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Date: May 21, 2007

To: Todd Woodsmall, WSRC

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Subject: SAND2007-#### (update to SAND2007-0095)
3-month 150°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 study, documented in Sandia Report SAND2007-0095, included HiTop getter material aged for 3 months at 70°C. An update to the original study (Sandia Report SAND2007-1789P) included performance data for material aged for an additional 3 months for a total of 6 months at 70°C. A second sample of HiTop material was aged for 4 months at 70°C, and an additional 3 months at 150°C, and the performance of this getter material under recombination and gettering conditions was evaluated. A sample of the 3 months at 150°C aged getter was exposed to radiation at SRNL, and the performance of this sample was also evaluated.

The 3 months at 150°C aged material showed similar performance under recombination conditions and slightly decreased performance under gettering conditions compared to the 6 months at 70°C aged material results reported in the first update report: the recombination rate is well above the required rate of 45 std. cc H₂/h, and the gettering reaction occurs in the absence of oxygen at a slower rate. Both pressure drop measurements and ¹H NMR analyses support these conclusions. ¹H NMR analyses do not indicate any degradation of the material.

Testing Summary

HiTop polymer hydrogen getter, batch 26TS152, was aged at 70°C for 4 months, and then at 150°C for 3 months. ¹H NMR spectra of the unaged material (Appendix A, Spectrum 1), material aged for 3 months at 70°C (Spectrum 2), and material aged for 4 months at 70°C plus 3 months at 150°C (Spectrum 3) show that the thermal aging has not caused degradation of the material.

As noted in SAND2007-1789P, the 3A molecular sieves called for in the planned WSRC deployment of 375 g getter and 200-250 g molecular sieves have been removed for the aging study evaluations, to allow for more reproducible data and better comparison of performance over time. For a detailed description of the testing apparatus and method, please see Section 2 of SAND2007-0095.

Pressure Change Measurements

A sample of the 3 months at 150°C aged material was tested under recombination conditions (76% CO₂, 24% air with 5% H₂) at 20°C. The same sample was then degassed and tested under gettering conditions (76% CO₂, 24% N₂ with 5% H₂) at 20°C. The experimental details are listed in Table 1, and the pressure drop results are shown in Figure 1. Recombination results for samples aged for 3 months at 150°C, 6 months at 70°C, and 3 months at 70°C without molecular sieves are shown in Figure 2. Gettering results for samples aged for 3 months at 150°C and 6 months at 70°C without molecular sieves 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 1. Experimental details for 3-month at 150°C 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)
3-month aged at 150°C (recomb)	0.87207	2:10 at 70°C 20:20 at 20°C	123.76 (CO ₂ /Air)	6.12
3-month aged at 150°C (gettering)	0.87207	2:10 at 70°C 20:30 at 20°C	123.81 (CO ₂ /N ₂)	6.12
6-month aged at 70°C (recomb)	0.86036	2:10 at 70°C 20:00 at 20°C	123.82 (CO ₂ /Air)	6.12
6-month aged at 70°C (gettering)	0.86036	2:10 at 70°C 21:00 at 20°C	123.84 (CO ₂ /N ₂)	6.12
3-month aged at 70°C (recomb)	0.86420	2:10 at 70°C 15:00 at 20°C	123.62 (CO ₂ /Air)	6.14

