Performance Testing of Aged Hydrogen Getters Against Criteria for Interim Safe Storage of Plutonium Bearing Materials

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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 hydrogen getter HITOP was aged for 3 months at 70°C and tested under both recombination and hydrogenation conditions at 20 and 70°C; partially saturated and irradiated aged getter samples were also tested. The recombination reaction was found to be very fast and well above the required rate of 45 std. cc H_2/h. The gettering reaction, which is planned as the backup reaction in this deployment, is slower and may not meet the requirements alone. Pressure drop measurements and ^{1}H NMR analyses support these conclusions.

Although the experimental conditions do not exactly replicate the deployment conditions, the results of our conservative experiments are clear: the aged getter shows sufficient reactivity to maintain hydrogen concentrations below the flammability limit, between the minimum and maximum deployment temperatures, for three months. The flammability risk is further reduced by the removal of oxygen through the recombination reaction. Neither radiation exposure nor thermal aging sufficiently degrades the getter to be a concern. Future testing to evaluate performance for longer aging periods is in progress.

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1. Background

Legacy plutonium-bearing materials are stored in shipping containers at the Savannah River Site (SRS) until their final disposition can be determined. This material has been stabilized and is maintained per the Department of Energy's (DOE) standard for long-term storage of Pu-containing materials, DOE-STD-3013. As a part of its ongoing storage mission, Washington Savannah River Company's (WSRC) Nuclear Materials Management (NMM) organization is tasked with a surveillance program that will ensure these materials have remained in their expected condition over the several years of storage. Information from this program will be used by multiple entities to further validate the safe storage of Pu-bearing materials per DOE-STD-3013. Part of the program entails cutting open selected 3013 containers and sampling the materials inside. Savannah River National Laboratory (SRNL) will then analyze these samples. The remaining material not used for samples will then be repackaged in non-3013 containers to be placed back into shipping packages for storage until disposition at SRS. These repackaged materials will be stored per the requirements of DOE's Criteria for Interim Safe Storage of Plutonium Bearing Materials (ISSC).

One criterion of the ISSC is preventing flammable concentrations of gases from accumulating inside storage vessels. For the proposed storage mission, these gases are hydrogen and oxygen. Prevention can be accomplished via limits on material mass, periodic venting, or other means. SRNL personnel suggested that NMM explore the possibility of using a hydrogen getter material to prevent such flammable conditions. SRNL has performed prior research and testing on various getters with successful results. NMM subsequently contacted personnel from both Sandia National Laboratory/CA (SNL) and Vacuum Energy Inc. (VEI) to investigate options. The getter materials that SRNL had evaluated were limited by performance testing to approximately two months of service at up to 70°C and were substantially affected by temperatures in excess of 70°C. Performance had also not been proven in an atmosphere of carbon dioxide, the inerting gas of choice for the storage vessels. Even though SRNL had a relatively large quantity of this material in storage, shelf life, storage conditions, the need for revalidation, and assembling the material into manageable units were drawbacks to using existing material.

After consideration, SNL/VEI recommended that an appropriate material to consider was a formulation among the HITOP family of getter materials combined with a molecular sieve (zeolite). This was due to the performance requirements indicated below:

- Maximum rate of hydrogen generation of 45 std. cc H_2/h
- Successful performance at temperatures up to 70°C for as long as possible
- Sufficient capacity to remove 2.5 moles of hydrogen gas (based on a maximum wt.% of moisture absorbed by the Pu-bearing materials in storage)
- Successful performance in a carbon dioxide atmosphere (nom. 75 vol. %)
- Impervious to gamma/neutron radiation fields

Since the HITOP getters have not been tested in a carbon dioxide atmosphere, a test was commissioned by NMM for SNL to test performance. The scope of the tests is to ensure that at both minimum and maximum storage temperatures (getter temperatures of 20°C and 70°C, respectively), the getter is able to remove hydrogen at the specified rate and with the required capacity in a carbon dioxide atmosphere.

The HITOP getters are designed to remove hydrogen from enclosed spaces. HITOP has two modes of operation:

1.   When oxygen is present, the getter will preferentially recombine the oxygen/hydrogen mixture to make water. This catalytic reaction does not consume getter capacity. A molecular sieve will be formulated with the getter. Water or desiccants have no effect on getter performance with the exception that if sufficient liquid water forms to submerge the getter, the water will form a permeation restriction between the hydrogen source and the getter. Presence of a molecular sieve will preclude this formation.

2.   After all the oxygen is consumed, the HITOP can react directly with the hydrogen up to its formulation-dependent fixed capacity. The getter assemblies will include 375 grams of HITOP and 200 grams of molecular sieve, for a total getter assembly mass of 575 grams, and a rated capacity of 150 std. cc H_2/g HITOP or approx. 100 std. cc H_2/g active getter assembly including the molecular sieves. The actual amount of molecular sieves may vary in the deployed assembly. All calculations in this report are based on the 200 g of molecular sieves for consistency. Additional molecular sieves deployed would only add additional capacity to remove water.

The test apparatus will involve a series of fixed volumes connected to gas supply, vacuum, and pressure gages; a detailed description of the apparatus is below. The getter sample is loaded into the test chamber, the chamber sealed and all chambers evacuated to degas the sample. The carbon dioxide/air (24% air, balance carbon dioxide) is mixed with the hydrogen by a series of expansions into the various reservoirs, and then the gas mix is expanded into the getter test chamber. For these experiments the getter test chamber will be the highest point in the apparatus so that the configuration is most representative of the deployment conditions.

The HITOP sample that will be used will be a three-year-old sample that was aged according to a 2-month-long protocol at 70°C a few days after the material was first made, and was then aged for an additional 31 days at 70°C before these tests commenced, for a total aging time of 3 months at 70°C. The getter sample may not be the exact same formulation as the commercial sample, but the rated capacity is the same at 150 std. cc H_2/g and the ingredients are exactly the same except that the aged getter was not formulated with molecular sieves. The aged sample was used because of its availability. The exact formulation will be slightly different in the manufactured lots (per the commercial supplier Vacuum Energy Inc.) but the ingredients and proportions will be essentially the same. It should be noted that SNL has provided numerous formulations to various customers and that they perform similarly. The molecular sieves are added to the aged getter sample vial for the tested formulations. All production lots of the getter material will be deployed adjacent to bags of molecular sieves rather than mixed together as evaluated in these experiments. All production lots of the getter material made in the future can be (and at this time are scheduled to be) tested for reactivity in the SNL apparatus.

2. Test Plan

2.1 Experimental Procedure

The gas handling apparatus (Figure 1) has been used extensively by SNL for evaluation of numerous getters, and a high degree of confidence is held for the accuracy of the results obtained. However, since the stainless steel apparatus is opened to the air on a daily basis, high vacuum measurements are limited by the ability to degas the reactor of absorbed atmospheric species. As a practical matter, vacuum levels ≤ 0.01 torr require that extra attention be paid to the degas cycle. It is not possible to bake out the entire apparatus, so typically the system operates with a few millitorr of residual gas during long experiments with sealed volumes.
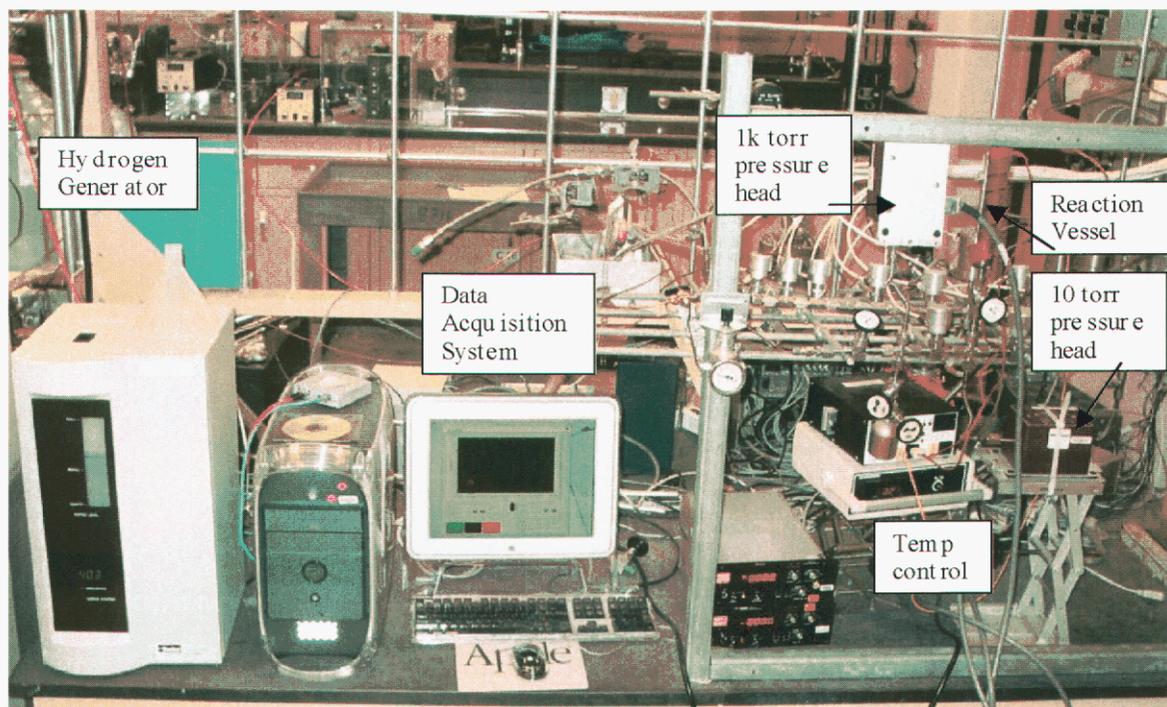
Figure 1.   A photograph of the Sandia getter testing apparatus.

The apparatus includes both 1000 torr and 10 torr MKS pressure heads manufactured by Baratron. Data is acquired with a National Instruments PCI-6035E data acquisition card in a PowerMac G4 running LabView Version 6i. The digital resolution of the PCI-6035E is 16 bits. With the system logging a data point at least every 10 minutes, these experiments have an uptake rate sensitivity of 2.9×10^{-9} std. cc s^{-1}.

The MKS pressure heads from Baratron and their controllers are accurate to 0.08% and were calibrated on June 2, 2006. Temperature measurements are made with a K type thermocouple and a model DP116-KC1-A-MDS meter manufactured by Omega with a maximum error of $\pm 1.5^\circ$C. Mass is measured on a calibrated Ohaus electronic balance model AP250D (calibrated on May 22, 2006) with a precision of 0.02 mg for masses up to 50 grams and then a precision of 0.1 mg up to 210 grams.

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2.2 Aged Getter Material and Sample Preparation

The getter material used for all testing was originally synthesized on May 2, 2003 (batch 26TS152) and aged for a total of 91 days, triple-bagged, in a 70°C oven. ^{1}H NMR analysis (see Appendix A, Spectra 1 and 2) shows the aged material to be similar to the unaged material, with no evidence of hydrogenation. The molecular sieve material, type 3A, was activated at 160°C for 48 hours, cooled to room temperature, and stored in a sealed jar to minimize air exposure. 99.99999% pure hydrogen was produced with a Whatman hydrogen generator model 75-32. The test gas mixtures (24% dry air/76% carbon dioxide and 24% nitrogen/76% carbon dioxide) were produced by Matheson Tri-Gas (see Appendix B for certifications).

Samples were prepared by first measuring the desired amount of molecular sieve material into a glass sample tube, sealed with a rubber septum. The desired amount of getter was weighed in a separate container and added to the sample tube, which was manually agitated for 2-3 minutes until a uniform color was achieved throughout the sample. Tissue was taped over the sample tube opening to avoid powder dispersion, and the sample tube was placed in the reactor vessel, labeled as Volume E in Figure 2. The reactor vessel was installed on the test apparatus and the system was degassed, typically by heating the reactor vessel for 15-20 hours at 70°C, followed by 2-3 hours at 20°C.
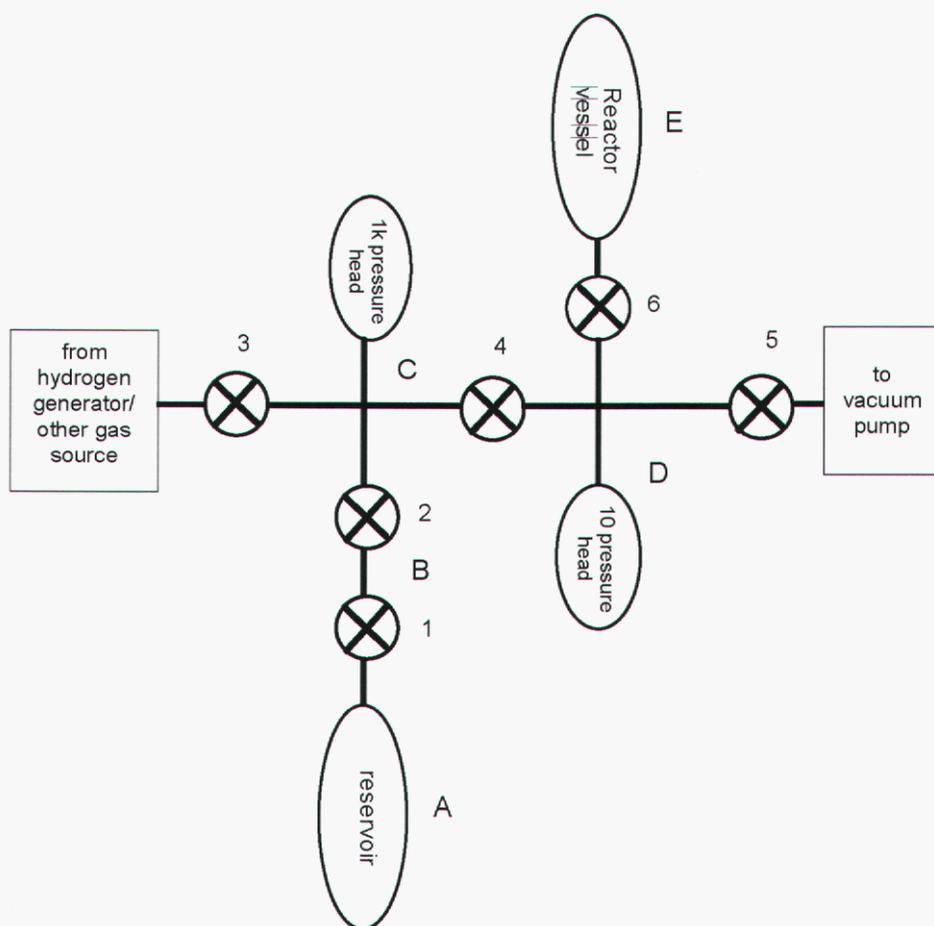
Figure 2.   Schematic of apparatus.

