HIPPO-NOAA-GMD RACK/DATA SET

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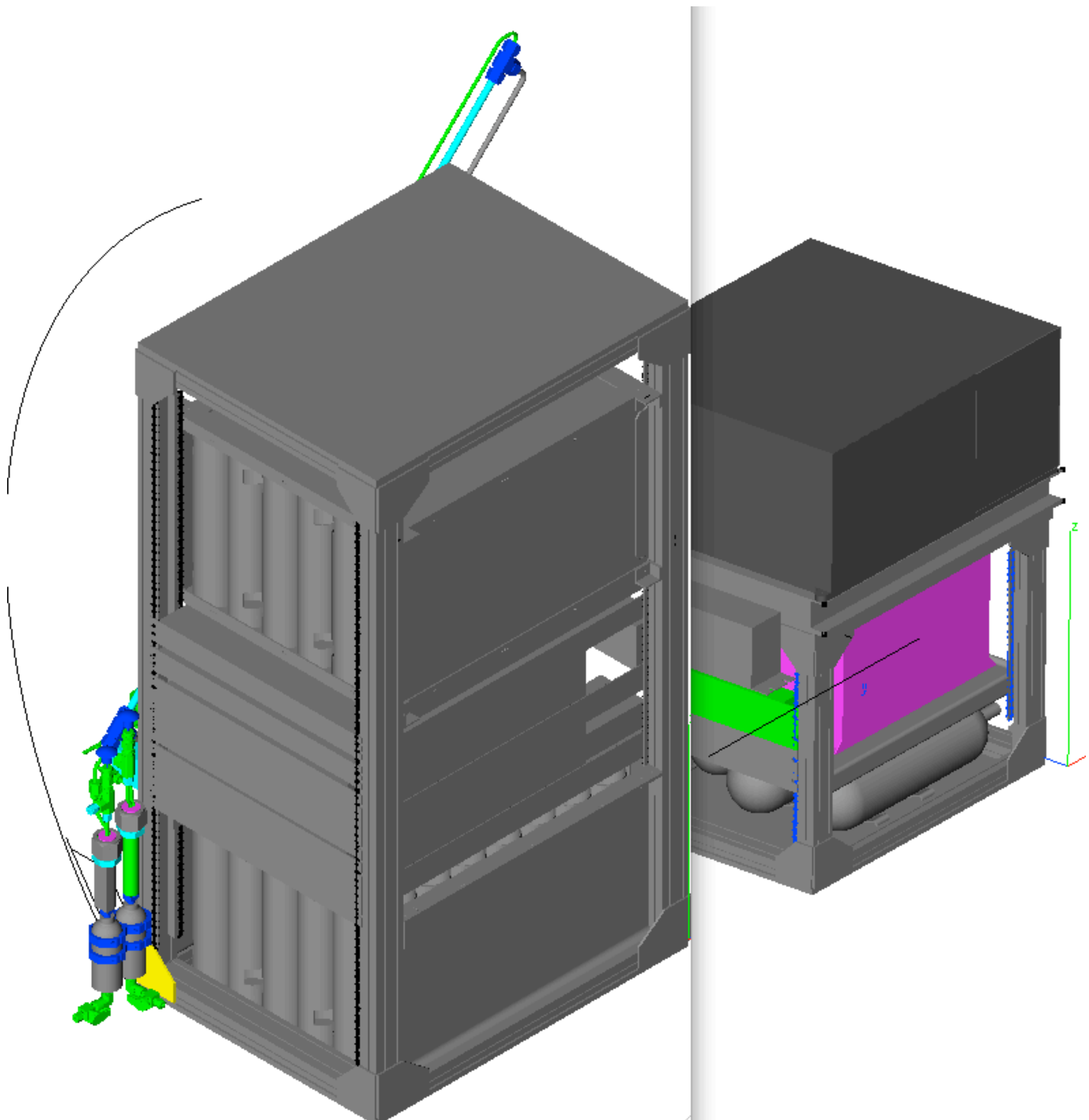
[1]GMD/ESRL, [2]CIRES/GMD/ESRL, [3] Science and Technology Corporation (STC) all in Boulder CO USA

Substantial Help from Elliot Atlas and group

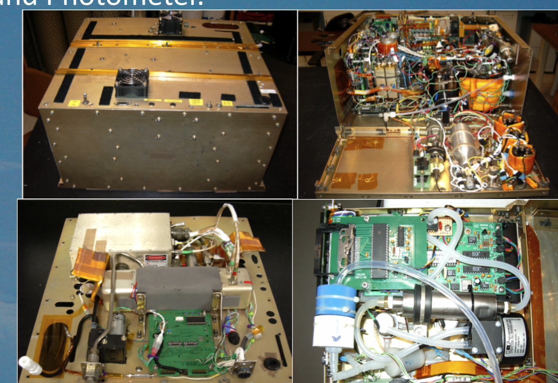


PANTHER: (PAN and other Trace Hydrohalocarbon ExpeRiment,) 200 lb., 6-channel GC (gas chromatograph).