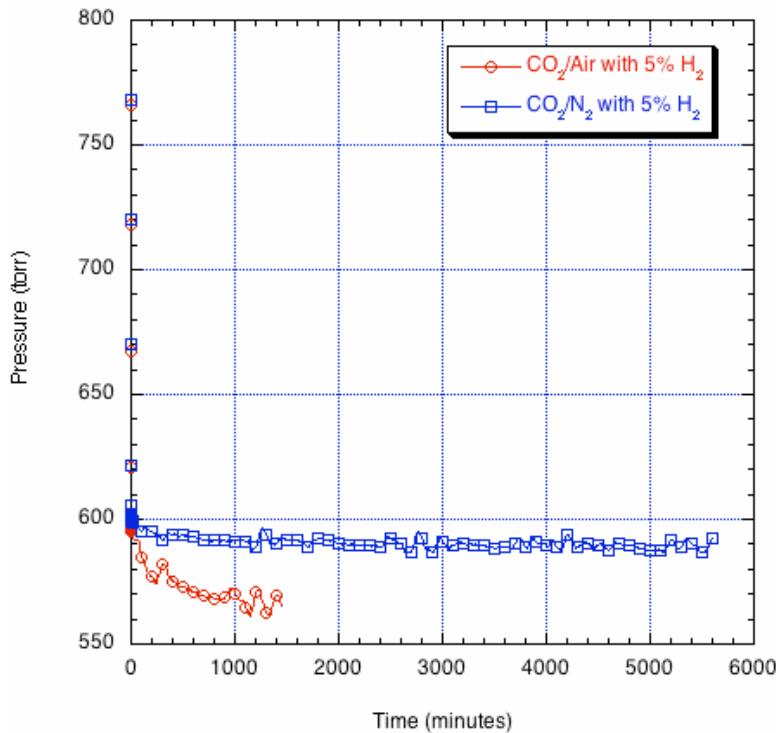


Figure 1. Pressure change over time for HiTop getter aged 3 months at 150°C plus 4 months at 70°C, under recombination (CO₂/Air with 5% H₂) and gettering (CO₂/N₂ with 5% H₂) conditions at 20°C.

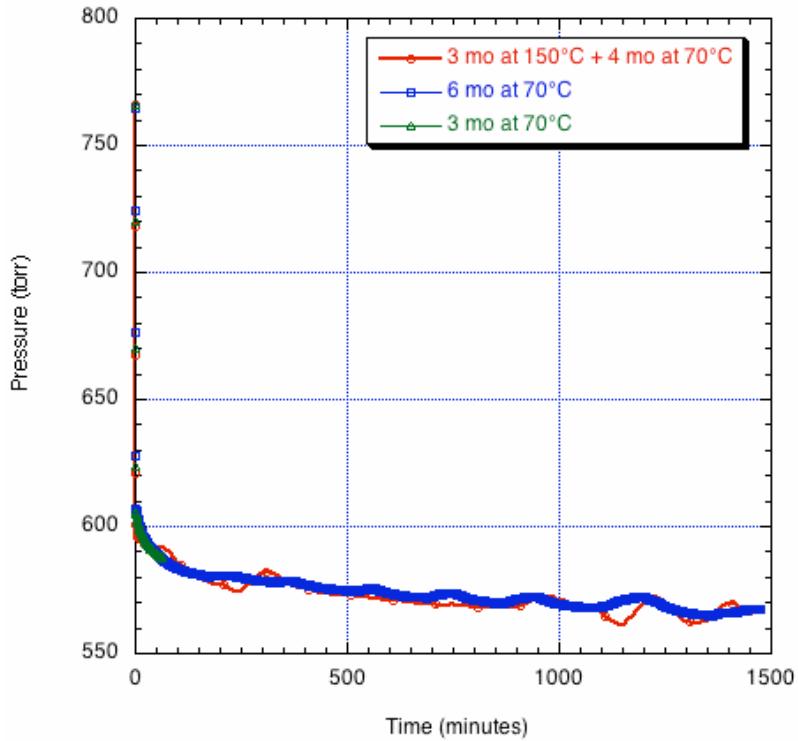


Figure 2. Pressure change over time for HiTop material, aged for 3 months at 70°C, 6 months at 70°C, and 3 months at 150°C plus 4 months at 70°C, under recombination conditions (CO₂/Air with 5% H₂) at 20°C.