The volumes of the apparatus, as labeled in Figure 2, are listed in the following table below; the volume of the sample and test tube together is 2.2 cc.

Table 1.   Volumes of getter testing apparatus

Section of apparatus	Volume (cc)	Measurement method
A	102.52	Calibration
B	3.89	Calibration
C	14.7	Gas expansion
D	18.3	Gas expansion
E	36.7	Gas expansion

The experiments took the form of general gas uptake tests. Two different gas mixtures were used as the background atmosphere for the testing: a mixture of 76% CO_2 and 24% dry air was used to create conditions for recombination of H_2 and O_2 into H_2O, and a mixture of 76% CO_2 and 24% N_2 was used to create hydrogenation/gettering conditions. Volume A was filled with approx. 980 torr of either the CO_2/air or CO_2/N_2 mixture, and, in some tests, Volumes B and C were filled with approx. 268 torr of hydrogen. The computer recorded the pressure fills for each experiment. Volumes A, B, and C were mixed, then expanded into Volume D, and finally slowly expanded over 2-3 minutes into Volume E, exposing the sample to the gas mixture. The reactor was left at room temperature (approx. 20°C) or preheated to 70°C before the experiment. After the experiment proceeded for several hours, the reactor was allowed to cool to room temperature before stopping the experiment.

During any experiment slight variations of temperature in the room can cause some uncertainty in the data. For an experiment measuring pressure drop at 500 torr, a 1°C fluctuation in room temperature represents about a 2 torr fluctuation in pressure. We record the temperature throughout the experiment and the temperature in the room is typically ±1°C, but the laboratory may be used by other persons who can open internal/external doors causing small temperature fluctuations. Care must be made not to over interpret minor pressure fluctuations over a multi-day/hour experiment.

^{1}H NMR was used to determine evidence of gettering, and in some cases, measure the amount of hydrogen absorbed by the getter. ^{1}H NMR samples were prepared by mixing excess quantity of 1,1-2,2 tetrachloroethane-d_2 (TCEd) with the getter to dissolve the organic component, and then filtering through (2) 0.45 μm PTFE filters, with magnesium sulfate added to dry samples where quantitative results were desired. A Varian INOVA 500 MHz NMR was used to acquire a ^{1}H proton spectrum. The relative integrals of the single and double bond regions were used to calculate the hydrogen uptake of the getters.

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3. Experimental Descriptions and Results

For each set of experiments, the experimental conditions are listed in a table, with the pressure change over the course of the experiment shown in a graph below the table. The experimental conditions to note include: the contents of each sample and the mass of each component, the total time (in hours) of previous experiments in which this sample was used, the degas conditions, and the gas fill amounts.

The previous exposure time is of interest because over the course of this study, it was found that the molecular sieve was not completely reactivating between experiments. Molecular sieve powder type 3A is typically reactivated through heating at 175-260°C for several hours, which is a condition not reached during the degassing phase of these experiments. During a longer experiment, a given sample would absorb an amount of many gases present in the system, including background gases (CO_2, O_2, N_2, and H_2) and gases generated during the experiment (H_2O). If this sample was then degassed and used again, the effect of the partially depleted molecular sieve was observed by a smaller pressure change in the second experiment. A previous exposure time of "0:00" means that the sample was used for the first time in that particular experiment.

3.1 Control Experiments

The first set of experiments was designed to estimate the effect of the entire apparatus on the gas absorption during an experiment, as many getter samples have been exposed to the apparatus over the years. In addition, the effect of the molecular sieve alone was measured at both 20°C and 70°C. Figure 3 shows the pressure change over the course of these three experiments; the experimental conditions are listed in Table 2 below.

Table 2.   Summary of conditions for control experiments.

Experiment	Getter (g)	Molecular sieve (g)	Previous exposure (hours)	Degas conditions (hours)	CO₂/Air fill (std. cc)	H₂ fill (std. cc)
Control	0	0	0:00	2:10 at 70°C 20:00 at 20°C	123.56	6.13
Molecular sieve at 20°C	0	0.46126	0:00	2:00 at 70°C 2:00 at 20°C	123.44	6.11
Molecular sieve at 70°C	0	0.46126	20:00	2:30 at 70°C	123.44	6.13
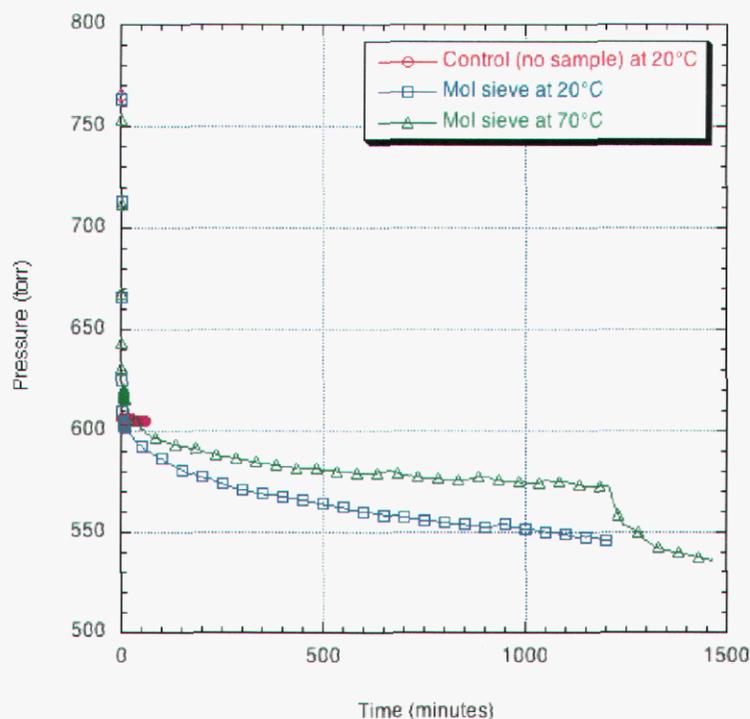
Figure 3. **Pressure change over time for control experiments, as described in Table 2.**

3.2 0% H_2 Adsorption Experiments

This set of experiments looked at the effect of the getter/molecular sieve material on the CO_2/air atmosphere with 0% H_2, at 20°C and 70°C. The experimental conditions are described in Table 3, and the results are shown in Figure 4. The masses of getter and molecular sieve vary slightly between samples because the molecular sieves were weighed out rapidly to minimize exposure to air and moisture, thus limiting ability to finely adjust the sample size. The effect of previous exposure of the molecular sieve, discussed on page 6, can be observed in the result for CO_2/Air at 20°C, run 2 (blue line) in Figure 4.

Table 3. **Summary of conditions for 0% H_2 adsorption experiments.**

Experiment	Getter (g)	Molecular sieve (g)	Previous exposure (hours)	Degas conditions (hours)	CO_2/Air fill (std. cc)	H_2 fill (std. cc)
CO_2/Air at 20°C (1)	0.85860	0.45797	0:00	11:00 at 70°C 2:00 at 20°C	123.44	0
CO_2/Air at 20°C (2)	0.85860	0.45797	51:30	1:00 at 20°C	123.42	0
CO_2/Air at 70°C	0.86568	0.51479	0:00	21:30 at 70°C	123.43	0
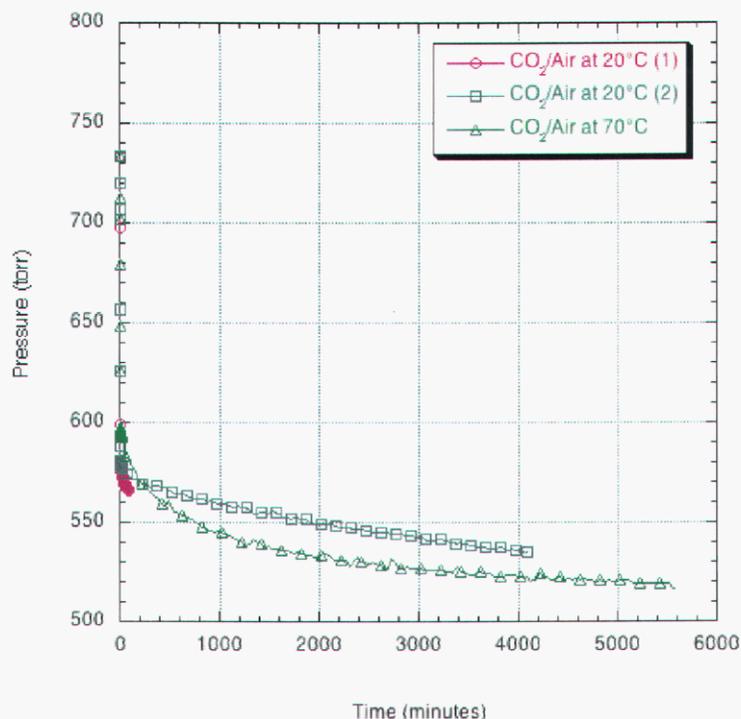
Figure 4. Pressure change over time for 0% H_2 adsorption experiments at 20°C and 70°C, as described in Table 3. Please note that the 70°C experiment was not cooled to room temperature at the end of the experiment, but remained at 70°C.

3.3 5% H_2 Recombination Experiments

This set of experiments looked at the effect of the getter/molecular sieve material on the CO_2/air atmosphere with 5% H_2, at 20°C and 70°C. The experimental conditions are described in Table 4, and the results are shown in Figure 5. ^{1}H NMR analysis of the getter material after recombination showed no evidence of hydrogenation (Appendix A, Spectra 3, 4, and 5).

Table 4. Summary of conditions for 5% H_2 recombination experiments.

Experiment	Getter (g)	Molecular sieve (g)	Previous exposure (hours)	Degas conditions (hours)	CO_2/Air fill (std. cc)	H_2 fill (std. cc)
CO_2/Air/H_2 at 20°C	0.85860	0.45797	1:30	1:00 at 20°C	123.46	6.14
CO_2/Air/H_2 at 70°C (1)	0.84683	0.45067	0:00	60:00 at 70°C	123.41	6.13
CO_2/Air/H_2 at 70°C (2)	0.86568	0.51479	92:40	3:00 at 70°C	123.37	6.13

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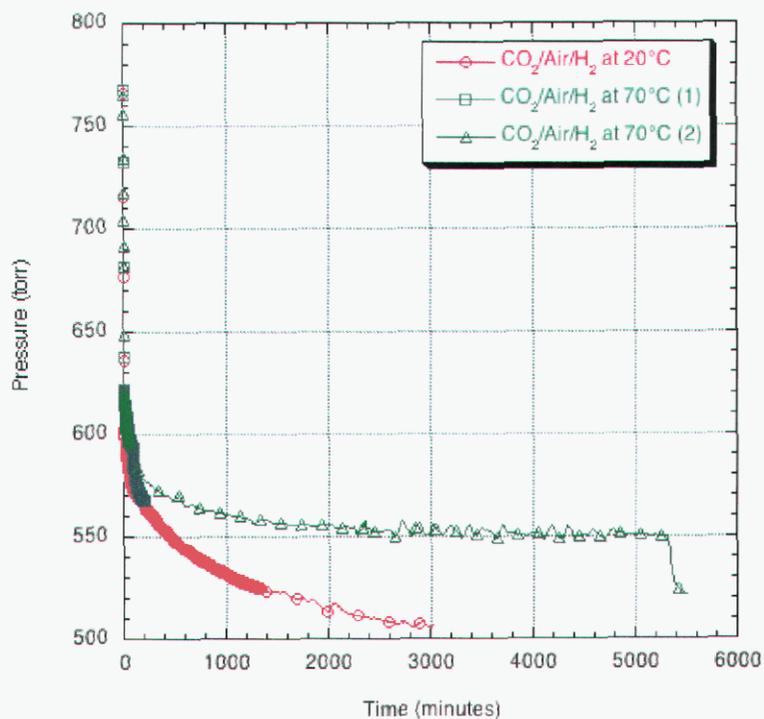
Figure 5. Pressure change over time for 5% H_2 recombination experiments at 20°C and 70°C, as described in Table 4.

