METHOD VALIDATION REPORT

Secondary (Lab) Standard Validation for the Analysis of δ^2H in Water Samples Using the GasBench and IRMS

Date: January 4, 2010

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SUMMARY

International Standards (IAEA Reference Material)	SLAP2 – Standard Light Antarctic Precipitation 2 GISP – Greenland Ice Sheet Precipitation VSMOW2– Vienna Standard Mean Ocean Water 2					
Primary Standard Absolute Values	**Primary Standard**		**$\delta^2H_{VSMOW/SLAP}$ ‰**			
	SLAP2		**-427.5**			
	GISP		**-189.5**			
	VSMOW2		**0.0**			
Primary Standard Experimental Values and Statistics	**Primary Standard**	**$\delta^2H_{VSMOW/SLAP‰}$**	**S.D.**	**%CV**	**%Acc**	**n**
	SLAP2	**-427.654**	7.07	1.65	100.04	12
	GISP	**-189.895**	6.84	3.60	100.21	12
	VSMOW2	**-1.645**	5.10	310.0*	*	12
	* Value skewed due to zero being the target value.					
Water Lab (Secondary) Standards	1. Vostok: Originally obtained as an ice core from Vostok Ice Core Team (member G. Domack) which subsequently melted due to freezer malfunction 2. Bottle Distilled: Fisher, Optima LCMS Grade, Lot: 086933 3. Well: D. Tewksbury (employee Hamilton College) home 4. Deuterium Prepared Lab Standard (see preparation section)					
Lab (Secondary) Standard Experimentally Determined δ^2H Values and Statistics	**Secondary Standard**	**$\delta^2H_{VSMOW/SLAP ‰}$**	**S.D.**	**%CV**	**N**	
	Vostok	**-430.609**	7.42	1.72	34	
	Bottle Distilled	**-44.704**	5.88	13.15	30	
	Well	**-76.705**	5.84	7.61	31	
	Prepared Lab Standard	**+245.566**	5.89	2.40	31	
Sample Analysis Volume	200 µL					

SIGNATURE PAGE

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Written by:

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1. INTRODUCTION

This report describes the qualification/validation process for Water δ^2H (or also referred to as D) Secondary (Lab) Standards using the automated H_2 equilibration GasBench Isotope Ratio Mass Spectrometry technique. Various water samples were analyzed to be evaluated as possible Secondary (Lab) standards. Three international (primary) standards were included in the analyses, they are GISP, SLAP2 and VSMOW2. The goal of the analysis was to identify the laboratory standards which provided acceptable experimental precision and encompassed the δ^2H ranges expected for samples submitted for analysis. The Lab Standards identified in the Summary section of this report fulfilled these requirements.

2. EXPERIMENTAL

2.1. CHEMICALS AND MATERIALS

Four water samples were chosen for this secondary (Lab) standard determination validation, as well as the three international (or primary) standards. The four laboratory standard candidates were as follows:

1. Vostok
2. Bottle Distilled
3. Well
4. Prepared Deuterium Laboratory Standard (50 ppm D_2O)

Note: The 50 ppm (v/v) D_2O laboratory standard was prepared as follows:

- ~ 100mL of Science Center RO water were first placed into a 1000 mL volumetric flask
- Using a pipette, exactly 50 µL of D_2O (Acros D_2O 100.0 Atom% D, Lot A020127801) were then placed into the volumetric flask
- Science Center RO water was then added to the flask to the mark
- A stir bar was inserted and the solution mixed for ~ 1 day

The three international standards were as follows:

1. SLAP2
2. GISP
3. VSMOW2

Other than the prepared lab standard, all waters were used neat “as received”.

A 2% H_2 in Helium gas was used as the equilibration gas which allowed for ^2H atom incorporation from the water sample into the H_2 gas introduced to each sample’s headspace. (Platinum catalyst “sticks” were inserted into each sample to facilitate this ^2H incorporation.)

Other materials were as follows:

Capillary Column – Varian PN: CP7551, PLOT Fused Silica, CP-PoraPLOT Q, length - 27.5 meter (including 2.5 m particle trap), (0.32 mm I.D., 0.45 mm O.D., 10 mm film thickness) held at 70ºC.

Exetainer Vials – 12 mL Borosilicate, obtained from LabConco with vial caps and disposable septa.

Valco Sample Loop in GasBench – 100 µL

GasBench Sample Block – set at 30ºC.

Platinum Catalyst sticks, (Thermo P/N 010207 1091831) one per sample vial.

He Gas - Grade 5.0 (50 psi tank gauge, 13-14 psi GasBench gauge)

2% H_2 /Balance Helium – P/N 105-MIX5E220C (45 - 50 psi tank gauge, adjust to give ~ 125 mL/min flush fill rate, check at vent of flush fill needle during the flush fill procedure.)

H_2 Reference Gas – Grade 5.0 (50 psi tank gauge, 40 – 50 psi GasBench gauge, adjust pressure at GasBench gauge to give ~ 6 – 7 volts m/z 2 signal, cup 1)

Pipettor – Finnpipette 40 – 200 µL range, S/N J57232 (Calibrated – 12/07)

Pipettor Tips – Eppendorf – "Yellow", capacity up to 200 µL (Fisher # 02-707-500)

2.2. INSTRUMENTATION (IRMS, GASBENCH AND PAL)

The IRMS instrument is a Thermo Scientific Delta V Advantage along with a ThermoFinnigan GasBench III and CTC Analytics PAL autosampler system. (The GasBench unit is equipped with a self-contained continuous flow interface.)

IRMS Data Acquisition System: Isodat 2.5 Gas Isotope Ratio MS Software

Acquisition - Used for running the analysis (acquiring data).

Workspace – Used for analysis setup, methods and sequence development, and data review.

Instrument Control – Used to monitor and control various aspects of the instrument.

2.3. ANALYSIS PROCEDURE, SAMPLE PREPARATION AND INSTRUMENT CONDITIONS

Analysis Procedure

Five analysis days (four Primary standard to Secondary standard evaluations and one Secondary to Primary standard evaluation) were performed during the course of the validation. The first four analysis days consisted of 50 samples, the final Secondary to Primary analysis consisted of 48 samples. The 50 samples used for the first analysis day had previously been analyzed for $\delta^{18}O$. It should be noted that a water sample subjected to $\delta^{18}O$ analysis can subsequently be subjected to $\delta^{2}H$ analysis. The reverse is not true, a $\delta^{18}O$ analysis cannot be performed on a water sample previously subjected to $\delta^{2}H$ analysis.

Ten peaks (consisting of ion current for m/z 2, and m/z 3) of decreasing signal are obtained for each sample (in addition to five reference pulses). The first peak is omitted (due to potential detector saturation) and the statistics (average, S.D., % accuracy, etc.) are generated on the $\delta^{2}H$ ‰ values given by the Isodat software on the remaining nine peaks. The final $\delta^{2}H$ ‰ values and associated statistical parameters given for each water sample were calculated two ways: using the average $\delta^{2}H$ ‰ value of the nine peaks for each sample (intra) and using each $\delta^{2}H$ ‰ value for every peak in each sample (inter). This latter method provided a much bigger population of experimental results (nine values per individual sample) than just using one value (average of nine values) per sample. Both statistical treatments of data yielded essentially identical results for each water sample given in the Summary.

Sample Preparation

The exetainer sample tubes were cleaned by washing in a soap bath and followed by multiple Science Center RO water rinses. Next, the vials were placed in a RO water bath to soak (as a final rinse) at least overnight. Each vial was then removed from the bath and given an acetone rinse. The vials were then placed into an oven to be baked out. The oven was set at ~ 150°C, and the vials were left in at least overnight. After baking, the vials were wrapped in new, clean aluminum foil for storage.

The exetainer vials for the first analysis (samples which were previously subjected to $\delta^{18}O$ analysis) were subjected to the above cleaning procedure prior to their being analyzed for $\delta^{18}O$. After the $\delta^{18}O$ analysis the vial caps were removed and the used septa were replaced with new septa, a Platinum catalyst stick was placed in the vial and the vial cap (with new septa) was replaced.

The sample preparation was as follows:

- Into a clean, dry and labeled exetainer vial, 200 µL of water sample were placed using a pipette. (Sample blanks did not contain the water.)
- A Platinum catalyst stick was placed in the sample vial ensuring that the platinum was not submerged in the sample.
- A cap with a new septum was then placed on the exetainer tube to seal it.

- Vials were placed into the GasBench sample block (maintained at ~ 30ºC) and the cover was secured.
- Each sample vial was then flush-filled with 2% H_2 in Helium gas before the analysis.
    - Attach the two flush-fill needles to the PAL autosampler (two sample vials will be flush filled (FF) at the same time).
    - Turn the T-valve so it points away from the GasBench (towards the ConFlo for the mixed gas FF's, towards the GasBench is the He FF for carbonate analysis).
    - In Isodat Acquisition, verify instrument configuration is set for GasBench+PAL, click the mouse on the GasBench flush-fill button in the GasBench area, this will purge the 2% H_2 in Helium gas flush-fill line. Note: If open, always close Isodat Instrument Control before using Isodat Acquisition.
    - Allow the 2% H_2 in Helium gas line to purge for ~ 15 minutes.
    - Use the ***FlushFill_H2He_6min.seq*** (see Figure 10) as a template (in Workspace), create a flush-fill sequence for the appropriate number of samples.
    - Ensure the sequence contains the correct method, ***H2He_Vial_Flush_6min.met.***
    - Ensure the use of an appropriate AS Method, **Internal No 1, (A200S-1) 6 injections of 61 seconds each** (see Figure 5).
    - Rename and save the sequence just created. Close the sequence.
    - In Acquisition, start the flush-fill sequence just created. Identify the folder for the data with the date and type of analysis. Note: To minimize potential computer issues, it is recommended to reset the computer before starting any extended analysis sequence.
    - Once started, verify the flush-fill flow rate by placing a flow meter onto the vent tube of the flush-fill needle (check this on both needles!), the flow rate should be ~ 125 mL/min.
- When the Helium flush-fill has been completed, turn the T-valve back 90° to point to the back wall and shut off the 2% H_2 gas in Helium at the cylinder.
- Remove both flush-fill needles from the PAL autosampler.
- The ^2H incorporation/equilibration from the H_2O to the H_2 in the vial headspace is finished within ~ 40 minutes after the addition of the flush-fill gas mixture. The analysis process can typically commence as soon as the flush-fill sequence is completed.
- Attach the sampling needle to the left position on the PAL autosampler syringe holder, leave the right position empty.
- Open Instrument Control software, check and record the MS pressure.
- Open the GasBench inlet valve on the IRMS.
- Wait a few minutes for the pressure to stabilize, and record the pressure.
- Turn on the filament.
- Monitor m/z 18 (H_2O) on cup 3. (The m/z 18 signal should drop below 1000 mV within 1 – 2 hours of turning on the filament.)
- Open the H_2 reference gas cylinder.
- ***DANGER!!!:*** *Due to the explosive nature of H_2 gas, the H_2 cylinder is only open when a δ^2H analysis is being performed. Shut off the H_2 gas at the cylinder after the δ^2H analysis is complete.*

