommended that KAC perform periodic surveillance of the getter material. An example of such a surveillance program would be removal of one getter assembly per year and sending the assembly or a sample of the getter material to SNL or SRNL for analysis. If SRNL would be utilized, SNL would provide guidance for SRNL personnel to ensure consistency with previous testing. SNL personnel may elect to travel to SRNL to assist with the analysis. It is expected that the outcome of this analysis would continue to support the posture of indefinite storage based on the recombination reaction being unaffected by storage conditions. For the purposes of modifying future surveillance, this report may be reissued at a later date. Initially, it is suggested that prior to the end of FY 2009, one getter assembly be removed from storage and analyzed to establish its current ability to remove hydrogen. For this first assembly, small samples (<100 mg) would be removed from several locations within the assembly and ¹H NMR compositional testing would be used to demonstrate that the getter has not degraded. The entire assembly of getter material would then be homogenized, and the recombination and gettering rates would be measured as previously tested. This report can then be reissued to include results from the first annual analysis and outline future analyses' scope and periodicity (e.g. annual, biennial, etc.). Further, the results of the initial analysis are expected to be able to conclude that the getter assemblies may be reused in future deployments without recycling or reprocessing.

Conclusion

Based on the testing performed to date, subject matter experts' opinions on the viability of the recombination reaction after deployment in KAC storage conditions, and anticipated future periodic test results, the HiTop getter material may be used for indefinite storage of oxide inside 9975 shipping containers after the performance of 3013 container DE. This judgment replaces the current limit of 18 months of storage. It is expected that the analyses outlined above will further strengthen this posture and may lead to the discontinuation of future analyses.