To demonstrate the effect of recombination with the addition of H_2 to the system, Figure 6 compares the adsorption and recombination results at 20°C, and Figure 7 includes the results at 70°C; Figures 6a and 7a include the same data as Figures 6 and 7, but focused on the first 200 minutes of each experiment. The effect of previous exposure on the molecular sieve performance can be seen in Figure 7, where the second recombination experiment at 70°C (green line), which had seen a previous exposure of 92:40 hours, shows much less pressure change than expected.
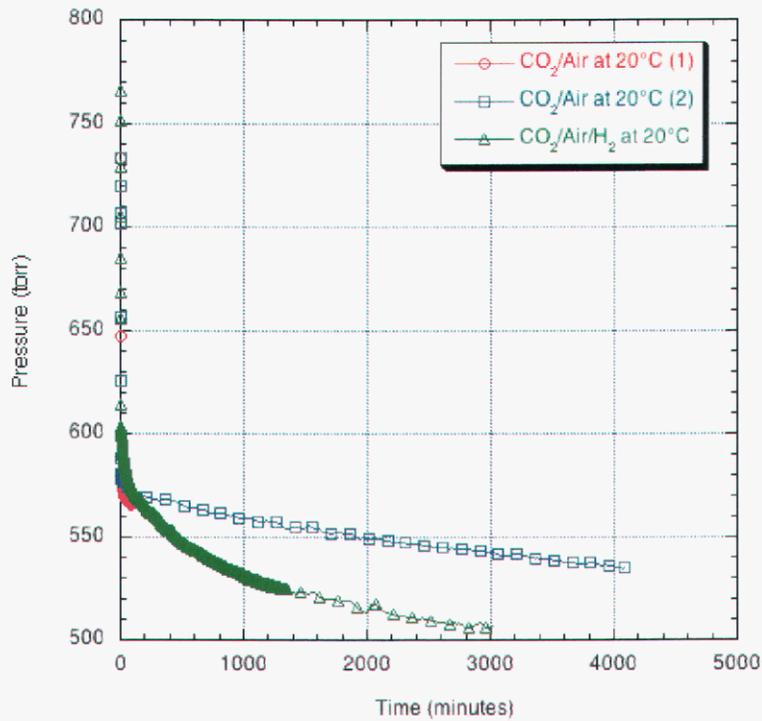
Figure 6. Pressure change over time at 20°C, comparing adsorption (0% H_2) and recombination (5% H_2) results.
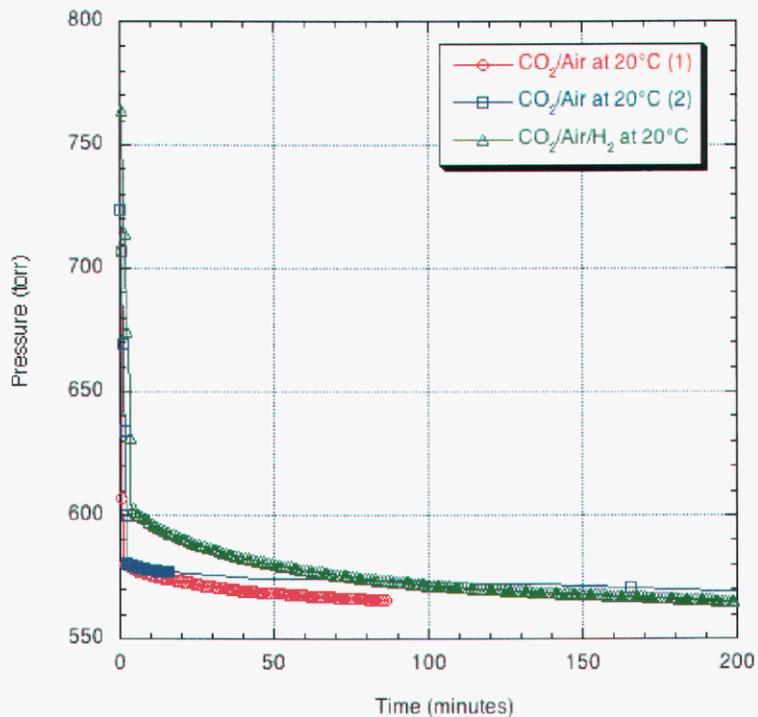
Figure 6a. (First 200 min of Figure 6.) Pressure change over time at 20°C, comparing adsorption (0% H_2) and recombination (5% H_2) results, focused on the first 200 minutes of the experiments.
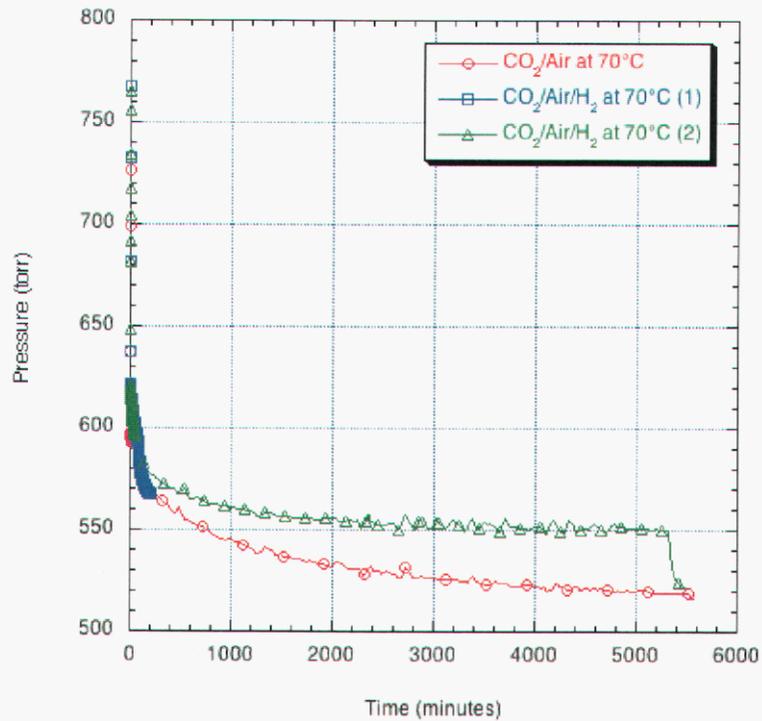
Figure 7. Pressure change over time at 70°C, comparing adsorption (0% H_2) and recombination (5% H_2) results.
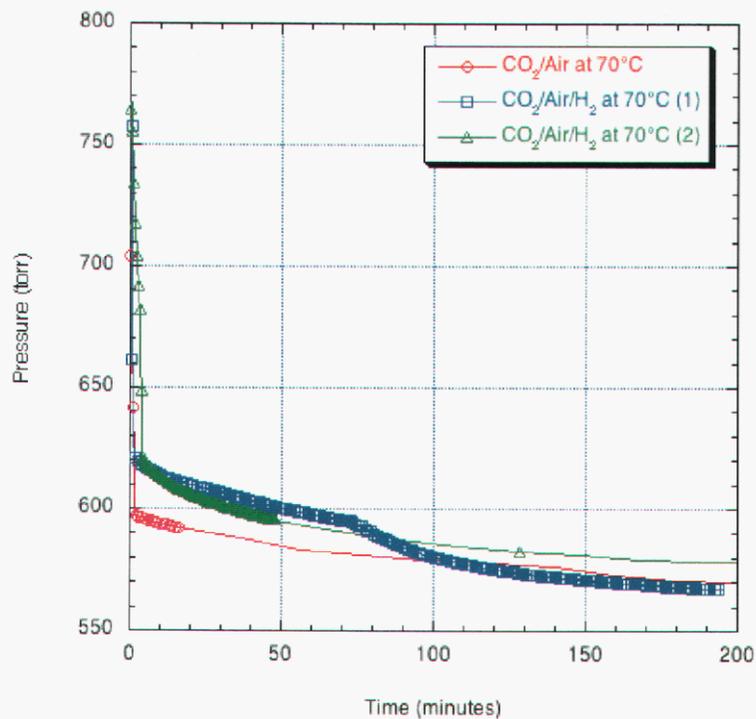
Figure 7a. (First 200 min of Figure 7.) Pressure change over time at 70°C, comparing adsorption (0% H_2) and recombination (5% H_2) results, focused on the first 200 minutes of the experiments.

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3.4 Hydrogenation of partially saturated getter experiments

To simulate performance of a partially saturated getter/molecular sieve system after some length of deployment, a sample of aged getter combined with molecular sieve was partially hydrogenated by exposure to pure hydrogen under the conditions described below. A sample made of 1.01535 g aged getter and 0.55568 g molecular sieve was degassed for 13:20 hours at 70°C. 85.72 std. cc H_2 was added to the system, and the reactor vessel was then heated to 125°C for 8:10 hours (25:00 hours total H_2 exposure). The remaining H_2 volume was 5.68 std. cc, for a total H_2 uptake of 80.04 std. cc. This is equivalent to approx. 50.9% of the rated capacity of 100 std. cc/g total material (getter plus molecular sieve).

The material was further hydrogenated during experiments under CO_2/N_2, and then used for a recombination experiment under CO_2/air. After these experiments, ^1H NMR shows 61.3 std. cc H_2 was taken up by the getter, or for the sample size of 0.83658 g getter and 0.45785 g molecular sieve, 47.4% of the rated capacity of 100 cc / g total material (getter plus molecular sieve) (Appendix A, Spectrum 6), which is comparable to the measured H_2 uptake. This quantitative ^1H NMR analysis conservatively assumes that all hydrogenated material is fully hydrogenated, while the actual material may have some double bonds left, and thus have more capacity available for further hydrogenation.

This partially saturated material was then used in an experiment to test the hydrogenation performance of a partially saturated getter material in a non-recombination environment of 24% N_2/76% CO_2 at 20°C. The experimental conditions are described in Table 5, and the results are shown in Figure 8. The hydrogen uptake rate for the 575 g getter assembly (375 g getter and 200 g molecular sieve) calculated from the hydrogen fill is 12 std. cc H_2/h. The same uptake calculated from the differential ^1H NMR spectra is 25 std. cc H_2/h. The large difference between these rates represents the cumulative errors among the multiple experiments and spectra. Regardless, the getter only uptake rate falls below the 45 std. cc H_2/h required for the container; end-of-life gettering might not be sufficient to remove all the hydrogen. This experiment is extremely conservative as the 12-day experiment certainly shows slower rates due to hydraulic restriction in the apparatus.

As discussed earlier, minor temperature fluctuations can cause changes in the measured pressure during an experiment. This can be observed in Figure 8, where the 3 torr rise in pressure around time=7500 min corresponds to a temperature rise of 1.5°C for the apparatus.

Table 5. **Summary of conditions for 5% H_2 hydrogenation experiment with partially saturated getter.**

Experiment	Getter (g)	Molecular sieve (g)	Previous exposure (hours)	Degas conditions (hours)	CO_2/N_2 fill (std. cc)	H_2 fill (std. cc)
$CO_2/N_2/H_2$ at 20°C	0.66711	0.36510	100:30	15:30 at 70°C 2:30 at 20°C	123.67	6.12
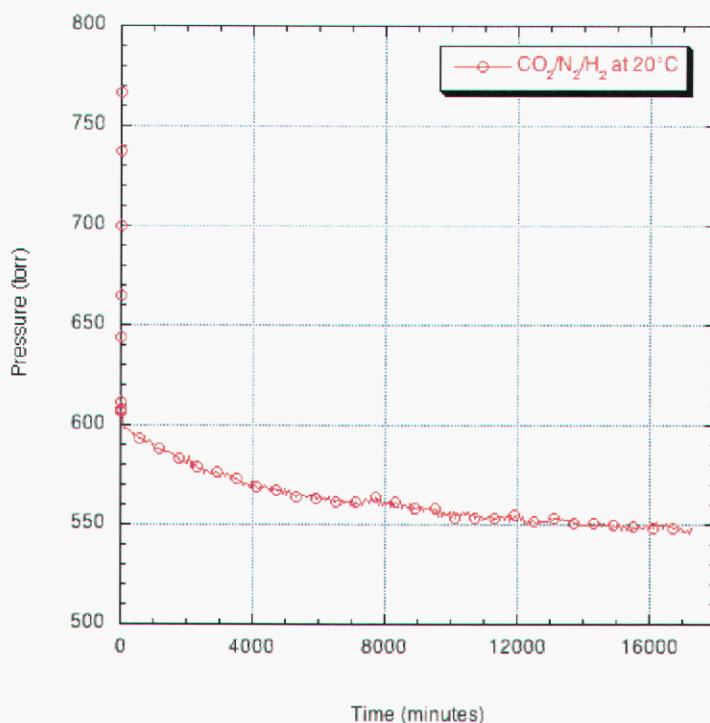
Figure 8. **Pressure change over time for partially hydrogenated getter/molecular sieve material under hydrogenation conditions (CO_2/N_2 with 5% H_2).**

3.5 Recombination of partially saturated getter experiment

The partially saturated getter/molecular sieve material was then placed under recombination conditions to test its performance at 20°C. The experimental conditions are described in Table 6, and the results are compared against a non-hydrogenated sample in Figure 9. ^{1}H NMR analysis after testing under hydrogenation and recombination conditions shows 74.3 std. cc H_2 was taken up by the getter, or for the sample size of 0.66711 g getter and 0.36510 g molecular sieve, 71.9% of the rated capacity of 100 cc / g total material (getter plus molecular sieve) (Appendix A, Spectrum 7).

Table 6. **Summary of conditions for 5% H_2 recombination experiment with partially saturated getter.**

Experiment	Getter (g)	Molecular sieve (g)	Previous exposure (hours)	Degas conditions (hours)	CO_2/Air fill (std. cc)	H_2 fill (std. cc)
CO_2/Air/H_2 at 20°C	0.59647	0.32643	390:15	21:30 at 70°C 2:00 at 20°C	123.62	6.12

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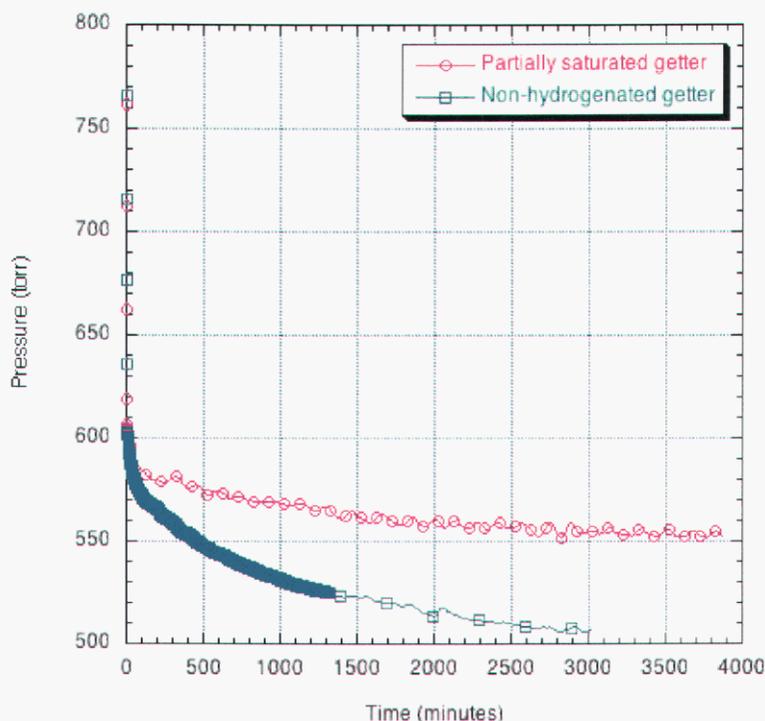
Figure 9. Pressure change over time for getter/molecular sieve samples under recombination conditions (CO_2/air with 5% H_2) at 20°C, comparing the partially saturated (hydrogenated) getter with non-hydrogenated getter.

3.6 Recombination and hydrogenation experiments with irradiated getter

To test the performance of the getter/molecular sieve material under the radiation conditions that will exist during deployment, samples of the aged HITOP and molecular sieve materials were 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 irradiated samples were then tested under recombination and hydrogenation conditions at 20°C. The experimental conditions are described in Table 7, and the results are shown in Figure 10. The irradiated sample results are compared against non-irradiated samples in Figures 11 (recombination) and 12 (hydrogenation).

The sample vials were cracked open slightly during the irradiation to avoid pressure buildup, allowing the molecular sieves to be exposed to air for some amount of time. Thus, while the molecular sieves were most likely somewhat deactivated during the irradiation, the exact amount of "previous exposure" was unknown; for the two experiments described in Table 7, each sample was used for first time. ^{1}H NMR spectra of the irradiated aged HITOP is similar to the aged HITOP before irradiation (Appendix A, Spectra 8 and 2). ^{1}H NMR analysis after hydrogenation (Spectrum 9) shows an uptake of 7.4 std. cc H_2 by the getter. This uptake represents a rate of 32.3 cc/h for the 575 g getter assembly (only 4000 min of the 5780 min uptake is shown in Figure 10).

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Table 7. Summary of conditions for 5% H_2 recombination and hydrogenation experiments on irradiated samples.