- Determine the optimal Electron Energy setting. This is done to reduce the contribution to peak distortion of doubly charged He ions (He^{2+}) created in the ion source. This needs to be performed before the first δ^2H analysis sequence, and does not need to be repeated unless a different analysis (i.e. $\delta^{18}O$) has been performed.
    - Perform a peak center with the H_2 reference On.
    - Switch the H_2 reference Off.
    - Record the signal intensity of m/z 2 versus the electron energy.
    - Adjust the electron energy up or down and repeat the previous three steps at multiple electron energy settings.
    - The preferred electron energy setting is just below the appearance of the He^{2+} signal, where the sensitivity for H_2 is optimal.
    - When the optimal electron energy has been determined, set the value in the Focus Delta administrative panel, and then click *Pass to Gasconfiguration*. Note: If this is not done, the electron energy will revert back to its previous value.
- Adjust the Hydrogen Calibration, (this needs to be performed before the first δ^2H analysis sequence, it does not need to be repeated unless a different analysis (i.e. $\delta^{18}O$) has been performed).
    - Switch the H_2 reference gas on.
    - Set the magnet to approximately 1000 magnet steps (right clicking on the magnet steps value allows the magnet steps to be edited).
    - Select *Pass to Gasconfiguration* in the Focus Delta administrative panel.
    - Force the IRMS to jump to m/z 2 by changing the Gas Configuration to CO_2 and back to H_2.
    - Adjust the magnet steps value to hit the peak center (maximize signal), then repeat the last two steps. The setting is precise enough if the jump finds 50% of peak intensity. The IRMS will now correctly jump to m/z 2 and m/z 3 (cups 1 and 5).
- With the m/z 18 signal below ~1000 mV, perform an autofocus for H_2 using Autofocus_H2_(Date) file in Instrument Control. Turn on the H_2 reference gas.
- Typically use the following parameters in the Autofocus dialog box (see Figure 2):
    - Measuring Channel: 2
    - Integration Time: 0.100(s)
    - Minimum Step Width: 1
    - Maximum Step Width: 10
    - Minimum delay time(ms): 50
    - Maximum delay time(ms): 500
    - Maximum iterations: 3
    - Simulated Poti Turns: 2
    - Accelerating Voltage: unchecked
    - Electron Energy: unchecked
    - Emission: unchecked
    - Trap: unchecked
    - X-Deflection: **Checked**
    - Focus Voltage: **Checked**
    - Extraction Voltage: unchecked

    - Y-Defl Voltage: **Checked**
    - Focus Symmetry: **Checked**
    - Extraction Symmetry: **Checked**
    - Y-Defl Symmetry: **Checked**
- Repeat the autofocus until there is no further H_2 signal improvement.
- Select *Pass to Gasconfiguration* in the Focus Delta administrative panel.
- Perform on-off (H**2_On-Off.met**) and linearity (H**2_On-Off.met**) system suitability using H_2 as the reference gas. **δ^2H - On-Off: std.dev. < 0.5‰, δ^2H - Linearity: regression slope std. dev. < 1.0‰ with increasing H_2 pressure** (see Figures 12 and 13).
- Calculate the H_3^+ Factor using the latest H_2 linearity file.
- Click on the H_3^+ button then on "Top CF Document" and choose a linearity file for the calculation of the H_3^+ Factor. Click on "Determine". The H_3^+ Factor will be calculated by Isodat. A low and stable H_3^+ Factor is needed for good δ^2H determination. An H_3^+ factor of 10 or less is desirable, but 12 or less is acceptable (see Figure 3).
- If the H_3^+ Factor is not acceptable, click cancel and perform another linearity test and repeat the H_3^+ Factor determination until an acceptable factor is obtained.
- Confirm the calculated H_3^+ value by clicking Ok. This H_3^+ factor will be used for further data acquisitions (see Figure 4).
- Adjust the H_2 reference gas to give a reference peak (m/z 2, cup 1) signal of between 6000 and 8000 mV (m/z 3 ~ 2000 mV). Close Instrument Control, open Isodat Acquisition.
- Create, identify, and save a new analysis sequence using the file ***H2_50_Samples.seq*** as a template (see Figure 11). The limiting factor for analyzing 50 samples per sequence is due to the current supply of 50 Platinum catalyst sticks on-hand. An analysis sequence can be performed on up to 96 samples (limited by the capacity of the sample tray).
- Use ***H2_100uL_Loop_Sample.met*** as the analysis method (see Figures 6 – 9).
- Ensure the correct autosampler method is entered in the sequence, **Internal No. 9 (A200S-9) 11 injections of 59 seconds each** (See Figure 5).
- Verify that Isodat Acquisition, and Isodat Workspace programs are open (and Instrument Control is closed). Note: To minimize potential computer issues, it is recommended to reset the computer before starting any extended analysis sequence.
- In Acquisition, check and record mass spectrometer pressure, the CO_2, N_2, H_2, m/z 18 (cup 3), m/z 32 (cup 3), and m/z 40 (cup 3) intensities.
- Verify system readiness for analysis, e.g., Helium tank pressures, capillary column temperature, T-valve position, alignment of syringes, vial location and identification, etc.
- Verify that the correct sequence has been selected and double check the information.
- When all is correct, click "Start".
- Identify the folder in which the data files are to be stored (typically use H2 followed by an underscore and then the analysis date).
- Next choose how to identify the data files.
- Un-check the "Auto Enum" button.
- Start the analysis by checking the "OK".

- Completed files can be reviewed in Isodat Workspace…\Results\filename. (see Figures 14 – 16, respectively, for example chromatograms of a blank, a Primary standard, and a Lab standard).
- When the analysis is complete, review the files in Workspace to verify all samples were properly acquired and analyzed. (It is useful to record any anomalous findings or notes on the analysis worksheet.)
- Turn off the H_2 gas at the gas cylinder.
- Print the data files in Workspace.
- Re-process the data files using the export file ***GB_H2_Export.wke***, this will put the data into EXCEL format (see Figure 17).
- Transfer the re-processed data via an appropriate technique to another computer for statistical analysis.
    - First copy the data into a new worksheet.
    - Clean up the spreadsheet, set significant figures, alignments, headings, etc, to make the spreadsheet easier to handle and interpret.
    - Sort on "Peak No." to separate out the reference peaks.
    - Cut and paste the reference peak data into a new worksheet.
    - After the reference peaks have been removed, sort on the sample ID.
    - Create a calibration curve for δ^2H ‰ using the primary standards, plot the known values vs. the IRMS determined values.
    - Plot the trend line, the equation of the trend line is the regression formula used to determine the corrected δ^2H ‰ values.
    - Perform statistical analysis (mean, standard deviation, accuracy, and %CV) on all average δ^2H ‰ values determined for each sample. This is the intra-statistical analysis.
    - Next, perform the same statistical analysis on all the individual peaks of each sample. This is the inter-statistical analysis.

Instrument Conditions

GasBench

- Capillary Column Temperature - 70ºC
- Capillary Column Flow Rate – 1.0 ml/min - 1.5 ml/min
- Sample Block Temperature - 30ºC
- Flush-Fill Flow rate - ~125mL/min
- He Pressure (at Tank) – 50 psi
- He pressure (at GasBench) – 13 – 14 psi (flow rate ~ 0.8 ml/min)
- 2% H_2 in He pressure (at Tank) - ~ 45 psi (adjust to give ~ 125ml/min FF rate)
- H_2 pressure – at Tank – ~35 psi
  at GasBench – adjust to 6 – 8 volts m/z 2 signal in cup 1

PAL

- Syringe Configuration – 10 µL
- FlushFill method – Internal 1
- Analysis method – Internal 9

IRMS

- Electron Energy – ~ 96 eV
- Tune File – e.g.: autofocus_H2_(Date of last tune)
- High Vacuum (MS Valve open) – ~ 5.5e-7 mB
- High Vacuum (MS Valve closed) - ~9.5e-8 mB
- Instrument configuration – GasBench+PAL
- H_2 reference peak intensity (m/z 2 cup 1) - ~ 6000 mV
- Method – FlushFill – H2He_Vial_Flush_6min.met
  Analysis – H2_100uL_Loop_Sample.met

2.4. WATER STANDARD VALIDATION DATA

The Excel files used for this validation can be found on the Hamilton College network, the path is Campus on ESS P:\Instrumentation\Geosciences\Data\Thermo_IRMS\GasBench\Water\Deuterium\Validation(file names). The file names and contents are listed below:

1. H2_082509_After_18O.xlsx – Validation day 1 results, after $\delta^{18}O$ analysis
2. H2_082809_Val_1.xlsx – Validation day 2 results
3. H2_083109_Val_2.xlsx - Validation day 3 results
4. H2_090209_Val_3.xlsx - Validation day 4 results
5. H2_090909_Sec_Primary.xlsx – Day 5, experimentally determined values for Secondary standards used to determine Primary standard values
6. H2_Validation_Summary.xlsx – Accuracy and precision analysis for all analyses performed during validation

Table 1:

Summary Statistics for Day 1 Validation - Primary Standards

File Name: H2_082509_After_18O.xlxs

Primary Standards Statistics	
SLAP2	**δ^2H ‰**
average	-432.503
Std. Deviation	4.805
%CV	1.11
%Acc	101.17
n	3
Known $\delta^2H_{VSMOW/SLAP}$	-427.5
VSMOW2	**δ^2H ‰**
average	-4.762
Std. Deviation	3.733
%CV	78.39*
%Acc	*
n	3
Known $\delta^2H_{VSMOW/SLAP}$	0.00
GISP	**δ^2H ‰**
Average	-191.705
Std. Deviation	6.566
%CV	3.43
%Acc	101.16
n	3
Known $\delta^2H_{VSMOW/SLAP}$	-189.5

Note: %CV = Coefficient of Variation

%Acc = Accuracy

* Value skewed due to zero being the target value

Table 2:

Summary Statistics for Day 1 Validation – Secondary Standards

File Name: H2_082509_After_18O.xlxs

Secondary Standards Statistics	
Well	**δ^2H ‰**
average	-78.430
Std. Deviation	4.897
%CV	6.24
n	7
Prepared Lab Standard	**δ^2H ‰**
average	+245.975
Std. Deviation	4.831
%CV	1.96
n	7
Bottled Distilled	**δ^2H ‰**
average	-47.222
Std. Deviation	4.582
%CV	9.70
n	6
Vostok	**δ^2H ‰**
average	-434.889
Std. Deviation	5.835
%CV	1.34
n	7

Note: %CV = Coefficient of Variation

%Acc = Accuracy

Table 3:

Summary Statistics for Day 2 Validation - Primary Standards

File Name: H2_082809_Val_1.xlxs

Primary Standards Statistics	
SLAP2	**δ^2H ‰**
Average	-427.897
Std. Deviation	4.443
%CV	1.04
%Acc	100.09
n	3
Known $\delta^2H_{VSMOW/SLAP}$	-427.5
VSMOW2	**δ^2H ‰**
Average	-0.745
Std. Deviation	3.714
%CV	498.52*
%Acc	*
n	3
Known $\delta^2H_{VSMOW/SLAP}$	0.00
GISP	**δ^2H ‰**
Average	-191.843
Std. Deviation	4.804
%CV	2.50
%Acc	101.24
n	3
Known $\delta^2H_{VSMOW/SLAP}$	-189.5

Note: %CV = Coefficient of Variation

%Acc = Accuracy

* Value skewed due to zero being the target value

Table 4:

