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Subject: update to SAND2008-301530150095, SAND2008-301530151789P, and SAND2008-301530157165P.
18-month 70°C aging study of HiTop Hydrogen Getter for WSRC

Abstract

Hydrogen getters were tested for use in storage of plutonium-bearing materials in accordance with DOE's Criteria for Interim Safe Storage of Plutonium Bearing Materials. The original studies, documented in Sandia Report SAND2008-301530150095, included HiTop getter material aged for 3 months at 70°C. This material was aged for an additional 3 months for a total of 6 months at 70°C, and the performance of the getter was evaluated again and documented in Sandia Report SAND2008-301530151789P. This material was then aged for an additional 7 months for a total of 13 months at 70°C, and the performance of the getter under recombination and gettering conditions was evaluated. A sample of the 13 months aged getter was exposed to radiation at SRNL, and the performance of this sample was also evaluated. The results of the 13 months study is reported in SAND2008-301530157165P. The HiTop material was aged for an additional 5 months for a total of 18 months. This material was split into two samples with the second sample being exposed to radiation at SRNL. The performance of the 18 month aged HiTop material is covered in this report.

The 18-month aged material showed similar performance under gettering conditions to the previously aged material: the recombination rate is well above the required rate of 45 std. cc H_2/h, and the gettering reaction occurs in the absence of oxygen at a slower rate. Both pressure drop measurements and ^{1}H NMR analyses support these conclusions. ^{1}H NMR analyses show extremely minor changes in the 18-month aged material, which can be possibly attributed to slight decomposition of the HiTop material or absorption of contaminants during the aging process.

Testing Summary

HiTop polymer hydrogen getter, batch 26TS152, was aged at 70°C for a total of 18 months. ^{1}H NMR spectra of the unaged material (Appendix A, Spectrum 1), material aged for 6 months at 70°C (Spectrum 2), and material aged for 13 months at 70°C (Spectrum 3) show subtle differences to the spectrum of the 18-month aged material (Spectrum 8). These changes can be attributed to multiple causes, including slight decomposition of the getter material or absorption of airborne contaminants during the aging process. However slight, some thermal degradation of the organics may have

occurred. This degradation appears not to have affected the recombination with respect to minimum required rates. The gettering may or may not have been affected. We measure the gettering by two methods, pressure drop and ^{1}HNMR spectral integration. For the pressure drop experiments, quantification of the getter rates is approaching the signal to noise resolution of the data. Though as expected for gettering, the general trend in pressure is downward, the scatter in the data does not allow for high confidence in the calculated rate. Additionally, the ^{1}HNMR spectral determination of the gettering rate depends on measuring the hydrogenated species in a previously vacant portion of the spectrum. After 18 Months at 70 °C. this region of the spectrum (1–2.5 ppm, except the water peak at ≈1.7 ppm), is starting to be populated with traces of contamination or thermal degradation species thus confusing the non-selective integration measurements. The integration algorithm yielded negative values, which makes no physical sense for the chemical species involved. A logical explanation is contamination of this region of the spectrum from some species that is now present after the prolonged aging. Regardless of our inability to confidently quantify the ^{1}HNMR or pressure drop results for gettering, we are confident that gettering at some rate is occurring. We cannot rule out that in the 6 and 13 Month sample, smaller amounts of these thermal degradation/contamination products could have yielded smaller apparent gettering rates per the ^{1}HNMR calculation than actual rates.

The planned WSRC deployment includes 375 g getter along with 200-250 g molecular sieves, type 3A. As reported in the original report, the 3-month aged getter was mixed with molecular sieves and then tested under various conditions. In those results, the non-reproducible behavior of the molecular sieves in each test, due to incomplete reactivation of the molecular sieves between tests, caused the previously reported pressure drop results to be somewhat complicated.

It should be noted that in the actual deployment, the molecular sieves and getter material will be enclosed in separate containers. In addition, the molecular sieves do not appear to have a negative effect on the performance of the getter; the removal of water by the molecular sieves can only help the getter performance. Removing the molecular sieves from these aging study evaluations provides a lower bound to the hydrogen removal rate, which would be expected to increase under the deployment conditions with molecular sieves.

Thus, to allow for less complicated pressure change results, molecular sieves were not used for the testing of the 6-month, 13-month, and 18-month aged getter. This prevents direct comparison to a majority of the 3-month data, but the overall performance can still be evaluated. For a detailed description of the testing apparatus and method, please see Section 2 of the original report.

In this report, the various samples will be referred to by code names, as described in Table 1.

Table 1. Code names for HiTop samples described in report

Code Name	Description
3mo70	3 months aged at 70°C
6mo70	6 months aged at 70°C
13mo70	13 months aged at 70°C
18mo70	18 months aged at 70°C
6mo70irr	6 months aged at 70°C, irradiated with 1 MRad gamma radiation (^{60}Co)
13mo70irr	13 months aged at 70°C, irradiated with 1 MRad gamma radiation (^{60}Co)

18mo70irr	18 months aged at 70°C, irradiated with 1 MRad gamma radiation (^{60}Co)

Pressure Change Measurements

A sample of the 18-month aged material was tested under recombination conditions (76% CO_2, 24% air with 5% H_2) at 20°C. The same sample was then degassed and tested under gettering conditions (76% CO_2, 24% N_2 with 5% H_2) at 20°C. The experimental details are listed in Table 2, and the pressure drop results are shown in Figure 1. Recombination results for the 18-month aged material and comparable results from 3-month, 6-month, and 13-month aged samples without molecular sieves are shown in Figure 2, and gettering results for the 6-month, 13 month, and 18-month aged materials are shown in Figure 3.

Note that minor temperature fluctuations in the laboratory have a significant effect on the pressure reading during an experiment: for an experiment measuring pressure drop at 500 torr, a 1°C fluctuation in room temperature represents about a 2 torr fluctuation in pressure. Care must be made not to over interpret minor pressure fluctuations over a multi-day/hour experiment.

Table 2. Experimental details for 18-month aged HiTop experiments

Sample	**Mass (g)**	**Degas conditions (hours)**	**CO_2/Air or CO_2/N_2 fill (std. cc)**	**H_2 fill (std. cc)**
18mo70 (recomb.)	0.86323	2:10 at 70°C ~36 at 20°C	123.67 (CO_2/Air)	6.15
18mo70 (gettering)	0.86323	2:10 at 70°C ~60 at 20°C	123.69 (CO_2/N_2)	6.15
13mo70 (recomb.)	0.93020	2:10 at 70°C 71:15 at 20°C	123.65 (CO_2/Air)	6.22
13mo70 (gettering)	0.93020	2:10 at 70°C 23:00 at 20°C	123.66 (CO_2/N_2)	6.20
6mo70 (recomb.)	0.86036	2:10 at 70°C 20:00 at 20°C	123.82 (CO_2/Air)	6.12
6mo70 (gettering)	0.86036	2:10 at 70°C 21:00 at 20°C	123.84 (CO_2/N_2)	6.12
3mo70 (recomb.)	0.86420	2:10 at 70°C 15:00 at 20°C	123.62 (CO_2/Air)	6.14

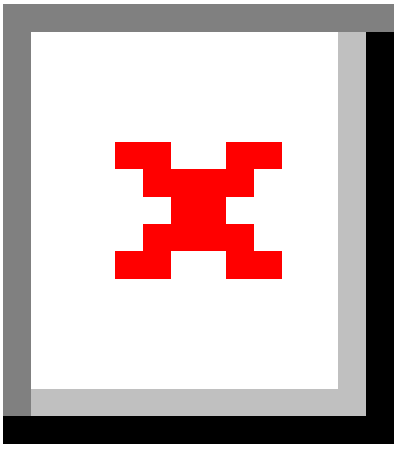


Figure 1. Pressure change over time for HiTop getter aged 18 months at 70°C, under recombination (CO_2/Air with 5% H_2) and gettering (CO_2/N_2 with 5% H_2) conditions at 20°C.