* 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: H2O, N2O, SF6 , CCl2F2 (CFC-12), CCl3F (CFC-11), CBrClF2 (halon-1211), H2, CH4 , CO, PAN (peroxyl acetyl nitrate), methyl halides CH3I, CH3Br, CH3Cl, the sulfur compounds COS, CS2, hydrochlorofluorocarbons CHClF2 (HCFC-22), C2H3Cl2F (HCFC-141b), C2H3ClF2 (HCFC-142b), and hydrofluorocarbon C2H2F4 (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: N2O, SF6 , H2 , CH4, CO, O3 and H2O.

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

* Total 48 flask per flight, 6 flasks per profile. [2 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, CO2 CH4 and isotopes, H2 , SF6 , N2O, tetrachloroethylene (C2Cl4), CCl4 , 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 (CHCl3), methyl chloroform (CH3CCl3), chloroethane (CH3CH2Cl), dichloromethane (CH2Cl2), methyl halides (CH3Cl CH3I CH3Br), bromoform (CHBr3), dibromomethane (CH2Br2), acetylene (C2H2), propane (C3H8), benzene (C6H6), perfluoropropane (PFC-218),
iso-pentane (C5H12), n-butane (C4H10), n-pentane (C5H12), n-hexane (C6H14),
carbonyl sulfide (OCS), and carbon disulfide (CS2).

NOAA_GMD generates **8** separate submission **files** for each flight.

GCMS-M2_	**Mass Spec Flask Data.**	*S. Montzka etal.*
MAGICC_gmd_	**Carbon Cycle Group Flask Data** (CO_2, CO, CH_4, H_2, SF_6, N_2O)	*C. Sweeney et. al.*
SIL_isotopes_	**Isotope Flask Data.** (^{18}O , ^{13}C on CO_2)	(*J. White and B. Vaughn INSTARR*)
UCATSO3_	2B Photometer (O_3)	*J. Elkins et. al.*
UCATSGC_	In Situ Chromatograph-ECD (N_2O, SF_6, CH_4, CO, H_2)	*J. Elkins et. al.*
UCATSH20_	MayComm TDL (H_2O)	*J. Elkins et. al.*
GC_ECD_	In Situ Chromatograph-ECD (N_2O, SF_6, CH_4, CO, H_2, CFC-11, -12, -131, halon-1211, PAN)	*J. Elkins et. al.*
GC_MSD_	In Situ Chromatograph-MSD (CH3Cl, CH3Br, CH3I, HCFC-22, HCFC-141b, HCFC-142b, HFC-134a, OSC, CS2)	*J. Elkins et. al.*

95% of HIPPO-1 _SUBMIT, _TIMED data submitted.

F = final data

= Data OK not submitted yet.

ND = No Data

RF#	01	02	03	04	05	06	07	08	09	10	11
GCMS-m2_	ND	F	F	F	F	F	F	F	F	F	F
MAGICC_	ND	ND	F	F	F	F	F	F	F	F	F
SIL_isotopes_	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
GC_ECD_	F	F	F	F	F	F	F				F
GC_MSD	F	F	F	F	F	F	F		F	F	F
UCATSH2O_	F	F	F	F	F	F	F	F	F	F	F
UCATSO3_	F	F	F	F	F	F	F	F	F	F	F
UCATSGC_	F	F	F	F	F	F	F	F	F	F	F

76% of HIPPO-2 _SUBMIT Data Submitted

F = final data
F = final-ish data typically problem with on molecule.
= Data OK not submitted yet.
ND = No Data

RF#	01	02	03	04	05	06	07	08	09	10	11
GCMS-m2_	F	ND	F	F	F	F	F	F	F	F	F
MAGICC_	F	ND	F	ND	F	F	F	F	F	F	F
SIL_isotopes_	F	ND	F	ND	F	F	F	F	F	F	F
GC_ECD_	F	F	F		F	F	F	F			
GC_MSD											
UCATSH2O_	F	F	F	ND	F	F	F	F	F	F	F
UCATSO3_	F	F	F	ND	F	F	F	F	F	F	F
UCATSGC_	F	F	F		F	F	F	F	F	F	F

55 % of HIPPO-3, move to _SUBMIT Data Submitted.

F = final data

= Data OK not submitted yet.

ND = No Data

note: UCATS was not on GV.

UCATSH2O_ submitted from MayComm TDL in PANTHER.