Summary Statistics for Day 2 Validation - Secondary Standards

File Name: H2_082809_Val_1.xlxs

Secondary Standards Statistics	
Well	**δ^2H ‰**
Average	-80.117
Std. Deviation	4.079
%CV	5.09
n	8
Prepared Lab Standard	**δ^2H ‰**
average	+244.474
Std. Deviation	4.773
%CV	1.95
n	8
Bottled Distilled	**δ^2H ‰**
Average	-46.925
Std. Deviation	3.796
%CV	8.09
n	8
Vostok	**δ^2H ‰**
average	-435.027
Std. Deviation	4.372
%CV	1.00
n	9

Note: %CV = Coefficient of Variation
%Acc = Accuracy

Table 5:

Summary Statistics for Day 3 Validation - Primary Standards

File Name: H2_083109_Val_2.xlxs

Primary Standards Statistics	
SLAP2	**δ^2H ‰**
average	-423.879
Std. Deviation	12.142
%CV	2.86
%Acc	99.15
n	3
Known $\delta^2H_{VSMOW/SLAP}$	-427.5
VSMOW2	**δ^2H ‰**
average	0.480
Std. Deviation	8.874
%CV	1848.75*
%Acc	*
n	3
Known $\delta^2H_{VSMOW/SLAP}$	0.00
GISP	**δ^2H ‰**
average	-187.129
Std. Deviation	9.435
%CV	5.04
%Acc	98.75
n	3
Known $\delta^2H_{VSMOW/SLAP}$	-189.5

Note: %CV = Coefficient of Variation

%Acc = Accuracy

* Value skewed due to zero being the target value

Table 6:

Summary Statistics for Day 3 Validation - Secondary Standards

File Name: H2_083109_Val_2.xlxs

Secondary Standards Statistics	
Well	**δ^2H ‰**
Average	-73.403
Std. Deviation	9.229
%CV	12.57
n	8
Prepared Lab Standard	**δ^2H ‰**
average	+245.069
Std. Deviation	8.880
%CV	3.62
n	8
Bottled Distilled	**δ^2H ‰**
Average	-41.077
Std. Deviation	9.225
%CV	22.46
n	8
Vostok	**δ^2H ‰**
average	-425.854
Std. Deviation	11.810
%CV	2.77
n	9

Note: %CV = Coefficient of Variation

%Acc = Accuracy

Table 7:

Summary Statistics for Day 4 Validation - Primary Standards

File Name: H2_090209_Val_3.xlxs

Primary Standards Statistics	
SLAP2	**δ^2H ‰**
Average	-426.339
Std. Deviation	6.900
%CV	1.62
%Acc	99.73
n	3
Known $\delta^2H_{VSMOW/SLAP}$	-427.5
VSMOW2	**δ^2H ‰**
Average	-1.554
Std. Deviation	4.093
%CV	263.34*
%Acc	*
n	3
Known $\delta^2H_{VSMOW/SLAP}$	0.00
GISP	**δ^2H ‰**
average	-188.905
Std. Deviation	6.562
%CV	3.47
%Acc	99.69
n	3
Known $\delta^2H_{VSMOW/SLAP}$	-189.5

Note: %CV = Coefficient of Variation

%Acc = Accuracy

* Value skewed due to zero being the target value

Table 8:

Summary Statistics for Day 4 Validation - Secondary Standards

File Name: H2_090209_Val_3.xlxs

Secondary Standards Statistics	
Well	**δ^2H ‰**
Average	-74.871
Std. Deviation	5.160
%CV	6.89
n	8
Prepared Lab Standard	**δ^2H ‰**
average	+246.748
Std. Deviation	5.077
%CV	2.06
n	8
Bottled Distilled	**δ^2H ‰**
Average	-43.591
Std. Deviation	5.906
%CV	13.55
n	8
Vostok	**δ^2H ‰**
average	-426.665
Std. Deviation	7.645
%CV	1.79
n	9

Note: %CV = Coefficient of Variation

%Acc = Accuracy

Table 9:

Summary Statistics for Day 5 (Secondary-to-Primary) Primary Standards

File Name: H2_090909_Sec_Primary.xlxs

Primary Standards Statistics	
SLAP2	**δ^2H ‰**
average	-430.999
Std. Deviation	2.971
%CV	0.69
%Acc	100.82
n	6
Known $\delta^2H_{VSMOW/SLAP}$	-427.5
VSMOW2	**δ^2H ‰**
average	-3.399
Std. Deviation	3.416
%CV	100.50*
%Acc	*
n	6
Known $\delta^2H_{VSMOW/SLAP}$	0.00
GISP	**δ^2H ‰**
average	-190.771
Std. Deviation	2.641
%CV	1.38
%Acc	100.67
n	6
Known $\delta^2H_{VSMOW/SLAP}$	-189.5

Note: %CV = Coefficient of Variation

%Acc = Accuracy

* Value skewed due to zero being the target value

Table 10:
Summary Statistics for Day 5 (Secondary-to-Primary) Secondary Standards

File Name: H2_090909_Sec_Primary.xlxs

Secondary Standards Statistics	
Well	**δ^2H ‰**
average	-79.509
Std. Deviation	2.682
%CV	3.37
%Acc	103.66
n	5
Experimentally Determined $\delta^2H_{VSMOW/SLAP}$	-76.705
Prepared Lab Standard	**δ^2H ‰**
average	+244.141
Std. Deviation	2.949
%CV	1.21
%Acc	99.42
n	5
Experimentally Determined $\delta^2H_{VSMOW/SLAP}$	+245.566
Bottled Distilled	**δ^2H ‰**
Average	-46.467
Std. Deviation	2.698
%CV	5.81
%Acc	103.94
n	6
Experimentally Determined $\delta^2H_{VSMOW/SLAP}$	-44.704
Vostok	**δ^2H ‰**
Average	-434.992
Std. Deviation	2.829
%CV	0.65
%Acc	101.02
n	5
Experimentally Determined $\delta^2H_{VSMOW/SLAP}$	-430.609

Note: %CV = Coefficient of Variation
%Acc = Accuracy

Table 11:

Regression Line Equations used to correct δ^2H‰ Instrument Values

Analysis Date	Validation Day	Regression Line	R^2
08/25/2009	Day 1	y = 3.7948x + 2816.1	0.9985
08/28/2009	Day 2	y = 3.7631x + 2801.5	0.9998
08/31/2009	Day 3	y = 3.8216x + 2807.2	0.9943
09/02/2009	Day 4	y = 3.7656x + 2794.2	0.9969
09/09/2009	Day 5	y = 3.8092x + 2819.8	1.0000

3. COMMENTS

Three standards, in duplicate (one at the beginning of the analysis and one at the end) were used to generate the regression line.

The Primary Standards that were used in the regression line generation were not used in the calculations of the experimentally determined δ^2H ‰ read-back values or the statistics generated for them. Only the additional Primary Standards (n=3) analyzed in each run were used for this purpose.

An analysis of the δ^2H ‰ value determined for each sample was plotted versus acquisition time. It was determined that there was no temporal bias and as such no drift corrections of determined δ^2H ‰ values were made.

δ^2H ‰ values given in the above Tables originate from the "intra" values determined in the Excel spreadsheets since the "intra" and "inter" values were essentially identical.

Day 5 Validation (Secondary to Primary Standard experiment) was performed only to evaluate the integrity of the Lab (Secondary) Standards for regression line generation and subsequent sample read-backs. This data was not used in any statistical calculations. (Vostok, Well water, and the prepared Laboratory Standard sample were used to generate the regression line.)

%Accuracy = Experimental Value/Known (Established) Value X 100

4. DATA RETRIEVAL

The raw data files are stored on the Thermo IRMS instrument computer in the GeoSciences laboratory in the following location:
C:\Thermo\Isodat NT\Global\User\Gas Bench\Results\H2_Analysis Folder\
H2_082509\filename.dxf
H2_082809\filename.dxf
H2_083109\filename.dxf
H2_090209\filename.dxf
H2_090909_Sec_to_Primary\filename.dxf

The Excel Worksheets are stored on the Hamilton College network in the following location:

Campus on "ESS"(P:)\Instrumentation\Geosciences\Data\Thermo_IRMS\ GasBench\Water\Deuterium\Validation\filename.xlsx, and Campus on "ESS"(P:) \Instrumentation\Geosciences\Data\Thermo_IRMS\GasBench\Water\Deuterium\Analysis Worksheets\filename.xlsx.

5. CONCLUSIONS

This analysis identified water samples which could be used for Lab (Secondary) Standards during unknown δ^2H ‰ investigations. This validation also provided δ^2H ‰ values for these Lab Standards (to be used for regression line generation) along with statistical evaluations of those values. The following is a summary of the results:

Table 12: Secondary Standard Statistics Summary (Four Analysis Days)

Water Sample	$\delta^2H_{VSMOW/SLAP}$‰	Std. Dev.	%CV	n
Vostok	**-430.609**	7.42	1.72	34
Bottled Distilled	**-44.704**	5.88	13.15	30
Well	**-76.705**	5.84	7.61	31
Prepared Lab Standard	**+245.566**	5.89	2.40	31

The experimentally determined values and the statistics for the Primary Standards are given below to assess method accuracy and variability across the 4 days of validation:

Table 13: Primary Standard Statistics Summary (Four Analysis Days)

Primary Standard	δ^2H_{VSMOW}‰	Std. Dev.	%CV	% Acc	n
SLAP2	**-427.654**	7.07	1.65	100.04	12
GISP	**-189.895**	6.84	3.60	100.21	12
VSMOW2	**-1.645**	5.10	310.0*	*	12

* Value skewed due to zero being the target value

6. REFERENCES

Thermo Electron Delta V Advantage Operating Manual
Finnigan GasBench II Operating Manual

7. FIGURES

Figure 1: δ^2H Experimentally Determined Values, Sorted by δ^2H (average of four runs)