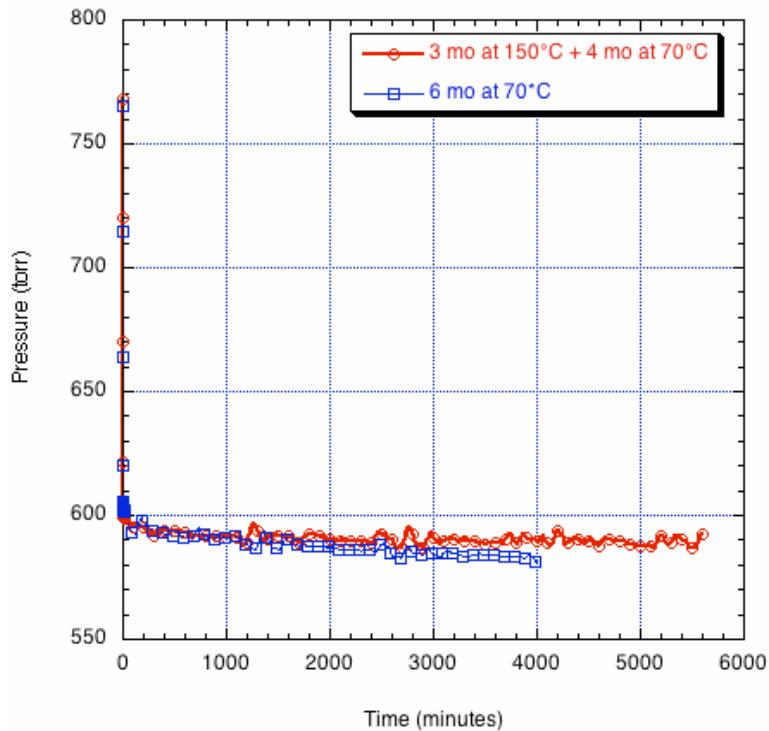


Figure 3. Pressure change over time for HiTop material, aged for 6 months at 70°C and 3 months at 150°C plus 4 months at 70°C, under gettering conditions (CO₂/N₂ with 5% H₂) at 20°C.

A small sample of 3 months at 150°C aged HiTop was exposed to a sealed gamma source (⁶⁰Co) 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 2, 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).

Table 2. Experimental details for 3-month aged at 150°C 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)
3-month aged at 150°C, irradiated (recombination)	0.87792	2:10 at 70°C 20:00 at 20°C	123.65 (CO ₂ /Air)	6.11
3-month aged at 150°C, irradiated (gettering)	0.87792	2:10 at 70°C 19:30 at 20°C	123.60 (CO ₂ /N ₂)	6.13

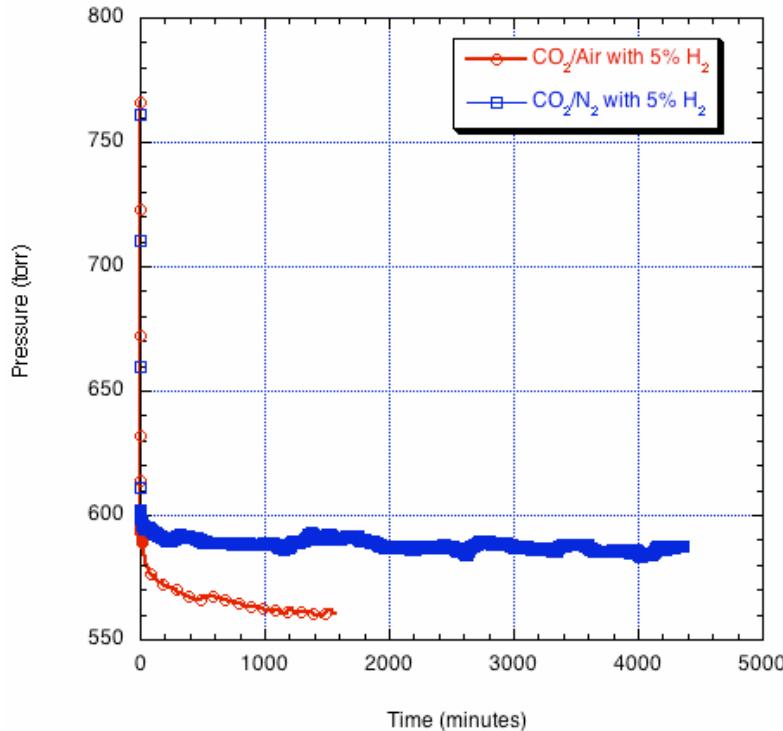


Figure 4. Pressure change over time for HiTop getter aged 3 months at 150°C plus 4 months at 70°C and irradiated with 1 MRad ^{60}Co , under recombination (CO₂/Air with 5% H₂) and gettering (CO₂/N₂ with 5% H₂) conditions at 20°C.