RF#	01	02	03	04	05	06	07	08	09	10	11
GCMS-m2_	F	F	F	F	F	F	F	F	F	F	ND
MAGICC_	F	F	F	F	F	F	F	F	F	F	ND
SIL_isotopes_	F	F	F	F	F	F	F	F	F	F	ND
GC_ECD_											
GC_MSD											
UCATSH2O_	F	F	F	F	F	F	F	F	F	F	F
UCATSO3_	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
UCATSGC_	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

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_3 (0.1 Hz) (target 2% +2 ppb precision)

H2O (1 Hz) (target 3% + 1 ppb precision)

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Correlate with Fast Data sets.

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Sample Volume information:

Integrate over Fast Data sets.

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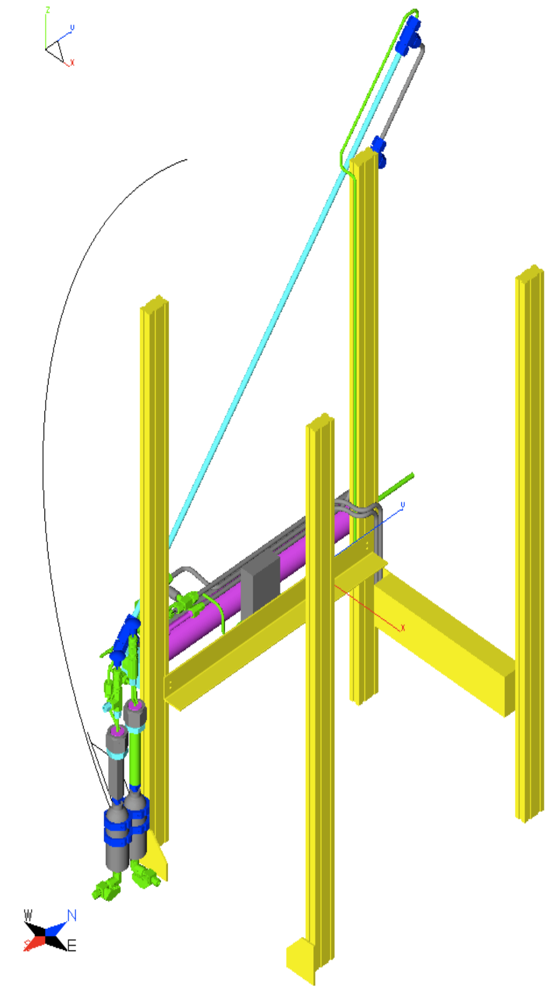
Instrument Improvements: HIPPO-1,2,3

#1 Water traps for flasks:

Removed water to below saturated at 2 ^{o}C and 40 psia.

To improve Isotope and CO_2 data.



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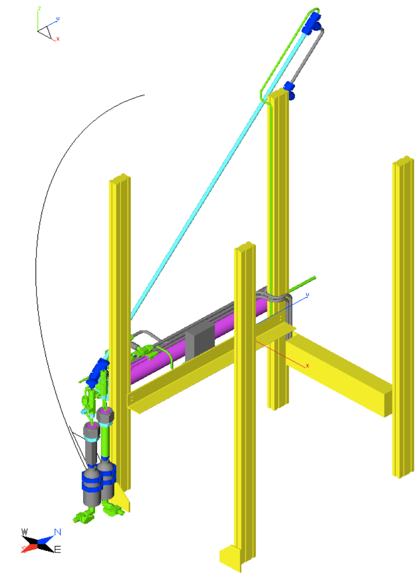

#1 Water traps for flasks:

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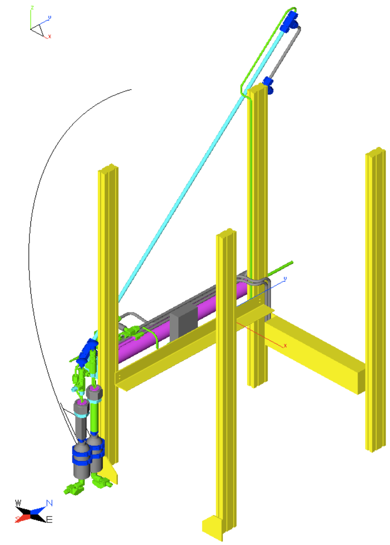
#2 Improved Flask data rate:

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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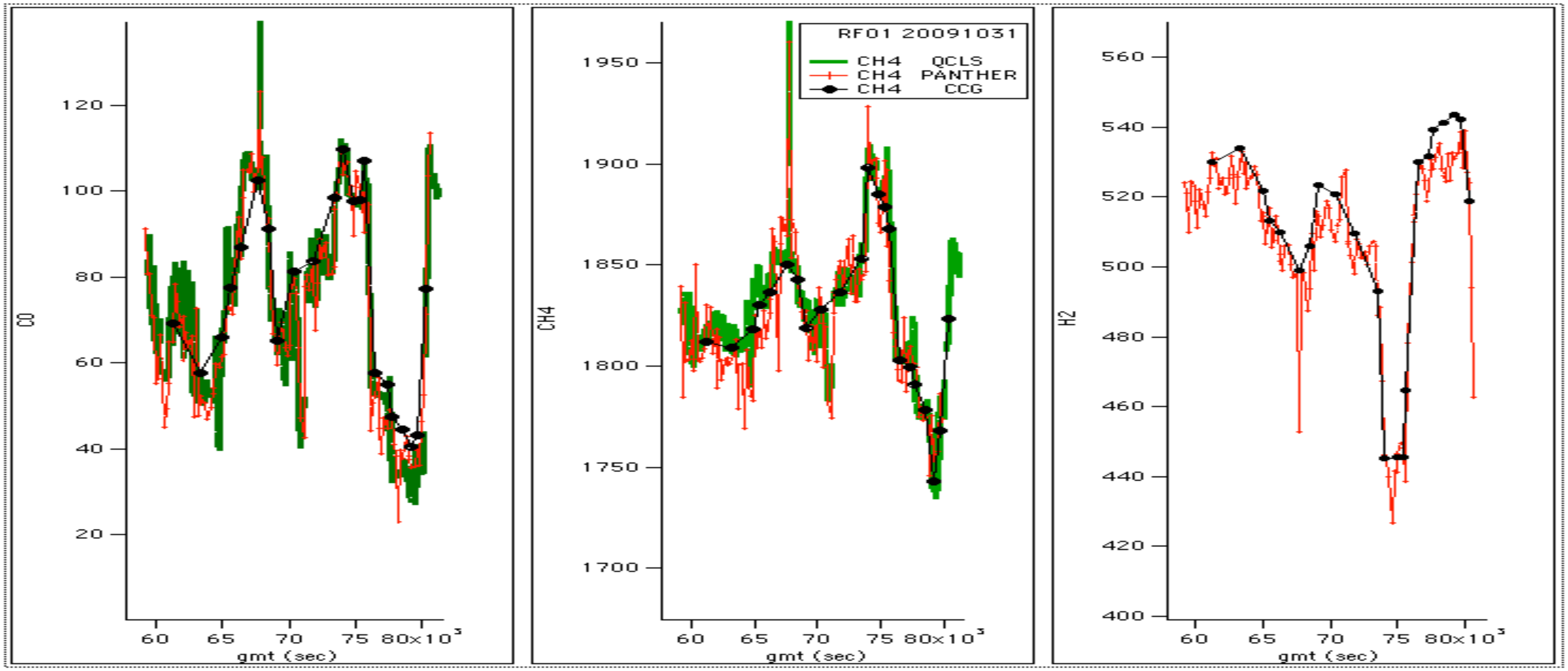
#3 PANTHER CH4, CO, H2 channel improved for HIPPO_2,3,4,5 (NRC temp limitations)



GC Calibrations:

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

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

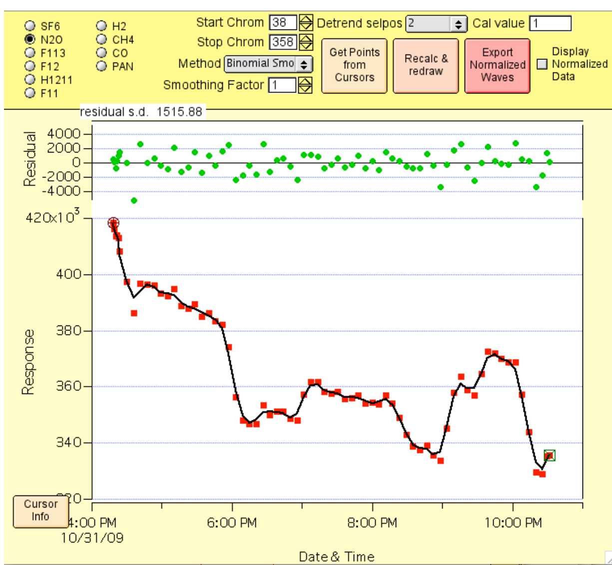
Uncertainty in data is 1-sigma spread in the residuals to this fit, added in quad with uncertainty in a calibration curve.

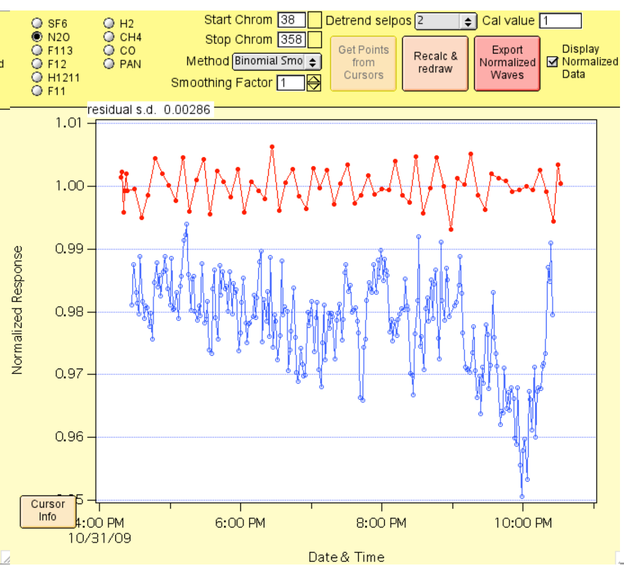
Normalize flight data to this smooth fit through the in-flight calibration data.

