

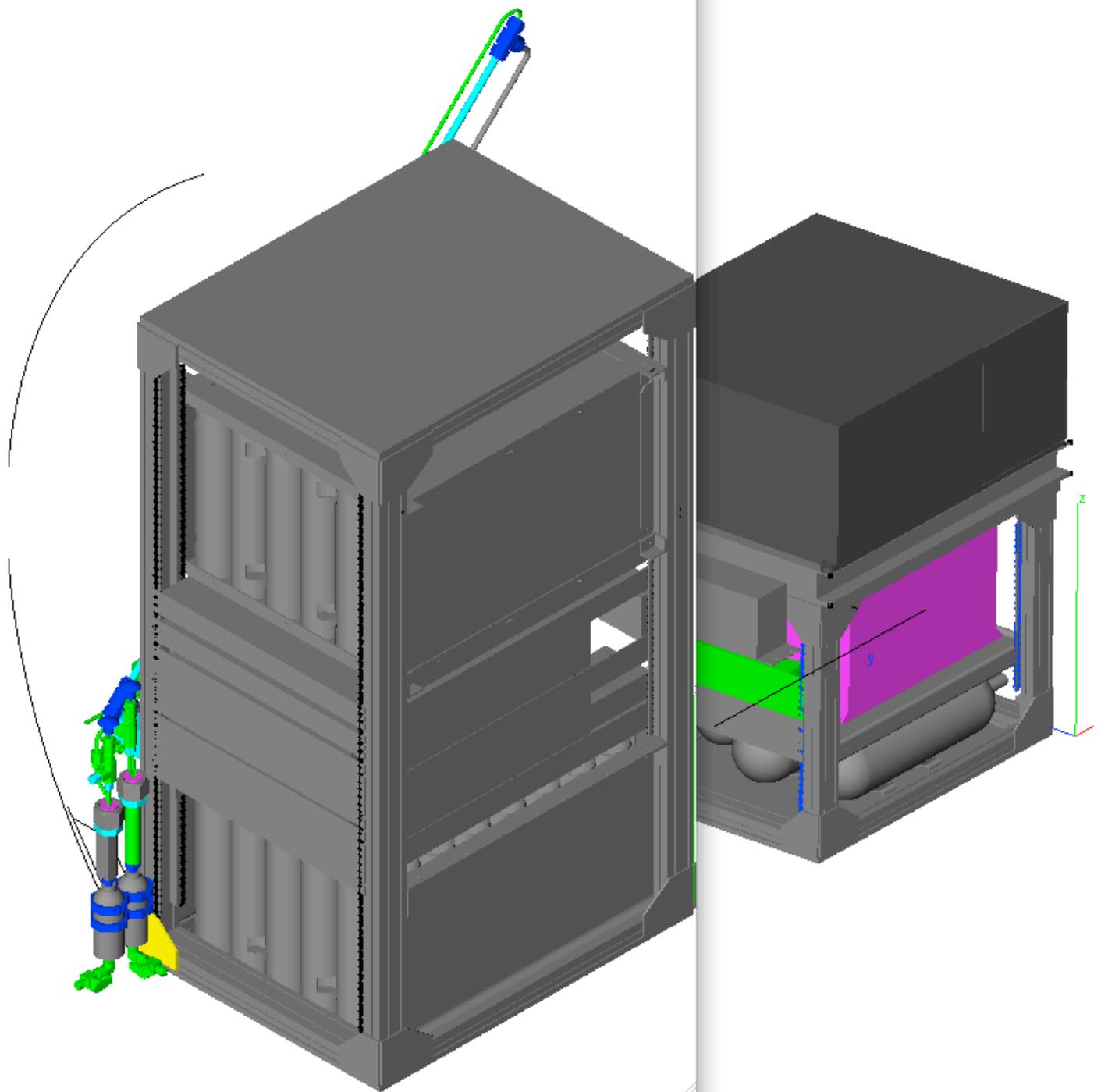
## HIPPO-NOAA-GMD RACK/DATA SET

J. Elkins<sup>1</sup>, F. Moore<sup>2</sup>, E. Hints<sup>2</sup>, J.D. Nance<sup>2</sup>, G.Dutton<sup>2</sup>, B. Hall<sup>1</sup>, S. Montzka<sup>1</sup>, B. Miller<sup>2</sup>, L. Miller<sup>3</sup>, D. Hurst<sup>2</sup>, L. Patrick<sup>2</sup>, S. Oltmans<sup>1</sup>, D. M. Heller<sup>2</sup>, P. Lang, J. Higgs<sup>3</sup>, D. Neff<sup>2</sup>, C. Sweeney<sup>2</sup>, Guenther<sup>2</sup>, S. Wolter<sup>2</sup>, *J. White<sup>4</sup> and B. Vaughn<sup>4</sup>*

<sup>1</sup>GMD/ESRL, <sup>2</sup>CIRES/GMD/ESRL, <sup>3</sup> Science and Technology Corporation (STC) all in Boulder CO USA

Substantial Help from Elliot Atlas and group





**PANTHER:** (PAN and other Trace Hydrohalocarbon Experiment,) 200 lb., 6-channel GC (gas chromatograph).

- \* 3 ECD (electron capture detectors), packed columns.
- \* 1 ECD with a TE (thermal electric) cooled RTX-200 capillary column.
- \* 2-channel MSD (mass selective detector). 2 independent samples concentrated onto TE cooled Haysep traps, two temp programmed RTX-624 capillary columns.
- \* Tunable diode laser hygrometer (May Comm Inst.)

Measures: H<sub>2</sub>O, N<sub>2</sub>O, SF<sub>6</sub>, CCl<sub>2</sub>F<sub>2</sub> (CFC-12), CCl<sub>3</sub>F (CFC-11), CBrClF<sub>2</sub> (halon-1211), H<sub>2</sub>, CH<sub>4</sub>, CO, PAN (peroxyl acetyl nitrate), methyl halides CH<sub>3</sub>I, CH<sub>3</sub>Br, CH<sub>3</sub>Cl, the sulfur compounds COS, CS<sub>2</sub>, hydrochlorofluorocarbons CHClF<sub>2</sub> (HCFC-22), C<sub>2</sub>H<sub>3</sub>Cl<sub>2</sub>F (HCFC-141b), C<sub>2</sub>H<sub>3</sub>ClF<sub>2</sub> (HCFC-142b), and hydrofluorocarbon C<sub>2</sub>H<sub>2</sub>F<sub>4</sub> (HFC-134a)



**UCATS:** (Unmanned aircraft systems Chromatograph for Atmospheric Trace Species), 60 lb. GC, TDL and Photometer.

- \* 2-Channel ECD GC, packed columns.
- \* Tunable diode laser hygrometer (May Comm Inst.)
- \* Dual-beam ozone photometer (2B Inst.)

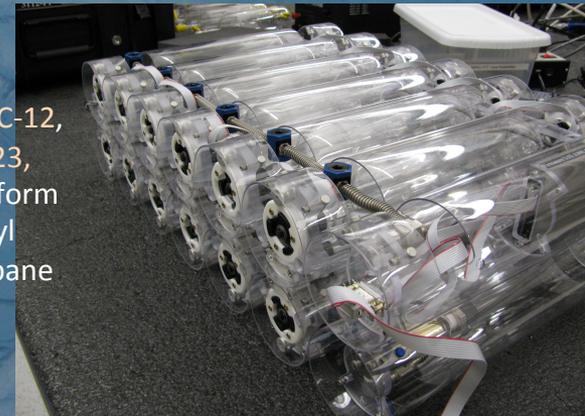
Measures: N<sub>2</sub>O, SF<sub>6</sub>, H<sub>2</sub>, CH<sub>4</sub>, CO, O<sub>3</sub> and H<sub>2</sub>O.