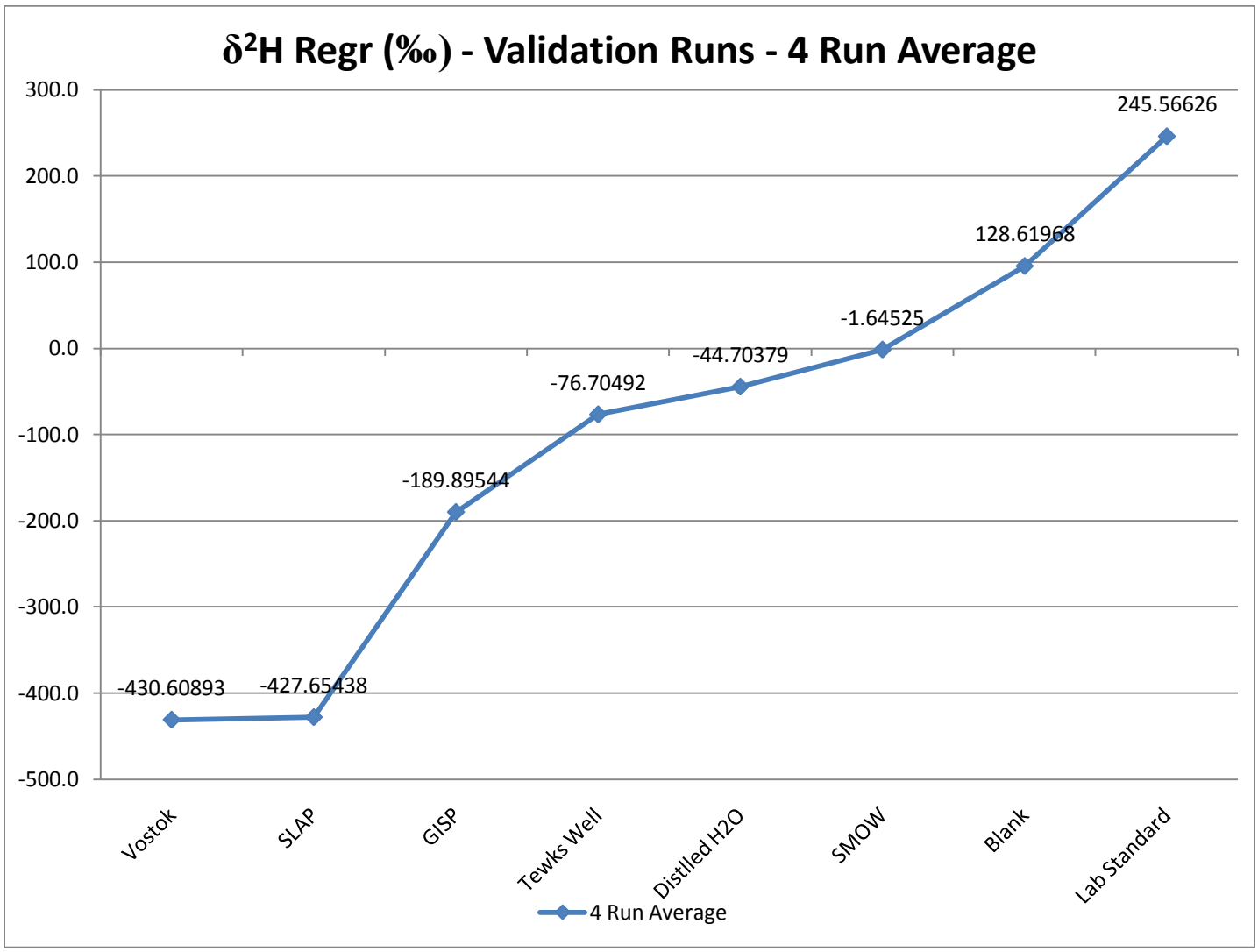


Figure 2: H_2 Autofocus Settings

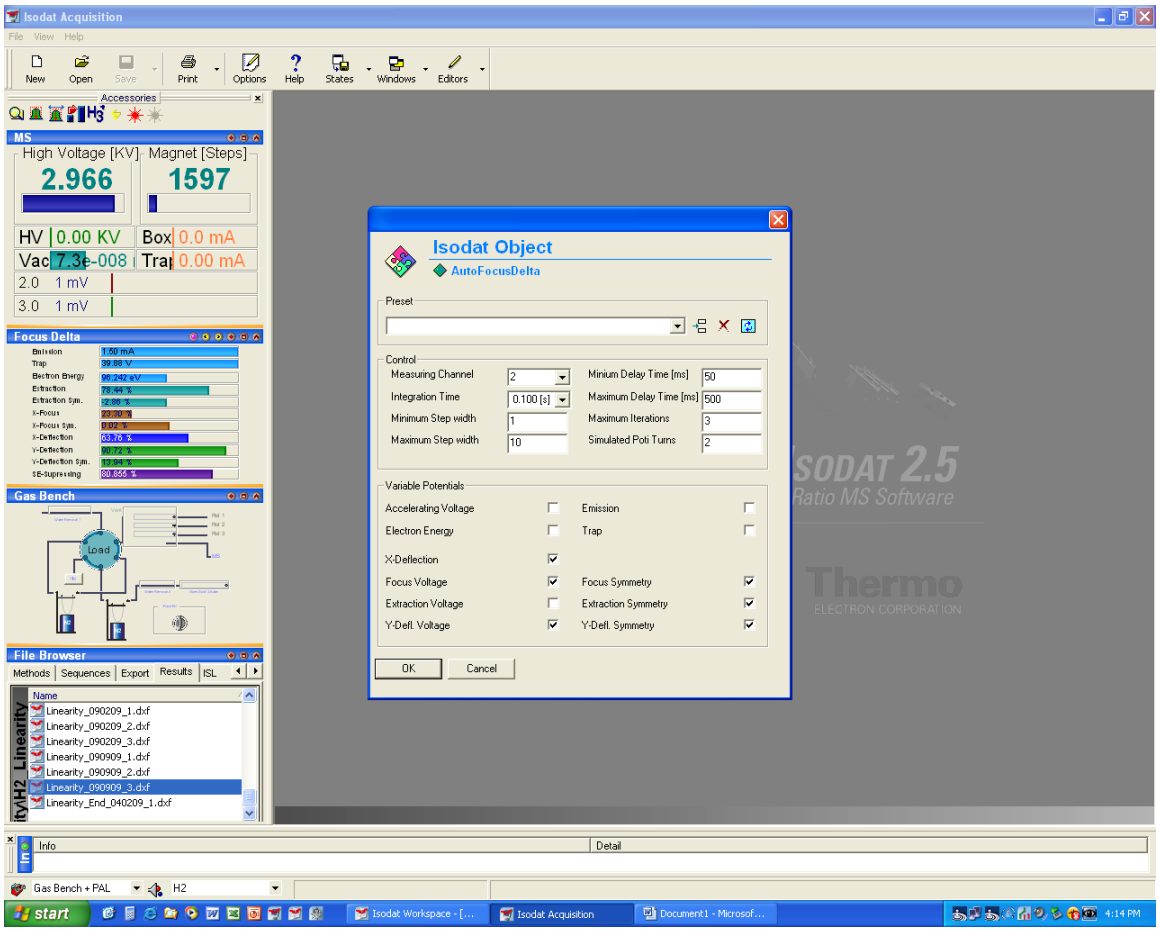


Figure 3: H_3^+ Factor Determination Screen

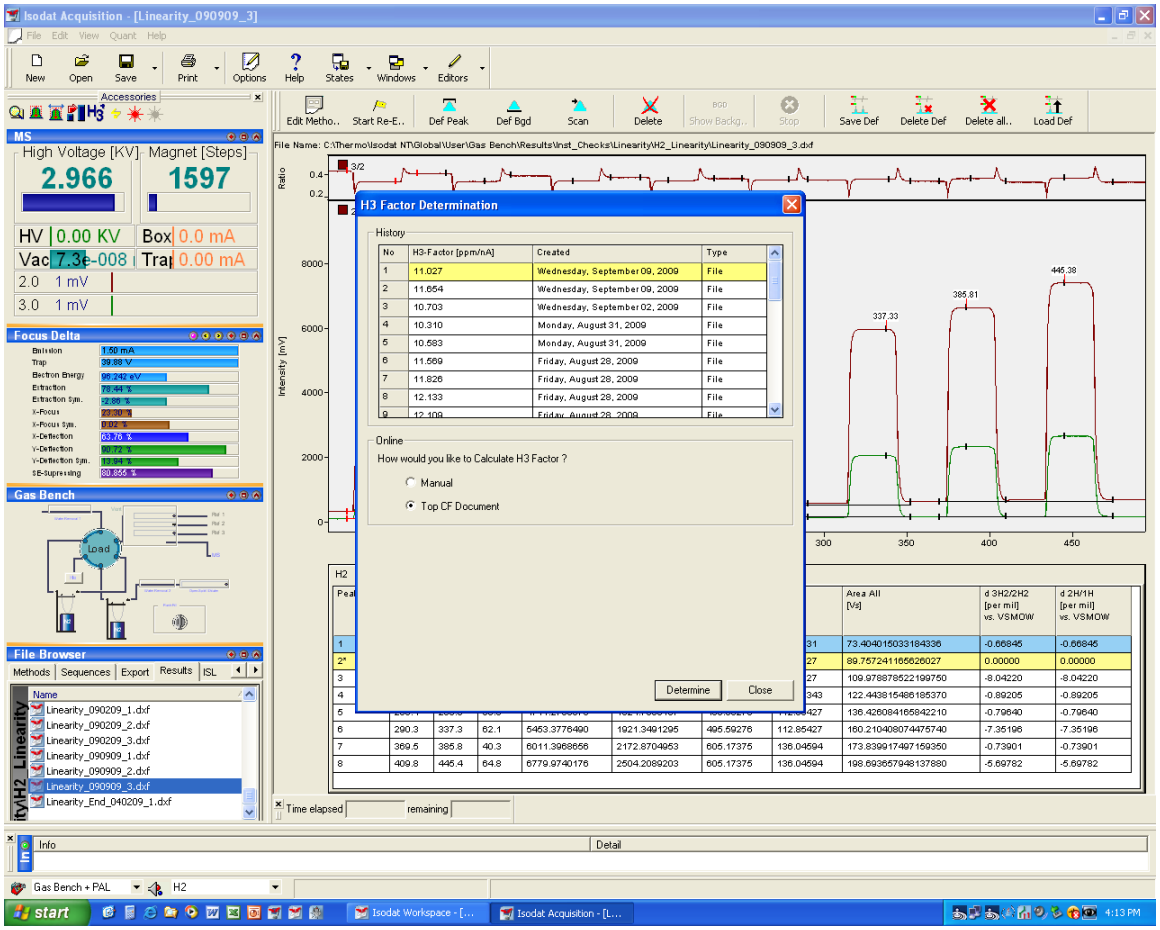


Figure 4: H_3^+ Factor Save Screen

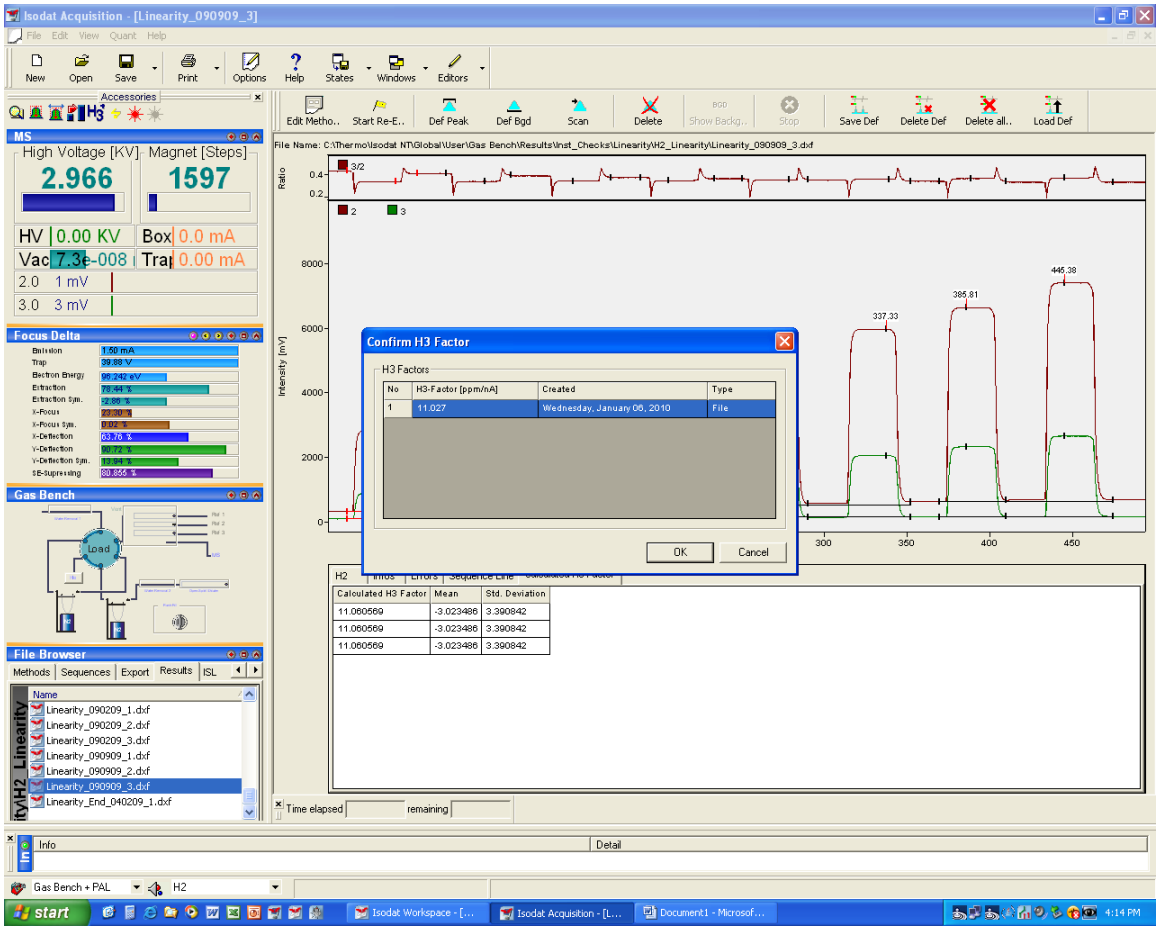


Figure 5: PAL Autosampler Setup

PAL Autosampler Methods for δ^2H Analysis and δ^2H FlushFill

Internal No. 1 (A200S-1) (FlushFill)	
Cycle	GC-Inj
Syringe	10 µL
Sample Volume	10.0 µL
Air Volume	0 µL
Pre Cln Slv1	0
Pre Cln Slv2	0
Pre Cln Spl	0
Fill Volume	0 nL
Fill Speed	5.0 µL /s
Fill Strokes	6
Pullup Del	61
Inject to	Flush
Inject Speed	50 µL /s
Pre Inj Del	0 ms
Pst Inj Del	0 ms
Pst Cln Slv1	0
Pst Cln Slv2	0

Internal No. 9 (A200S-9) (Analysis)	
Cycle	GC-Inj
Syringe	10 µL
Sample Volume	10.0 µL
Air Volume	0 µL
Pre Cln Slv1	0
Pre Cln Slv2	0
Pre Cln Spl	0
Fill Volume	0 nL
Fill Speed	5.0 µL /s
Fill Strokes	11
Pullup Del	59 s
Inject to	Flush
Inject Speed	50 µL /s
Pre Inj Del	0 ms
Pst Inj Del	0 ms
Pst Cln Slv1	0
Pst Cln Slv2	0

