HATS in situ Program

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There are six custom-built gas chromatographs (GCs) deployed at remote NOAA and cooperative institute facilities where continuous background air measurements conducted nearly every hour. These instruments make up the HATS ground-based in situ program. The current set of instruments called the Chromatograph for Atmospheric Trace Species (CATS) were installed in 1998 (at BRW, MLO, SMO, and SPO), 2000 (at NWR) and 2007 (at SUM) and replaced the older Radiatively Important Trace Species (RITS) instruments. The CATS GCs compose of four chromatographic channels each equipped with gas sample valves, flow controllers, packed columns, and an electron capture detector (ECD). The GCs were built at NOAA in the 1990s and have undergone field maintenance, repairs, and upgrades; many of the significant changes to each CATS instrument are documented in the accompanying table (table 1) and text.

The CATS instrumentation measures and reports hourly, weekly and monthly median mixing ratios for the following gases: N2O, SF6, CFC-11, CFC-12, CFC-113, CCl4, CH3CCl3, and halon-1211. CATS also measures and reports CH3Cl, HCFC-22, and HCFC-142b; however, the chromatography for these gases can be affected by a whole host of problems leading to poor accuracy and/or precision. This GC channel relies on pre-concentrating a large air sample (80cc) onto a cold trap (a packed column from Restek: Hayesep-D, 80/100 mesh, 2-inches of column material in the center of a one foot 1.0mm ID tube), then flash heating the sample onto a megabore capillary column (25ft Chrompack Poraplot Q-HT). Problems encountered in the field include sample contamination, variability in sample volume, failure of the chiller or flash heating electronics, and unstable calibration cylinders. These problems lead to many data gaps and accuracy issues for the CATS CH3Cl, HCFC-22, and HCFC-142b measurements. For these gases, long-term trends and tropospheric gradients should be evaluated from the HATS MSD flask program, however hourly and day-to-day variability can be estimated from the CATS data.

The CATS data is online and regularly updated at the Earth System Research Laboratory (ESRL) Global Monitoring Division (GMD) Halocarbons and other Atmospheric Trace Gases (HATS) Chromatograph for Atmospheric Trace Species (CATS) in situ Halocarbons Program website. They and also used in several GMD data products including the combined N2O, SF6, CFC-11, CFC-12, CFC-113, and CCl4 data sets, as well as the NOAA indices: Annual Greenhouse Gas Index (AGGI) and Ozone Depleting Gas Index (ODGI). Several national and international assessments and publications use CATS data.

Improvements to all CATS instruments

All of the CATS GCs were constructed in the 1990s with some custom designed parts, as well as commercially available power supplies, sensors, and controllers. Routine maintenance has repaired and replaced many components in the instruments. However, there have also been improvements made to the GCs during the last decade. Most significantly, all six of the carrier gas digital flow controllers (Tylan, Model FC-260) were replaced by a less expensive precise unit (Pneucleus Technologies LLC, 100 cc/min). The new controllers improved the stability of the gas flows and ultimately the precision of the GCs' measurements.

Both air and calibration gas samples are dried before injection via a custom packed, inline magnesium perchlorate trap. The lifetime of these traps is much shorter at wet sampling locations. From 2008 to 2009 Nafion membrane dryers (Perma Pura, ¼" OD S.S. tubing) were installed upstream to the magnesium perchlorate trap. This improvement lengthened the duration a magnesium perchlorate trap could be used, thus simplifying field maintenance.

Instrument Changes at Niwot Ridge, Colorado

During the summer of 2006 at Niwot Ridge, Colorado (NWR) the protective cover over the air inlet was blown off by strong winds. Subsequently, rainwater was drawn into the GC severely damaging most of the valves, traps, columns, and flow controllers. The GC was removed from the field site and later refurbished in Boulder. All of the valves were disassembled, cleaned and new rotors installed. It was also an opportune time to replace the aging Tylan flow controllers with new, smaller and more stable controllers from Pneucleus Technologies LLC. The N_2O/SF_6 chromatographic channel was also modified to improve measurement precisions by changing the carrier gas, columns, and chromatography [Hall et al., 2011].