**NWAS:** (NOAA Whole Air Sampler) 20 lb. per 12 flask pkg., 2 to 4 NWAS pkg per flight, 6 in rack.

- \* Total > 48 flask per flight, 6 flasks per profile. [2 to 4 NWAS pkg +2 AWAS-Elliot Atlas]
- \* MSD (analysis by HATS/ESRL flask lab - Steve Montzka *et al.*)
- \* ECD, NDIR, FID and RGA (analysis by CCGG/ESRL flask lab - Pat Lang *et al.*)
- \* MSD (analysis by INSTARR/CU isotopes flask lab - James White *et al.*)

Measures: CO, CO<sub>2</sub>, CH<sub>4</sub> and isotopes, H<sub>2</sub>, SF<sub>6</sub>, N<sub>2</sub>O, tetrachloroethylene (C<sub>2</sub>Cl<sub>4</sub>), CCl<sub>4</sub>, CFC-11, CFC-12, CFC-13, CFC-113, CFC-114, CFC-115, HCFC-22, HCFC-124, HCFC-141b, HCFC-142b, HCFC-227ea, HFC-23, HFC-125, HFC-134a, HFC-143a, HFC-152a, HFC-365mfc, halon-1211, halon-1301, halon-2402, chloroform (CHCl<sub>3</sub>), methyl chloroform (CH<sub>3</sub>CCl<sub>3</sub>), chloroethane (CH<sub>3</sub>CH<sub>2</sub>Cl), dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>), methyl halides (CH<sub>3</sub>Cl, CH<sub>3</sub>I, CH<sub>3</sub>Br), bromoform (CHBr<sub>3</sub>), dibromomethane (CH<sub>2</sub>Br<sub>2</sub>), acetylene (C<sub>2</sub>H<sub>2</sub>), propane (C<sub>3</sub>H<sub>8</sub>), benzene (C<sub>6</sub>H<sub>6</sub>), perfluoropropane (PFC-218), iso-pentane (C<sub>5</sub>H<sub>12</sub>), n-butane (C<sub>4</sub>H<sub>10</sub>), n-pentane (C<sub>5</sub>H<sub>12</sub>), n-hexane (C<sub>6</sub>H<sub>14</sub>), carbonyl sulfide (OCS), and carbon disulfide (CS<sub>2</sub>).



NOAA\_GMD generates **8** separate submission **files** for each flight.

GCMS-M2_	Mass Spec Flask Data.	<i>S. Montska et al.</i>
MAGICC_gmd_	Carbon Cycle Group Flask Data (CO <sub>2</sub> , CO, CH <sub>4</sub> , H <sub>2</sub> , SF <sub>6</sub> , N <sub>2</sub> O)	<i>C. Sweeney et. al.</i>
SIL_isotopes_	Isotope Flask Data. ( <sup>18</sup> O , <sup>13</sup> C on CO <sub>2</sub> )	<i>(J. White and B. Vaughn INSTARR)</i>
UCATSO3_	2B Photometer (O <sub>3</sub> )	<i>J. Elkins et. al.</i>
UCATSGC_	In Situ Chromatograph-ECD (N <sub>2</sub> O, SF <sub>6</sub> , CH <sub>4</sub> , CO, H <sub>2</sub> )	<i>J. Elkins et. al.</i>
UCATSH20_	MayComm TDL (H <sub>2</sub> O)	<i>J. Elkins et. al.</i>
GC_ECD_	In Situ Chromatograph-ECD (N <sub>2</sub> O, SF <sub>6</sub> , CH <sub>4</sub> , CO, H <sub>2</sub> , CFC-11, -12, -131, halon-1211, PAN)	<i>J. Elkins et. al.</i>
GC_MSD_	In Situ Chromatograph-MSD (CH <sub>3</sub> Cl, CH <sub>3</sub> Br, CH <sub>3</sub> I, HCFC-22, HCFC-141b, HCFC-142b, HFC-134a, OSC, CS <sub>2</sub> )	<i>J. Elkins et. al.</i>











## Sample Volume information:

PFP Flask data is altitude targeted (on dives) with ~ 10-20 seconds of sample width.  
(24 to 36 flask samples per flight).  
(target precision 0.05% on up depending on species )

In situ MDS data is similar to flask data except for a higher 3 min. data rate and a sample width integration of ~ 150 sec , or about an 80% sample duty cycle.  
(target 1% precision)

In situ ECD data have even higher data rate of 1 or 2 min ( 2-3 second sample width).  
(target 0.5% precision)

O<sub>3</sub> (0.1 Hz) (target 2% +2 ppb precision)

H<sub>2</sub>O (1 Hz) (target 3% + 1 ppb precision)

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Correlate  
with  
Fast Data sets.