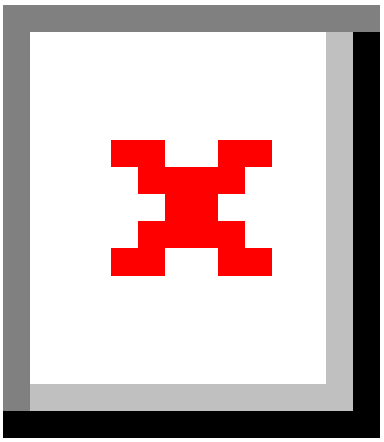


Figure 2. Pressure change over time for HiTop material, aged for 3 months, 6 months, 13 months, and 18 months at 70°C, under recombination conditions (CO_2/Air with 5% H_2) at 20°C.

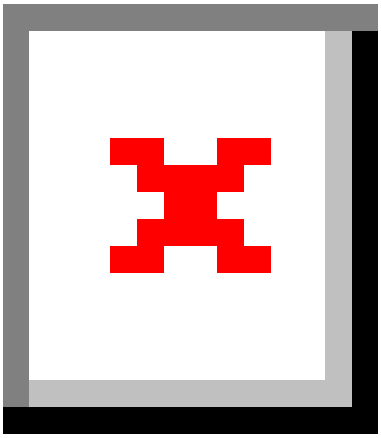


Figure 3. Pressure change over time for HiTop material, aged for 6 months, 13 months, and 18 months at 70°C, under gettering conditions (CO_2/N_2 with 5% H_2) at 20°C.

A small sample of 18-month aged HiTop was exposed to a sealed gamma source (^{60}Co) for a total dose of 1 MRad. The irradiation exposure was conducted by David Hathcock at WSRC. The performance of the irradiated HiTop was evaluated under recombination and gettering conditions at 20°C. The experimental details are listed in Table 3, and the pressure change results are shown in Figure 4. The irradiated material performance is compared against the non-irradiated material in Figure 5 (recombination) and Figure 6 (gettering). The 18-month aged material is compared against similar samples aged for 6 months and 13 months in Figure 7 (recombination) and Figure 8 (gettering).

Table 3. Experimental details for 18-month aged irradiated HiTop experiments

Sample	Mass (g)	Degas conditions (hours)	CO_2/Air or CO_2/N_2 fill (std. cc)	H_2 fill (std. cc)
18mo70irr (recomb.)	0.82021	2:10 at 70°C 22:15 at 20°C	123.66 (CO_2/Air)	6.15
18mo70irr (gettering)	0.82021	2:10 at 70°C 86:10 at 20°C	123.66 (CO_2/N_2)	6.15
13mo70irr (recomb.)	0.93072	2:10 at 70°C 71:15 at 20°C	123.63 (CO_2/Air)	6.19
13mo70irr (gettering)	0.93072	2:10 at 70°C 23:00 at 20°C	123.55 (CO_2/N_2)	6.26
6mo70irr (recomb.)	0.80862	2:10 at 70°C 47:00 at 20°C	123.83 (CO_2/Air)	6.12
6mo70irr (gettering)	0.80862	2:10 at 70°C 21:00 at 20°C	123.58 (CO_2/N_2)	6.12

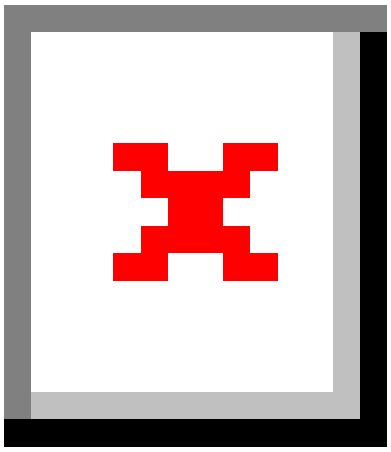


Figure 4. Pressure change over time for HiTop getter aged 18 months at 70°C and irradiated with 1 MRad ^{60}Co, under recombination (CO_2/Air with 5% H_2) and gettering (CO_2/N_2 with 5% H_2) conditions at 20°C.

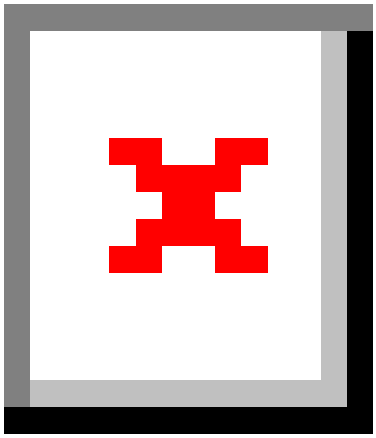


Figure 5. Pressure change over time for HiTop getter aged 18 months at 70°C under recombination (CO_2/Air with 5% H_2) conditions at 20°C, comparing irradiated and non-irradiated samples.

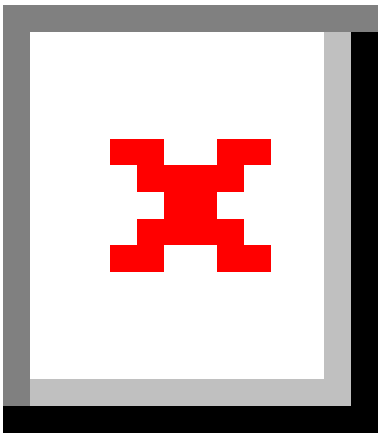


Figure 6. Pressure change over time for HiTop getter aged 18 months at 70°C under gettering (CO_2/N_2 with 5% H_2) conditions at 20°C, comparing irradiated and non-irradiated getter.

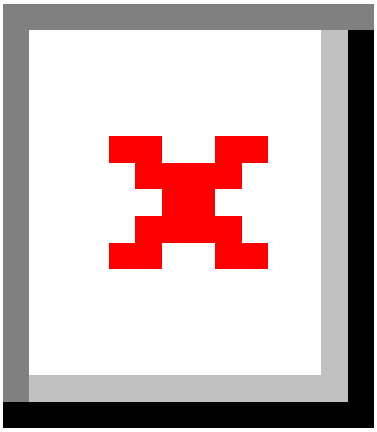


Figure 7. **Pressure change over time for HiTop getter irradiated with 1 MRad ^{60}Co and aged 6 months, 13 months, and 18 months at 70°C, under recombination (CO_2/Air with 5% H_2) conditions at 20°C.**

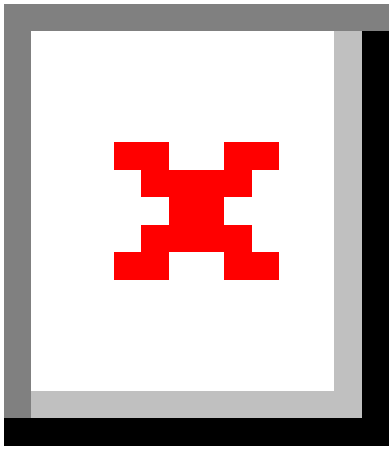


Figure 8. Pressure change over time for HiTop getter irradiated with 1 MRad ^{60}Co and aged 6 months, 13 months, and 18 months at 70°C, under gettering (CO_2/N_2 with 5% H_2) conditions at 20°C. Temperature change over time is also shown.