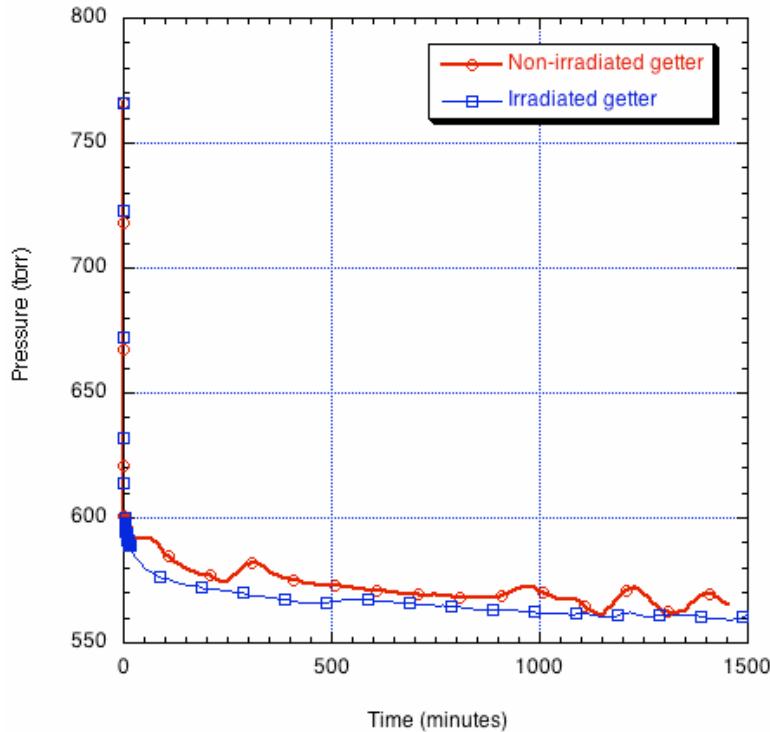


Figure 5. Pressure change over time for HiTop getter aged 3 months at 150°C plus 4 months at 70°C under recombination (CO₂/Air with 5% H₂) conditions at 20°C, comparing irradiated and non-irradiated getter.

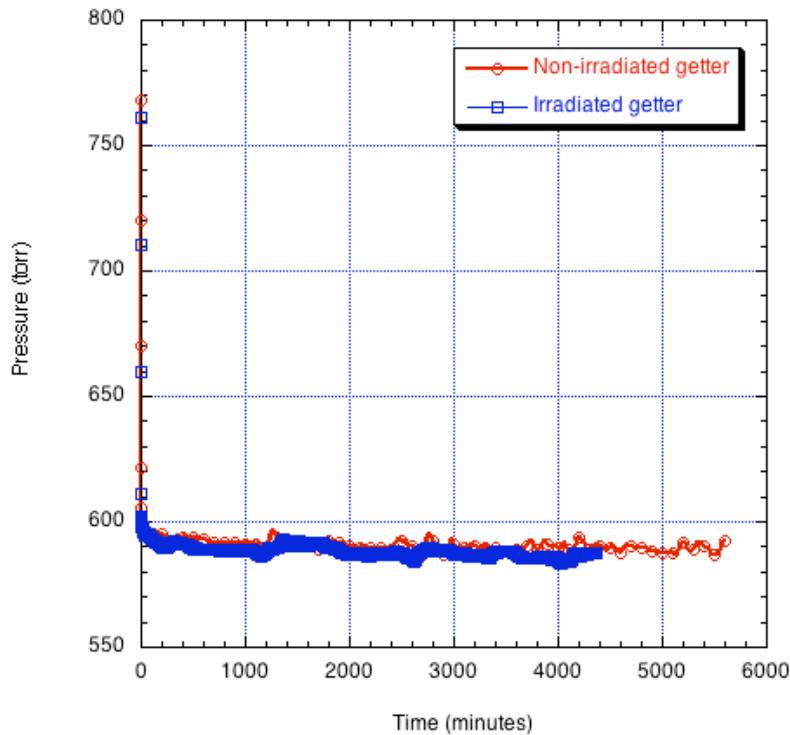


Figure 6. Pressure change over time for HiTop getter aged 3 months at 150°C plus 4 months at 70°C under gettering (CO₂/N₂ with 5% H₂) conditions at 20°C, comparing irradiated and non-irradiated getter.

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 3.

Table 3. Summary of approximate H₂ removal rates for the 575 g getter assembly under various experimental conditions

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	3-months at 150°C aged getter	Recombination	1454	139	903
CO ₂ /N ₂ /H ₂	3-months at 150°C aged getter	Gettering	5597	9	378
CO ₂ /air/H ₂	3-months at 150°C aged getter, irradiated	Recombination	1567	144	2033
CO ₂ /N ₂ /H ₂	3-months at 150°C aged getter, irradiated	Gettering	4362	17	542
CO ₂ /air/H ₂	6-months at 70°C aged getter	Recombination	1477	131	1347
CO ₂ /air/H ₂	6-months at 70°C aged getter, irradiated	Recombination	1405	146	1363
CO ₂ /air/H ₂	3-months at 70°C aged getter	Recombination	61.3	1193	1193

¹H NMR spectra of the materials after hydrogenation (gettering) (Appendix A, Spectra 4 and 5) were analyzed to calculate the hydrogen uptake of the aged getter with and without irradiation, and the results are summarized in Table 4. For descriptions of the assumptions and errors associated with this analysis method, please see Section 4.1 of the original report.

