Objective-

Atmospheric methane today is nearing 2000 ppb, more than 2X preindustrial concentrations. Cumulatively, methane is the second most important anthropogenic greenhouse gas, but with a per molecule potency at trapping heat 25X greater than CO_2. While NOAA has monitored global methane concentrations since 1983, our ice core records have accurately extended atmospheric methane records going back 800 000 years and more with recent work under COLDEX.

Today, we are measuring gas samples that will start off in the pre-industrial period and cover the industrial rise in methane and other greenhouse gases. The plan is to measure 12 samples covering 7 unique depths from the GISP2 ice core in Greenland. We will also measure 5 replicates of the same depth giving us an error associated with the measurements. Our objective is to re-affirm measurements of the preindustrial rise that were made more than 15 years ago.

The start of a typical sampling day:
A typical sampling day starts off with loading samples into glass flasks and transporting them from the freezer to the lab where they are bolted onto a 12-port sampling array. Each port corresponds to a single sample which we can open and close individually to the vacuum line and GC. Once the samples are bolted onto to line, while being kept at -70°C, we open the flasks to the vacuum line to remove any modern air from the flasks. We do this for 1 hour, ensuring that the final flask pressure is just the vapor pressure over ice at -70°C, the temperature of the ethanol cold bath.

Releasing air from a sample:
To measure a gas sample from ice we must first liberate the ancient air from the ice it was trapped in. In the case of making methane measurements, we do this by melting the sample. As the sample melts, sample air bubbles into the headspace leaving the meltwater at the bottom of the flask. This is the air that we will later expand into the GC to make a concentration measurement, but first we must refreeze the sample. We don't want water vapor interfering with our measurements and the freezing minimizes this.

Calibration and standards

While our ice sample is going through the melt-refreeze process we start preparing for the sample measurements by creating a standard curve. A standard curve gives us a reference so that we can convert the measurement that the GC produces into a methane concentration.

To make a measurement, gas is expanded first into a sample loop (known volume) with a pressure gauge attached to it. Once the gas is expanded and reaches an equilibrium pressure we record the pressure value. In the case below, standard gas was added to the sample loop and a pressure was 39.37torr.

A valve (6 port gas sampling valve) then switches position and allows a stream of clean nitrogen gas to push the sample air through a chromatographic column in the gas chromatograph (GC). The column separates the components of air so that different gases exit the column at different times. A detector at the end of the column (flame ionization detector) generates an electrical signal proportional to the amount of methane passing the detector and the instrument software displays and records the detector signal. In the image below the second peak is the methane signal.