Hydrogen Removal Rates

The hydrogen removal rates for the tests described above were calculated based on the 575 g getter assembly (375 g getter and 200 g molecular sieves) and are summarized in Table 4. The rate of the 13-month aged irradiated sample appears to be lower than expected; however, the 6-month aging results also show a similar drop in hydrogen removal after irradiation. The higher temperatures recorded during the experiment with the 13-month aged irradiated material, as shown in Figure 8, would also contribute to a lower-than-expected hydrogen removal rate, based on a final pressure reading that would be higher than expected.

Table 4. Summary of approximate H_2 removal rates for the 575 g getter assembly under various experimental conditions. The starred value was calculated using a temperature-adjusted pressure value, as the original reading at 1 hour was greater than the nominal 20°C.

Gases present	Materials	Dominant reaction	Length of test (min)	Rate (std. cc H_2/h)	First hour rate (std. cc H_2/h)
CO_2/air/H_2	18mo70	Recombination	1565	114	1268
CO_2/N_2/H_2	18mo70	Gettering	4003	11	65*
CO_2/air/H_2	18mo70irr	Recombination	989	186	771
CO_2/N_2/H_2	18mo70irr	Gettering	4883	18	122
CO_2/air/H_2	13mo70	Recombination	1456	112	1109
CO_2/N_2/H_2	13mo70	Gettering	1482	32	383
CO_2/air/H_2	13mo70irr	Recombination	1474	106	862
CO_2/N_2/H_2	13mo70irr	Gettering	1470	9	334*
CO_2/air/H_2	6mo70	Recombination	1477	131	1347
CO_2/N_2/H_2	6mo70	Gettering	3996	29	710
CO_2/air/H_2	6mo70irr	Recombination	1405	146	1363
CO_2/N_2/H_2	6mo70irr	Gettering	3974	19	46
CO_2/air/H_2	3mo70	Recombination	61.3	1193	1193

^{1}H NMR spectra of the 6-month, 13-month, and 18-month aged materials before and after hydrogenation (gettering) (Appendix A: Not all of the spectra are shown in this report, see previous reports for spectra not shown here). were analyzed to calculate the hydrogen uptake of the aged getter with and without irradiation, and the results are summarized in Table 5. For descriptions of the assumptions and errors associated with this analysis method, please see Section 4.1 of the original report.

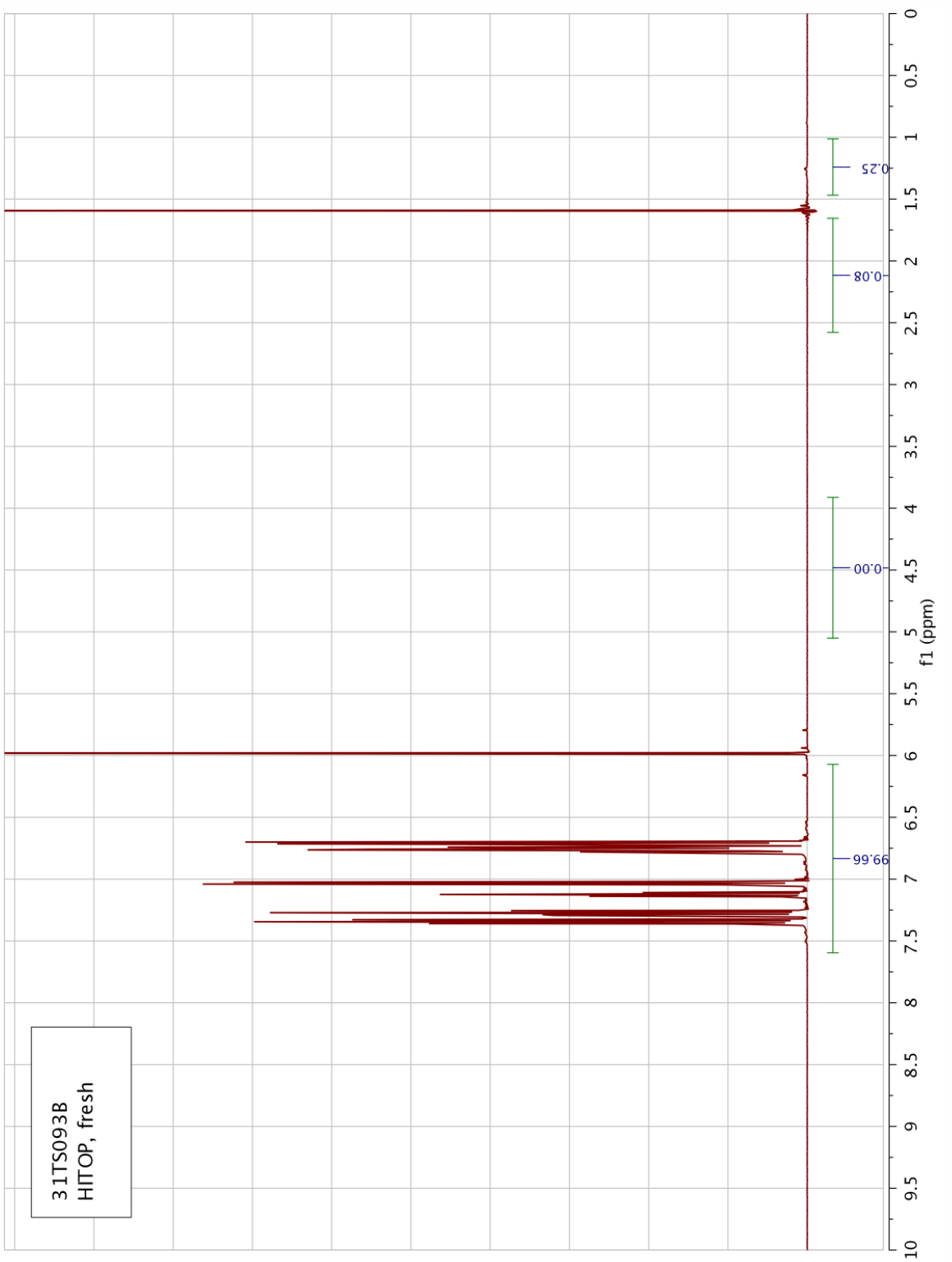
Table 5. Summary of hydrogen uptake values based on ^{1}H NMR analysis and pressure change data. Double starred data could not be accurately determined do to low the signal to noise ratio.