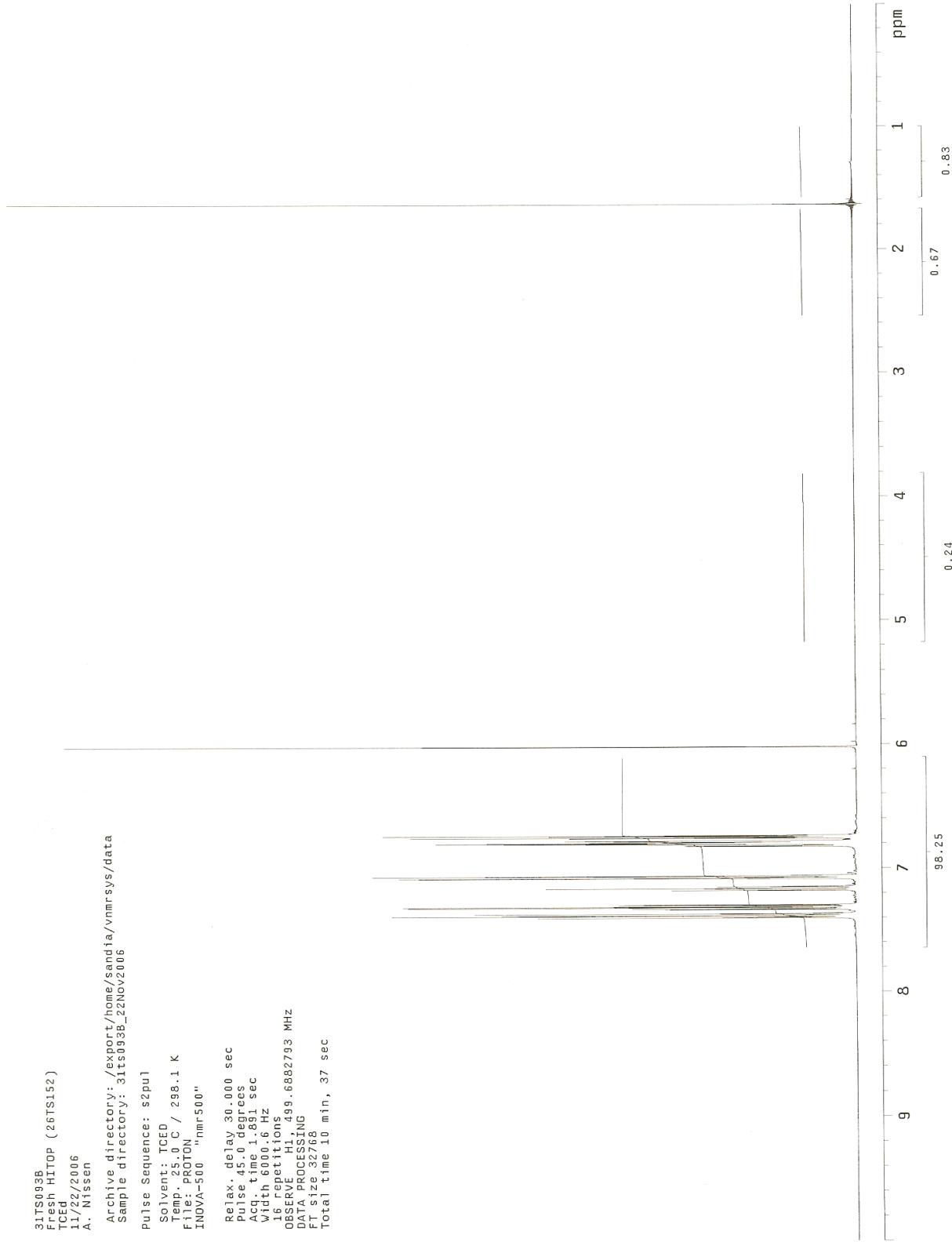
Table 4. Summary of hydrogen uptake values based on ¹H NMR analysis and pressure change data