Figure 6: δ^2H Method File – Instrument Screen

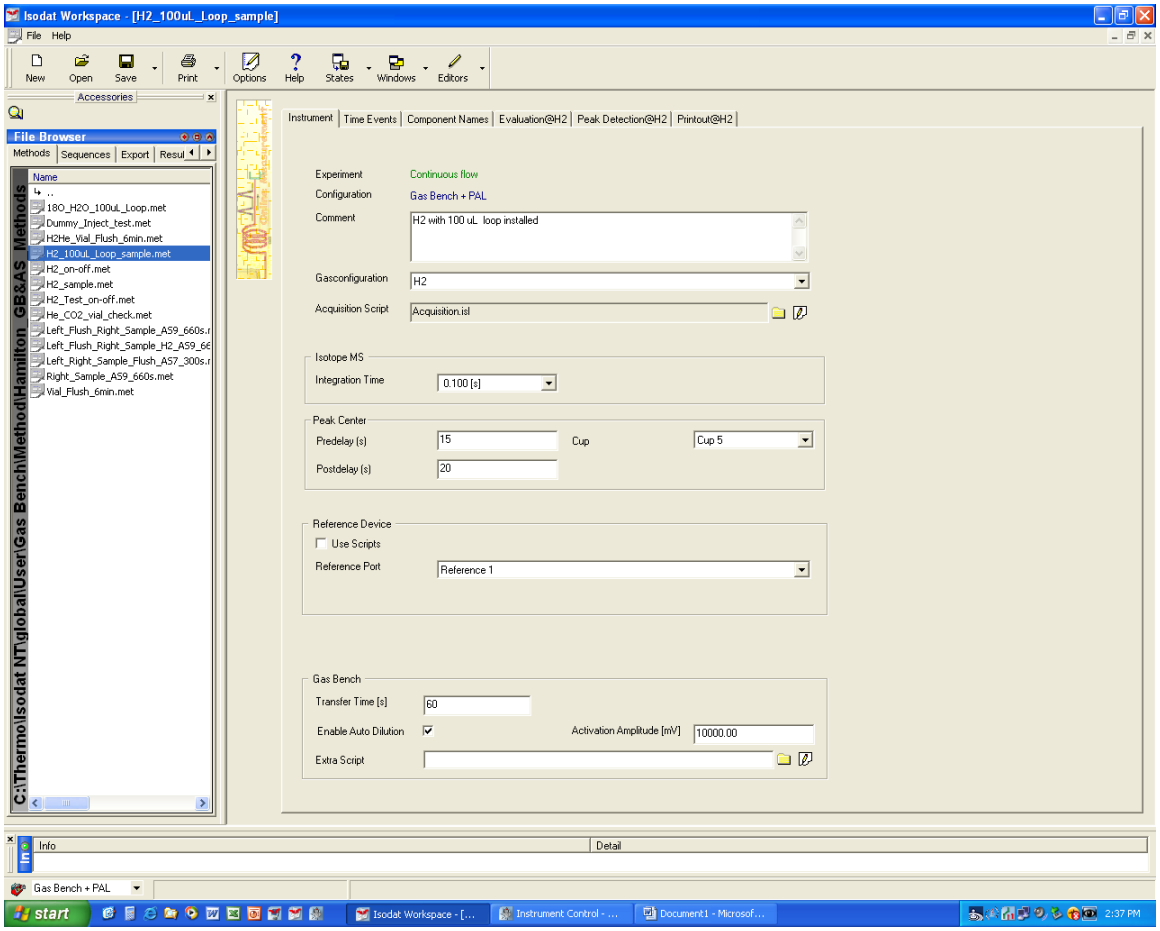


Figure 7: δ^2H Method File – Time Events Screen

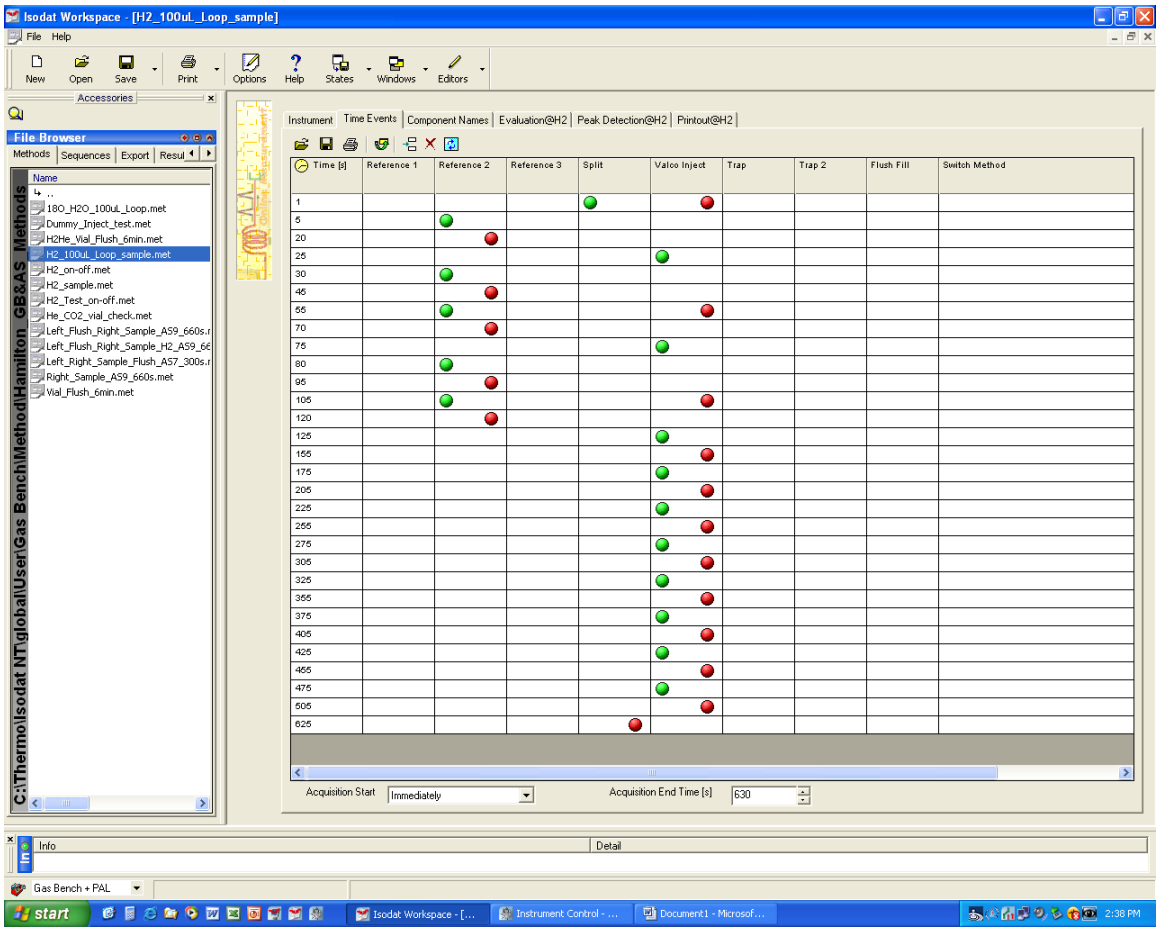


Figure 8: δ^2H Method File – Evaluation@H2 Screen

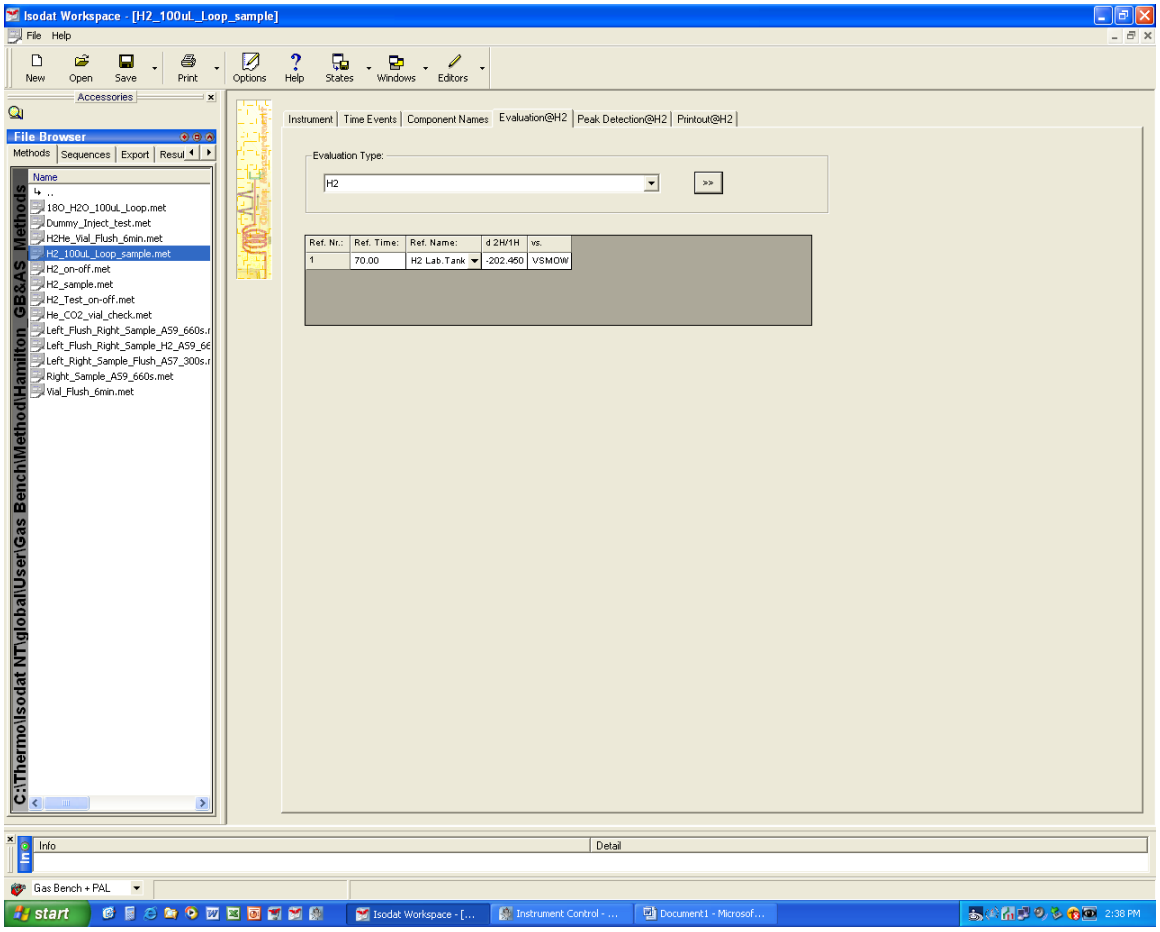