Gases present	Materials	Dominant reaction	Length of test (min)	^{1}H NMR H_2 uptake (std. cc)	Pressure change H_2 uptake (std. cc)
CO_2/N_2/H_2	18mo70	Gettering	4003	**	1.7
CO_2/N_2/H_2	18mo70irr	Gettering	4883	**	3.2
CO_2/N_2/H_2	13mo70	Gettering	1482	7.9	2.1
CO_2/N_2/H_2	13mo70irr	Gettering	1470	6.7	0.6
CO_2/N_2/H_2	6mo70	Gettering	3996	11.5	4.5
CO_2/N_2/H_2	6mo70irr	Gettering	3974	12.5	2.6

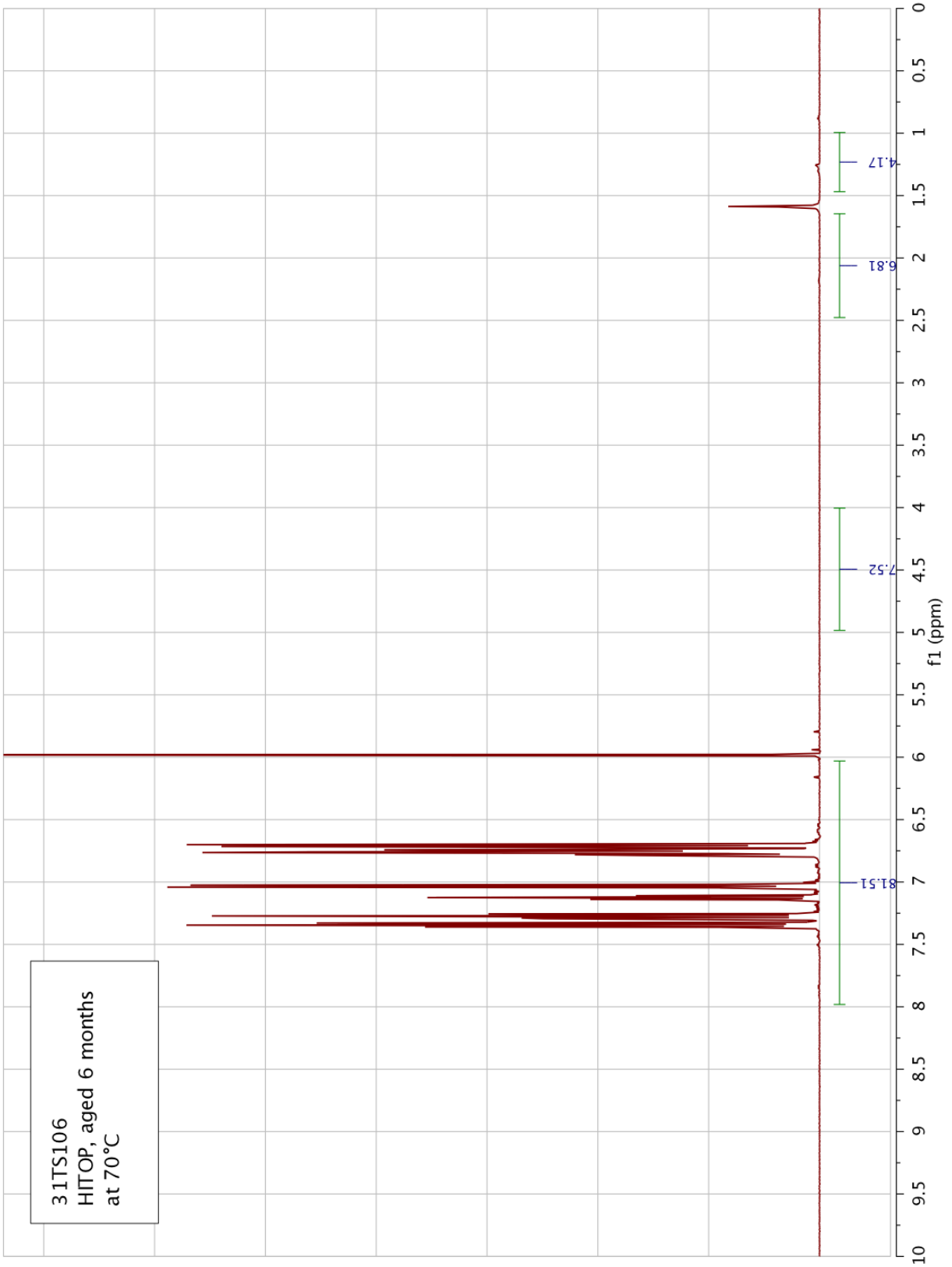
While the NMR-based hydrogen uptake values are higher than the pressure change values, both methods confirm that hydrogenation/gettering had taken place in each experiment.