Experiment	Getter (g)	Molecular sieve (g)	Previous exposure (hours)	Degas conditions (hours)	CO_2/N_2 or CO_2/Air fill (std. cc)	H_2 fill (std. cc)
CO_2/Air/H_2 at 20°C	0.86091	0.46400	Unknown	21:00 at 70°C 2:00 at 20°C	123.44	6.13
$CO_2/N_2/H_2$ at 20°C	0.89091	0.47219	Unknown	20:40 at 70°C 2:00 at 20°C	123.38	6.12
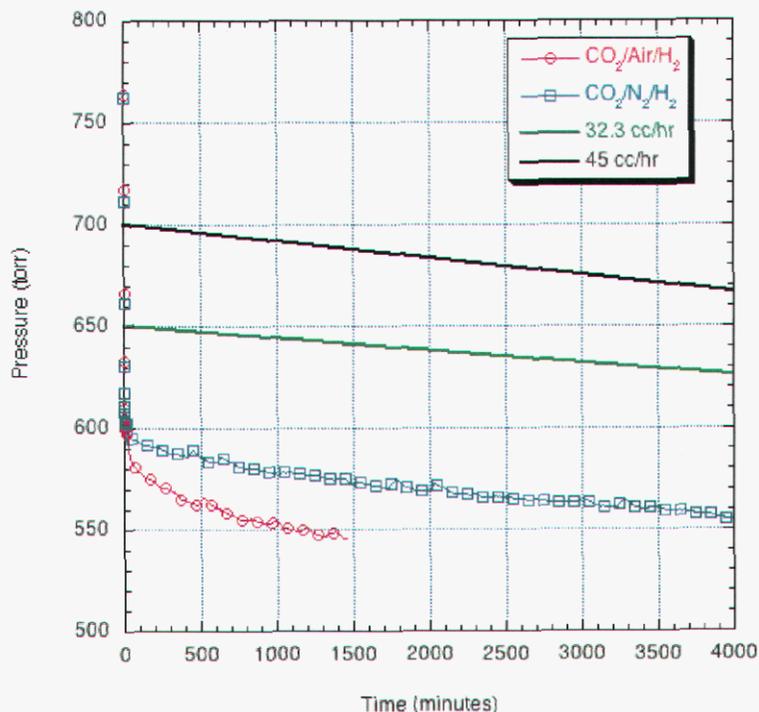
Figure 10. Pressure change over time for irradiated getter/molecular sieve samples under recombination (CO_2/air with 5% H_2) and hydrogenation (CO_2/N_2 with 5% H_2) conditions at 20°C. Lines reflecting the theoretical change in pressure for rates of 45 std. cc/h (black) and 32.3 std. cc/h (green) are also included; these rates are for the entire 575 g getter assembly.

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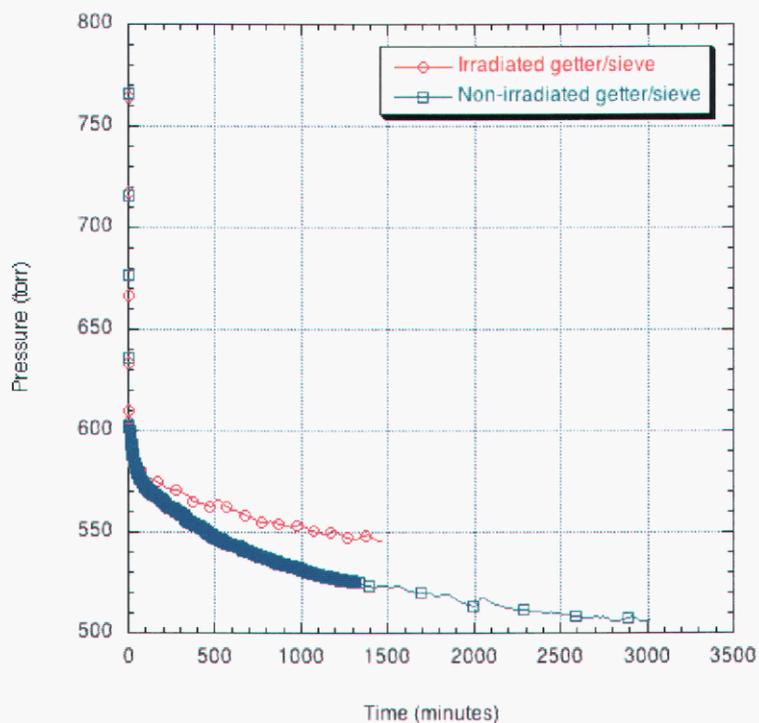
Figure 11. Pressure change over time for irradiated and non-irradiated getter/molecular sieve samples under recombination (CO_2/air with 5% H_2) conditions at 20°C.
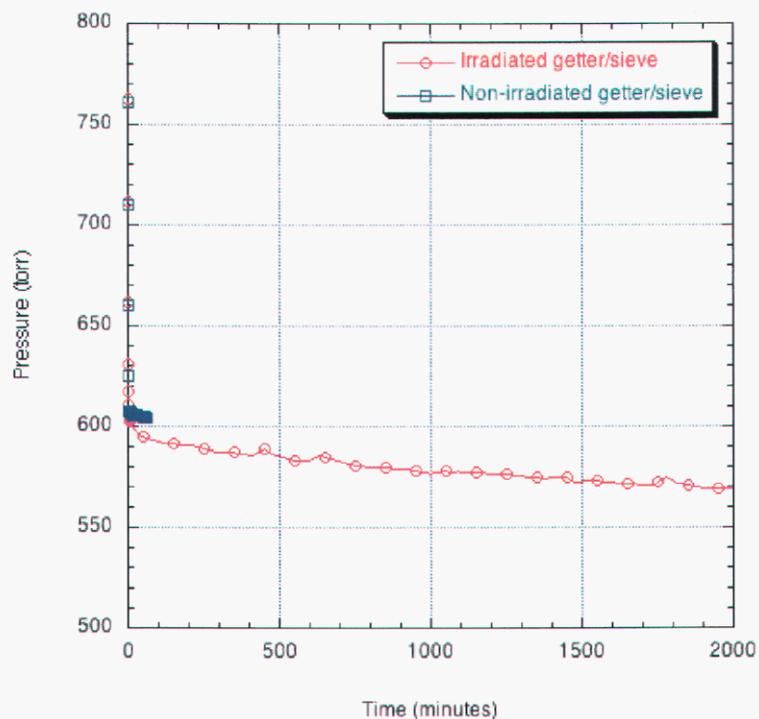
Figure 12. Pressure change over time for irradiated and non-irradiated getter/molecular sieve samples under hydrogenation (CO_2/N_2 with 5% H_2) conditions at 20°C.

3.7 Measurement of recombination rate with aged getter

To estimate the overall removal rate of hydrogen by the getter under recombination conditions, 0.86420 g of aged HITOP getter, without molecular sieves, was placed in the system and degassed for 2:10 at 70°C and 15:00 at 20°C. 123.62 std. cc of the CO_2/air mixture and 6.14 std. cc H_2 were added to the system, and the getter sample was exposed to the gas mixture for 61.3 minutes. At the conclusion of the experiment, the final gas volume remaining was 126.95 std. cc, for a change of 2.81 std. cc. The rate is calculated to be 8.837×10^{-4} std. cc H_2/ sec/ g getter or 1193 std. cc H_2/h for the 575 g getter assembly, assuming that all pressure change during the experiment was due to H_2 recombination or gettering. A summary of H_2 removal rates under various experimental conditions can be found in Table 8 below.

Table 8. Summary of approximate H_2 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	Aged getter	Recombination	61.3	1193	1193
CO_2/air/H_2	Aged getter/ molecular sieve	Recombination	3013	184	2546
CO_2/N_2/H_2	Aged partially saturated getter/ molecular sieve	Gettering	17263	25	972
CO_2/air/H_2	Aged partially saturated getter/ molecular sieve	Recombination	3868	67	1399
CO_2/N_2/H_2	Aged irradiated getter/ molecular sieve	Gettering	5780	32.3	998
CO_2/air/H_2	Aged irradiated getter/ molecular sieve	Recombination	1454	225	2352

4. Discussion

4.1 Discussion of the experiments

Control experiments were performed to verify that the reactor itself was not reacting with the gases and to establish the baseline adsorption of the activated molecular sieves. These experiments detailed in Figure 3 and Table 2 show the prolonged adsorption of CO_2. The adsorption at 70°C is less than at 20°C but when the 70°C sample was cooled to 20°C the data pressure dropped so that the two 20°C samples showed similar results. Additional controls were run with the addition of getter to the setup but without hydrogen (see Figure 4 and Table 3). One might have expected that the blue trace (CO_2/Air 20°C (2)) would have shown a larger pressure drop, but this sample had a long previous exposure of the molecular sieves and thus was no longer so reactive.

The first gettering experiments were recombination experiments done at 20°C (Figures 6 and 6a, Tables 3 and 4) and 70°C (Figures 7 and 7a, Tables 3 and 4). The 20°C experiments showed that without hydrogen, the gases rapidly expanded and then there was only the slow adsorption process. With hydrogen, there is a rapid expansion of the gases upon opening the valve then a second process causing the pressure drop. Within about one hour, a comparison of the red and green plots (the exact same sample with and without H_2) in Figure 6a shows that the sample with H_2 is about 10 torr higher pressure than the control. Considering the 6 std. cc additional gas (H_2) in the gettering experiment (green trace), this represents over 2/3 of the hydrogen being scavenged. Absolute determination of the relative rates in these experiments is problematic because of the large background adsorptions. The approximate first hour uptake rate here is 2000 std. cc H_2/h. A similar analysis made from the experiments at 70°C (also, the same sample with and without H_2) shows a nearly identical recombination rate over the first hour. Post-test analysis of the getters shows no gettering occurred (Spectra 3, 4, and 5) compared to the control (Spectrum 2). The conclusion of these experiments is that recombination occurs rapidly on the getter when oxygen is abundant.

The next experiments demonstrated gettering rather than recombination. Getter was pre-hydrogenated to partial gettering capacity then that sample was exposed to gettering and recombination experiments. The partially saturated aged getter clearly still functions under both gettering and recombination conditions. The uptake rate of the getter assembly falls below 45 std. cc H_2/h as gettering capacity is used. If the getter is required to perform without recombination far into its rated capacity, some pressure build up will likely occur after oxygen is consumed and flammability concerns removed. Recombination is an independent catalytic chemical process that remains unaffected by partial/complete saturation of the getter. The overall rate of 67 std. cc H_2/h for the 575 g getter assembly shown in Figure 9 clearly demonstrates this.

Because of the radioactivity present with the getter deployment, samples of the getter were pre-exposed to 1 MRad and then tested (Figures 10, 11, & 12, Table 7) under gettering and recombination conditions. Comparison of the ^1H NMR spectra of the aged HITOP getter showed no obvious degradation as evidenced by the appearance of new chemical species. The hydrogenation experiment represented in Figure 10 (blue trace, no oxygen) demonstrated an uptake rate of 32.3 std. cc H_2/h for the 575 g getter assembly as calculated from the ^1H NMR integration results. Importantly, the uptake rate is independent of whatever adsorption (CO_2)

occurred as the ^{1}H NMR integration does not rely on the pressure drop. Lines representing the measured uptake rate and the 45 std. cc H$_2$/h rate have been placed on Figure 10.

This experiment would appear to show the uptake rate as less than required. The experimental conditions of the test need to be considered. The H$_2$ uptake by the getter was calculate to be 7.4 std. cc H$_2$ by ^{1}H NMR. Only 6.12 std. cc H$_2$ was added to the reaction chamber. The error here comes from the assumptions necessary in interpreting the NMR spectra. We do not know which of the phenyl rings in the getter material are hydrogenated or if they are internal or terminal phenyl groups. Our assumption is that each molecule is completely hydrogenated before another begins hydrogenates. This assumption simplifies the integration calculation and can lead to an error of $\leq$20% (4/5). The result of this experiment also demonstrate that the hydrogen was essentially used completely during the gettering so the end of the experiment is diffusion restricted through the apparatus yielding a slower apparent reaction rate that would manifest with free access of gas to the getter.

Considering all the different experiments performed in this study, every recombination experiment yielded a hydrogen removal rate greater than the required 45 std. cc H$_2$/h, as summarized in Table 8. These tests are extremely conservative. The hydraulic restrictions inherent in the apparatus uniformly slow the rates recorded over many hours. The first hour rate is more representative of recombination/gettering without hydraulic restriction. Admittedly, reaction during the first hour will be faster than in later stages of the experiments even when there is no hydraulic restriction. An accurate measurement of the rate profile is impossible without a detailed mockup of the shipping container. The gettering experiments showed rates that were greater than the 45 std. cc H$_2$/h but then decayed to rates slower than those required after many hours. It is impossible to separate the two causes of the slower rates (hydraulic restrictions and reduced capacity).

Several aspects of the experiments are conservative. The hydraulic restriction slows the apparent long-term reaction rate. The fact that we start the experiments above the flammability limit and then watch hydrogen concentrations decrease is different than the deployment scenario, where hydrogen concentrations start at zero and then slowly increase. Gettering/recombination will occur immediately when hydrogen is formed and hydrogen concentrations will be maintained below the flammability limit. Depending on the amount of water present inside the container when sealed, there may be no need for any gettering, which will occur after recombination is complete. Because gettering is a backup mechanism to the recombination reaction, we are fully confident that the hydrogen removal rates represented in our suite of experiments are sufficient to stay below flammability limits. We conclude that if any recombination is possible in the actual deployment, the getter assembly will be adequate to maintain hydrogen concentrations below the flammability limit.

4.2 Effect of experimental conditions on gettering performance

Hydrogen gettering is a proven phenomenon involving simple chemical reactions. The hydrogen may catalytically recombine with oxygen to make water or be directly gettered. The data from the above experiments reveal that the catalytic recombination dominates the two processes while oxygen is present and that the hydrogen is gettered directly by the polymer in the getter when oxygen is not present. To certify the getter, the baseline gettering rate of 45 std. cc/h is required. We measured a rate in abundant oxygen without molecular sieves of >1190 std. cc H$_2$/h (see above paragraph) which at first glance might seem to easily meet the requirement; however, a number of factors particular to this qualification complicate the measurement of the rates. A

28

discussion of the experiments and these phenomena and how they affect the perceived and real performance of the getter follows.

Consider that gettering/recombination is measured by pressure drop in the system. Any process that produces, condenses, or removes gas within the reactor will affect a pressure change. We must understand all these processes and run appropriate control experiments if we are to make meaningful conclusions from the data in this study.

The testing required to qualify these getters in this application involves a number of complicating phenomena that make it difficult to quantify the exact rate of hydrogen removal. First, follows a discussion of general factors impacting gettering experiments. Later will follow a discussion of the factors impacting these particular gettering experiments.