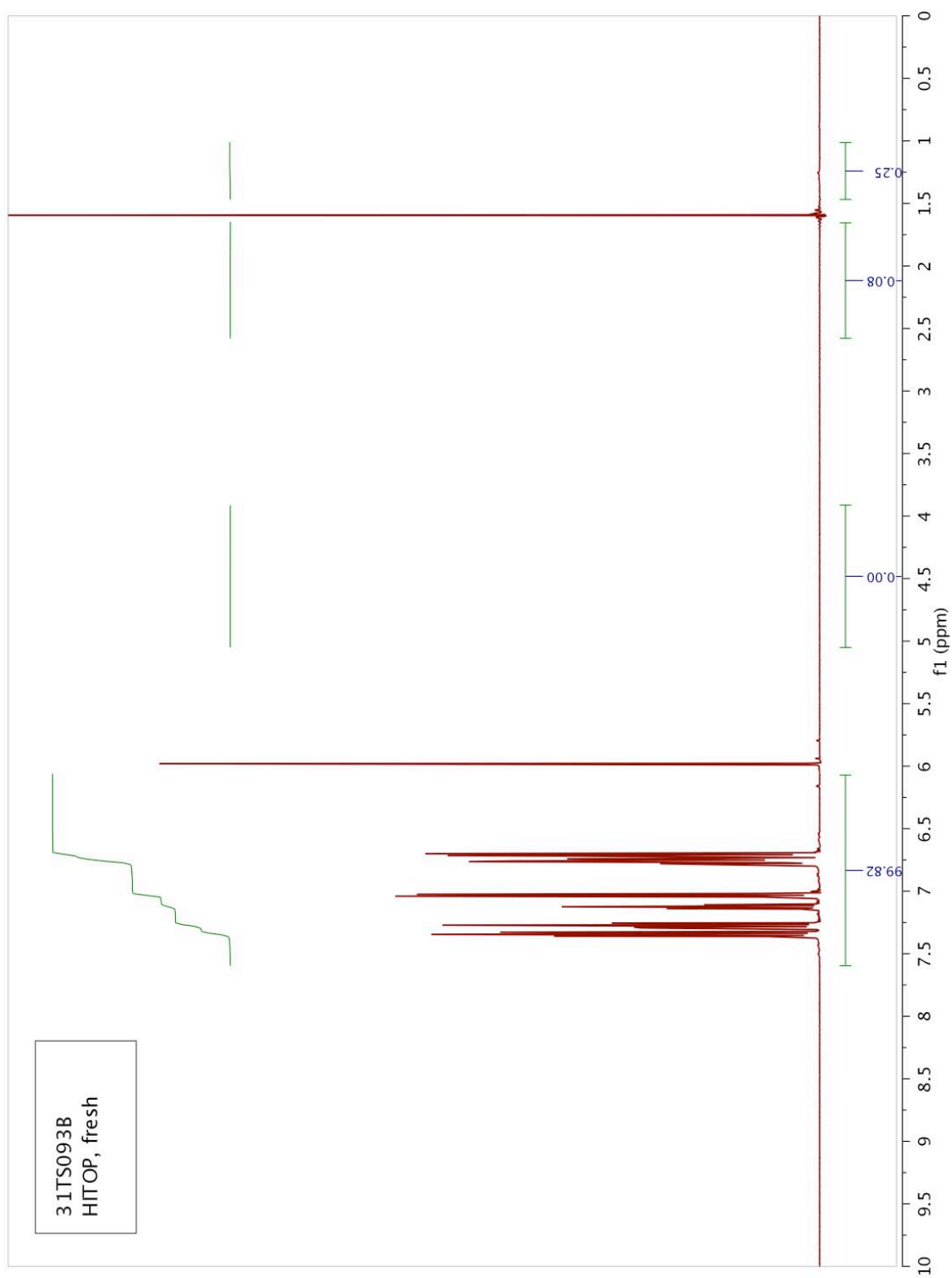
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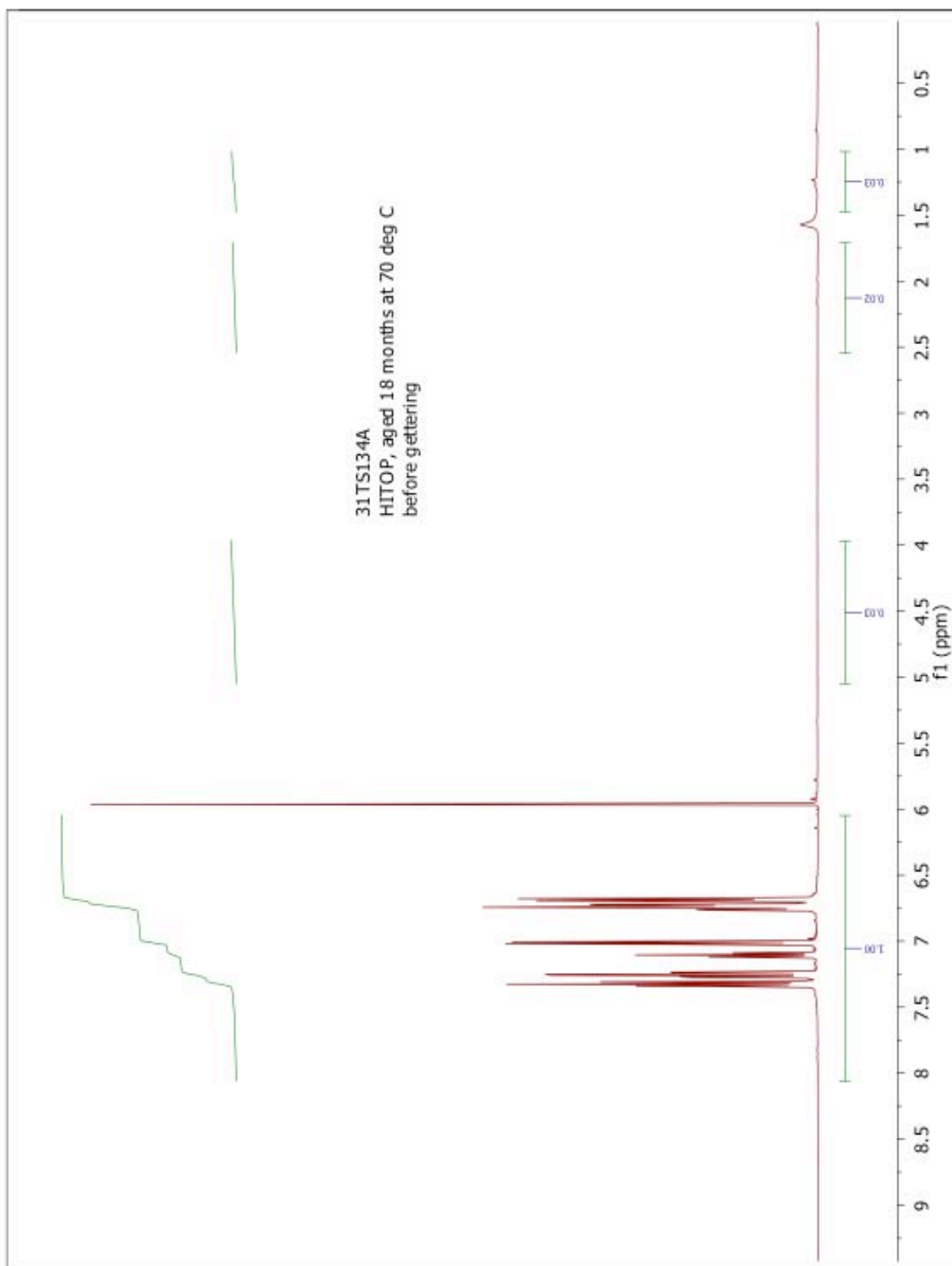
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Appendix A: ^1H NMR Spectra