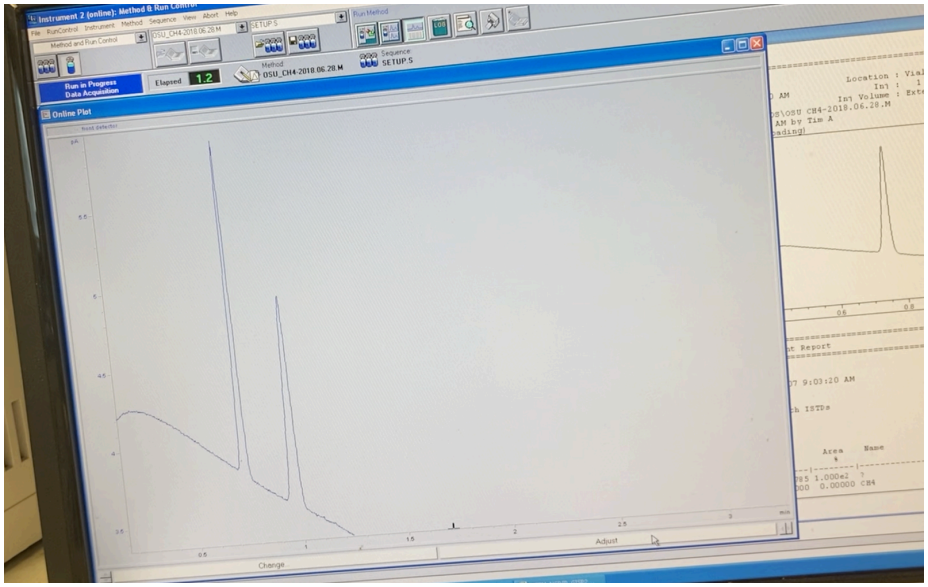


Figure2. Signal from the flame ionization detector for an air sample run through the GC column. The second peak corresponds to methane.
The methane peak in the recorded detector signal is integrated from the baseline of the signal. The GC software does this for us and records the results in a “peak report”. The ratio of peak area to pressure is determined by the methane concentration of the injected gas. We use the peak area to pressure ratio of a standard gas as a reference point for our sample measurements.

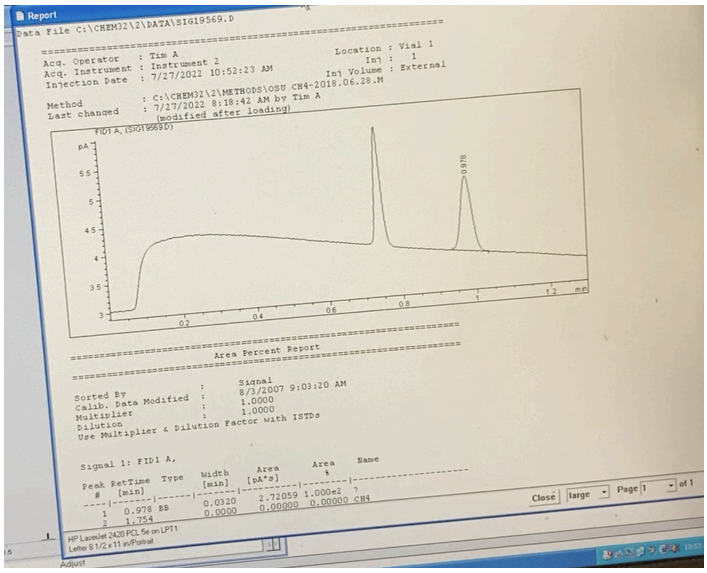
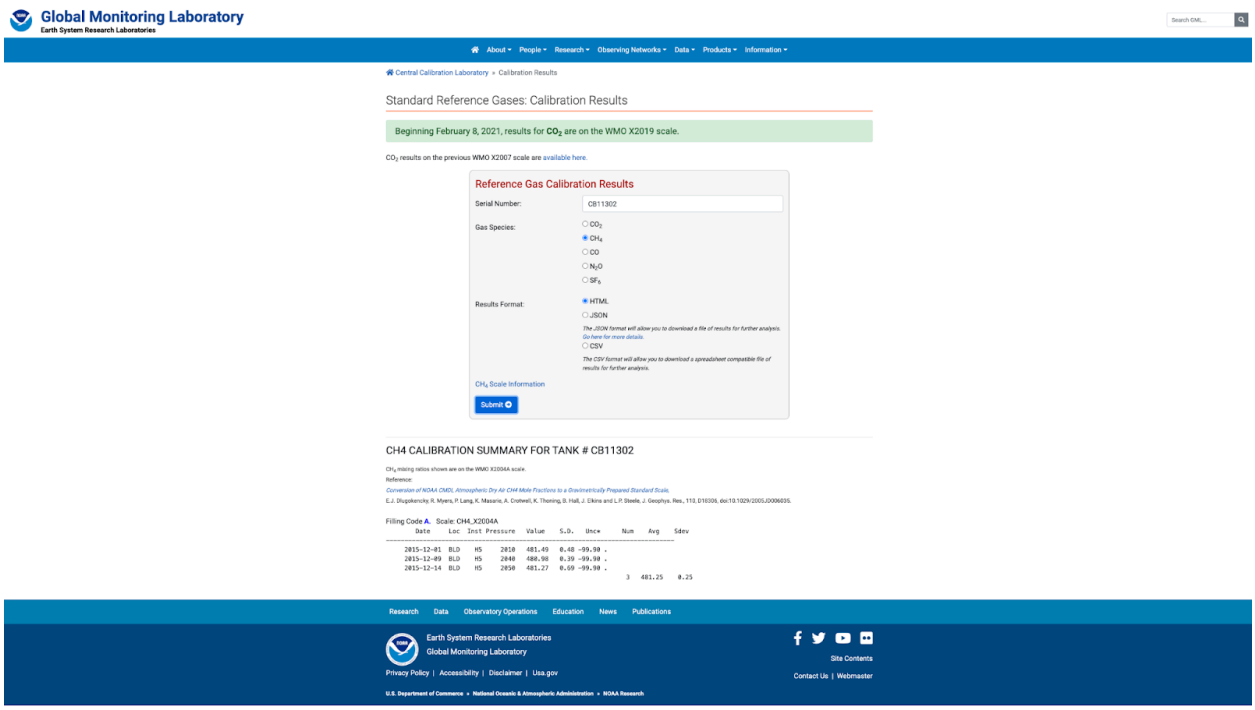