For all gettering experiments numerous experimental conditions influence the reaction rate:

Temperature: Increased temperature typically increases gettering rates as the viscosity of the polymer is decreased and thus its diffusion to the active catalyst sites is faster. The reaction is sufficiently exothermic to overcome the decrease in entropy associated with gas becoming a solid. At some temperature, typically >500°C, the entropic terms dominate the equilibrium, and hydrogen is pyrolyzed from the getter. The slow maximum reaction rate of 45 std. cc H_2/h will not generate sufficient heat to cause anything but localized warming. The presence of local warmer and cooler within the package actually enhances system performance compared to the small scale testing because gas circulation is promoted. The laboratory evaluation of gettering rates is conservative compared to deployment conditions.

Hydraulic restriction/diffusion barriers: The ideal performance of the getter requires free access of the reactive gases to the getter and free access of any product gases (namely water from recombination) to diffuse from the getter location. The perforated can containing the getter and molecular sieve represents such an environment. The powder has high free volume and the getter has access to the surrounding gases. Hydrogen easily diffuses among gases, but can be restricted from access to the getter if narrow and tortuous geometries restrict free gas movement. Such restrictions exist in the getter test apparatus because of the multiple needle valves. The getter testing is thus a conservative demonstration of getter reaction rates. The reaction rates represented by the pressure decline curves are slowed to an unquantified extent by the delay in diffusing gases to/from the getter/molecular sieves.

Impurities: The getter is manufactured from the highest grade of raw materials specifically designed to release minimum volatiles. The carbon black and molecular sieves used in the getter package are active solids that can and will absorb organics, water and other impurities from their environment. The getter can should remain in its sealed packaging until ready for immediate use. Short exposure to ambient hydrogen (typically ≈ 1 ppm), background trace organics, or humidity will not affect getter performance, but might introduce chemical species into the system that are "discovered" when the package is opened leading to unnecessary concerns regarding impurities. Exposure to ambient humidity will quantitatively diminish the molecular sieve water uptake capacity. The exposure time of the molecular sieves to the ambient environment should be minimized and the package should be immediately assembled after insertion of the air-exposed getter can.

4.3 Effect of deployment conditions on gettering performance

Particular to this getter deployed in this package are some additional factors that must be understood.

The molecular sieves co-deployed with the getter confuse the results because they adsorb CO_2 and water: The molecular sieves are deployed so that the water produced from the recombination reaction is trapped in the gettering region of the can. Isolating the water minimizes the opportunity for liquid water to form. Liquid water might form a diffusion-limiting layer that could affect performance of the filter and/or the getter. Water in the gettering region of the package will also be subject to lower radiation doses and thus be less subject to radiolysis that could yield hydrogen gas again.

The 3A molecular sieves also adsorb carbon dioxide. This adsorption does not interfere with water adsorption, gettering or recombination but serves to confuse the measurement of hydrogen gettering, which is followed by pressure drop in the sealed apparatus. The magnitude and rate of CO_2 adsorption onto the molecular sieves is certainly influenced by the water content of the molecular sieves, as CO_2 is highly soluble in water. The interdependency of these rates is not the subject of this study and likely has no meaningful impact on hydrogen removal rates, but again is simply a source of error when we try to measure an accurate gettering rate. We were not provided the resources to measure gas compositions throughout the testing though this can be done with a significant increase in cost and effort. A further complication is that the CO_2 adsorption is dependent on temperature as demonstrated in Figure 3.

The hydrogen gettering experiments involve a preliminary degassing step under vacuum at 70°C meant to ensure the getter starts each of the different experiments in the same physical state. The 70°C degas removes adsorbed water and CO_2 from the getter, but not the water from the molecular sieves. The residual water content – and thus slower reaction rate towards additional water – causes the slower pressure drops found on samples that have been previously exposed to recombination conditions.

CO_2 and other gases have been reported as "poisons" for hydrogen getters: Indeed CO_2 will slow the reaction of hydrogen with either oxygen or the organic polymer when compared to these reactions in the absence of other gases. We conducted all experiments in atmospheres representative of actual deployment conditions. Experiments that measured gettering/recombination contained ≥70% CO_2 and still removed the hydrogen at the required rates.

The affect of CO_2 and other gases is more pronounced when getters use a palladium catalyst. For this reason, more expensive platinum catalyst is used in the getters tested here.

The hydrogen gettering rate slows as capacity is used: This phenomenon is real and a representation of two individual processes. First, the inhomogeneous getter powder represents a distribution of reaction sites. Some sites, because of the physical access of the polymer to the catalyst, or the local make up of the platinum nanoparticles, will be more reactive than others. Second, as the gettering capacity is used, the consumed getter dilutes the remaining getter. It just takes longer for a dilute solution to react than the original 100% pure getter. For example, if 90% of the polymer molecules diffusing across the catalyst surface are fully hydrogenated, then there are ten times less molecules to react. This issue was addressed by evaluating getter that

had be pre-hydrogenated to ~47% of its rated capacity (this getter assembly including molecular sieves is rated by the manufacturer, Vacuum Energy Inc., at 100 std. cc/g).

Other chemical reactions might occur in the presence of oxidizing agents (CO_2), reducing agents (hydrogen), and catalysts (Pt): We did consider the possibility of hydrogen reducing the carbon dioxide to form different one carbon species (formic acid, formaldehyde, methanol, or methane). We found no literature evidence of these processes occurring at ambient temperature and pressures. Analyzing the ^1H NMR spectra of the getter/recombination samples showed no evidence of methanol or formic acid. If methane were formed, we would not see it. None of these reactions, if they did occur would affect performance of the getter.

Old (aged) getter might react slower than the "as produced" material: The getter was aged for a total of 3 months during 2 separate periods and without molecular sieves present. Aging at 70°C represents the most severe environment envisioned during deployment or storage. A small, unquantifiable (likely <<1%) amount of chemical impurities were observed by ^1H NMR spectroscopy. It is not obvious that the thermal aging, or radiation exposure produced significant impurities other than those present in the starting materials. The pressure drops were slower for the aged material, but for many of the reasons stated above, exact quantification of the results is impossible. The polymer used as the hydrogen getter is a specialty product designed for prolonged use at temperatures >150°C. in air. We do not expect (or witness by ^1H NMR) significant aging over the course of 3 months at ≤70°C. We have returned the remaining getter to the aging oven so that we can reliably quantify the effects of 6 months aging at 70°C. Plans for accelerated aging studies are in progress.

4.4 Discussion of ^1H NMR spectroscopy interpretation.

The ^1H NMR spectra are plotted on a scale of 10-0 ppm, left to right. The multiple peaks around 7 ppm are the phenyl rings of the getter. Small baseline peaks in this area are impurities, either natural or generated by degradation. The sharp peak at 5.98 ppm is the residual proton signal in the 99+% deuterated solvent 1,1-2,2 tetrachloroethane-d_2. The tall sharp solvent peak is symmetrically bracketed by its ^{13}C satellite peaks and a minor solvent impurity. If gettering occurs, the phenyl rings are reduced to cyclohexyl moieties. The saturated cyclohexyl peaks appear around 1 ppm. The cyclohexyl ether peak (quintet) appears at 4.2 ppm. Olefin peaks resulting from the partial reduction of phenyl rings appear at 5-6 ppm. Typical of getter reactions, little olefin concentration (representing partial hydrogenation of a phenyl ring) is ever seen. Once a ring starts to hydrogenate at the catalyst surface, complete hydrogenation to the cyclohexyl moiety is the dominant process. The peak around 1.5 ppm is residual water that is always seen unless samples and NMR tubes are handled in a dry glove box. The height of the solvent peak represents a fixed concentration of hydrogen and is indicative of the concentration of the other species. The smaller the solvent peak is, the more concentrated the sample. The horizontal lines that trace above the baseline is the integration of the signals below them.

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5. Conclusion

The getter performed as it was designed. Upon exposure to hydrogen, in the presence of oxygen, catalytic recombination dominates as a hydrogen removal mechanism, reducing the flammability of the atmosphere by removing both hydrogen and oxygen. After consumption of the oxygen, hydrogen reacts directly with the getter, permanently reducing its gettering capacity. Although the experimental conditions do not exactly replicate the deployment conditions, the results of our conservative experiments are clear: the aged getter shows sufficient reactivity to maintain hydrogen concentrations below the flammability limit, between the minimum and maximum deployment temperatures, for three months. Neither radiation exposure nor thermal aging sufficiently degrades the getter to be a concern. Future testing to evaluate performance for longer aging periods is in progress.

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Appendix A: ^{1}H NMR Spectra

Spectrum 1: Fresh HITOP/molecular sieve


```
31TS0936
Fresh HITOP (26TS152)
TCED
11/22/2006
A. Nissen

Archive directory: /export/home/sandia/vnmrsys/data
Sample directory: 31ts0936_22Nov2006
File: PROTON

Pulse Sequence: s2pul

Solvent: TCED
Temp. 25.0 C / 298.1 K
INOVA-500  "nmr500"

Relax. delay 30.000 sec
Pulse 45.0 degrees
Acq. time 1.891 sec
Width 6000.6 Hz
16 repetitions
OBSERVE   H1, 499.8882811 MHz
DATA PROCESSING
FT size 32768
Total time 10 min, 37 sec
```

31TS86A
HITOP aged 3 months ("fresh")
TCEd
10/27/2006
A. Nissen

Archive directory: /export/home/sandia/vnmrsys/data
Sample directory: 31ts86a_27Oct2006

Pulse Sequence: s2pul

Solvent: TCED
Temp. 25.0 C / 298.1 K
File: PROTON
INOVA-500 "nmr500"

Relax. delay 30.000 sec
Pulse 45.0 degrees
Acq. time 1.891 sec
Width 6000.6 Hz
16 repetitions
OBSERVE   H1, 499.6882994 MHz
DATA PROCESSING
FT size 32768
Total time 10 min, 37 sec

9   8   7   6   5   4   3   2   1   ppm

100.48

-0.38

-0.11
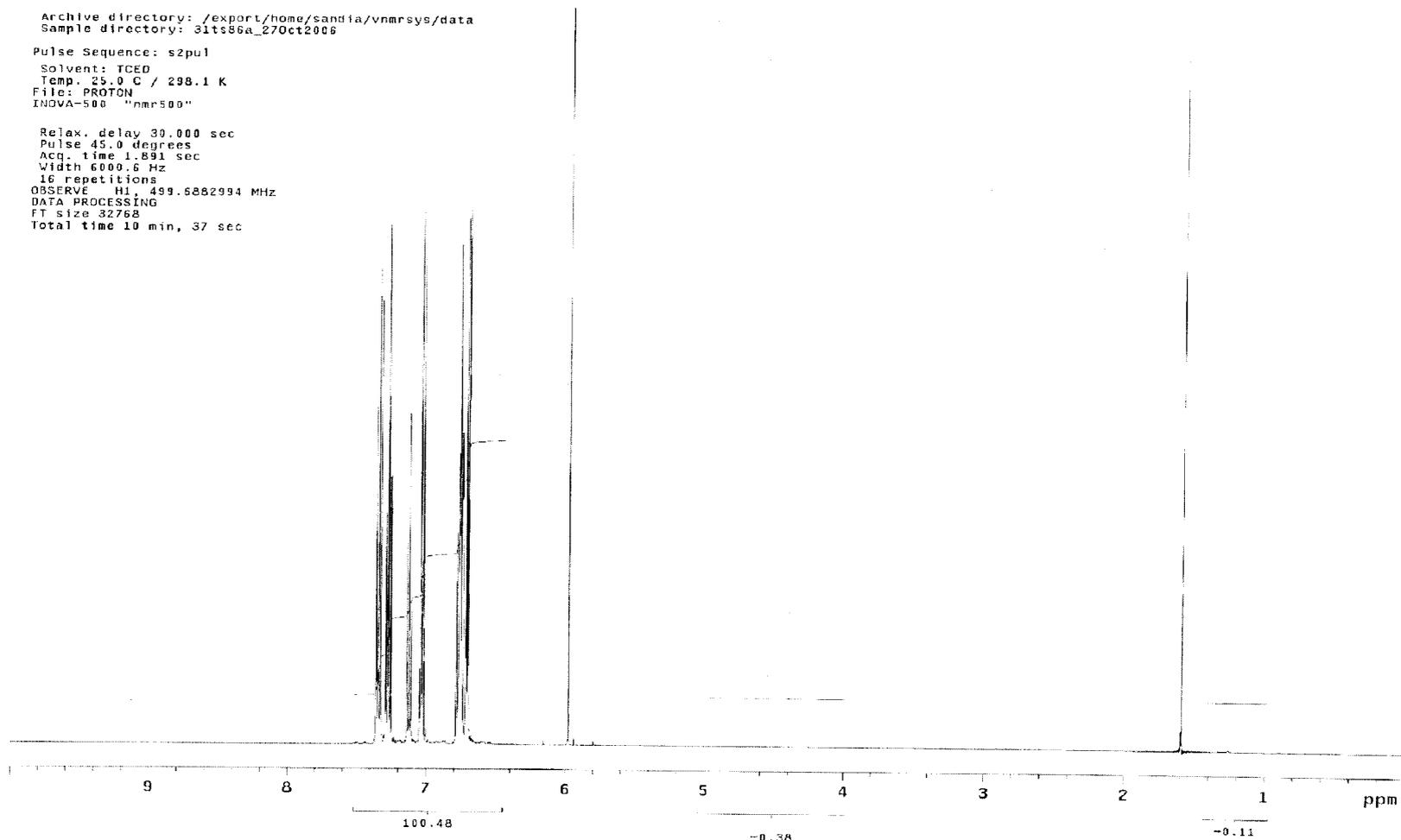
Spectrum 3: Recombination at 20°C


```
31ts78b (aged HITOP)
10/10/06
TCEd
G. Buffleben

 Archive directory: /export/home/sandia/vnmrsys/data
 Sample directory: 31ts78b_10Oct2006

Pulse Sequence: s2pul

 Solvent: TCED
 Temp. 25.0 C / 298.1 K
File: PROTON
INOVA-500  "nmr500"

 Relax. delay 30.000 sec
 Pulse 45.0 degrees
 Acq. time 1.891 sec
 Width 6000.6 Hz
 16 repetitions
OBSERVE   H1, 499.6882994 MHz
DATA PROCESSING
FT size 32768
Total time 10 min, 37 sec
```