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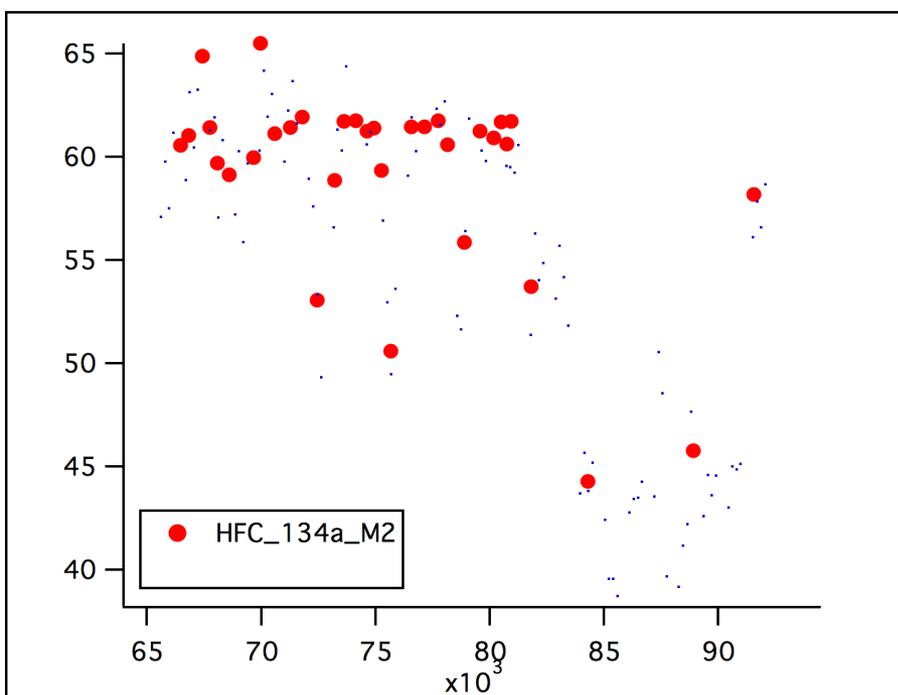
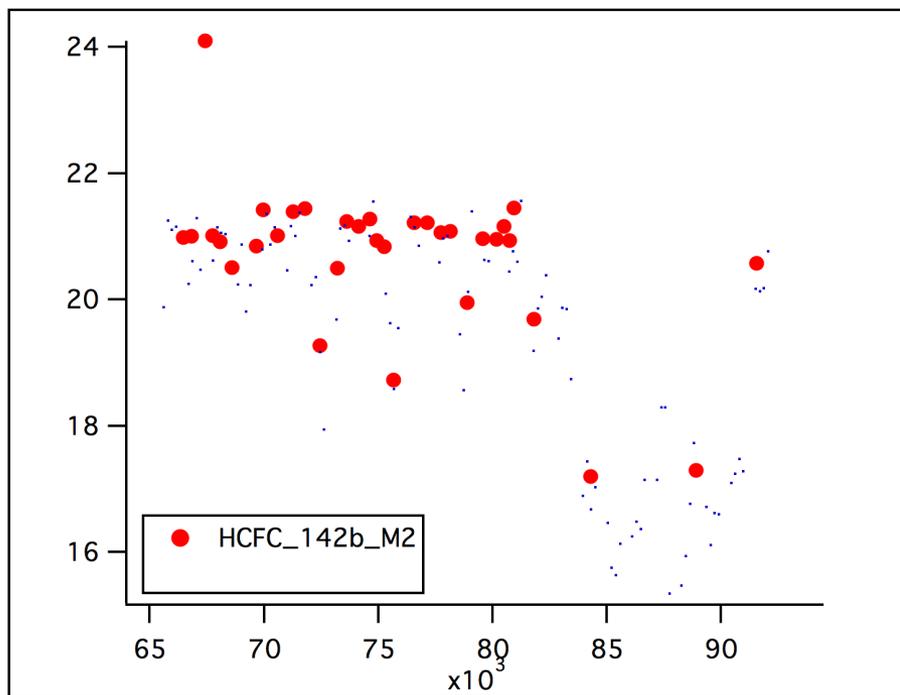
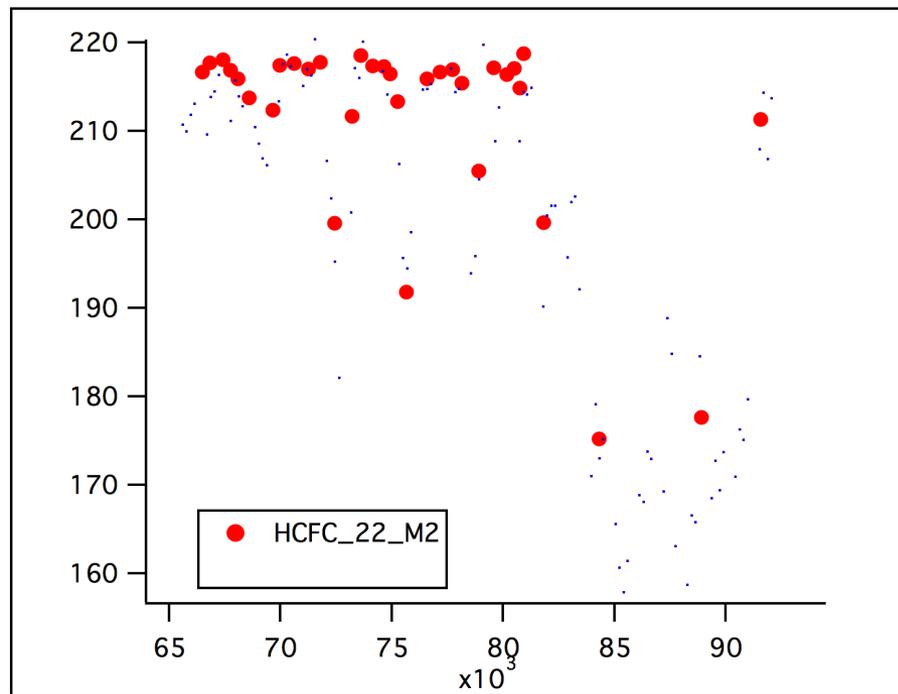
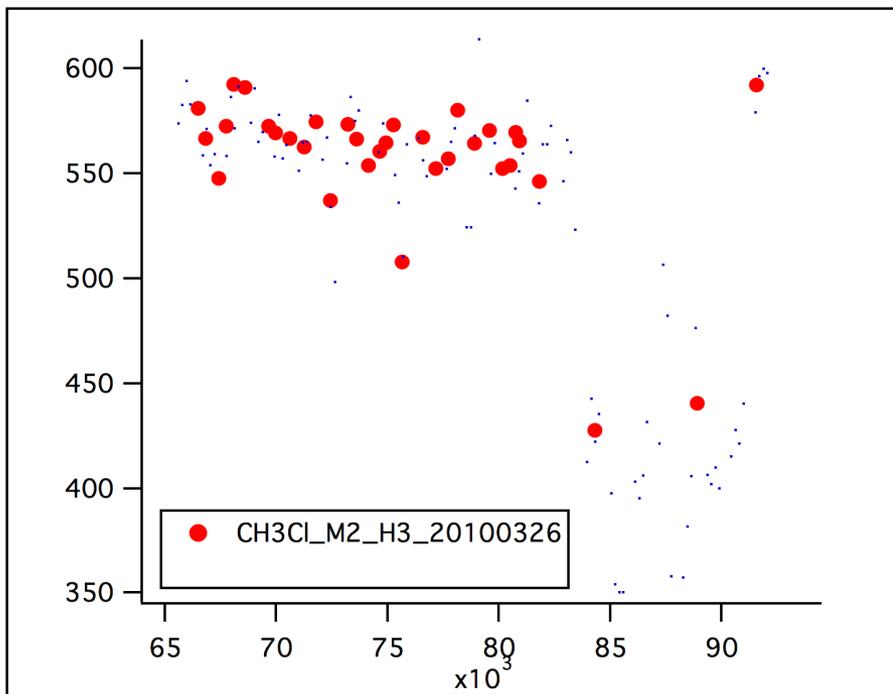
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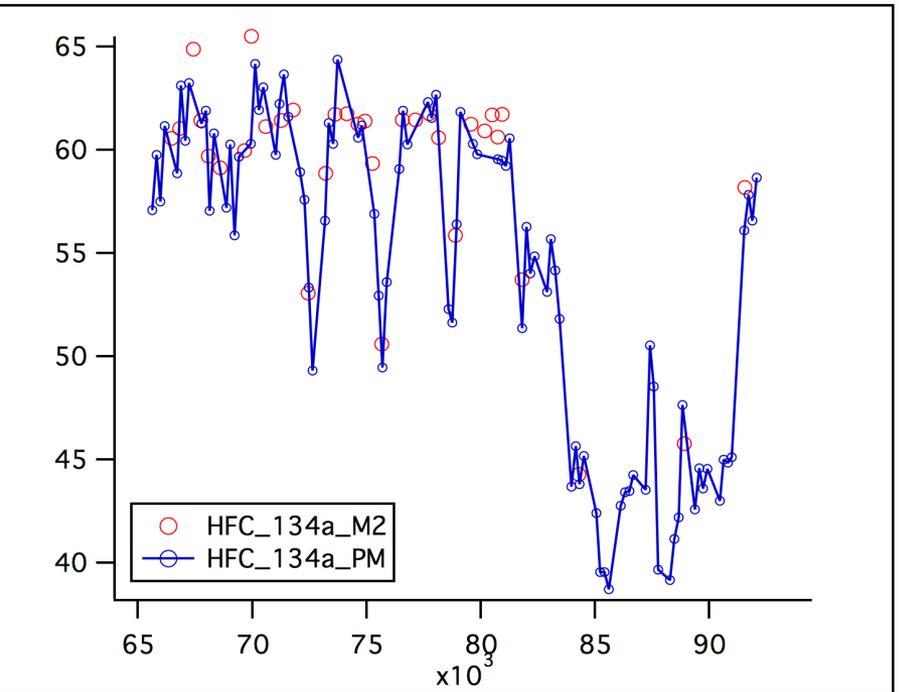
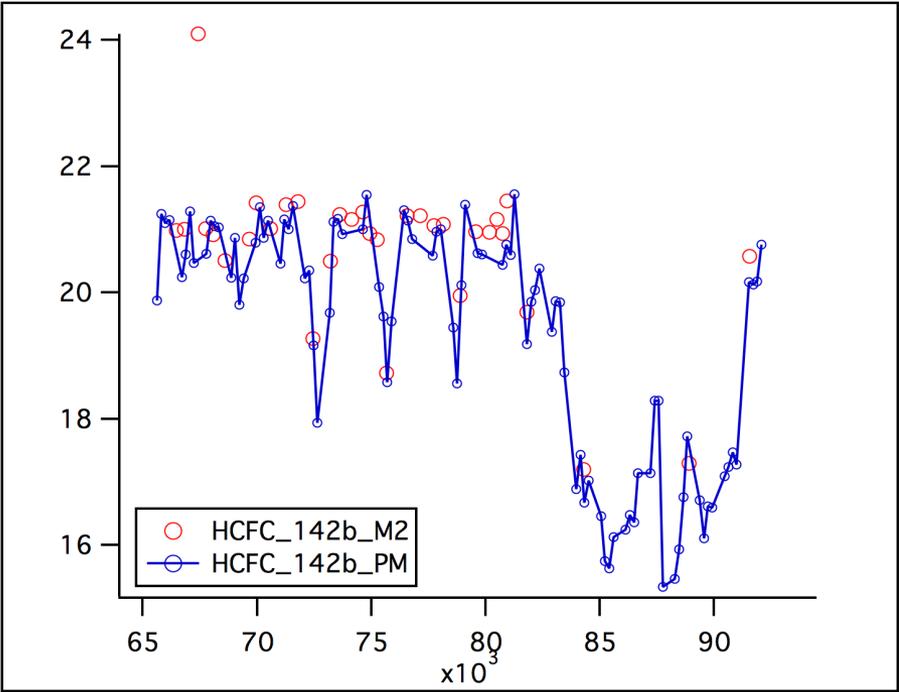
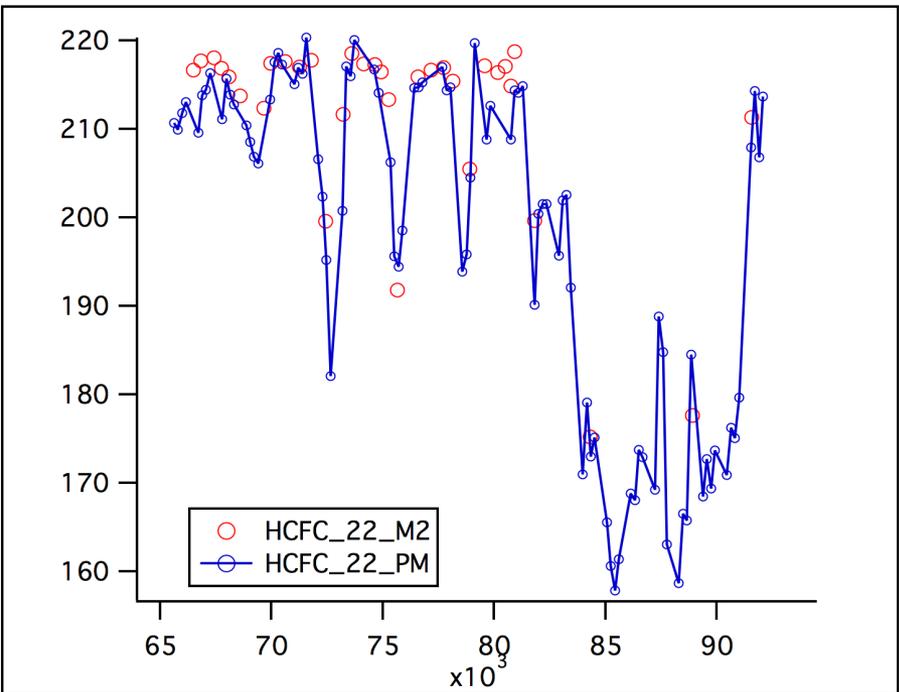
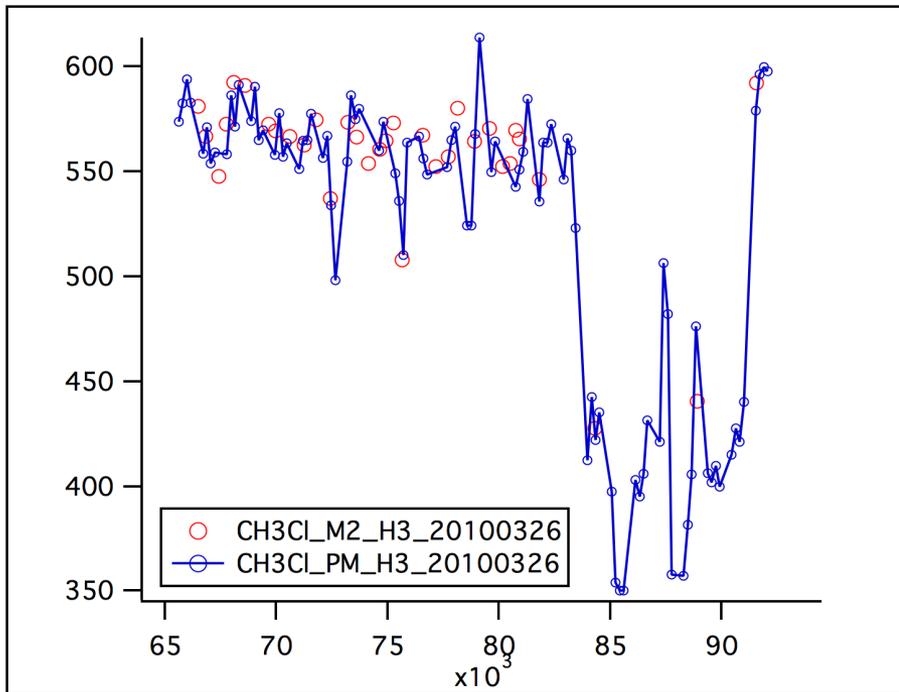