Figure 9: δ^2H Method File – Peak Detection@H2 Screen

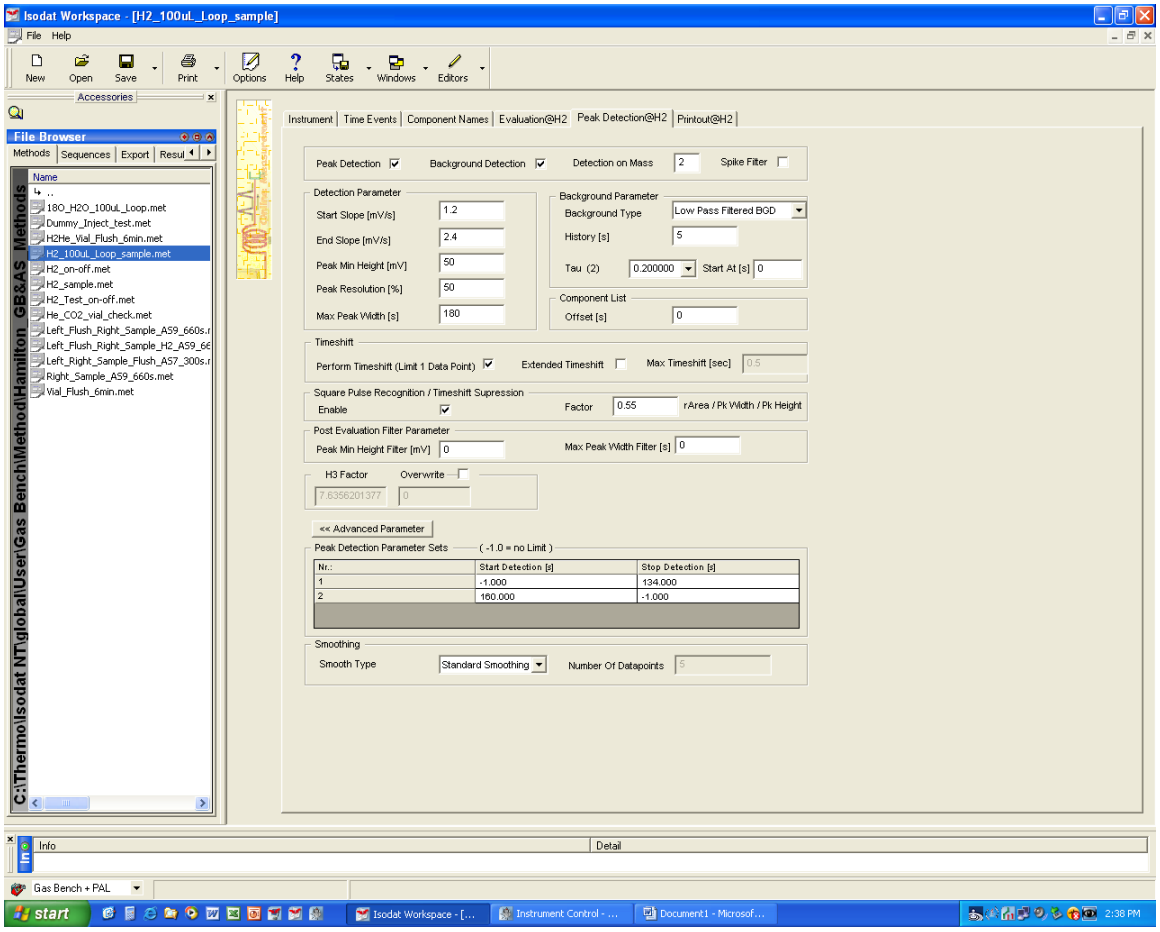


Figure 10: δ^2H Flush Fill Sequence File Example

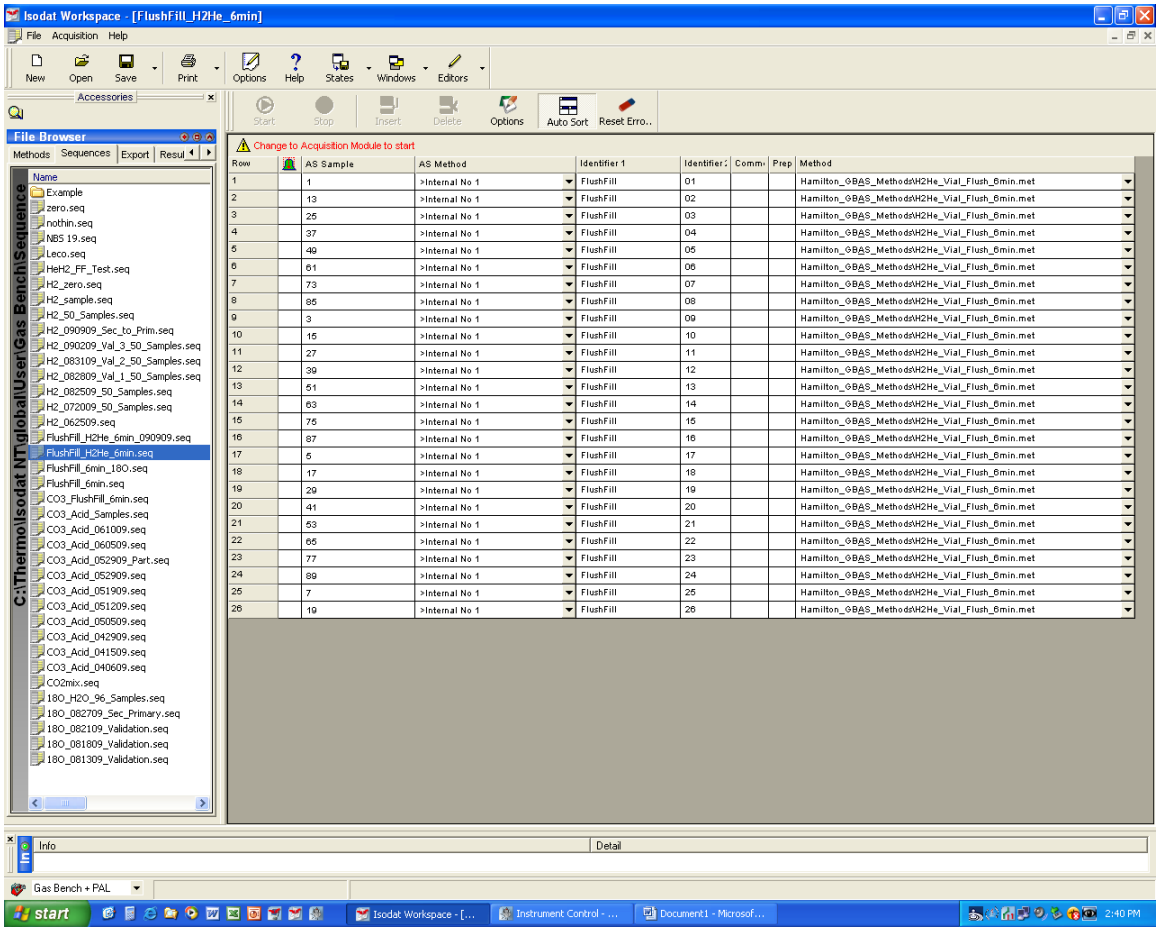


Figure11: δ^2H Analysis Sequence File Example

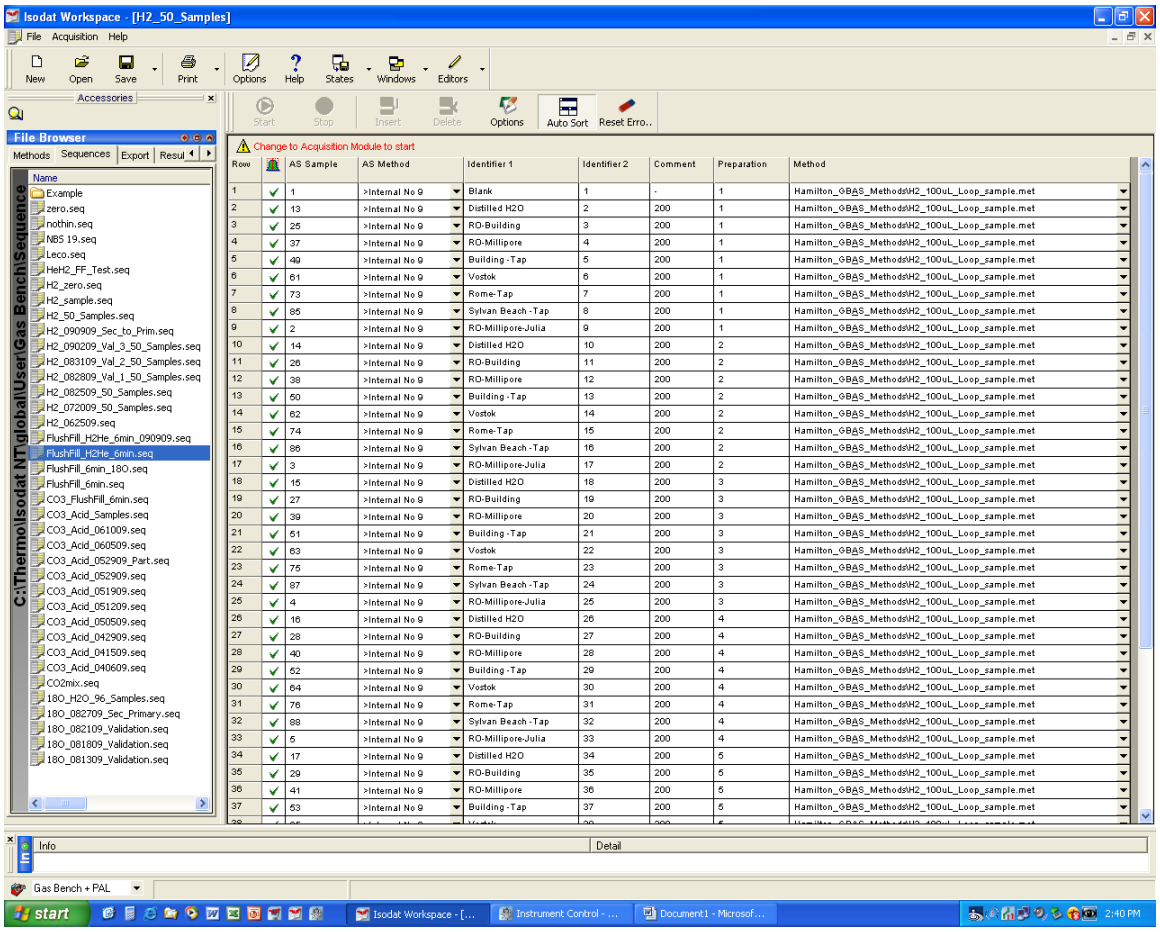


Figure 12: δ^2H On-Off Check (Using H_2)