10   9   8   7   6   5   4   3   2   1   -0   ppm

99.73   0.12   0.15
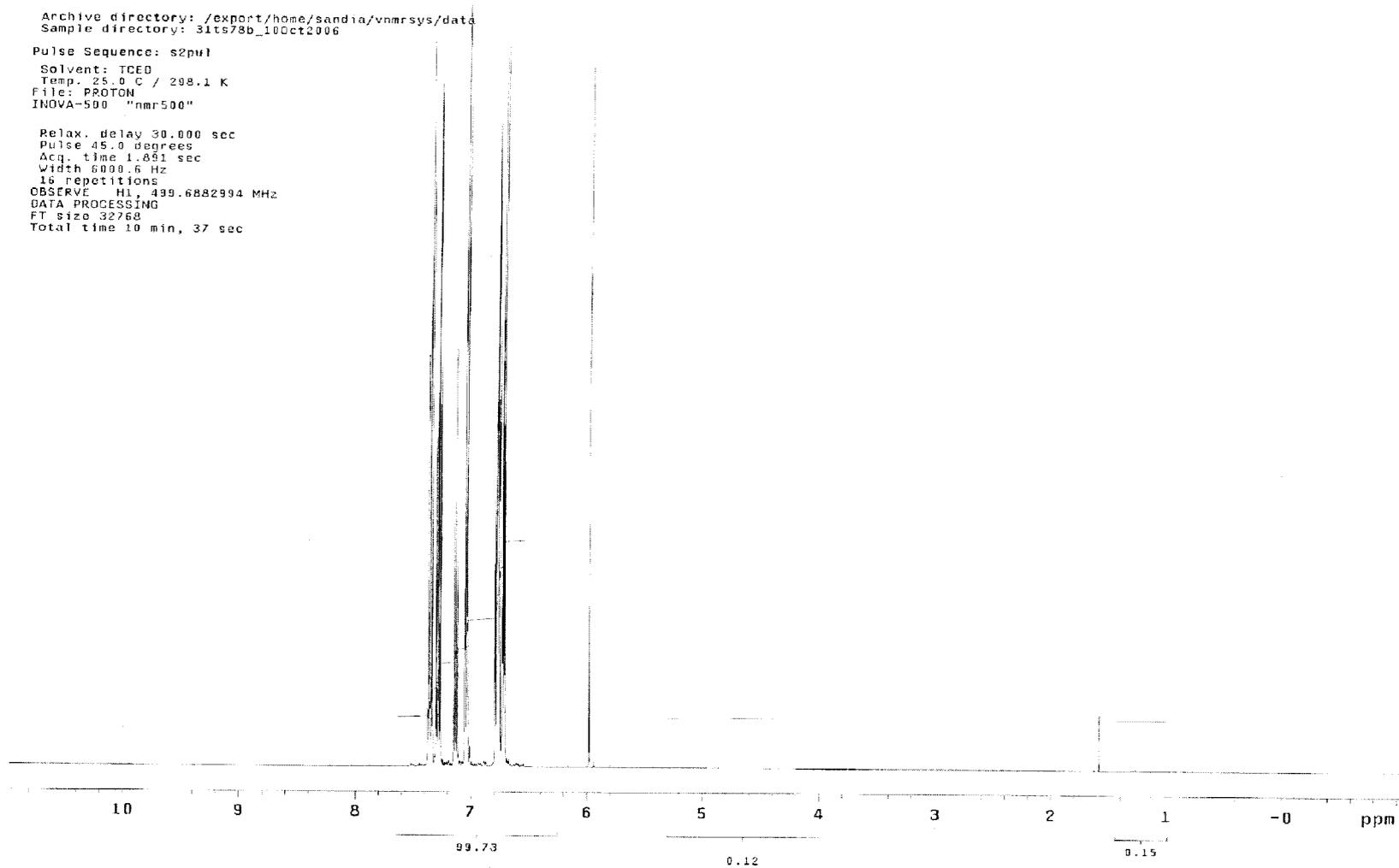
Spectrum 4: Recombination at 70°C (1)

31TS80
Aged HITOP
TCEd
10/16/2006
A. Nissen

Archive directory: /export/home/sandia/vnmrsys/data
Sample directory: 31ts80_16Oct2006

Pulse Sequence: s2pul

Solvent: TCED
Temp. 25.0 C / 298.1 K
File: PROTON
INOVA-500 "nmr500"

Relax. delay 30.000 sec
Pulse 45.0 degrees
Acq. time 1.891 sec
Width 6000.6 Hz
16 repetitions
OBSERVE   H1, 499.6882994 MHz
DATA PROCESSING
FT size 32768
Total time 10 min, 37 sec

9   8   7   6   5   4   3   2   1   ppm

99.82   0.16   0.02
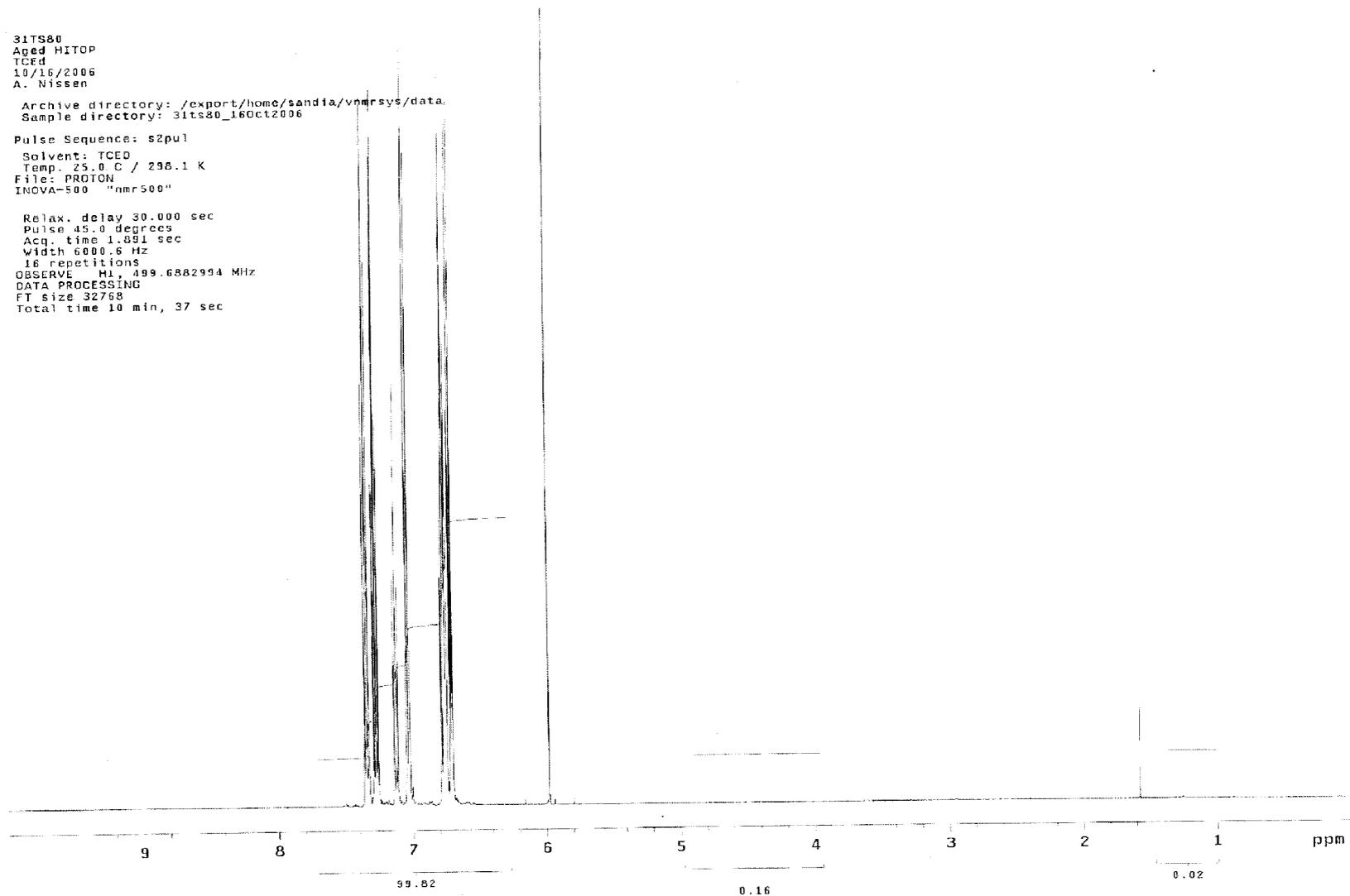
Spectrum 5: Recombination at 70°C (2)

31TS86B
31TS82 — HITOP, aged, at 70 deg C

TCEd
10/27/2006
A. Nissen

Archive directory: /export/home/sandia/vnmrsys/data
Sample directory: 31ts86b_27Oct2006
File: PROTON

Pulse Sequence: s2pul

Solvent: TCED
Temp. 25.0 C / 298.1 K
INOVA-500 "nmr500"

Relax. delay 30.000 sec
Pulse 45.0 degrees
Acq. time 1.891 sec
Width 6000.6 Hz
16 repetitions
OBSERVE   H1, 499.6882811 MHz
DATA PROCESSING
FT size 32768
Total time 10 min, 37 sec

10   9   8   7   6   5   4   3   2   1   -0   ppm
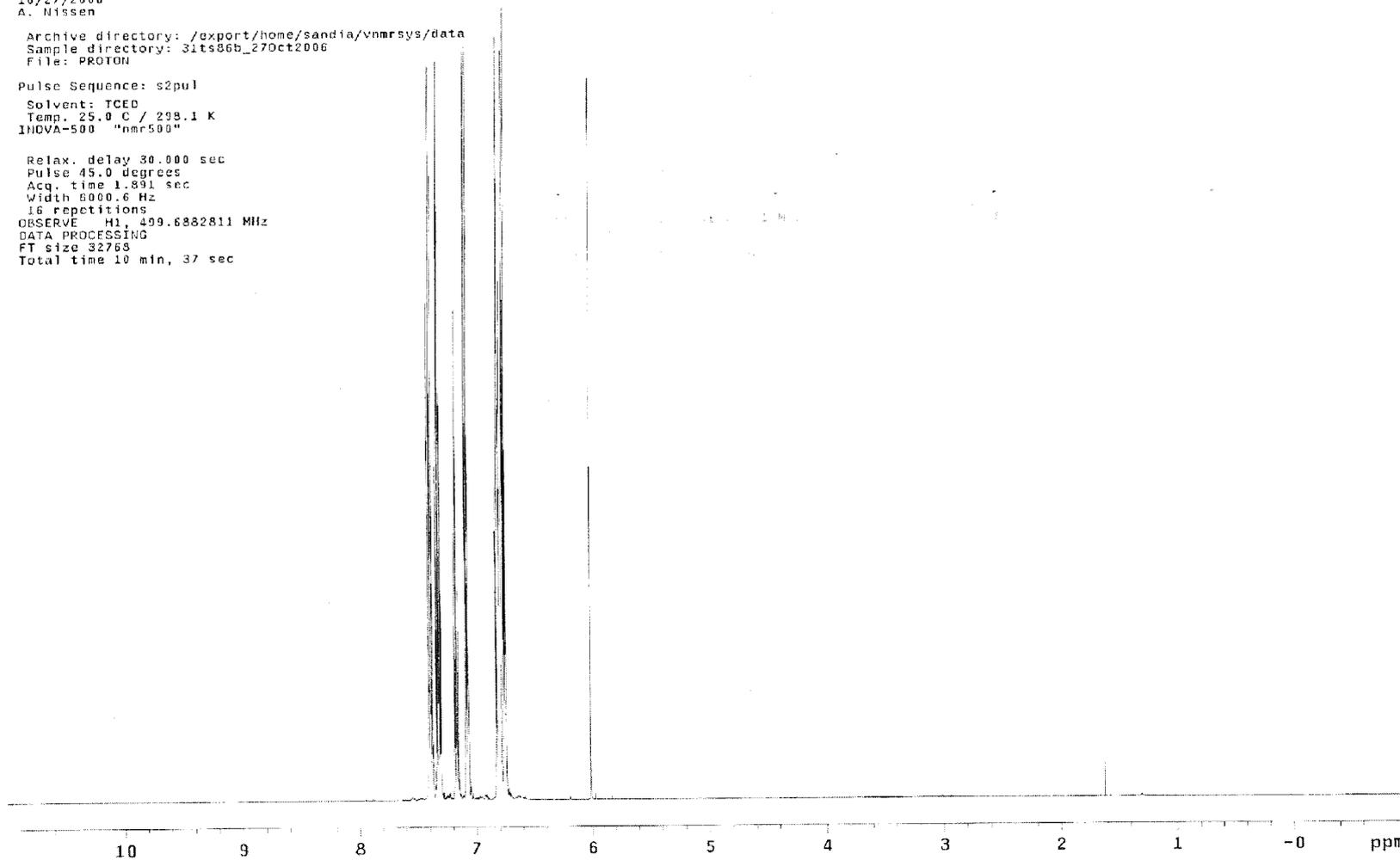
Spectrum 6: Partial hydrogenation of getter

31TS092A
31TS88: HITOP after hydro/recomb
TCEd
11/20/2006
A. Nissen

Archive directory: /export/home/sandia/vnmrsys/data
Sample directory: 31ts092A_20Nov2006

Pulse Sequence: s2pul

Solvent: TCED
Temp. 25.0 C / 298.1 K
File: PROTON
INOVA-500 "nmr500"

Relax. delay 30.000 sec
Pulse 45.0 degrees
Acq. time 1.891 sec
Width 6000.6 Hz
16 repetitions
OBSERVE   H1, 499.6882994 MHz
DATA PROCESSING
FT size 32768
Total time 10 min, 37 sec