Figure 3. Peak report. With each sample run through the GC we get a peak report. It contains the integration we use for calculating a methane concentration.

The standard curve is created by making measurements from a high pressure tank of air independently calibrated for methane concentration (done for us by a central laboratory maintained by the National Oceanic and Atmospheric Administration (NOAA) in Boulder, CO. . NOAA measures these tanks to get an absolute concentration and maintains a system of standards that all labs around the world can use. NOAA keeps careful track of every tank they calibrate. Each tank has a numbered associated with it and you can look up the information for any tank that has been calibrated by them.



CH4 CALIBRATION SUMMARY FOR TANK # CB11302

CH_4 mixing ratios shown are on the WMO X2004A scale.

Reference:

Conversion of NOAA CMDL Atmospheric Dry Air CH4 Mole Fractions to a Gravimetrically Prepared Standard Scale,

E.J. Dlugokencky, R. Myers, P. Lang, K. Masarie, A. Crotwell, K. Thoning, B. Hall, J. Elkins and L.P. Steele, J. Geophys. Res., 110, D18306, doi:10.1029/2005JD006035.

Filling Code **A.** Scale: CH4_X2004A

Date	Loc	Inst	Pressure	Value	S.D.	Unc*	Num	Avg	Sdev
2015-12-01	BLD	H5	2010	481.49	0.48	-99.90 .			
2015-12-09	BLD	H5	2040	480.98	0.39	-99.90 .			
2015-12-14	BLD	H5	2050	481.27	0.69	-99.90 .			
							3	481.25	0.25

From the standard tank we measure standard air over a range of pressures, and with each pressure we get a corresponding peak area. We do this for pressures ranging from 7 - 50 torr which covers the range of our sample measurements.