Installation and Removal at Summit, Greenland

There were two GCs built in the mid-1990s and installed at a pair of North American tall tower sites (WITN in North Carolina and WLEF in Wisconsin). These GCs were very similar to the CATS instruments; custom built, four channels equipped with electron capture detectors. Likewise, these instruments measured CFCs, N2O, SF6, and halon-1211; however in place of the complicated CH3Cl and HCFCs channel a doped ECD channel measuring H2, CH4 and CO was installed. After many years of successful measurements and publications [Hurst et al., 1997, 1998] these instruments were removed and returned to Boulder. One of them was refurbished and deployed to Summit, Greenland during the summer season of 2007 and incorporated into the HATS CATS in situ program.

Unfortunately, due to budgetary constraints, the NOAA GMD Summit, Greenland station was downsized during the summer of 2017. Most in-situ measurements were discontinued including the CATS GC.

World Meteorological Organization N_2O audit

In March 2008 a representative of the World Meteorological Organization (WMO) World Calibration Centre (WCC) for Nitrous Oxide visited the NOAA Barrow, Alaska station. They conducted a site assessment and several blind audits of trace gas measurements including the CATS

N2O channel. A calibrated N2O cylinder was substituted in place of an air sample on the CATS instrument. The tank was sampled eleven times over the course of 22 hours, and the data were processed with standard CATS algorithms as an air sample. Based on the NOAA-2006 N2O scale value of 315.74 ± 0.30 ppb (1σ) was obtained, which is in perfect agreement with the value assigned by the WCC-N2O [Zellweger et al., 2008].

Significant Events and Changes to CATS Instruments

Barrow, Alaska (BRW)

2018-02-22
Changed N_2O/SF_6 chromatography to use N_2 carrier gas and CO_2 doping.

2013-05-30
Significant improvements to ECD temp control affecting N_2O/SF_6.

2008-09-07
Installed Nafion dryer on sample lines.

2008-09-05
Installed new carrier gas flow controllers.

2008-03-13
WMO N20 audit.

2006-12 to 2007-05
N_2O/SF_6 ECD temperature control problems.

1998-06-15
Installation of CATS instrumentation.

Mauna Loa, Hawaii (MLO)

2014-07-23
Changed N_2O/SF_6 chromatography to use N_2 carrier gas and CO_2 doping.

2009-06-19
Installed Nafion dryer on sample lines.

2008-02-25
Installed new carrier gas flow controllers.

2007-09-27

ECD replaced. CFC-11, CFC-12, and CFC-113 precision effected.

2003-09-23
N_2O/SF_6 ECD replaced.

2001-11 to 2003-05
Very Noisey ECD affecting N_2O/SF_6 precision.

1998-10-11
Installation of CATS instrument.

Niwot Ridge, Colorado (NWR)

2008-10-28
Installed Nafion dryer on sample lines.

2007-10-31
GC rebuilt and installed.

2007-10-31
Changed N_2O/SF_6 chromatography to use N_2 carrier gas and CO_2 doping.

2006-07-01
Rainwater severely damaged GC, removed and refurbished.

2000-11-09
Installation of CATS instrument.

American Samoa (SMO)

2017-12 to 2018-02
Removal and installation of a new cell phone tower and air lines.

2009-09-29
Observatory hit by 8.3 mag. Earthquake. GC sustained minor damage.

2009-09-11
Installed Nafion dryer on sample lines.

2009-06-12
Installed new carrier gas flow controllers.

1998-12-02

Installation of CATS instrument.

South Pole, Antarctica (SPO)

2009-01-24
Installed new carrier gas flow controllers.

2007-05-18
Replace N_2O/SF_6 ECD due to poor precision.

1998-01-25
Installation of CATS instrument.

Summit Station, Greenland (SUM)

2017-07-24
CATS instrument turned off and returned to Boulder, CO.

2016-04-30
Changed N_2O/SF_6 chromatography to use N_2 carrier gas and CO_2 doping.

2013-07-30
Raised building and inlets about 10 ft.

2010-10-15
Building and tower moved to a new location.

2010-06-06
Installed new carrier gas flow controllers.

2009-08-19
Installed Nafion dryer on sample lines.

2007-06-26
Installation of CATS instrument.