Appendix A: NMR Spectra

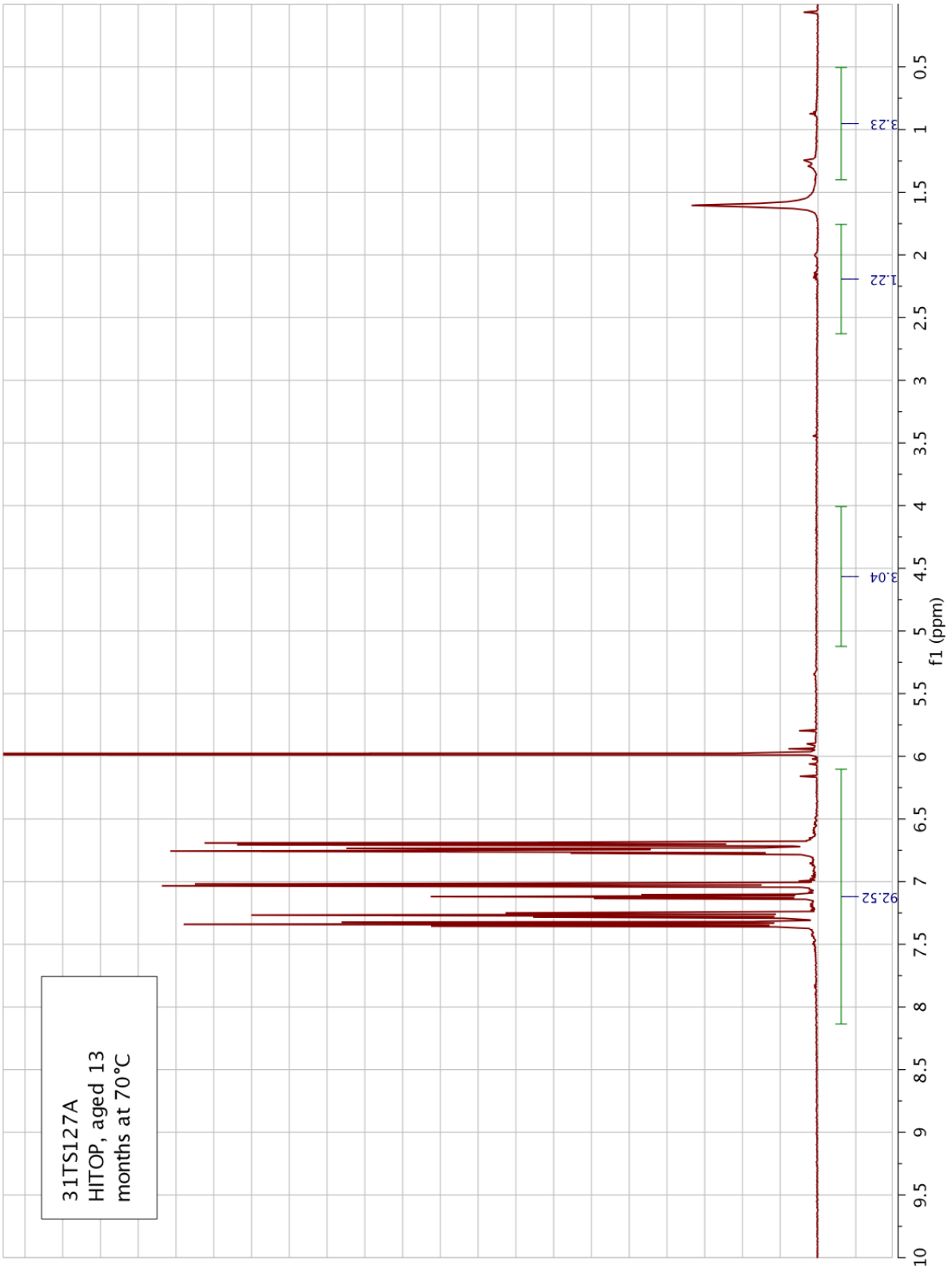
Spectrum 1: HiTop, unaged



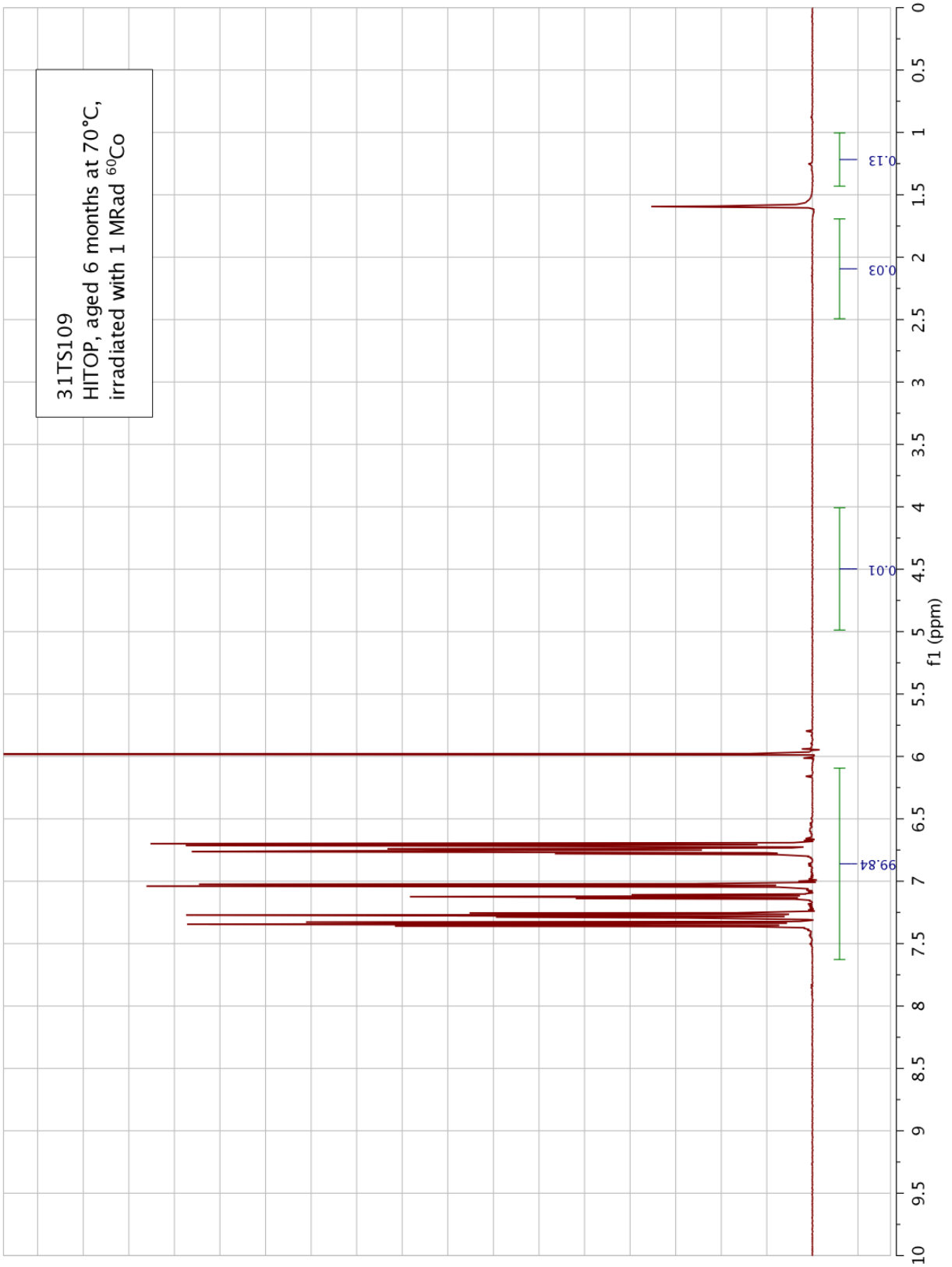
Spectrum 2: HiTop, aged 6 months at 70°C



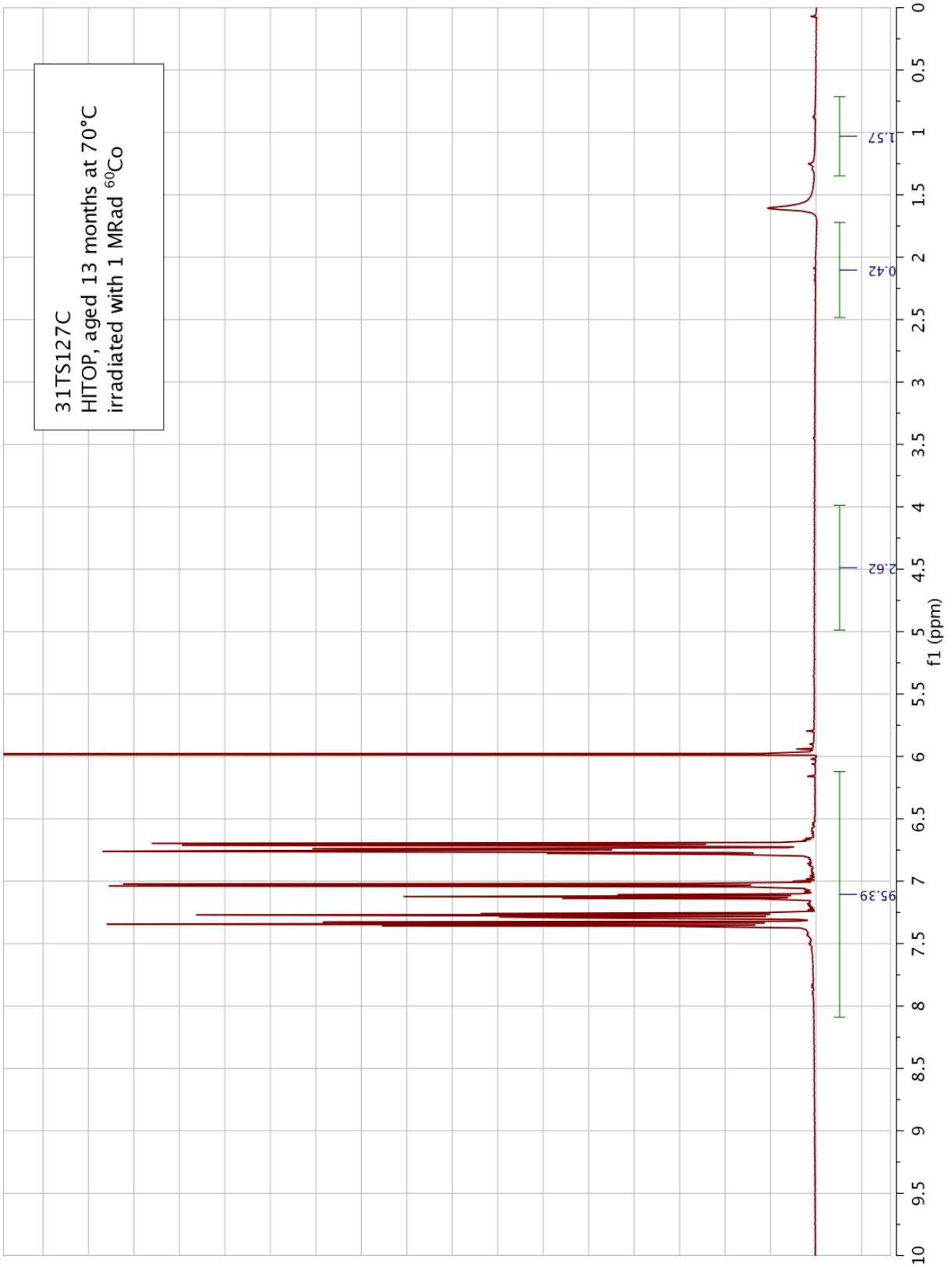
Spectrum 3: HiTop, aged 13 months at 70°C