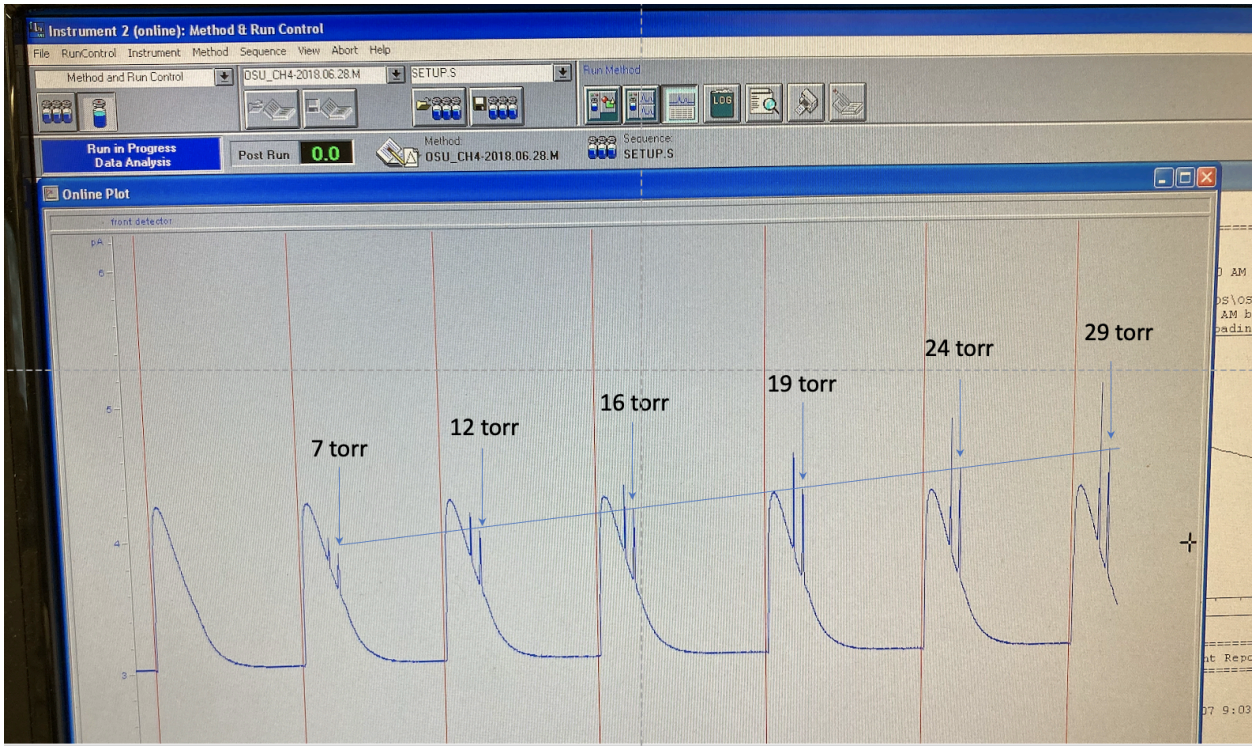


Figure 5. Standard measurements and their corresponding peaks for different pressures of gas added to the sample loop.

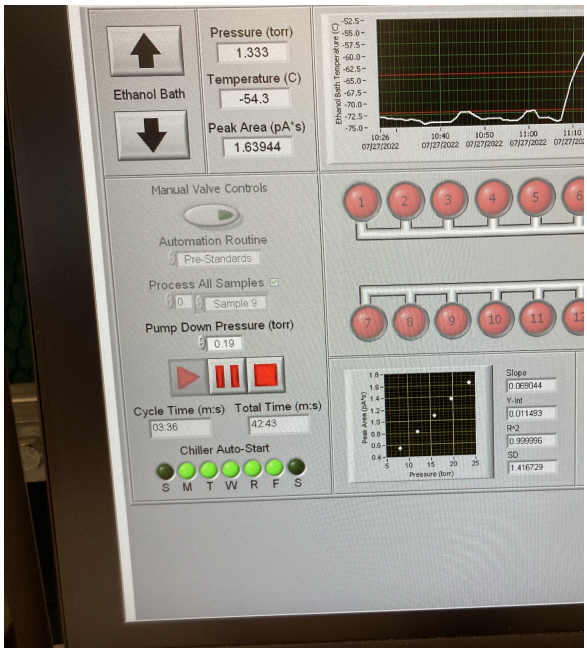


Figure 6. Each peak area is plotted against its corresponding pressure. This gives us a standard curve to compare our samples to.

Measuring samples

After we have created our standard curve and the sample are refrozen, we can begin the process of measuring samples. The air from each flask is expanded into the sample loop and analyzed in the same way as the standard. We are able to make 4 separate measurements from the gas of each sample.