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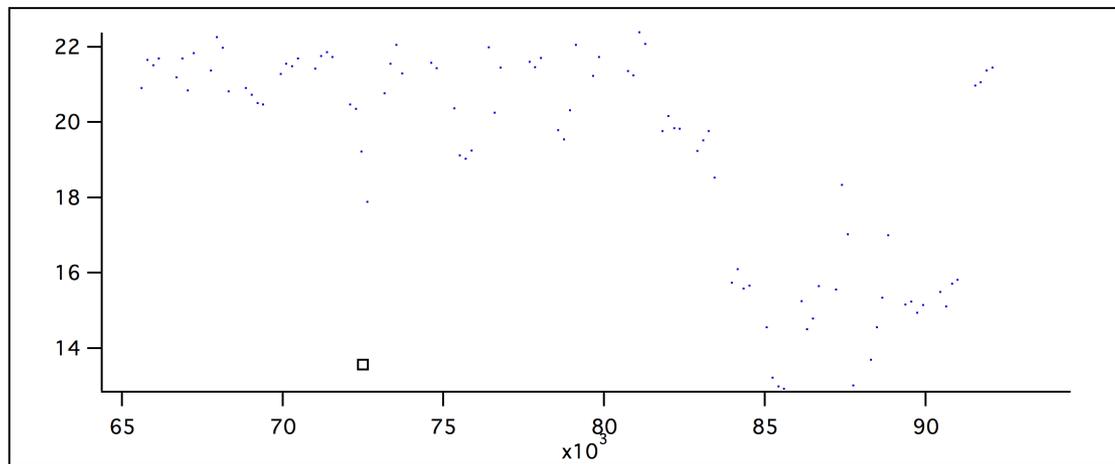
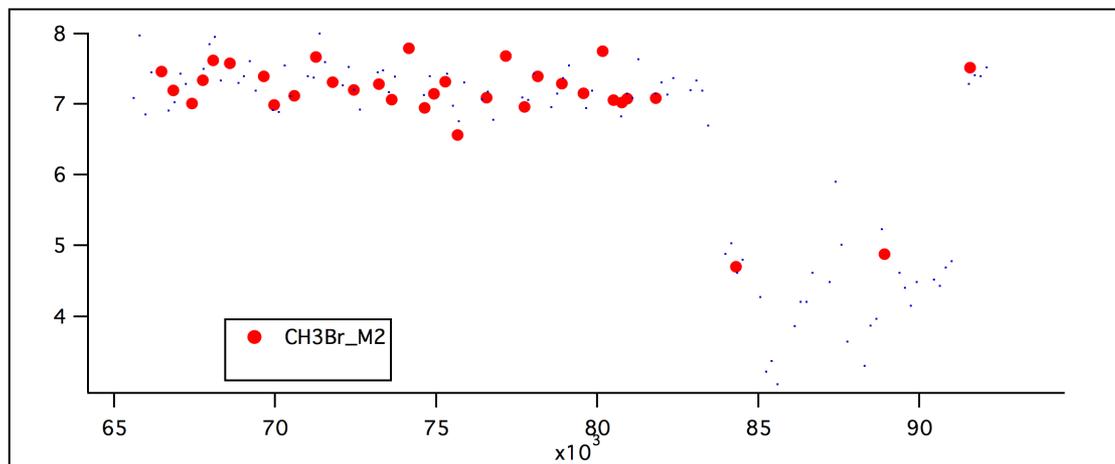
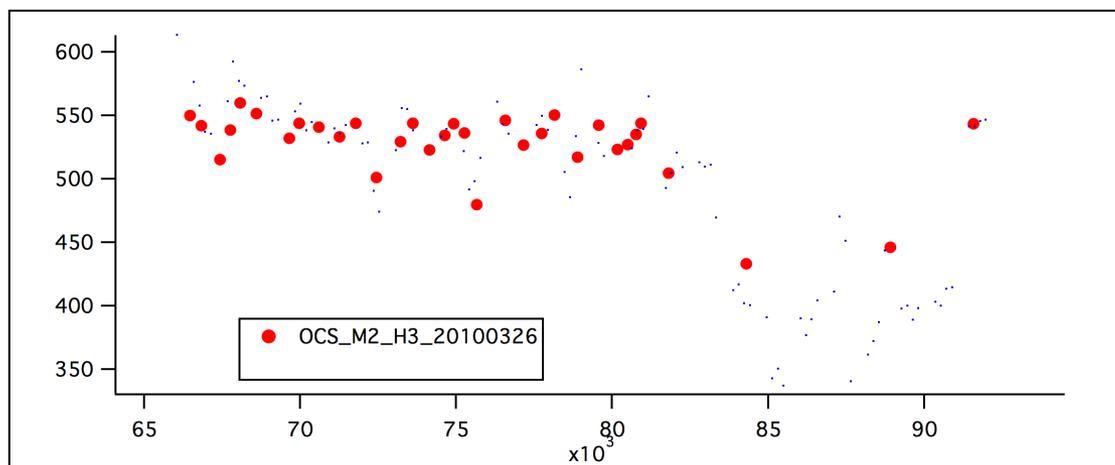
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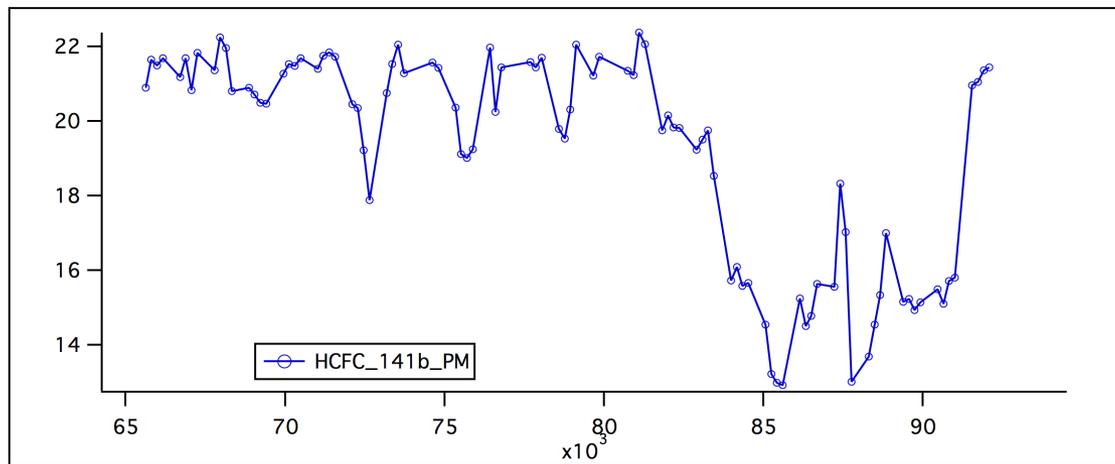
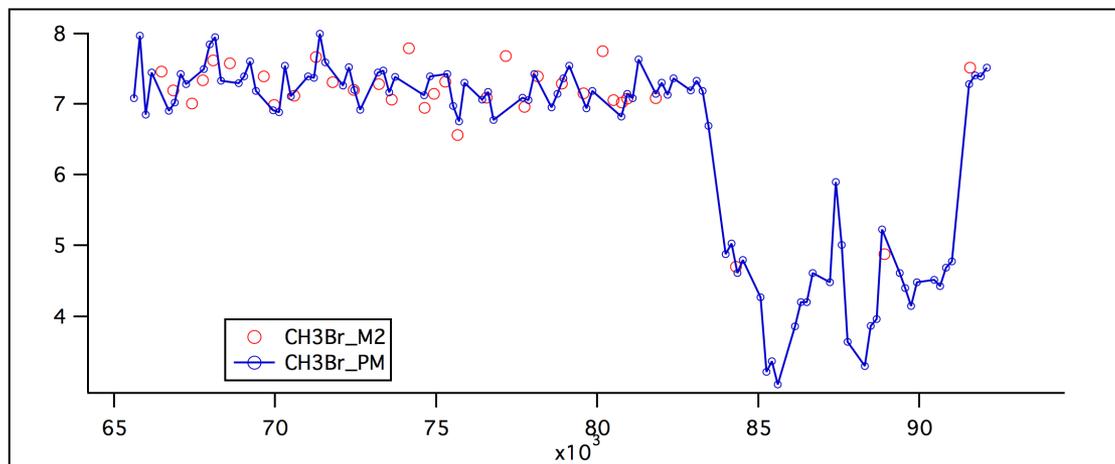
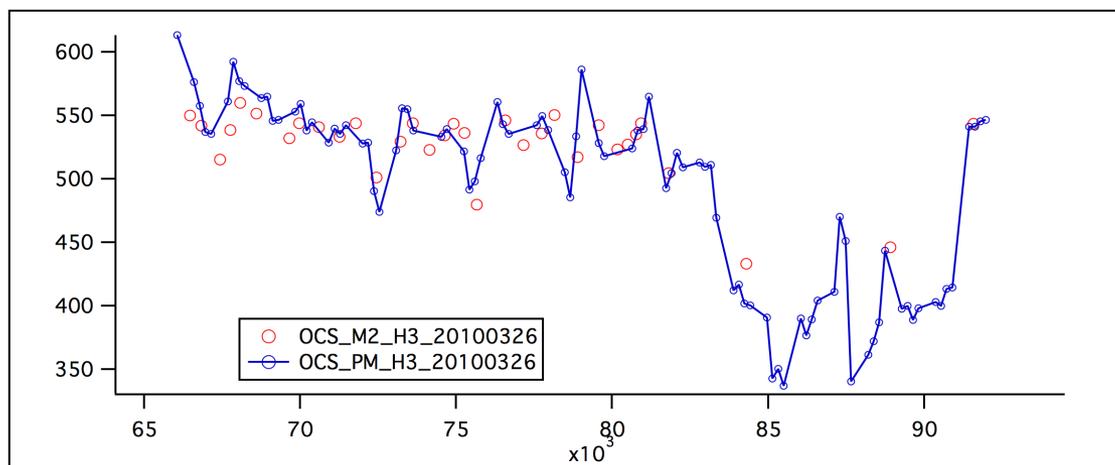
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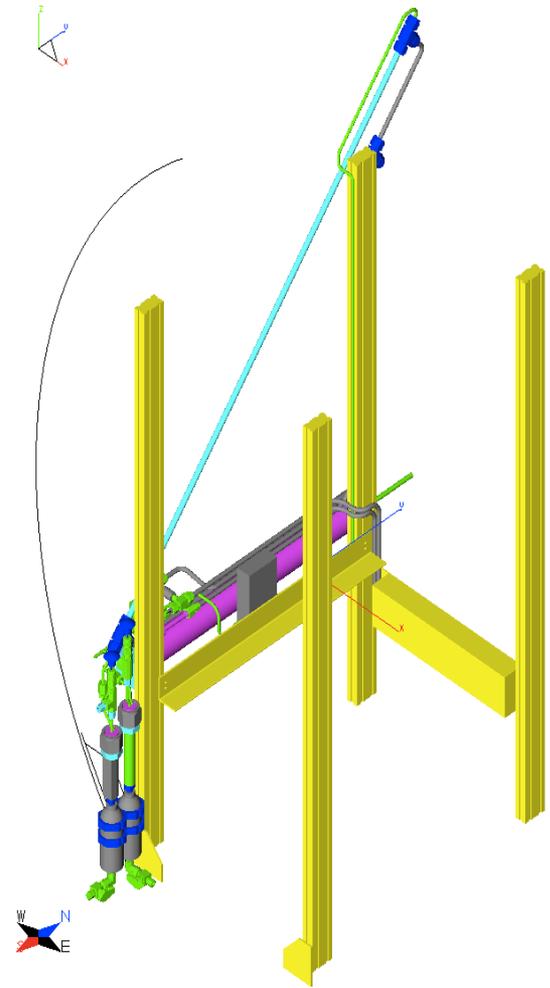