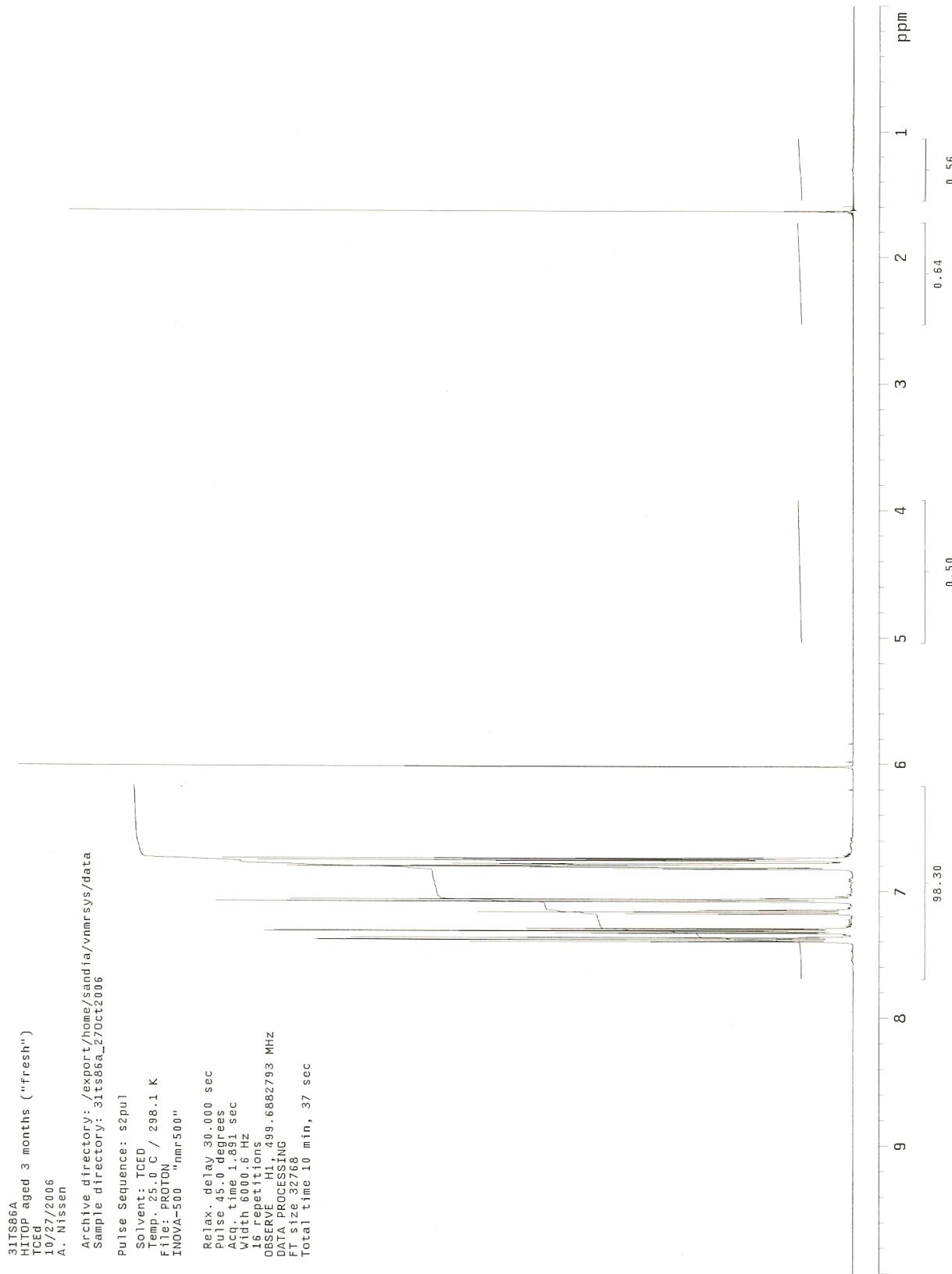
Gases present	Materials	Dominant reaction	Length of test (min)	¹ H NMR H ₂ uptake (std. cc)	Pressure change H ₂ uptake (std. cc)
CO ₂ /N ₂ /H ₂	3-months at 150°C aged getter	Gettering	5597	18	9
CO ₂ /N ₂ /H ₂	3-months at 150°C aged getter, irradiated	Gettering	4362	34	17