Calibration Scales for Various Trace Gases

NOAA ESRL GMD is the World Meteorological Organization (WMO), Global Atmospheric Watch (GAW) Central Calibration Laboratory (CCL) for CO_2, CH_4, N_2O, SF_6, and CO. NOAA ESRL also maintains internal scales for a number of trace gases that are not part of the set of WMO GAW CCL scales. Scales are defined by a specific set of primary standards. Mixing ratios (expressed as dry air mole fraction) are assigned to the primary standards based on the mean response observed on GC-ECD or GC-MSD instruments. The scales are tied to a specific set of primary standards and named according to the year in which they were adopted. Thus, the preparation and use of new primary standards for a particular compound results in a new scale for that compound. Additional information can be found on the National Oceanic and Atmospheric Administration (NOAA) Earth System Research Laboratory (ESRL) Global Monitoring Division (GMD) Halocarbons and other Atmospheric Trace Species Group (HATS) Central Calibration Laboratory website.

N_2O
Previous Scale: 2005
Current Scale: 2006A
Number of Primary Standards: 13
Note: WMO GAW CCL scale

SF_6
Previous Scale: 2006
Current Scale: 2014
Number of Primary Standards: 17
Range: 2-20 ppt
Conversion Equation: $Y = 2.6821e\text{-}3*X^2 + 9.7748e\text{-}1*X + 3.5831e\text{-}2$ (where Y = value of SF_6 on the 2014 scale and X is SF_6 on the 2006 scale)
Note: WMO GAW CCL scale

CFC-11
Previous Scale: 1992
Current Scale: 2016
Number of Primary Standards: 5
Range: 100-260 ppt
Conversion Equation: $Y = -1.7948e\text{-}6*X^3 + 7.4134e\text{-}4*X^2 + 0.89385*X + 6.54$ (where Y = value of CFC-11 on the 2016 scale and X = value of CFC-11 on the 1992 scale)

CFC-12
Previous Scale: 2001
Current Scale: 2008
Number of Primary Standards: 15
Range: 150-650 ppt
Conversion Equation: Y = 1.0021 * X + 5.807 (where Y = value of CFC-12 on the 2008 scale and X = value of CFC-12 on the 2001 (or 1997) scale)
Note: The 2008 CFC-12 scale is 1.3% higher than the 2001 scale, see scale page for more information. Update using Y = 1.002*X + 5.807 ppt.

CFC-113
Previous Scale: 2003
Current Scale: No Change
Number of Primary Standards: 10

Range: 20-110 ppt

CCl_4
Previous Scale: 1996
Current Scale: 2008
Number of Primary Standards: 7
Range: 25-150 ppt
Note: Seven standards prepared from 2001-2004 are now used to define the scale. These seven standards are consistent to within 0.5%. Four standards prepared in 1996 have been removed from the scale. For ECD-based results the conversion is 0.9954 at 95 ppt. For GCMS results the conversion is 0.9853.

CH_3CCl_3
Previous Scale: 2003
Current Scale: No Change
Number of Primary Standards: 10
Range: 10-180 ppt

Halon-1211
Previous Scale: 1996
Current Scale: 2006
Number of Primary Standards: 5
Range: 3-7 ppt
Conversion Equation: Y = 1.0175 * X - 0.0249 (where Y = value of Halon-1211 on the 2006 scale and X = value of Halon-1211 on the 1996 scale)
Note: The 2006 scale is 1% higher than the 1996 scale. The conversion factor is 1.011.

References

Hall, B. D., Dutton, G. S., Mondeel, D. J., Nance, J. D., Rigby, M., Butler, J. H., Moore, F. L., Hurst D. F., & Elkins, J. W.. (2011). Improving measurements of SF_6 for the study of atmospheric transport and emissions. *Atmospheric Measurement Techniques Discussions*, *4*(4), 4131-4163.

Hurst, D. F., Bakwin, P. S., Myers, R. C., & Elkins, J. W. (1997). Behavior of trace gas mixing ratios on a very tall tower in North Carolina. *Journal of Geophysical Research: Atmospheres (1984–2012)*, *102*(D7), 8825-8835.

Hurst, D. F., Bakwin, P. S., & Elkins, J. W. (1998). Recent trends in the variability of halogenated trace gases over the United States. *Journal of Geophysical Research: Atmospheres (1984–2012)*, *103*(D19), 25299-25306.

Zellweger, C., Klausen, J., & Buchmann, B. (2008). System and Performance Audit of Surface Ozone, Carbon Monoxide, Methane and Nitrous Oxide at the Global GAW Station Barrow, USA, March 2008, WCC-Empa Report 08/1.