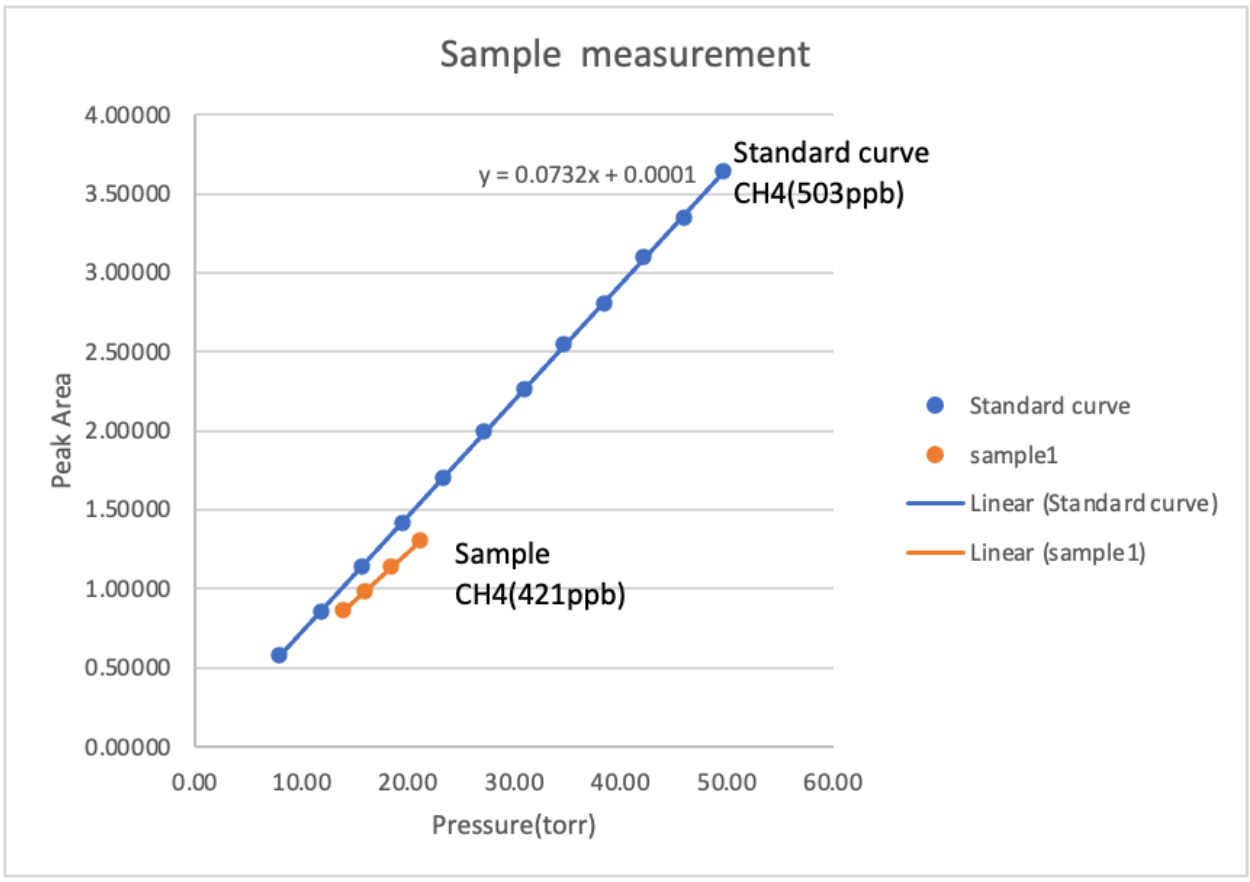


Figure 8. We take the peak areas of the samples and compare them to the standard curve to make a measurement of a sample. We use the slope equation of the standard curve to get a methane concentration as follows.

Sample concentration=standard CH4 concentration (peak area-intercept)/(pressure x slope)

The units of concentration are parts per billion (ppb), equivalent to the number of methane molecules per billion air molecules. This is sometimes called a mixing ratio or mole fraction.

Once we get a concentration, we still have some processing to do. Because CH_4 is more soluble in water than N_2 and O_2, the extra gas that dissolves in water causes our concentrations to be lower than expected. We correct for this small effect by adding a solubility correction which has been empirically determined.

We also must account for any blank, or extra methane signal associated with melting and refreezing the samples. We create air free ice and then add standard gas over it. We then melt that ice just like any other sample. Any deviation from the standard concentration is our blank measurement.

Finally, we generally make measurements in replicate. We use the average or pooled standard deviation of these replicates to determine the error of our measurements.