## Instrument Improvements: HIPPO-1,2,3

### #1 Water traps for flasks:

Removed water to below saturated at 2 °C and 40 psia.

To improve Isotope and CO<sub>2</sub> data.



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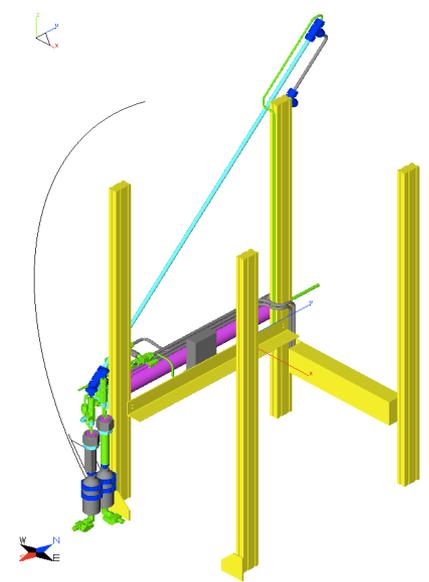
Removed water to below saturated at 2C and 40 psia.)

### #2 Improved Flask data rate:

HIPPO-1 228 PFP flasks.

HIPPO-2 264 PFP flasks.

HIPPO-3 336 PFP flasks.



# Instrument Improvements: HIPPO-1,2,3

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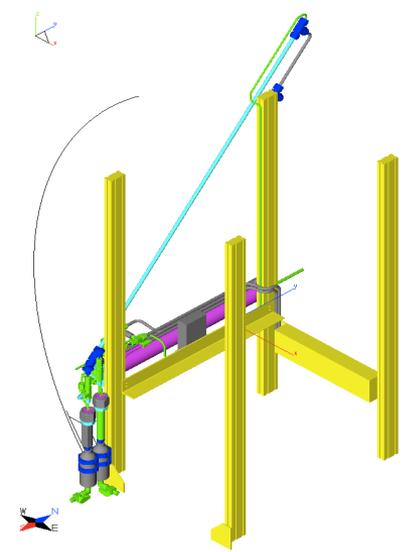
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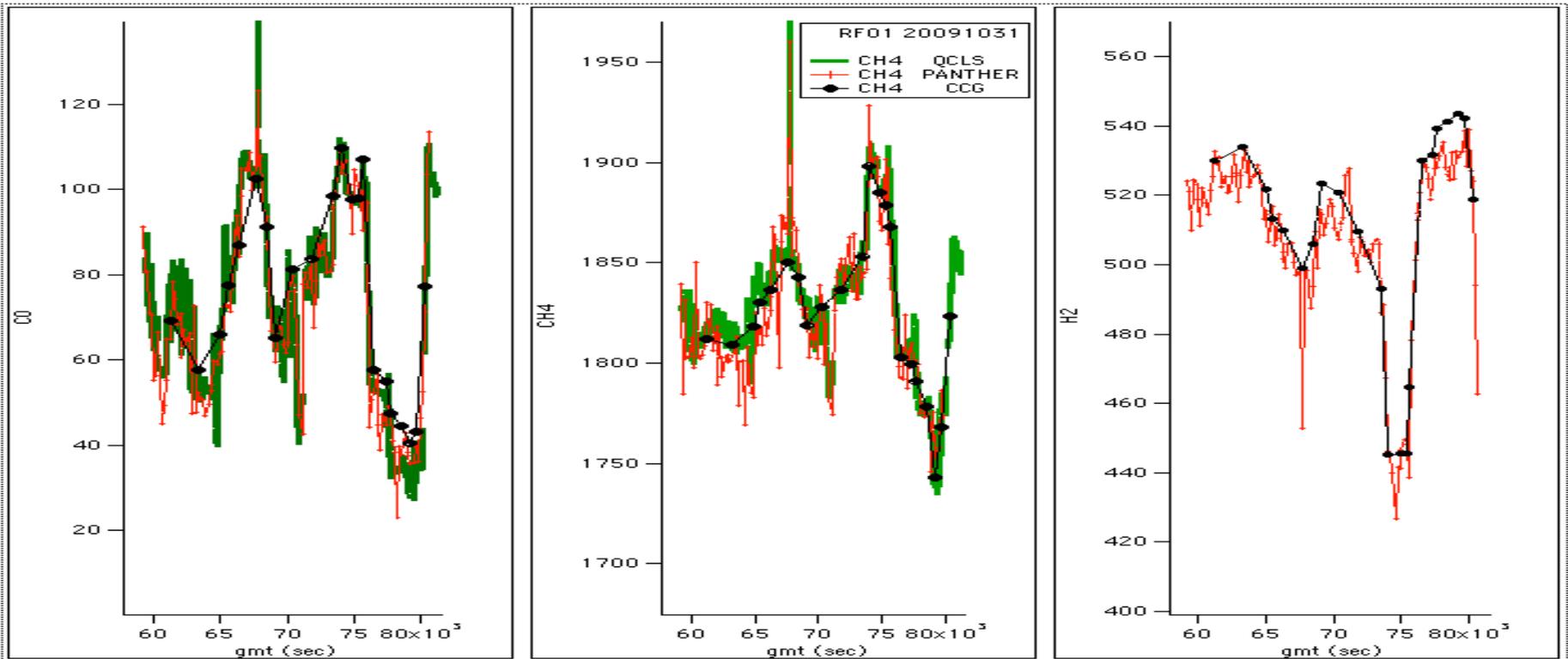
HIPPO-1 228 PFP flasks.