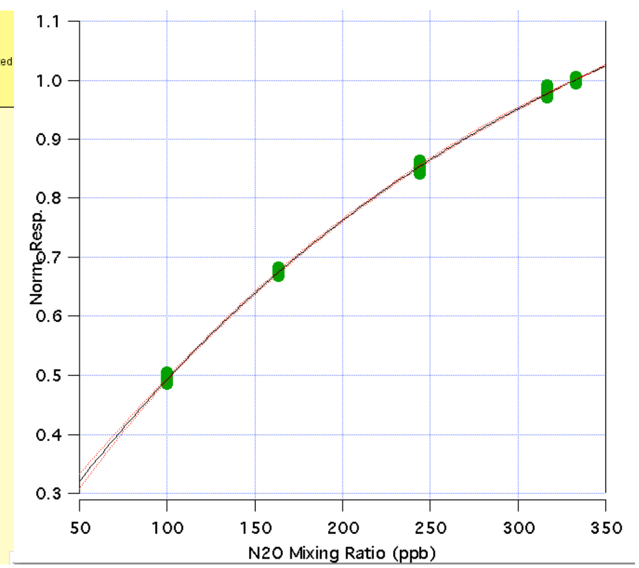
Convert normalized data to ppt via a calibration curve generated in the lab using multiple standards.
(tied to gravimetrically prepared Primaries.)

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

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





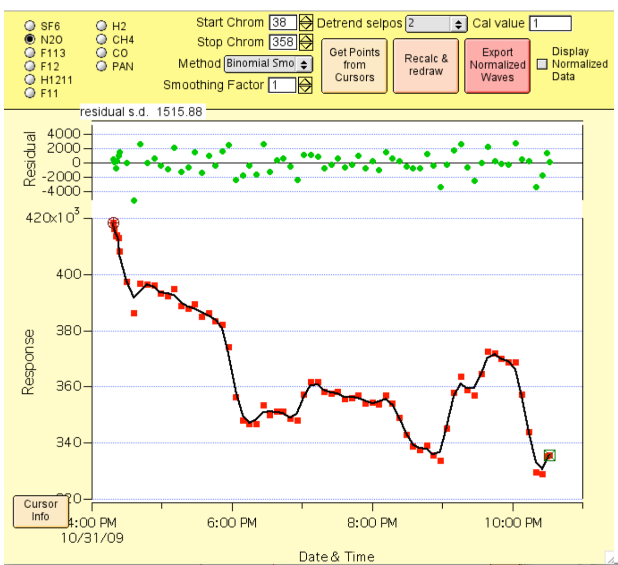


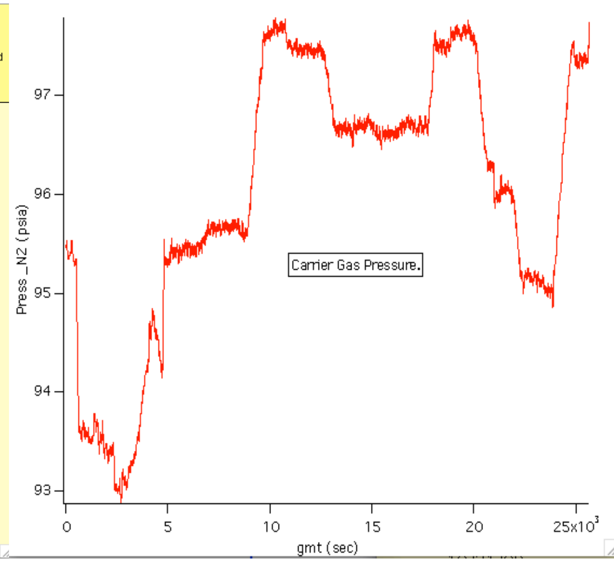
HIPPO GC Calibration issues.