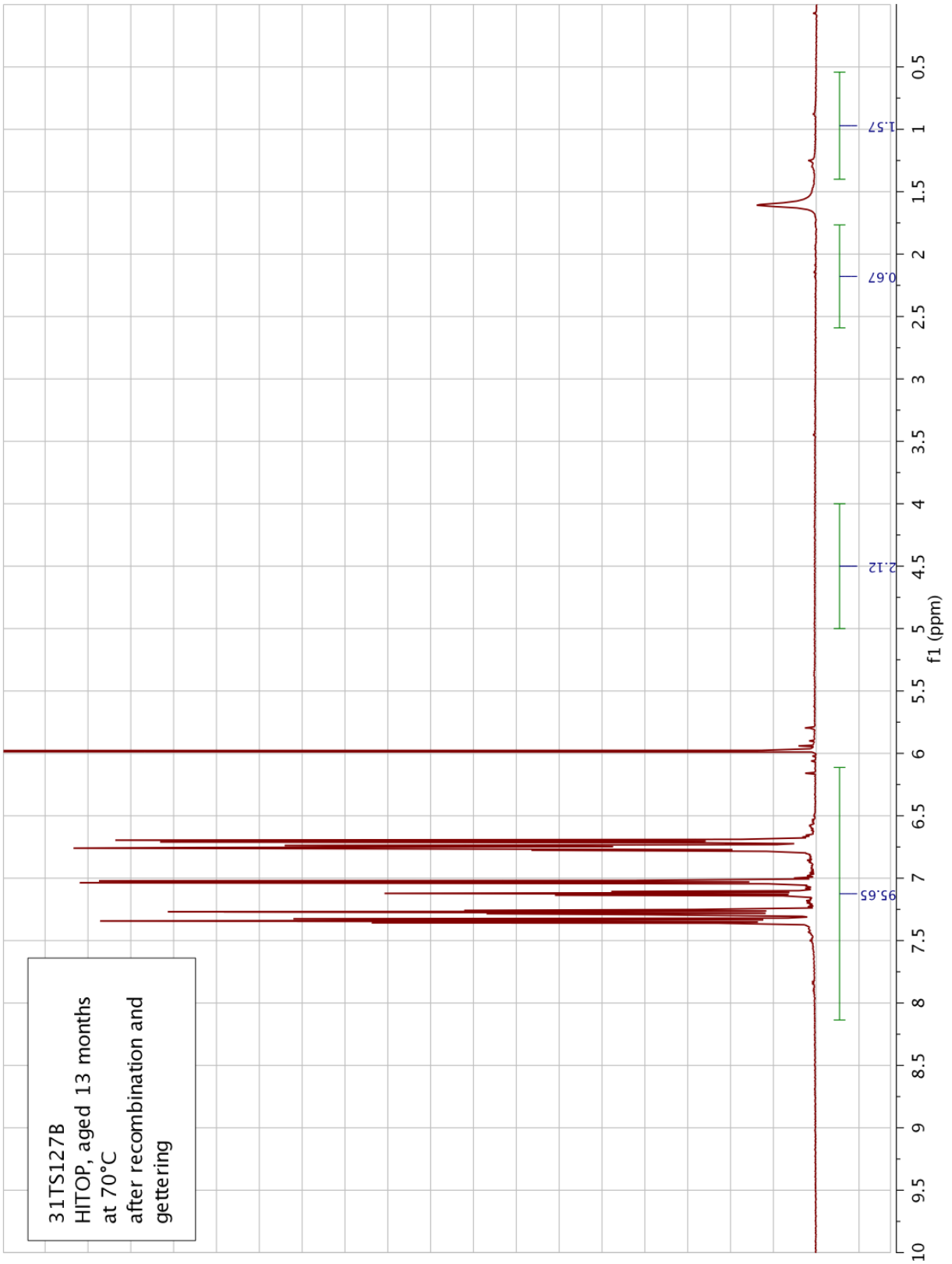
Spectrum 4: HiTop, aged 6 months at 70°C, irradiated