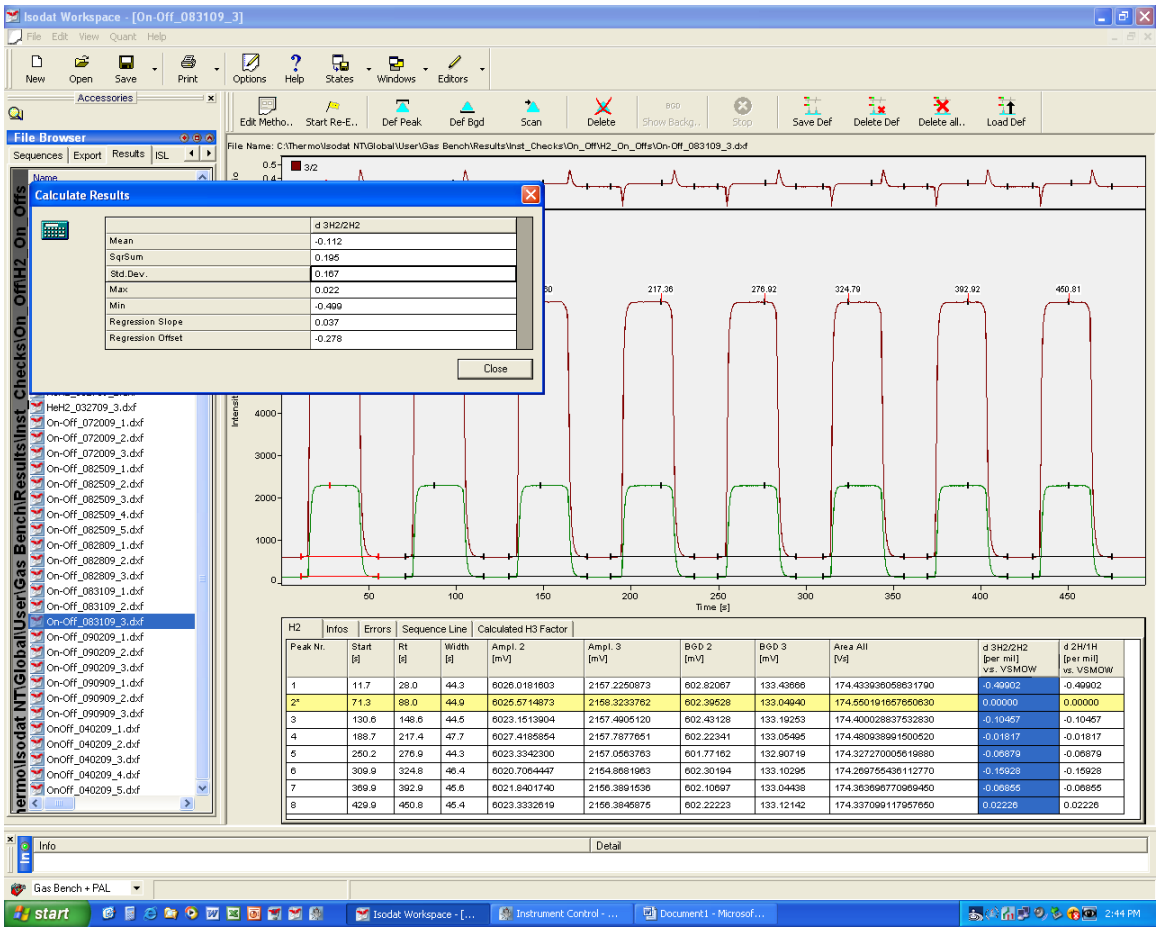


Figure 13: δ^2H Linearity Check (Using H_2)

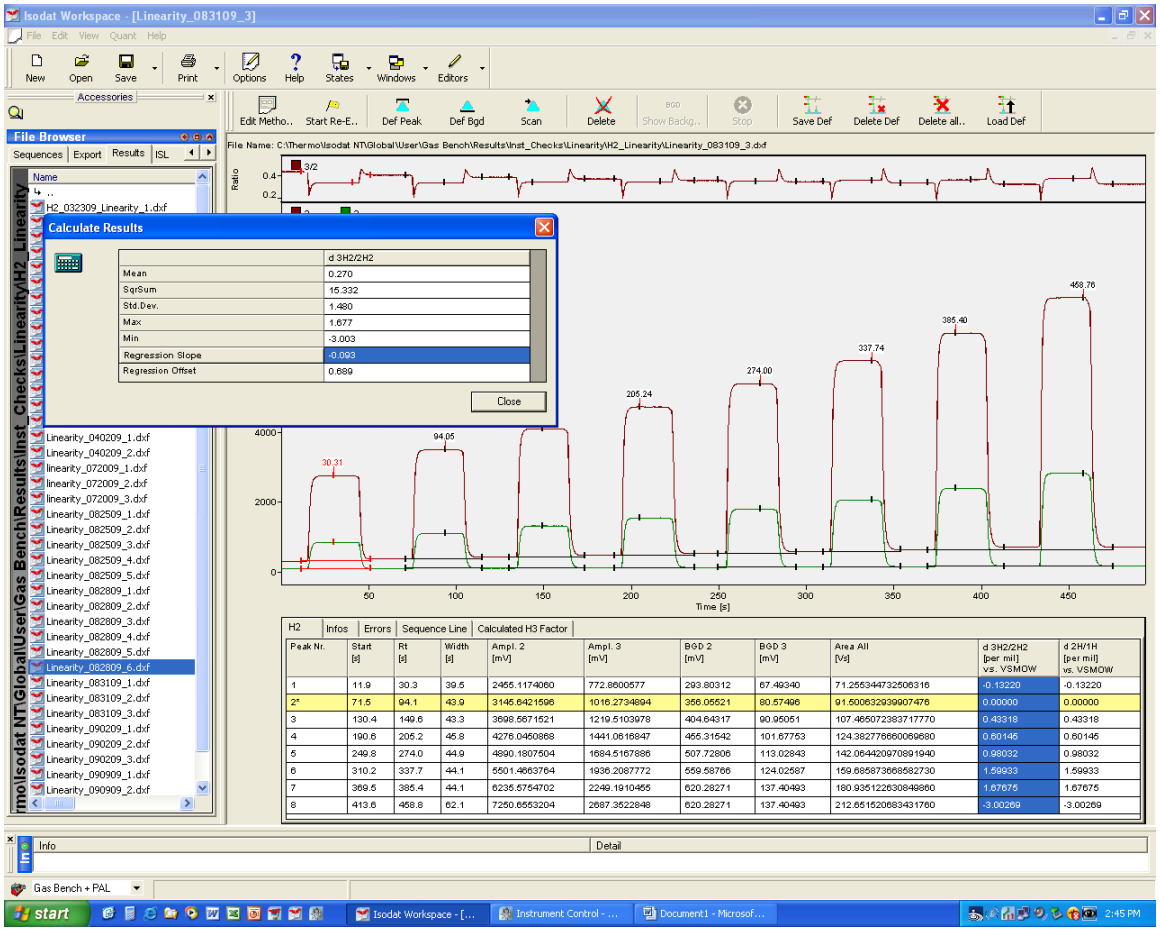


Figure 14: δ^2H Data Acquisition File – Blank

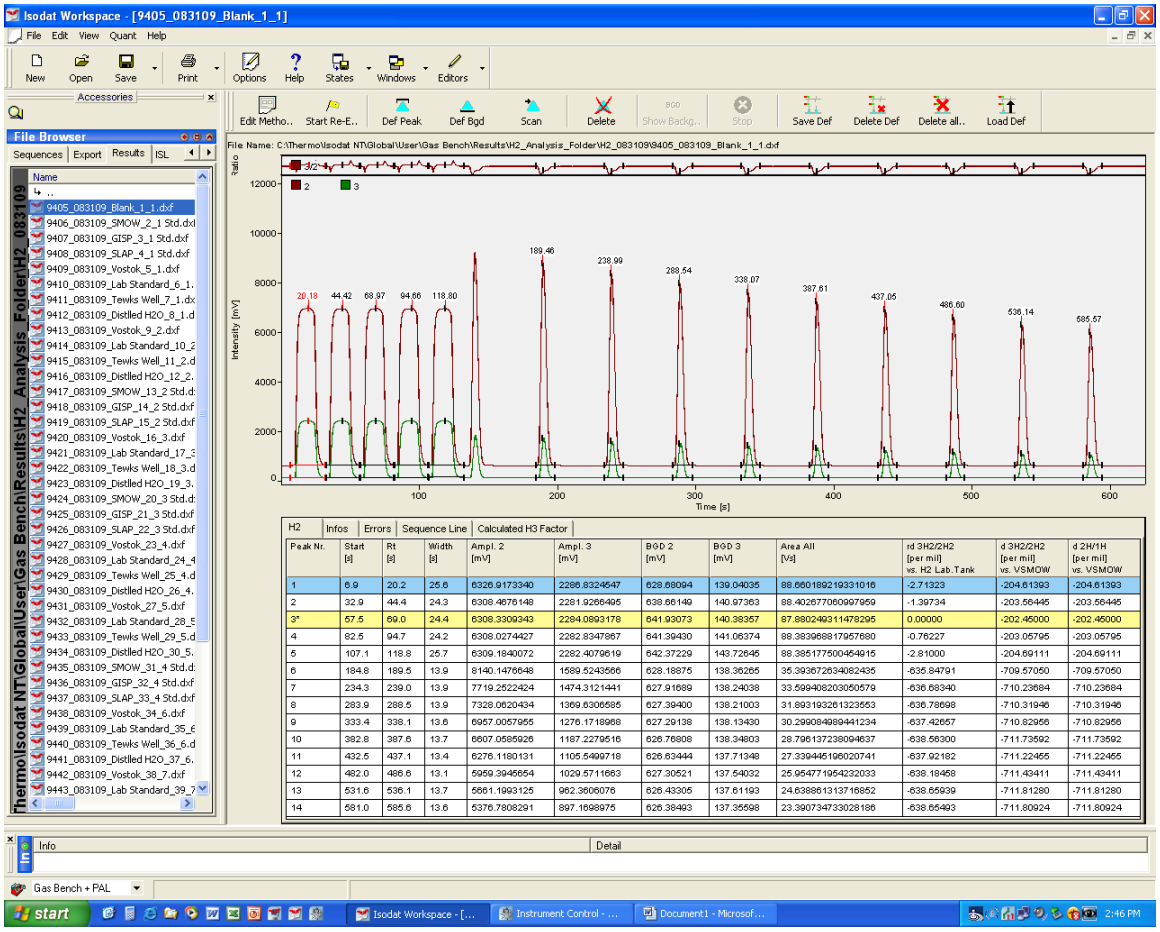


Figure 15: δ^2H Data Acquisition File – Primary Standard (GISP)