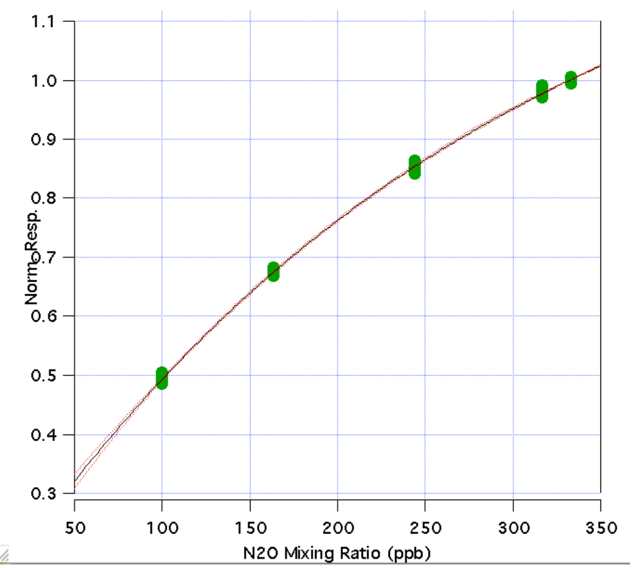
For HIPPO these gain changes are dominated by:

1) Changes in the Carrier Gas head pressure.

2) Water moving through columns onto the ECD.







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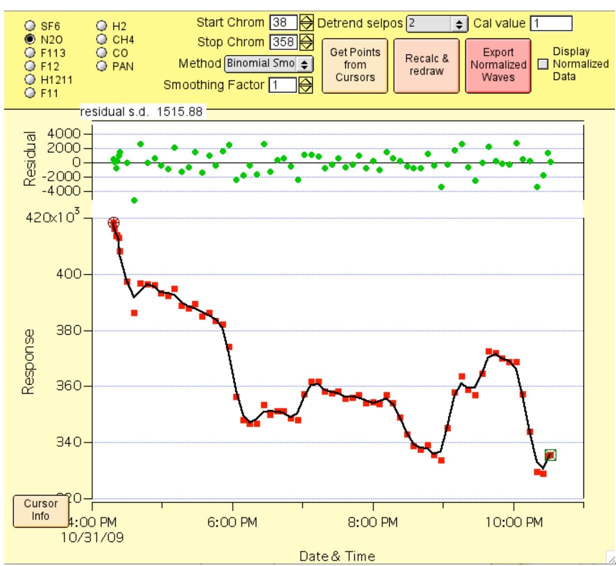
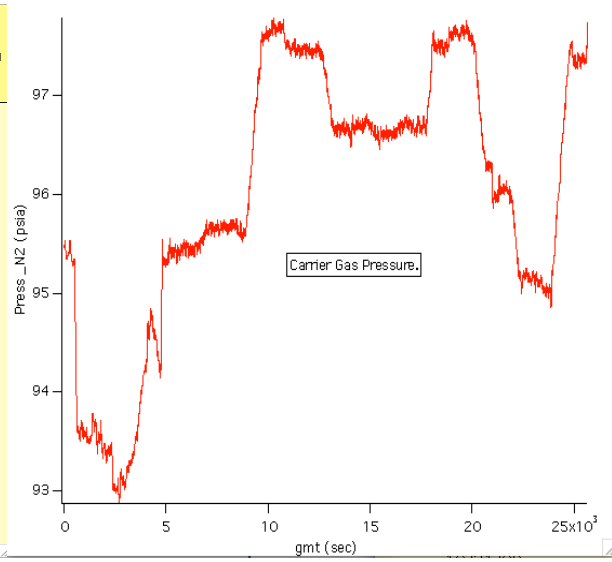
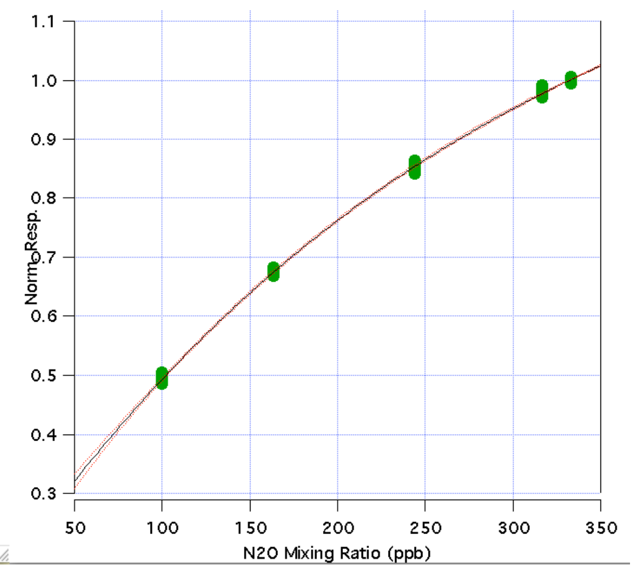
Curvature in cal curve implies detector is showing effects of saturation.