HIPPO-2 264 PFP flasks.

HIPPO-3 336 PFP flasks.



## #3 PANTHER CH4, CO, H2 channel improved for HIPPO\_2,3,4,5 ( NRC temp



## GC Calibrations:

Every 5<sup>th</sup> sample is from an in-flight calibration gas. (red points below.)

Fit smooth curve through in-flight data (black line).

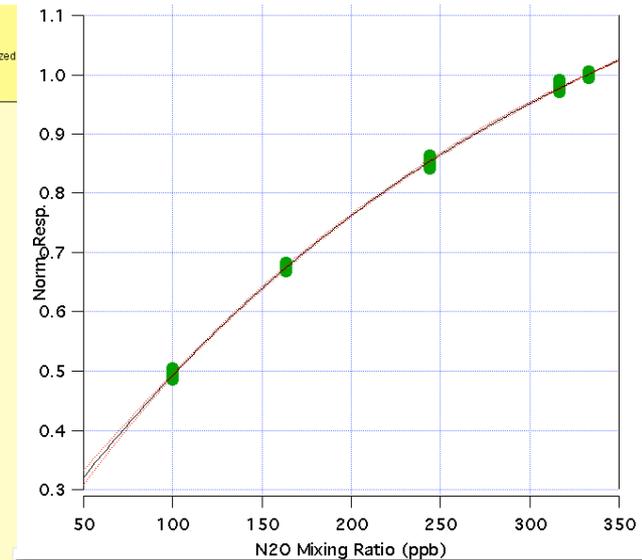
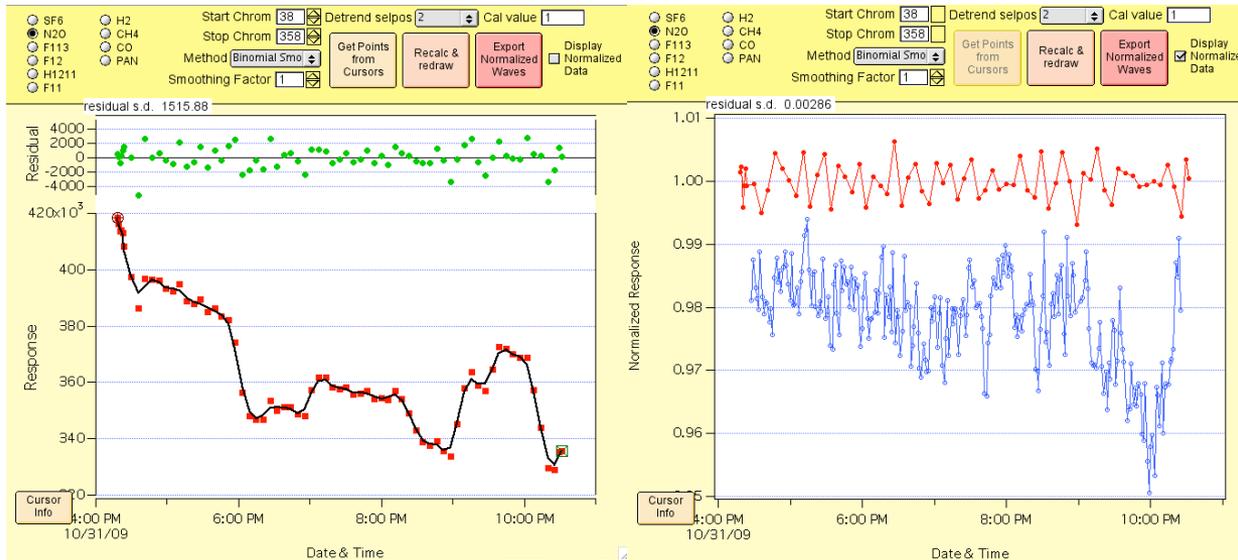
Uncertainty in data is 1-sigma spread in the residuals to this fit, added in quad with uncertainty in a calibration curve.

Normalize flight data to this smooth fit through the in-flight calibration data.

Convert normalized data to ppt via a calibration curve generated in the lab using multiple standards. (tied to gravimetrically prepared Primaries.)

This takes out the non-linearity and offsets associated with the chromatography and ECD's.

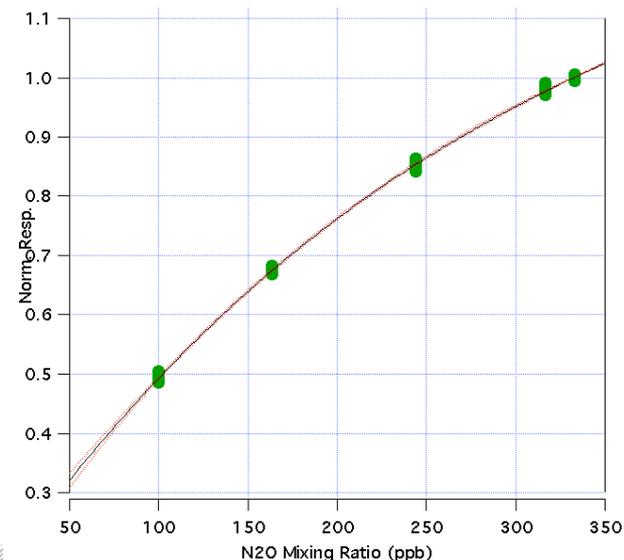
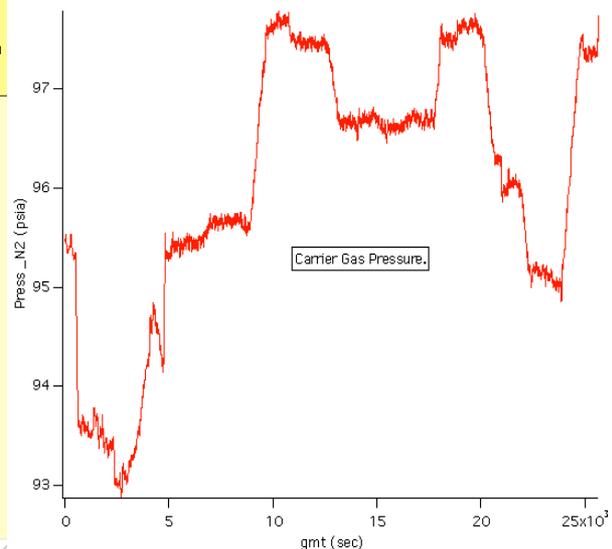
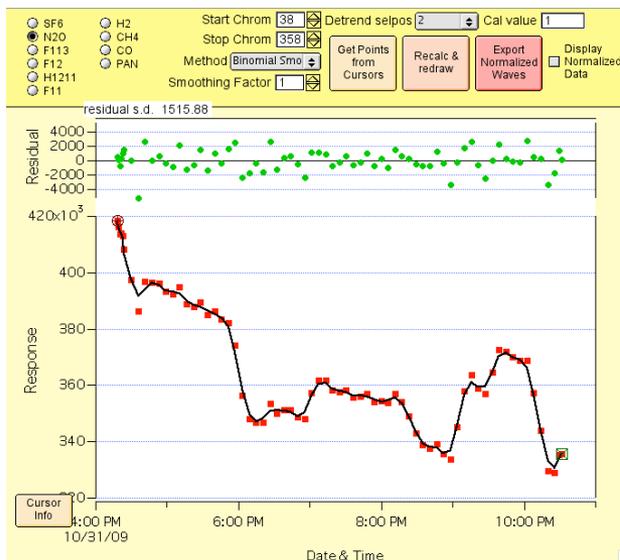
Lab cal-curves are generated Pre- and Post- mission.