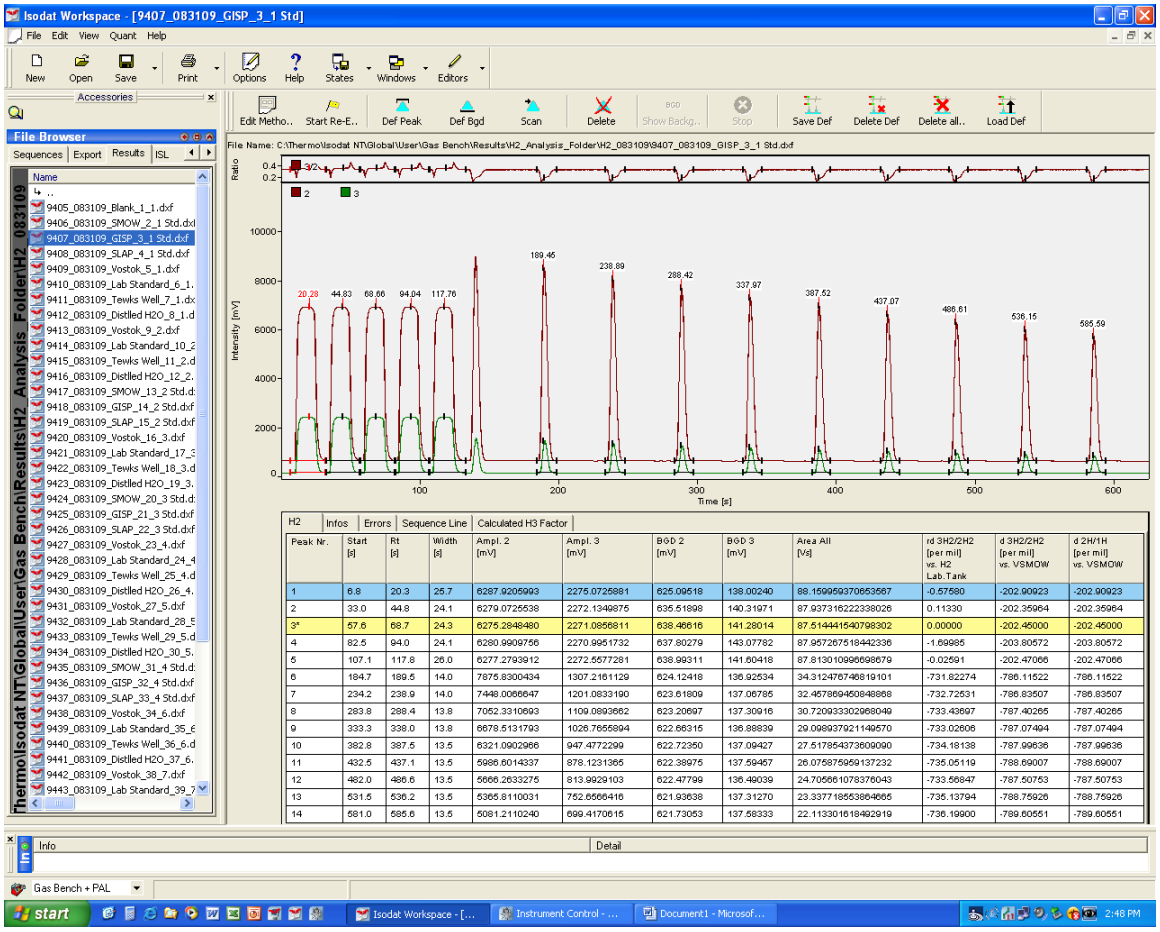
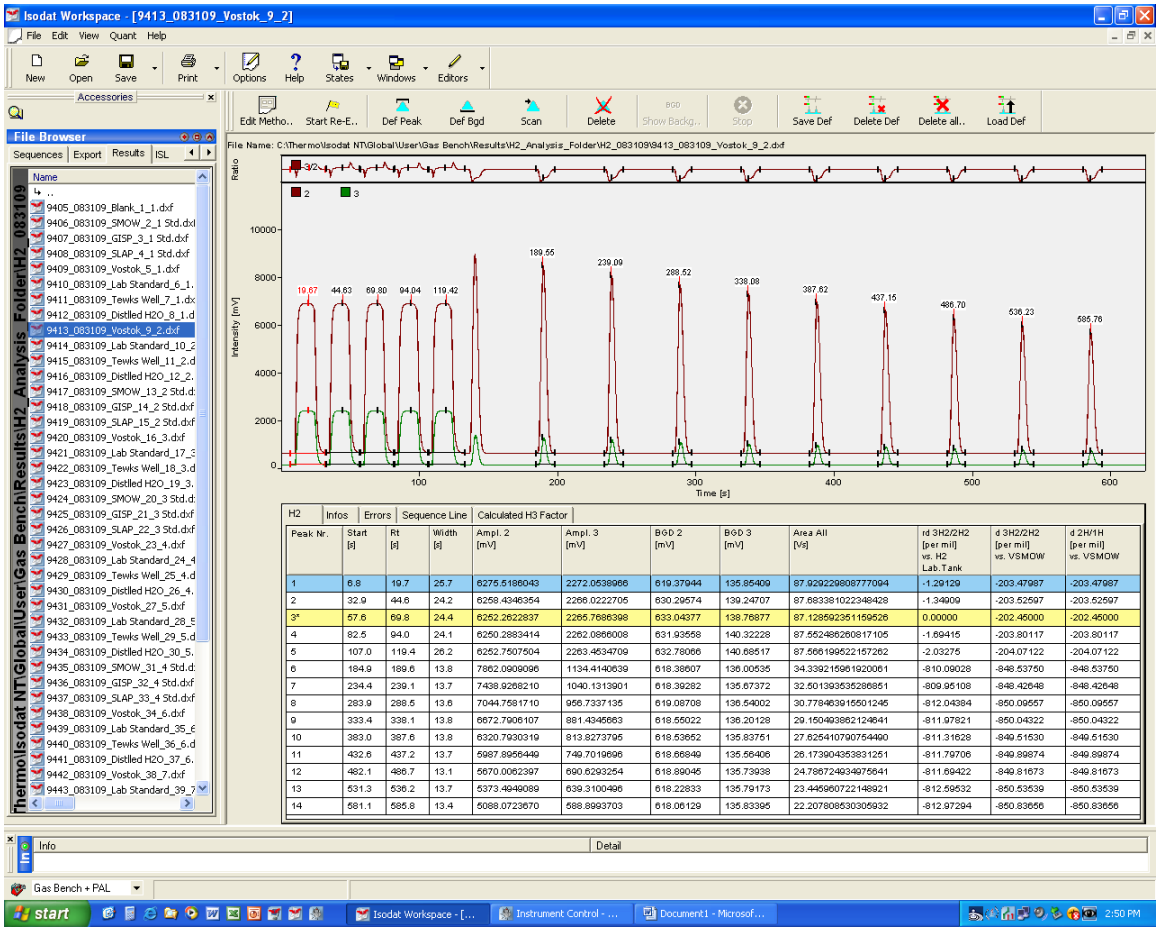


Figure 16: δ^2H Data Acquisition File – Sample (Vostok)



Peak Nr.	Start [s]	Rt [s]	Width [s]	Ampl. 2 [mV]	Ampl. 3 [mV]	BGD 2 [mV]	BGD 3 [mV]	Area All [Vs]	rd 3H2/2H2 [per mil] vs. H2 Lab.Tank	d 3H2/2H2 [per mil] vs. VSMOW	d 2H/1H [per mil] vs. VSMOW
1	6.8	10.7	25.7	6275.5186043	2272.0539966	619.37944	135.85409	87.929229808777094	-1.29129	-203.47987	-203.47987
2	32.9	44.6	24.2	6258.4346354	2266.0222705	630.29574	139.24707	87.683381022348428	-1.34909	-203.52597	-203.52597
3*	57.6	69.8	24.4	6252.2622837	2265.7686398	633.04377	138.76877	87.128592351159526	0.00000	-202.46000	-202.46000
4	82.5	94.0	24.1	6250.2883414	2262.0866008	631.93558	140.32228	87.552486260817105	-1.69415	-203.80117	-203.80117
5	107.0	119.4	26.2	6252.7507504	2263.4534709	632.78066	140.68517	87.566199522157262	-2.03275	-204.07122	-204.07122
6	184.9	189.6	13.8	7862.0909096	1134.4140639	618.38607	136.00535	34.339215961920061	-810.09028	-848.53750	-848.53750
7	234.4	239.1	13.7	7438.9268210	1040.1313901	618.39282	135.67372	32.501393535286851	-809.95108	-848.42648	-848.42648
8	283.9	288.5	13.6	7044.7581710	956.7337135	619.08708	136.54002	30.778463915501245	-812.04384	-850.09557	-850.09557
9	333.4	338.1	13.8	6672.7906107	881.4345663	618.55022	136.20128	29.150493862124641	-811.97821	-850.04322	-850.04322
10	383.0	387.6	13.8	6320.7930319	813.8273795	618.53652	135.83751	27.625410790754490	-811.31628	-849.51530	-849.51530
11	432.6	437.2	13.7	5987.8956449	749.7019696	618.86849	135.56406	26.173904353831251	-811.79706	-849.89874	-849.89874
12	482.1	486.7	13.1	5670.0062397	690.5293254	618.89045	135.73938	24.786724934975641	-811.69422	-849.81673	-849.81673
13	531.3	536.2	13.7	5373.4949089	639.3100496	618.22833	135.79173	23.445960722148921	-812.59532	-850.53539	-850.53539
14	581.1	585.8	13.4	5088.0723670	588.8993703	618.06129	135.83395	22.207808530306932	-812.97294	-850.83656	-850.83656

Figure 17: δ^2H Data Export File – GB_H2_Export