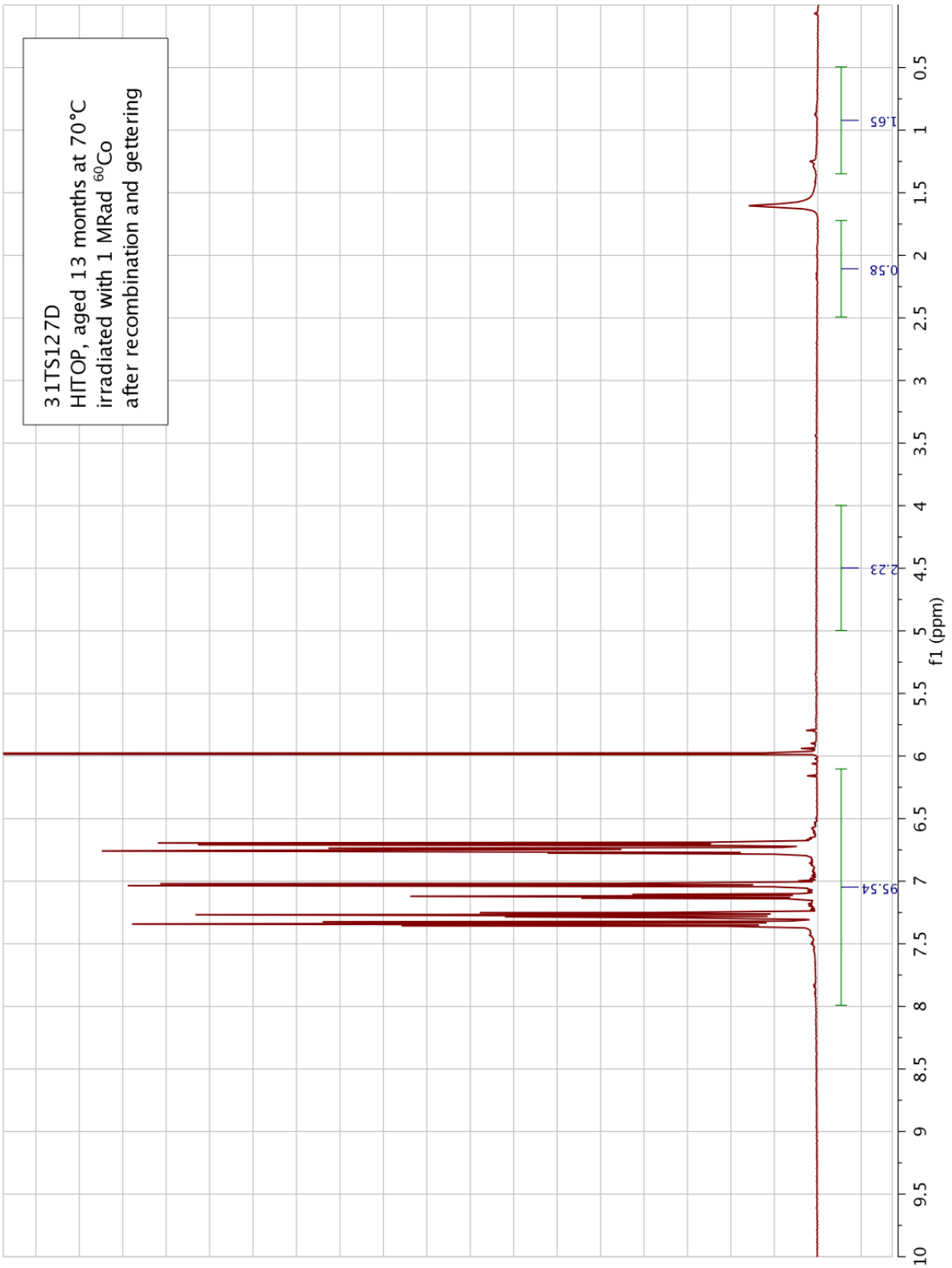
Spectrum 5: HiTop, aged 13 months at 70°C, irradiated



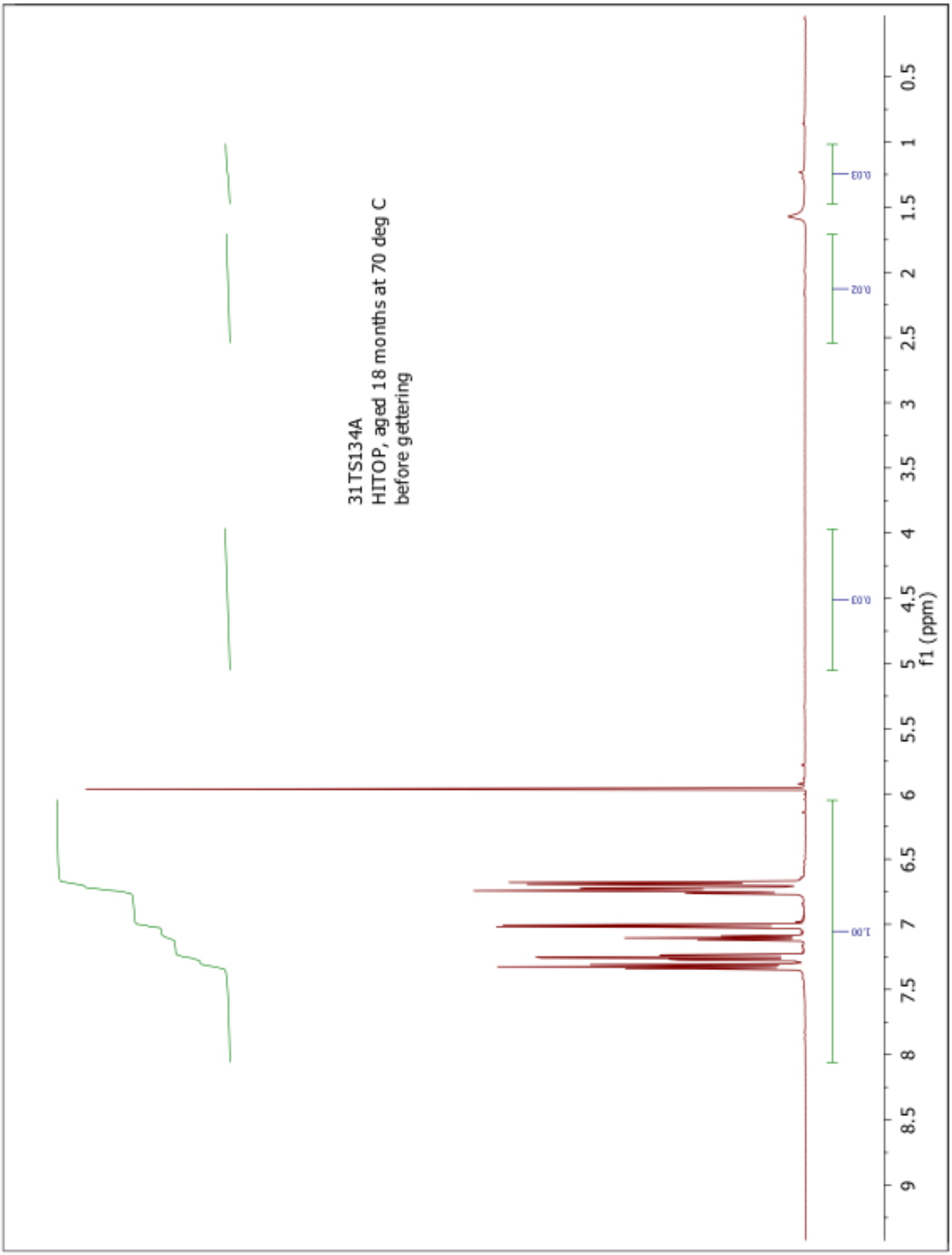
Spectrum 6: HiTop, aged 13 months at 70°C, after gettering (hydrogenation)