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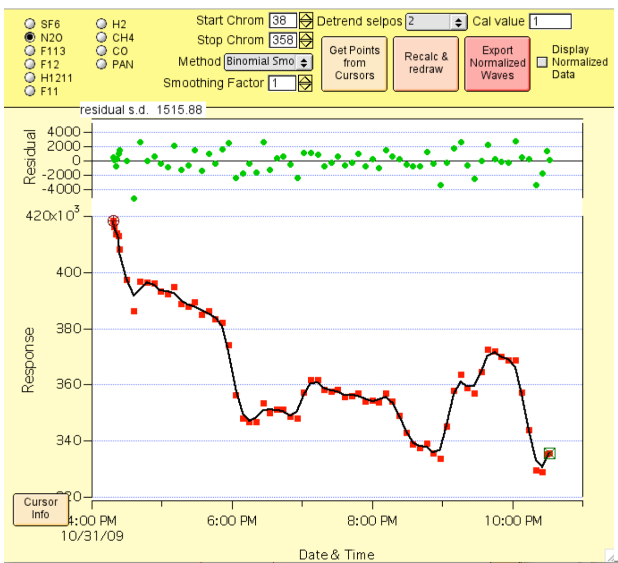
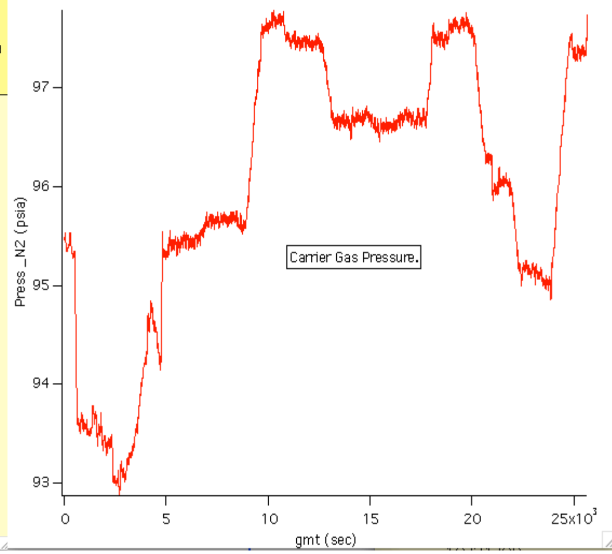
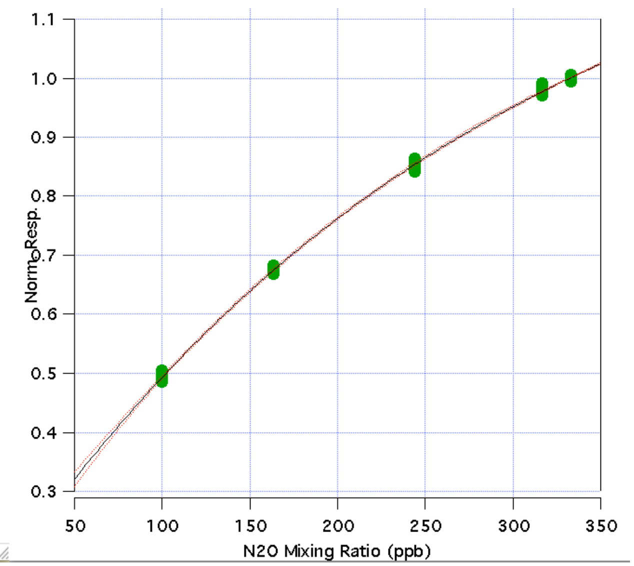
Solution: Reduce the gain changes > remove water and stabilize N2 carrier gas press.
Reduce calibration curvature with smaller sample size.







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HIPPO-3 336 PFP flasks.

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Future Instrument Improvements: HIPPO-4,5.

#4 More isotope data: (Ben Miller)

Add CH_4 isotope measurements.
Potential double flask fill to get isotope ^{14}C (CO_2) for outflow from China.

#5 Water removal for UCATS, PANTHER ECD sample flow.

#6 Stabilize N2 carrier gas regulator against cabin pressure changes.

#7 Reduce Sample Loop on PANTHER N2O channel to reduce calibration curvature.

And Now a Word From Eric

on

UCATS

HIPPO-2 UCATS Summary

Ozone:

- Cell and detectors not tightly fastened to each other - higher noise in flight.
- Lamp replaced after RF03; leak in system on RF04 (no data). Apparent change in calibration from RF05 to end.
- Problems fixed after HIPPO-2; tested in laboratory and in flight.
- Final data submitted.
- Pre- and post-mission calibrations with a NIST-traceable ozone instrument.