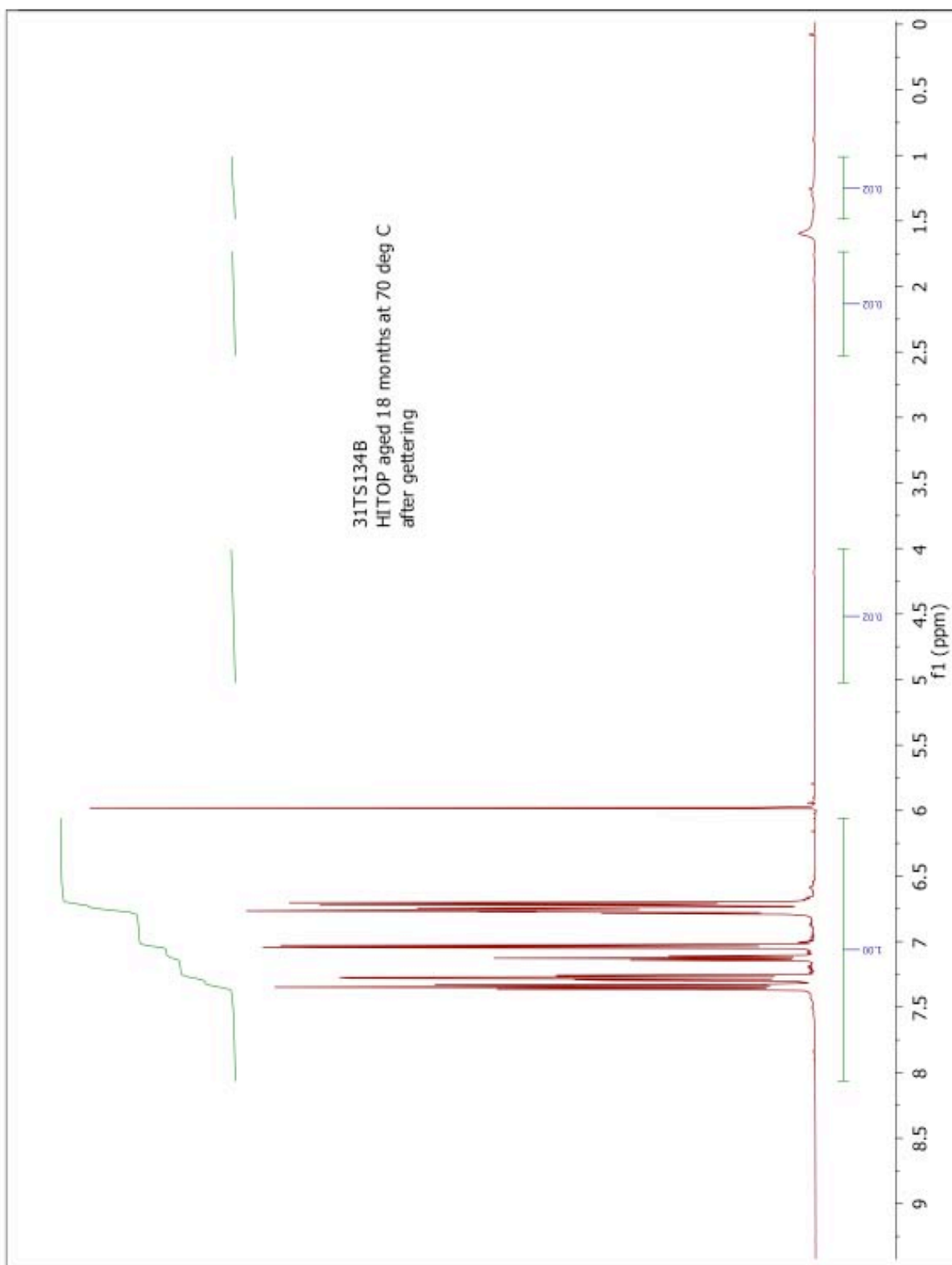
Spectrum 1: HiTop, unaged



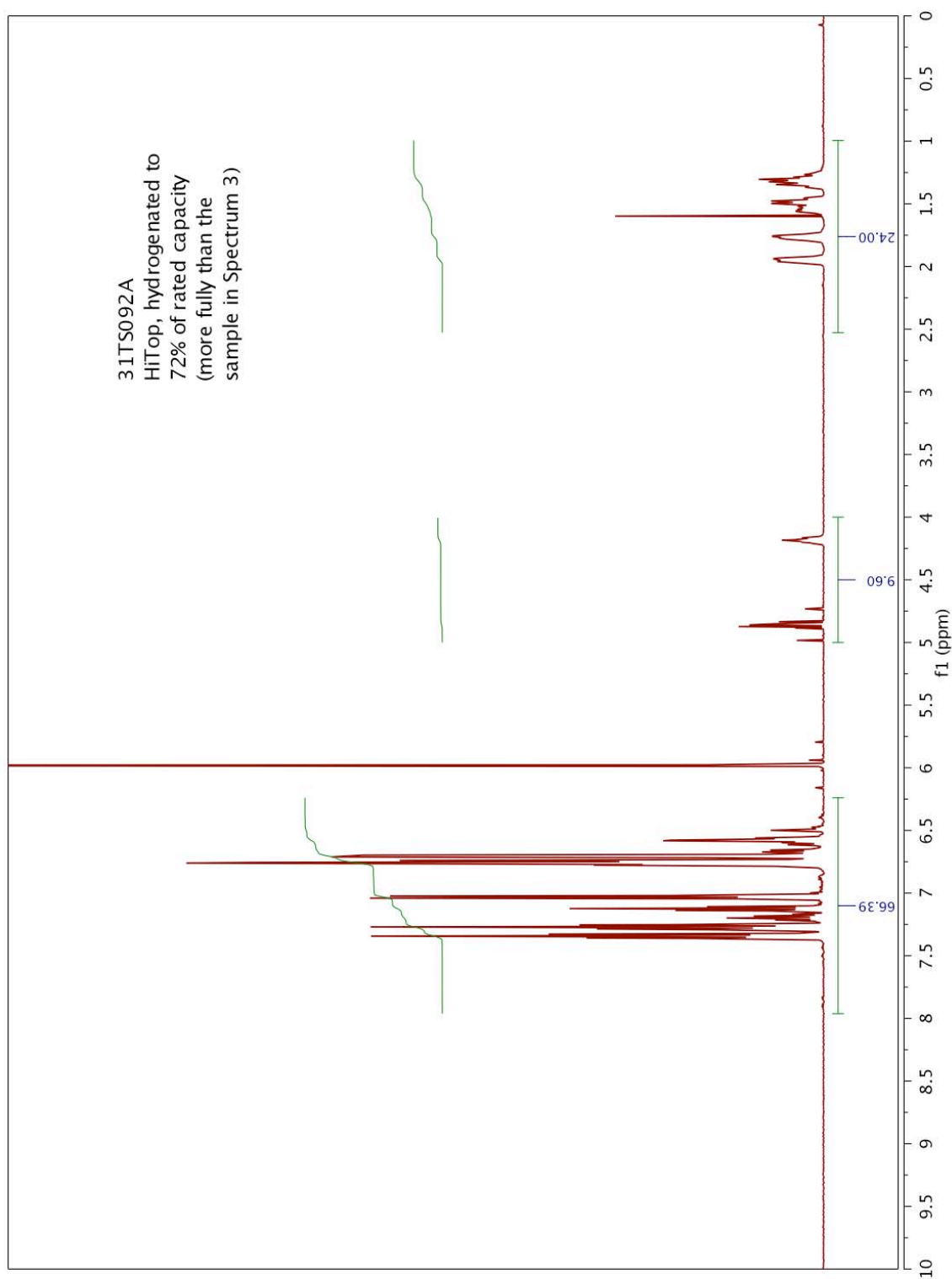
Spectrum 2: HiTop, aged 18 months at 70°C



Spectrum 3: HiTop, aged 18 months at 70°C, after gettering (hydrogenation)



Spectrum 4: HiTop, hydrogenated to 72% of rated capacity



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