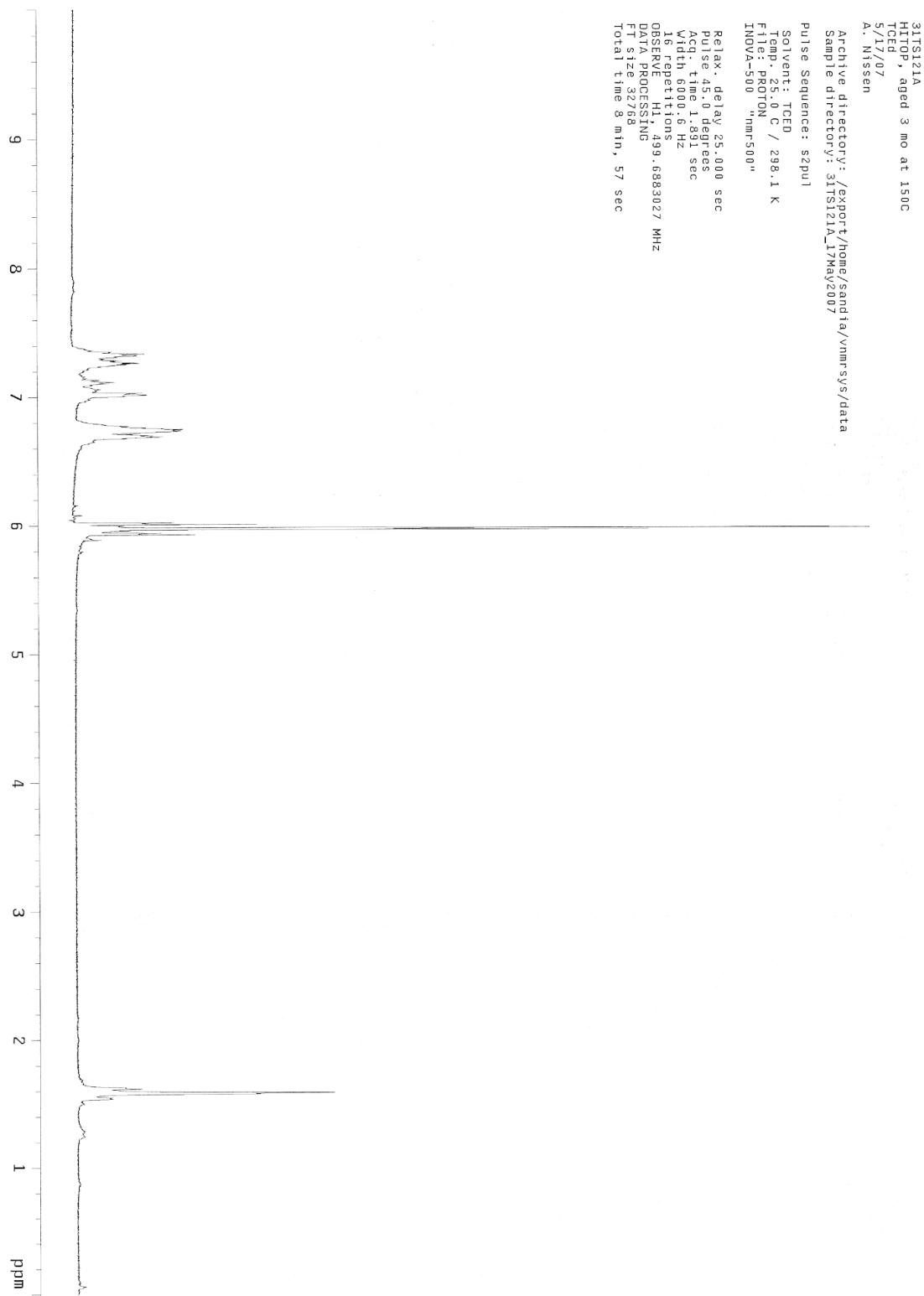
Appendix A: NMR Spectra

Spectrum 1: HiTop, unaged

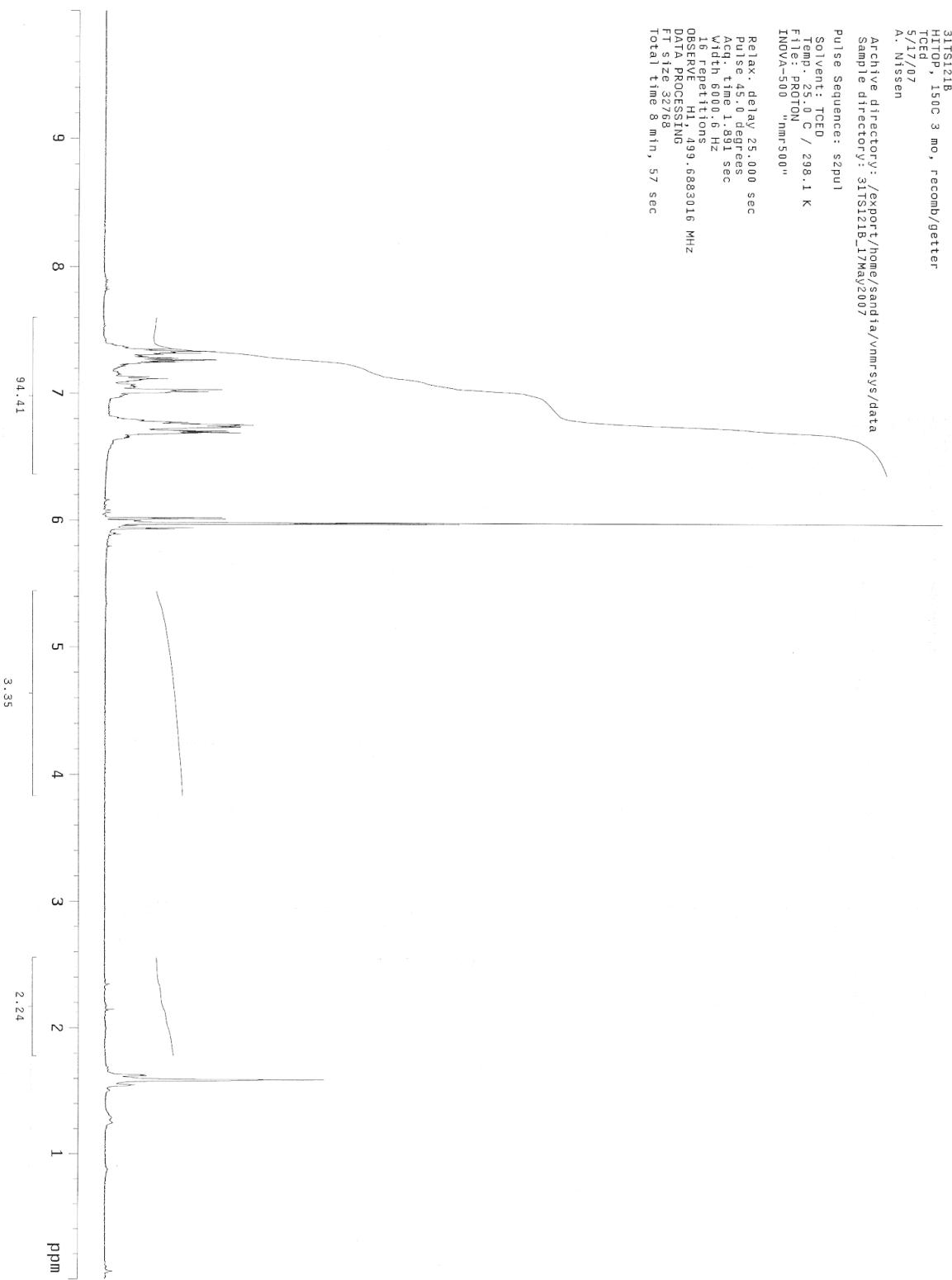
31TS093B
Fresh HiTOP (26TS152)
TCEd
11/22/2006
A. Nissen
Archive directory: /export/home/Sandia/vnmrsys/data
Sample directory: 31ts093B_22Nov2006
Pulse Sequence: s2pu1
Solvent: TCE
Temp: 25.0 C / 298.1 K
File: PROTON
INOVA-500 "nmr500"
Relax. delay 30.000 sec
pulse 45.0 degrees
Acq. time 1.81 sec
Width 600.6 Hz
16 repetitions
OBSERVE H1, 499.6882793 MHz
DATA PROCESSING
FT size 32768
Total time 10 min, 37 sec



Spectrum 2: HiTop, aged 3 months at 70°C

Spectrum 3: HiTop, aged 4 months at 70°C plus 3 months at 150°C

**Spectrum 4: HiTop, aged 4 months at 70°C plus 3 months at 150°C,
after gettering (hydrogenation)**



Spectrum 5: HiTop, aged 4 months at 70°C plus 3 months at 150°C, irradiated, after gettering (hydrogenation)