79.41   2.25   18.33

9   8   7   6   5   4   3   2   1   ppm

40
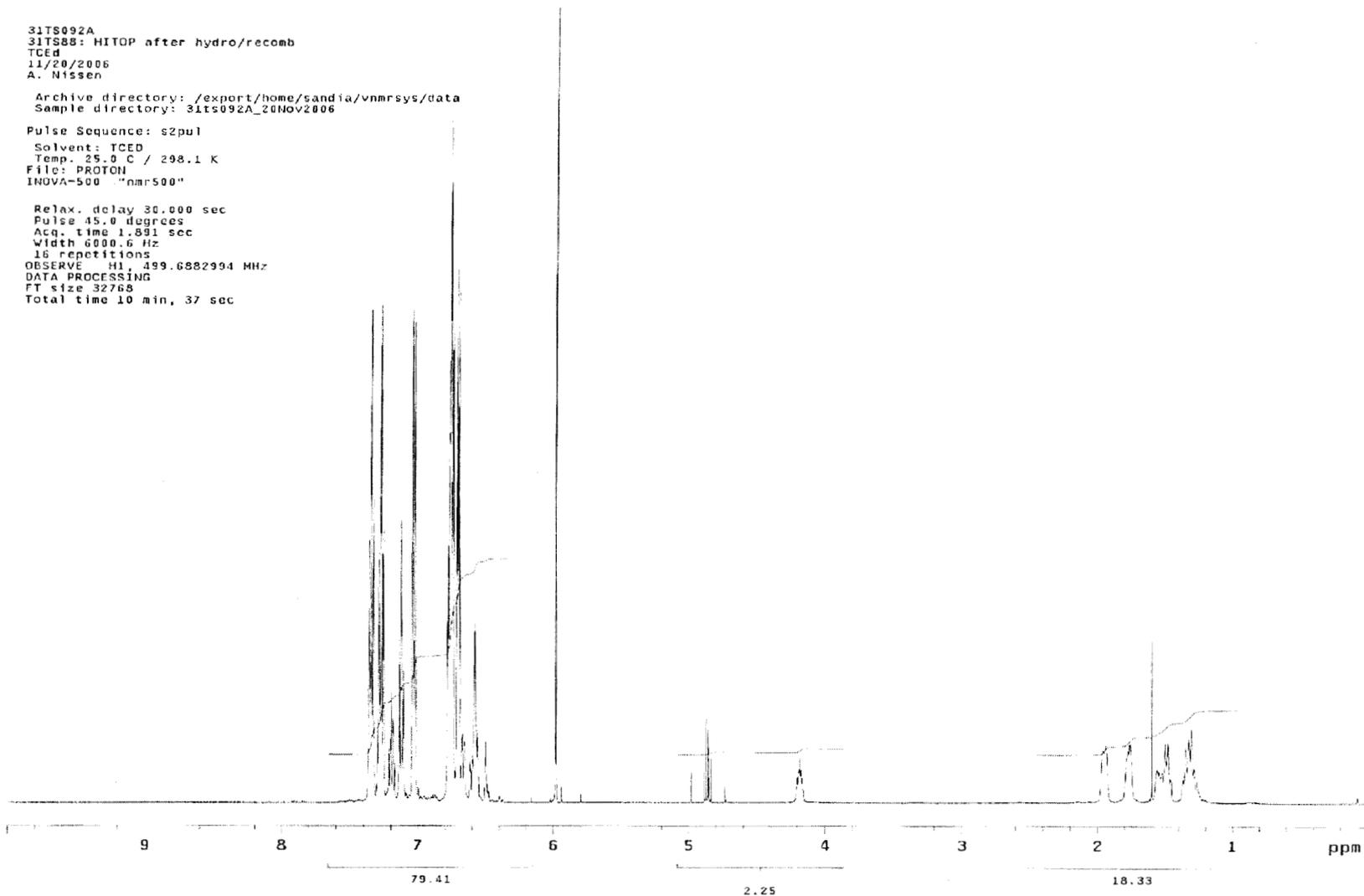
Spectrum 7: Hydrogenation of partially saturated getter

```
31TS097A
Sample 31TS95 (HITOP)
TCEd
3 Jan 2007
A. Nissen

 Archive directory: /export/home/sandia/vnmrsys/data
 Sample directory: 31TS097A_03Jan2007

Pulse Sequence: s2pul

 Solvent: TCED
 Temp. 25.0 C / 298.1 K
File: PROTON
INOVA-500  "nmr500"

 Relax. delay 30.000 sec
 Pulse 45.0 degrees
 Acq. time 1.891 sec
 Width 6000.6 Hz
 16 repetitions
OBSERVE  H1, 499.5582987 MHz
DATA PROCESSING
FT size 32768
Total time 10 min, 37 sec
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70.57	7.04	22.39
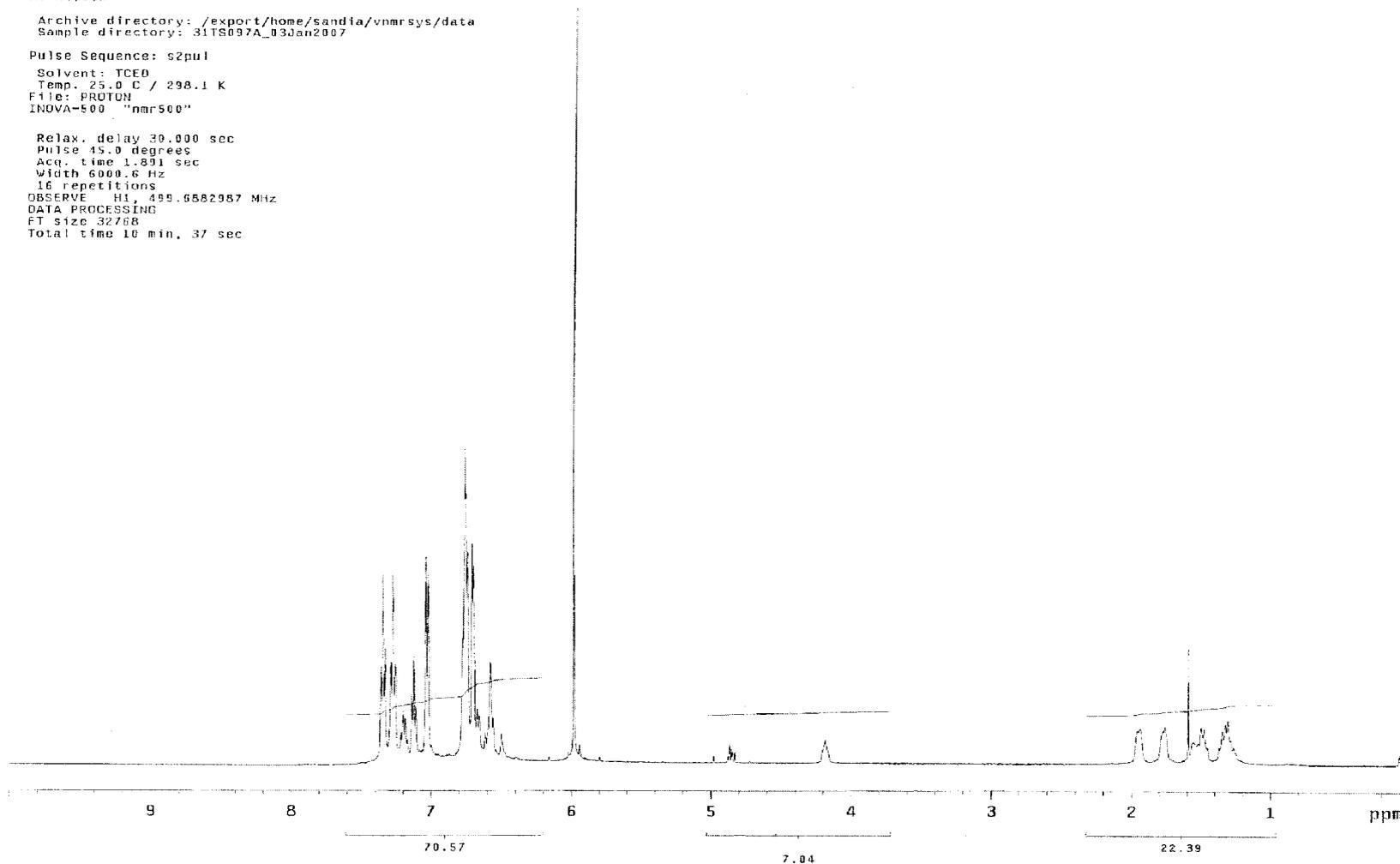
Spectrum 8: Irradiated aged HITOP

31TS093A
Aged HITOP, irradiated (31TS85C)
TCEd
11/22/2006
A. Nissen

Archive directory: /export/home/sandia/vnmrsys/data
Sample directory: 31ts093A_22Nov2006
File: PROTON

Pulse Sequence: s2pul

Solvent: TCED
Temp. 25.0 C / 298.1 K
INOVA-500 "nmr500"

Relax. delay 30.000 sec
Pulse 45.0 degrees
Acq. time 1.891 sec
Width 6000.6 Hz
16 repetitions
OBSERVE   H1, 499.6852811 MHz
DATA PROCESSING
FT size 32768
Total time 10 min, 37 sec
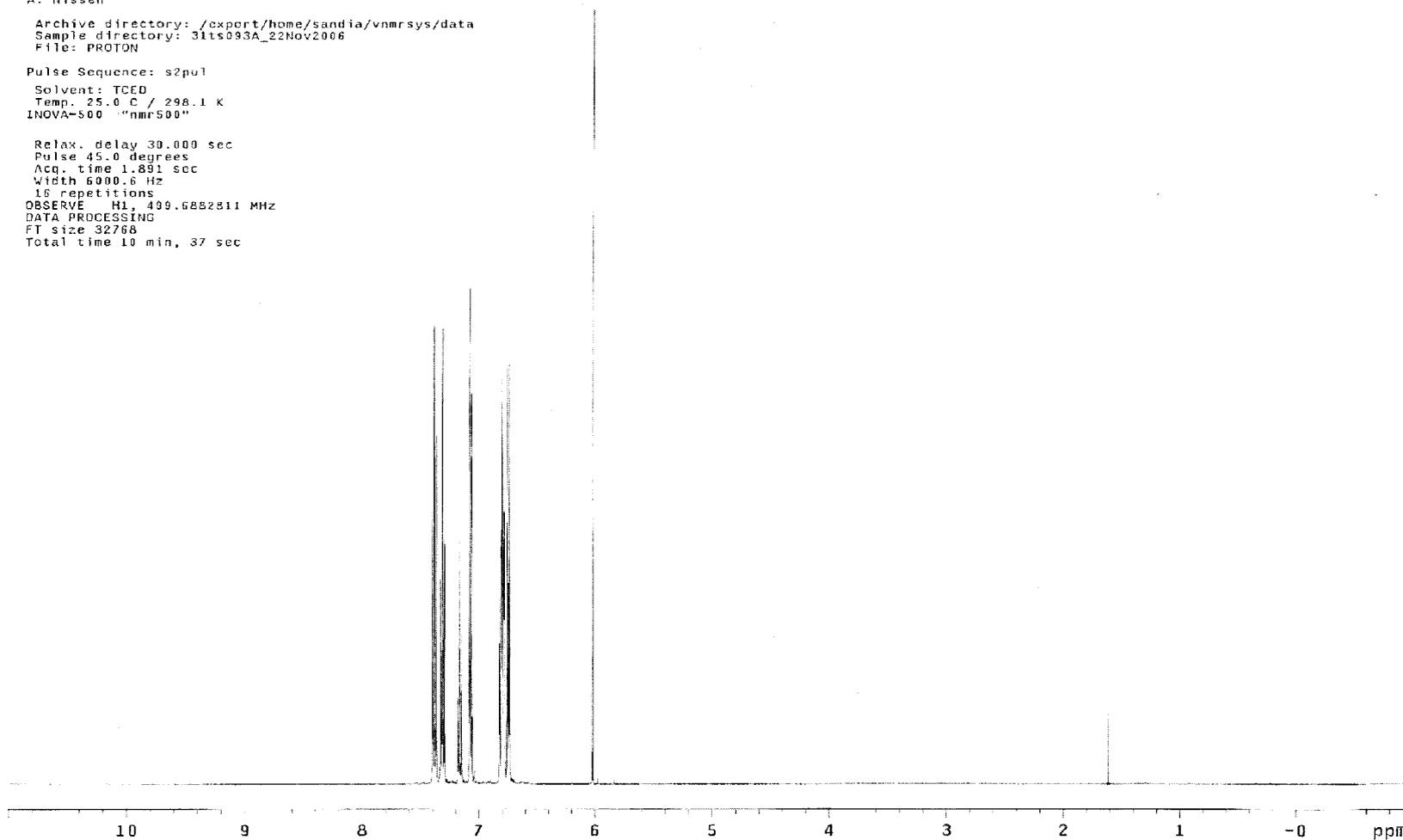
Spectrum 9: Irradiated aged HITOP after recombination/hydrogenation

```
31TS092B
31TS91: Irradiated HITOP, hydroge
nated
TCEd
11/20/2006
A. Nissen

 Archive directory: /export/home/sandia/vnmrsys/data
 Sample directory: 31ts092b_20Nov2006

Pulse Sequence: s2pul

 Solvent: TCED
 Temp. 25.0 C / 298.1 K
File: PROTON
INOVA-500  "nmr500"