# HIPPO GC Calibration issues.

For HIPPO these gain changes are dominated by:

- 1) Changes in the **Carrier Gas** head **pressure**.
- 2) **Water** moving through columns **onto the ECD**.



# HIPPO GC Calibration issues.

Curvature in cal curve implies detector is showing effects of saturation.

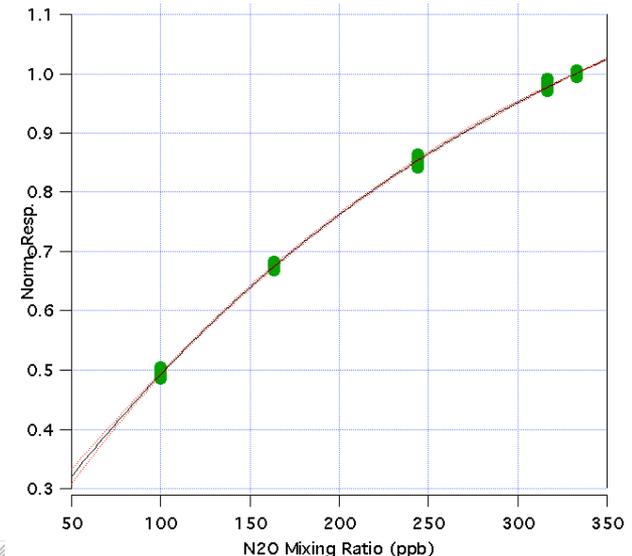
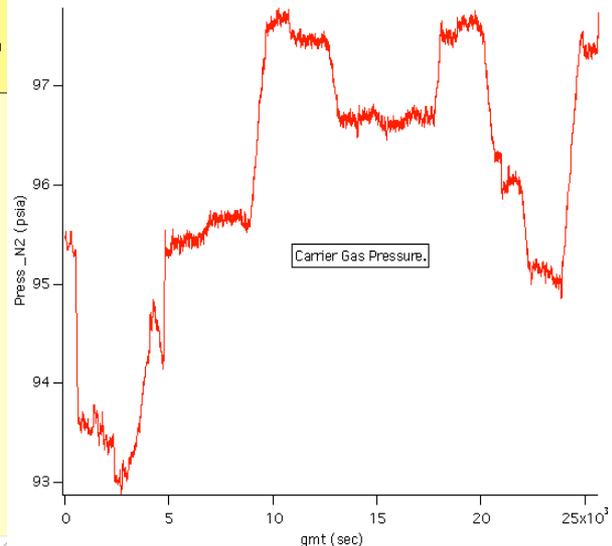
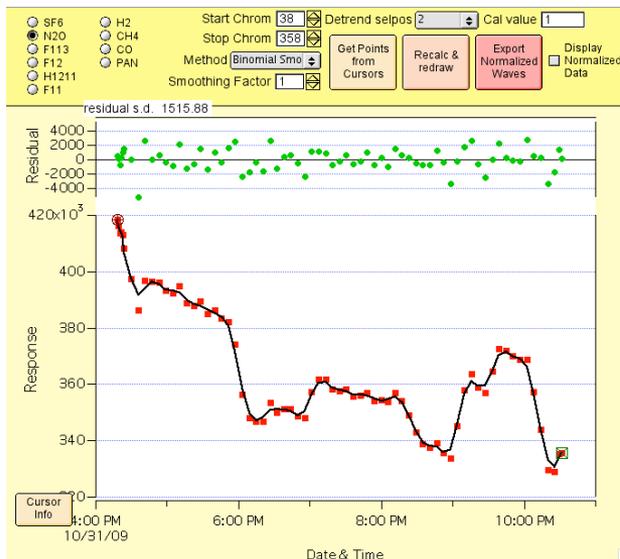
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As gain goes up or down you are effectively moving the normalizing cal to a different point on the cal-curve below..

This changes the effective cal-curve.

> **Systematic** for UCATS and PANTHER .



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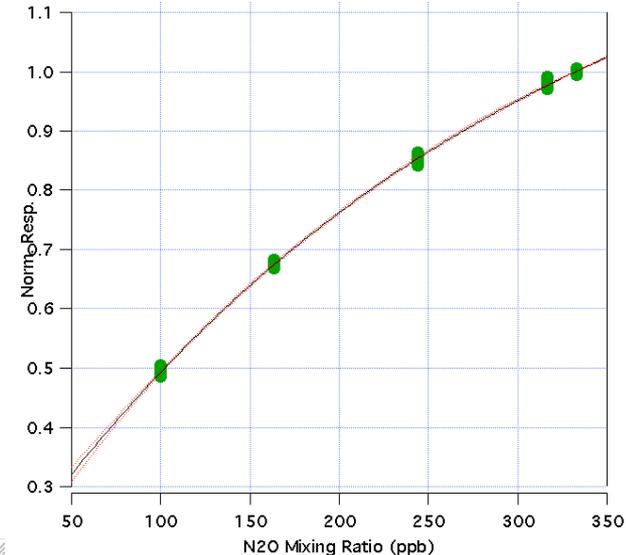
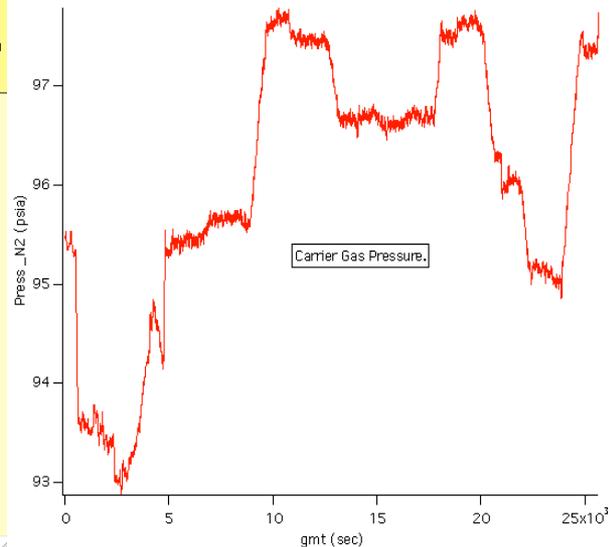
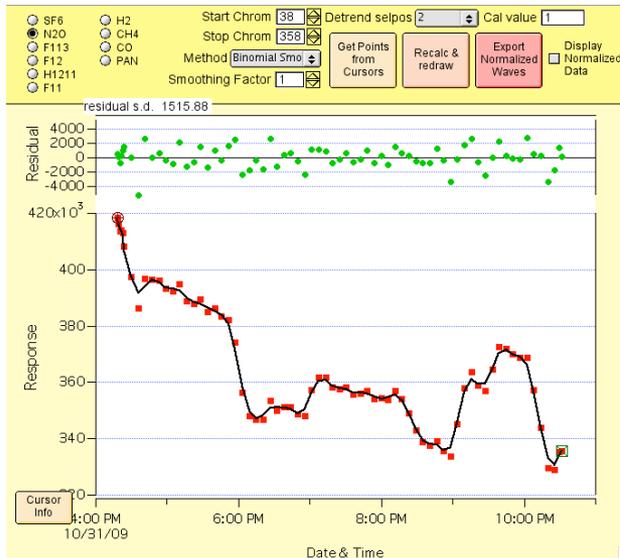
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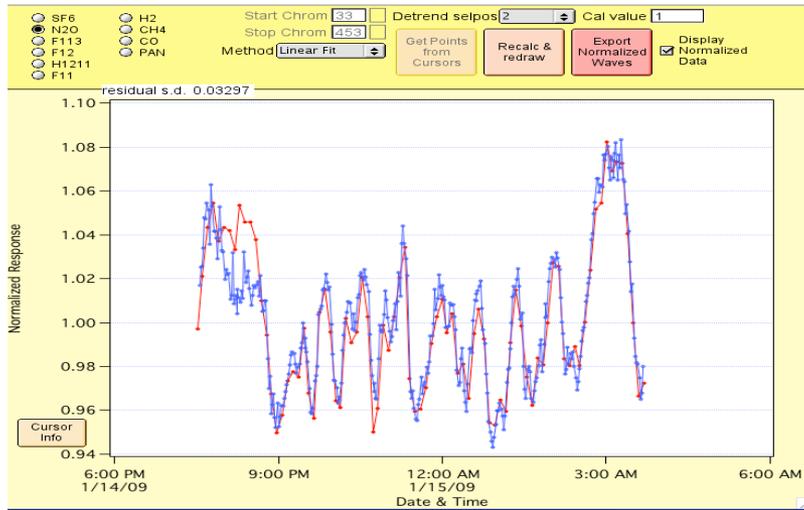
**Solution:** Reduce the gain changes > remove water and stabilize N2 carrier gas press.  
Reduce calibration curvature with smaller sample size.