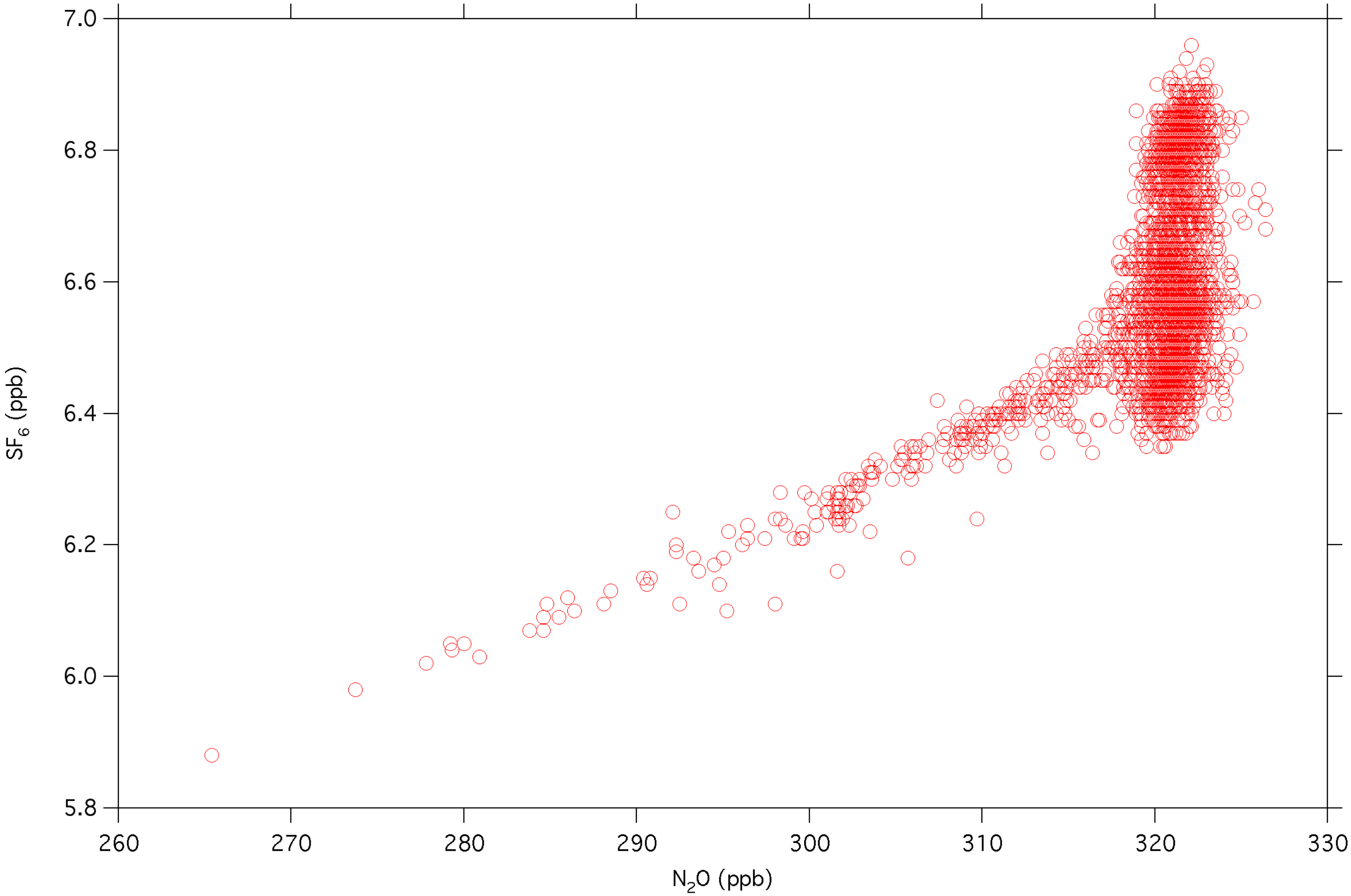
UCATS GC:

- CO_2 dopant flow for N_2O channel blocked. Calibration curve for N_2O depends on CO_2 in cal gas standards.
- N_2O/SF_6 electrometer not working for RF02-RF06 – no N_2O/SF_6 data for these flights.
- N_2O in flight standard bottle (on GV) higher than in standard tank. Using UCATS and PANTHER calibration data to calculate exact value of N_2O.

- Problems with chromatography on CH_4/H_2/CO channel. Precision is about half as good as in HIPPO-1.
- RF02 – instrument shutdowns because of pump current draw; warm-up period for GC.
- All of these problems have been fixed in hardware and software after HIPPO-2; tested in laboratory and in flight.
- All CH_4, H_2, CO, and SF_6 data submitted; N_2O in progress.

Water Vapor:

- Water and ozone plumbing are connected at outlet; leak during RF04 affected H_2O as well.
- Good data for all other flights, same as in HIPPO-1.
- Laboratory calibrations (based on frost point hygrometer) applied and all data submitted.
- The combination of VCSEL and TDL should yield a complete and consistent data set throughout HIPPO.



7.0
6.8
6.6
6.4
6.2
6.0
5.8
260
270
280
290
300
310
320
330
SF_6 (ppb)
N_2O (ppb)

And Now a Word from Eliot

on

AWAS