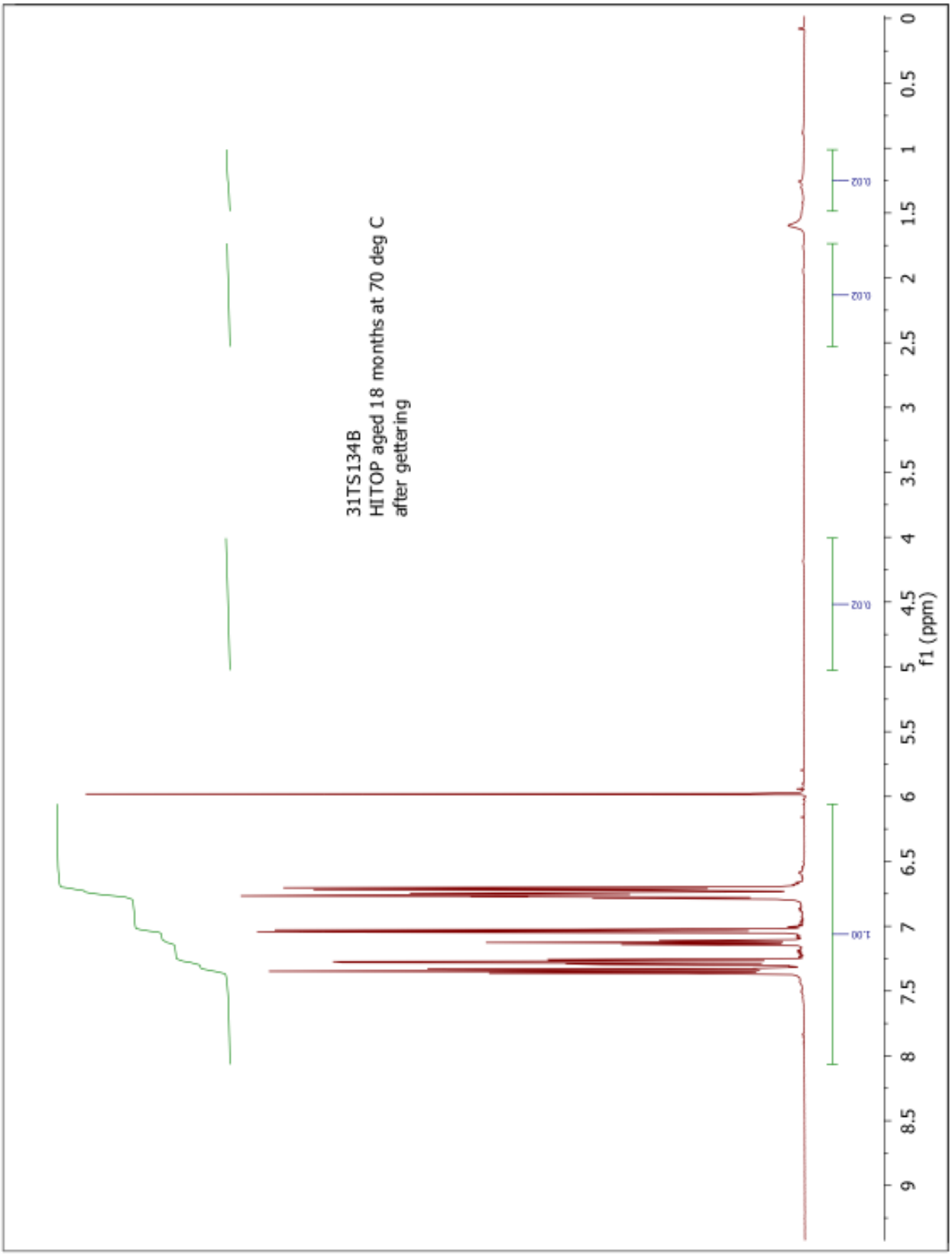
Spectrum 7: HiTop, aged 13 months at 70°C, irradiated, after gettering (hydrogenation)



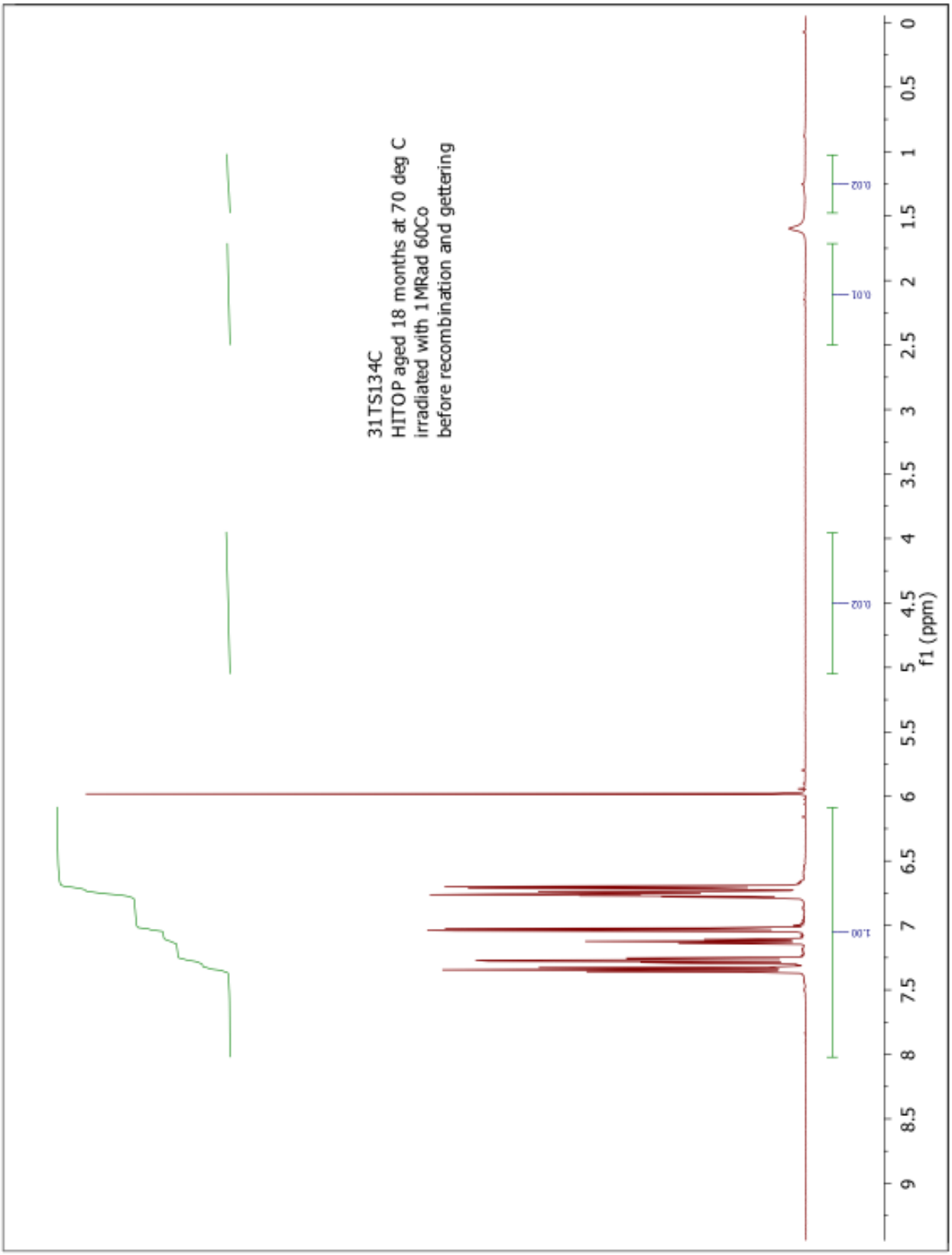
Spectrum 8: HiTop, aged 18 months at 70°C



Spectrum 9: HiTop, aged 18 months at 70°C, after gettering (hydrogenation)



Spectrum 10: HiTop, aged 18 months at 70°C, irradiated



Spectrum 11: HiTop, aged 18 months at 70°C, irradiated, after gettering.