 Relax. delay 30.000 sec
 Pulse 45.0 degrees
 Acq. time 1.891 sec
 Width 6000.6 Hz
 16 repetitions
OBSERVE   H1, 499.6882994 MHz
DATA PROCESSING
FT size 32768
Total time 10 min, 37 sec
```


| | 9 | 8 | 7 | 6 | 5 | 4 | 3 | 2 | 1 | ppm |

97.72

-0.05

2.33
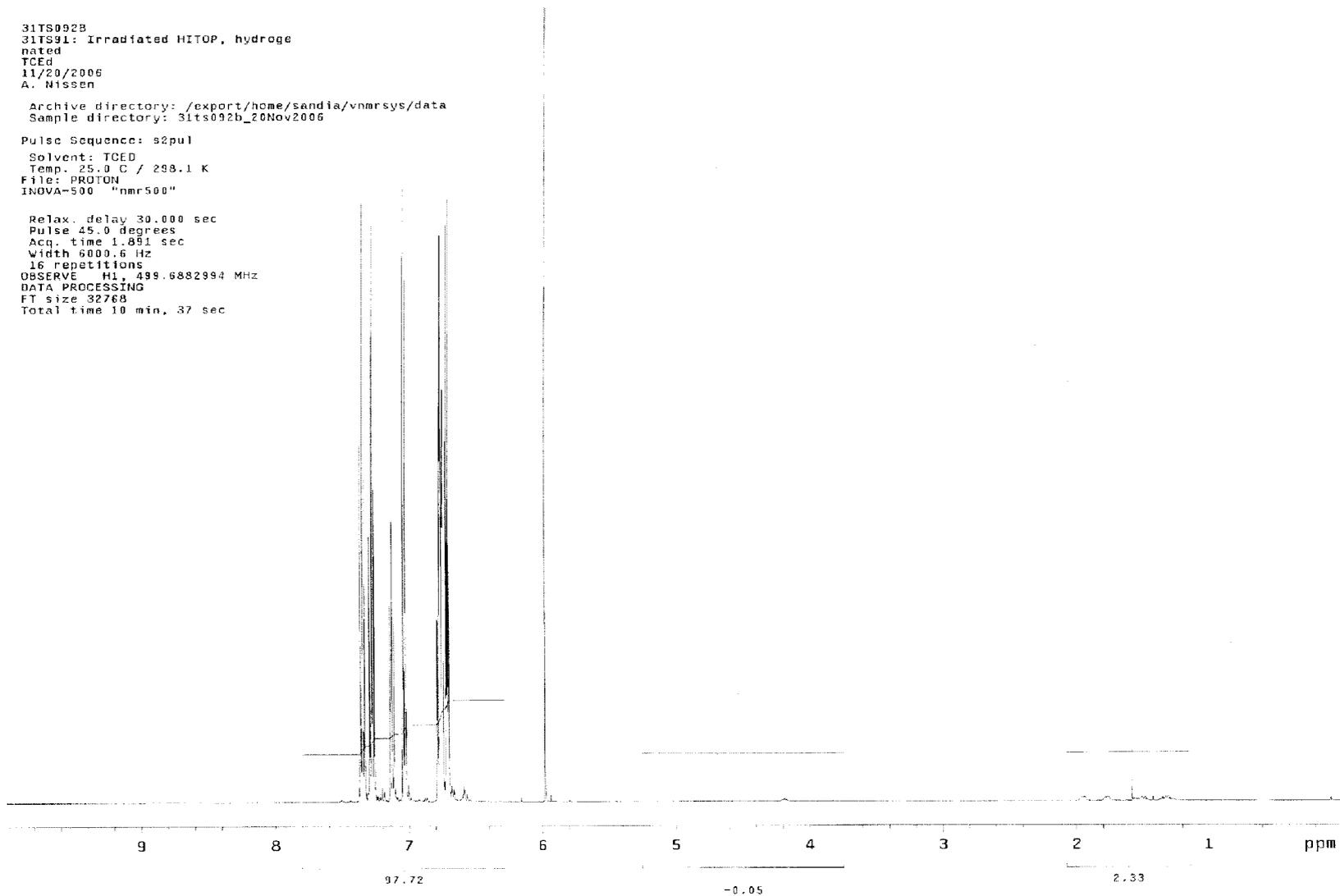
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Appendix B: Certificates of Analysis/Calibration

Manometers

PRIMARY STANDARDS LABORATORY
Sandia National Laboratories, Albuquerque, New Mexico 87185-0665

NVLAP

Accredited by the National Voluntary Laboratory Accreditation Program
for the scope of accreditation under Lab Code 105002

CERTIFICATE

Calibration
File: 49062

R 2ce4/3

R /c8 9c2

Instrument:	Pressure System
Manufacturer:	MKS Instruments Inc.
Model Number:	690A11TRB
Serial Number:	000170102

Submitted by: Organization 08236
Engineering Services
Dept. 08236, MS9133
Livermore, CA 94550-9133

As Found Condition: In Tolerance
As Left Condition: Left As Found (see note 1)
Certified: June 02, 2006
Expires: June 02, 2007

Note 1: new coefficients and uncertainties applied.

Test Method:
This artifact was calibrated by a force balance piston gauge (FPG) and a very low pressure controller, MMS-6110, for test points in the range of 1 to 10 torr. The FPG measures low gauge and absolute pressure by using a load cell to measure the force on the effective area of a 35 mm piston. A measurement mode specific lubricating pressure is applied to the annular gap of the piston/cylinder to provide a centering force on the piston. Compensation for the effects of the lubrication pressure on the load cell and piston are determined during the manufacturing process. The output of the load cell combined with the force components associated with the lubrication pressure determines the total force on the piston. This force divided by the temperature corrected effective area of the piston determines the differential pressure of the FPG.
Traceability for pressure is maintained through DH calibration report No. 44475 (3/20/2006) and NIST test report 267909-03 V321.

Test Parameters:
System Check – 9962   Head Temperature - Regulated
Range Select - X1   MUX   N/A
Pressure Fluid – Nitrogen   Indicator: MKS, 270D-4, S/N 94249213A
Multiplexer: N/A

Test Results: As Found/As Left

The calibration for true pressure, P(torr), in terms of the transducer reading, R(torr), are as follows:

$$1 \leq R \leq 10 \quad P = 1.35 \times 10^{-3} + 9.9786 \times 10^{-1} * R$$

Absolute Pressure Measurement

Reading	True Pressure	U_i, k=3
torr	torr	%
1.000	0.999	0.78
2.000	1.997	0.76
3.000	2.995	0.75
4.000	3.993	0.75
5.000	4.991	0.75
6.000	5.989	0.75
7.000	6.986	0.75
8.000	7.984	0.75
9.000	8.982	0.75
10.000	9.980	0.75

Where U_i is the certification uncertainty and k is the coverage factor when using the above equations to calculate true pressure. These results relate only to this test item.

Calibration Procedure: FPG8601/VLPC Version 1.0, 09/10/2001
Laboratory Temperature: 22.0 °C
Laboratory Humidity: 40.0 %
Calibration Start Date: May 26, 2006
Calibration Finish Date: May 30, 2006
Certificate Number: 177948
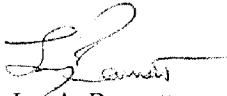
Metrologist: Jay A. Bennett
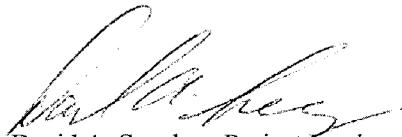
Approved by: David A. Sanchez, Project Leader

Copy to:
08236   (2)
PVL File (1)

MEASUREMENTS STANDARDS PROGRAM
SANDIA NATIONAL LABORATORIES
Albuquerque, New Mexico

File: 49062
Date: June 02, 2006

General Traceability Statement: Values and the associated uncertainties supplied by the Measurements Standards Program (MSP) are traceable to one or more of the following:

1. The values of the units (either base or derived) maintained and disseminated by the National Institute of Standards and Technology (United States of America) or, in special cases and where appropriate, to the National Standards Laboratory of another nation;
2. The accepted value(s) of fundamental physical phenomena (intrinsic standards);
3. Ratio(s) or other non-maintained standards established by either a self-calibration and/or a direct calibration technique;
4. Standards maintained and disseminated by the MSP in special cases and where warranted;
5. Values and uncertainties arising from participation in a National Measurement System.

Because of inherent complexity in the calibration process and the uncertainty contribution by both standards and calibrating instruments, traceability always requires evaluation of a "traceability tree." A "traceability tree" analysis can be assembled for a specific calibration and valid for a particular and specific point in time. The "traceability tree" will include copies of relevant certificates and reports, excerpted as appropriate for brevity. However, the cost of preparation of the "traceability tree" will be charged to the requester.

Note 1: This certificate or report shall not be reproduced except in full without the advance written approval of the Measurement Standards Program at Sandia National Laboratories.

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Note 3: The as received condition of the standard, set of standards, or measurement equipment described herein was as expected, unless otherwise noted in the body of the certificate or report.

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PRIMARY STANDARDS LABORATORY

Sandia National Laboratories, Albuquerque, New Mexico 87185-0665

NVLAP

Accredited by the National Voluntary Laboratory Accreditation Program
for the scope of accreditation under Lab Code 105002

CERTIFICATE

Calibration
File: 49063

R2oo 4/1

R 108 401

Instrument:	Pressure System
Manufacturer:	MKS Instruments Inc.
Model Number:	690A13TRB
Serial Number:	000166568

Submitted by: Organization 08236
Engineering Services
Dept. 08236, MS9133
Livermore, CA 94550-9133

As Found Condition:	In Tolerance
As Left Condition:	In Tolerance, Adjusted
Certified:	June 02, 2006
Expires:	June 02, 2007

Test Method:
This artifact was calibrated by the direct comparison method on MMS-167, for test points in the range of 100 to 1000 torr. The reference standard used to determine the true pressure was a Paroscientific quartz pressure transducer. The Paroscientific transfer standard was calibrated using a low range air piston gauge, which was calibrated at NIST.

Test Parameters:
System check: 9943   Head temperature: Regulated
Range select: X1   Pressure Fluid: Nitrogen
Indicator: MKS, Model 270D-4, S/N 000248119

Test Results: As Found

Absolute Pressure Measurement

Reading	True Pressure	2004 U_i, k=3	Tolerance
torr	torr	%	in/out
100.0	100.1	1.57	in
200.0	200.1	0.77	in
300.0	300.2	0.47	in
400.0	400.2	0.46	in
500.0	500.3	0.45	in
600.0	600.3	0.45	in
700.0	700.4	0.45	in
800.0	800.4	0.45	in
900.0	900.4	0.45	in
1000.0	1000.5	0.45	in

Test Results: As Left, Adjusted
NOTE: Zero adjustment on the MKS model 270 controller was at the extreme of its range. Centered controller zero and zeroed display via the head zero adjustment. Additionally the span was adjusted.

The calibration for true pressure, P(torr), in terms of the transducer reading, R(torr), are as follows:

$$100 \leq R \leq 1000 \quad P = 2.25 \times 10^{-1} + 1.00215*R - 3.88 \times 10^{-6}*R^2 + 1.32 \times 10^{-9}*R^3$$

Absolute Pressure Measurement

Reading	True Pressure	U_i, k=3
torr	torr	%
100.0	100.4	1.78
200.0	200.5	0.96
300.0	300.6	0.65
400.0	400.5	0.48
500.0	500.5	0.45
600.0	600.4	0.45
700.0	700.3	0.45
800.0	800.1	0.45
900.0	900.0	0.45
1000.0	999.8	0.45

Where U_i is the certification uncertainty and k is the coverage factor when using the above equations to calculate true pressure. These results relate only to this test item.

Calibration Procedure: Medium Vacuum Gauge Version 2.00, 08/25/2004
Laboratory Temperature: 22.0 °C
Laboratory Humidity: 40.0 %
Calibration Start Date: May 30, 2006
Calibration Finish Date: May 31, 2006
Certificate Number: 177947

Metrologist: Jay A. Bennett

Approved by: David A. Sanchez, Project Leader

Copy to:
08236   (2)
PVL File (1)

MEASUREMENTS STANDARDS PROGRAM
SANDIA NATIONAL LABORATORIES
Albuquerque, New Mexico

File: 49063
Date: June 02, 2006

General Traceability Statement: Values and the associated uncertainties supplied by the Measurements Standards Program (MSP) are traceable to one or more of the following:

1. The values of the units (either base or derived) maintained and disseminated by the National Institute of Standards and Technology (United States of America) or, in special cases and where appropriate, to the National Standards Laboratory of another nation;
2. The accepted value(s) of fundamental physical phenomena (intrinsic standards);
3. Ratio(s) or other non-maintained standards established by either a self-calibration and/or a direct calibration technique;
4. Standards maintained and disseminated by the MSP in special cases and where warranted;
5. Values and uncertainties arising from participation in a National Measurement System.

Because of inherent complexity in the calibration process and the uncertainty contribution by both standards and calibrating instruments, traceability always requires evaluation of a "traceability tree." A "traceability tree" analysis can be assembled for a specific calibration and valid for a particular and specific point in time. The "traceability tree" will include copies of relevant certificates and reports, excerpted as appropriate for brevity. However, the cost of preparation of the "traceability tree" will be charged to the requester.

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Gas mixtures

CO$_2$/Air

MATHESON TRI•GAS
ask...The Gas Professionals

Certified Mixture Grade

Matheson Tri-Gas Inc.
6775 Central Avenue
Newark, CA, 94560
Phone: 510-793-2559
Fax: 510-790-6241

TO: SANDIA NATIONAL LABS
7011 East Avenue
Bldg 916 Dock Door 6
Livermore, CA   94550

PHONE:
FAX:

TO AVOID BACKFILL, CYLINDER PRESSURE MUST BE GREATER THAN PROCESS PRESSURE

SALES ORDER NUMBER: 382363
P.O. NUMBER: 1BUFFLEBEN 9/11/06
LOT NUMBER: 103-06-04944

PRODUCT: 2 Component Mixture

CYLINDER NUMBER: 149827   FILL DATE: Sep 18, 2006
SIZE: 1A
CGA/DISS OUTLET: CGA 590
CONTENT: 68 cu. ft
PRESSURE: 650 psig

COMPONENT	REQUESTED CONCENTRATION	BLEND TOLERANCE (+/-)	CERTIFIED CONCENTRATION	CERTIFICATION ACCURACY
Air, DRY	24.0 %	5 %	24.0 %	+/- 2%
Carbon Dioxide, CO	BAL		BAL	

TRACEABLE TO REFERENCE STANDARD SOURCE/NUMBER:
TRACEABLE TO NIST TRACEABLE WEIGHT CERTIFICATE: 822/260017-98

SPECIAL INFORMATION / ADDITIONAL COMMENTS

The product listed above and furnished under the referenced purchase order has been tested and found to contain the component concentration listed above. All values in mole/mole basis gas phase unless otherwise indicated. Matheson Tri-Gas Inc. warrants that the above product(s) conform at the time of shipment to the above description. Matheson Tri-Gas Inc. liability does not exceed the value of the product purchased.

Sengthong Lamounthy   Sep 19, 2006
ANALYST   SIGNATURE   DATE SIGNED

Page 1 of 1

CO_2/N_2

MATHESON TRI•GAS
ask — The Gas Professionals

Certified Mixture Grade

Matheson Tri-Gas Inc.
6775 Central Avenue
Newark, CA, 94560
Phone: 510-793-2559
Fax: 510-790-6241

TO: SANDIA NATIONAL LABS
7011 East Avenue
Bldg 916 RM 120
Livermore, CA 94550

PHONE:
FAX:

TO AVOID BACKFILL, CYLINDER PRESSURE MUST BE GREATER THAN PROCESS PRESSURE

SALES ORDER NUMBER: 386426
P.O. NUMBER: TNISSEN 10/18/06
LOT NUMBER: 103-66-05899

PRODUCT: 2 Component Mixture

CYLINDER NUMBER: AJ 11907
SIZE: 1A
CGA/DISS OUTLET: CGA 320
CONTENT: 68 cu ft
PRESSURE: 650 psig

FILL DATE: Nov 3, 2006

COMPONENT	REQUESTED CONCENTRATION	BLEND TOLERANCE (+/-)	CERTIFIED CONCENTRATION	CERTIFICATION ACCURACY
Nitrogen, UHP	24 %	5 %	24.1 %	+/- 2%
Carbon Dioxide, BD	76 %	5 %	75.9 %	+/- 2%

TRACEABLE TO REFERENCE STANDARD SOURCE/NUMBER:
TRACEABLE TO NIST TRACEABLE WEIGHT CERTIFICATE: 822/260017-98

SPECIAL INFORMATION / ADDITIONAL COMMENTS

The product listed above and furnished under the referenced purchase order has been tested and found to contain the component concentration listed above. All values in mole/mole basis gas phase unless otherwise indicated. Matheson Tri-Gas Inc. warrants that the above product(s) conform at the time of shipment to the above description. Matheson Tri-Gas Inc. liability does not exceed the value of the product purchased.

Singthong Lamountry
ANALYST

SIGNATURE

Nov 3, 2006
DATE SIGNED

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