# Pre-Naf-Dryer flight: HIPPO-1,-2,-3

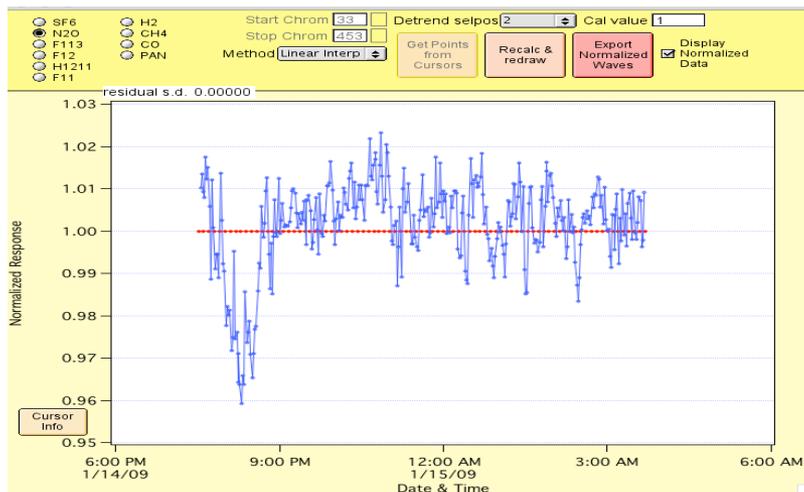
Big **change** in **gain** with the each vertical profile.

> due to **changing water** on detector etc.



Recoverable final precision **about 1.0%** with **outliers**.

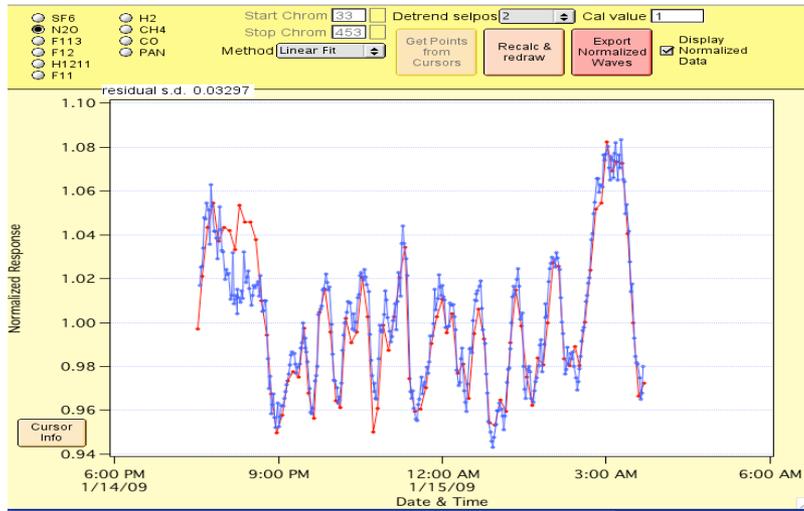
(Air sample in blue, flight-cal sample in red)



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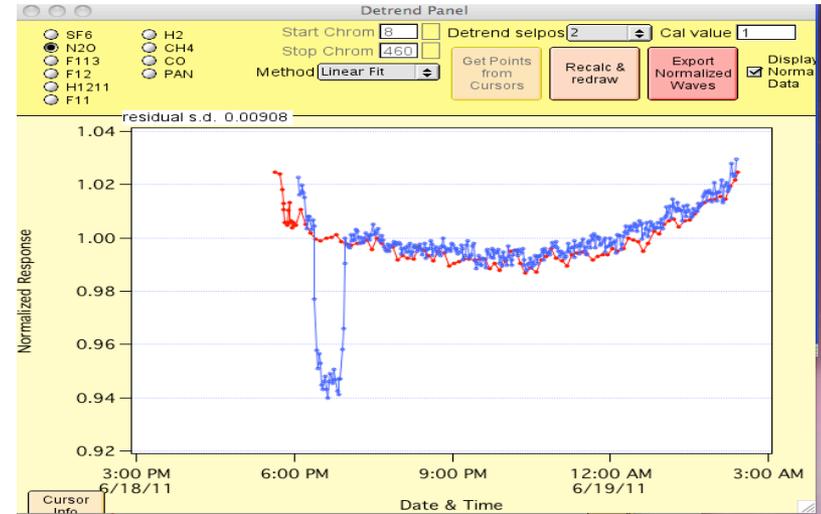


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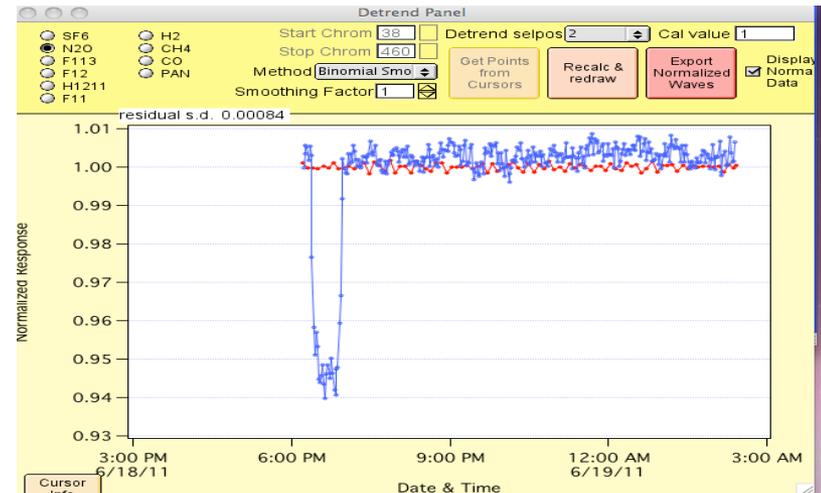
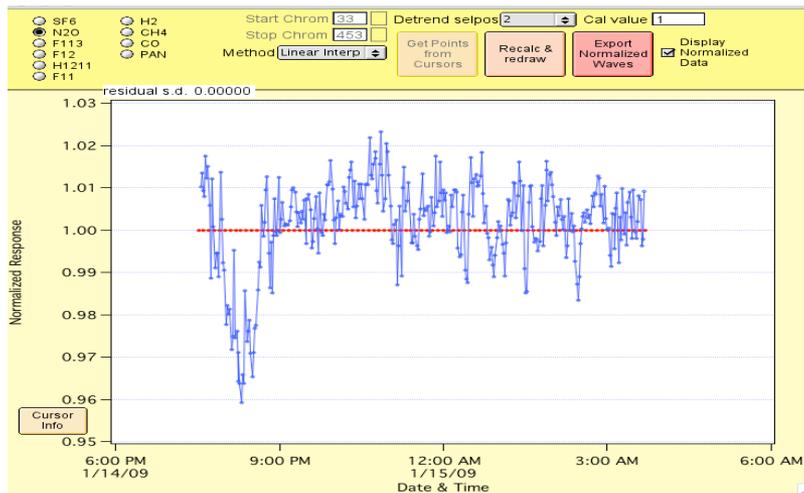
## Naf-Dryer in sample line HIPPO-4,-5

No **change** in **gain** with the each vertical profile.

> Stable **water** on detector etc.



Final precision **0.2%** with **no outliers**.



## Final data submitted for HIPPO.

- #1 All Flask data submitted as final. (GCMS-M2\_, MAGICC\_gmd\_, and SIL\_isotopes\_).  
\*Issues exist with drifting calibration tanks etc. that will result in re-submission soon.  
this will affect primarily OCS, SF6, and H2 data.
- #2 UCATS data is final through HIPPO\_2, no data for 3, and 4 and 5 are near final with time-sync and calibration issues to be resolved. (UCATSGC\_, UCATSH20\_, UCATS03\_.)
- #3 All PANTHER mass spec data will all be submitted as final by the end of the week with no mass spec data for HIPPO-5. (GC\_MSD\_). ECD data is final through HIPPO-2 and remaining ECD data will begin processing next week after final submission of MSD data.

## Instrument Improvements throughout HIPPO.

- #1 Water traps for flasks after HIPPO-1: Targeted water at saturation at 2C and 40 psia.
- #2 Progressively Improved Flask data rate : Averaged over 300 PFP flasks per mission.
- #3 PANTHER CH4, CO, H2 channel improved over HIPPO-1.
- #5 Water removal for PANTHER and UCATS ECD sample flow improving precision.
- #6 Stabilize N2 carrier gas regulator improving precision for PANTHER and UCATS.
- #7 Reduce Sample Loop size to reduce calibration curvature and reduce systematic.