

Instrumental Method

Inlet line and sample intake

The inlet point resides inside an inverted titanium cup with 1/2" bulkhead union and monel mesh covering and attached via hose clamps to a 1" vertical aluminum rod that is affixed to a 3 meter rod extending horizontally from the tower. The inlet line is 1/2" OD Synflex Type 1300/Dekabon tubing (Goodrich, Geneva, IL) drawn from the inlet cup to a pump module located in an adjacent building. A 1/4" guy wire was extended across the two buildings and clamped down using wire rope clamps. The Synflex tubing was affixed with hose clamps and zip ties approximately every meter to a tie-down point on the tower, along the guy wire and on rebars mounted along the sides of the buildings. There is no point where excessive stress is placed on the Synflex. The inlet line is connected directly to the pump module and totals ~65 feet in length.

The air sample is pumped into the instrument using a custom-built pump module. An oscillating aquarium-style pump (Gast Manufacturing, Inc., Benton Harbor, MI, model DDL8BS) continually flushes the line at 12 L/min to prevent buildup of condensation and to reduce the residence time between the sampling point and the instrument. This flushing pump contains components that could contaminate the air sample so the line is split upstream through a 7 micron filter and to a diaphragm pump (KNF Neuberger, Trenton, NJ, model UN86) that is switched on only during sampling. Air and any water that may have entered or condensed in the line pass through this pump and into a 'dip-tube' water trap. The water trap consists of an inner and outer tube, where water droplets fall to the bottom of the outer tube and air is pumped into the instrument from the top. Water and the bulk of air passes through a back pressure regulator (Go Regulator, Spartanburg, SC) where the majority of the flow is vented at 2 L/min. Only a small amount of sample is introduced into the GC system at 100 mL/min. A schematic of the intake system is shown in Figure 1.

Laboratory

The instrument is located on the first floor of an adjacent building equipped with an air conditioner and dehumidifier. The dehumidifier is used continuously between March-October and the air conditioner is only used for hot days during the summer, when air temperatures exceed 27°C. Most of the year, air temperatures are significantly below this threshold and the air conditioner is not needed. A small fan is used instead to ventilate air in the lab. The inlet line that is within the lab space has been insulated with pipe insulation to minimize the formation of condensation in the line when the air conditioner is being used.

Chromatography

A detailed schematic of the GC system is found in Figure 2, FID and ECD valve schematics in Figures 3 and 4 and chromatograms for the three gases in Figure 5. A 6-port 2-position gas sampling valve (GSV, VICI Valco, Houston, TX, model ED2C6UWEPH) and 10-port 2-position backflush valve (BFV, VICI Valco, Houston, TX, model ED2C10UWEPH) were used for each channel to control the chromatography. Note: A 8-port valve could be used in place of 10-port BFVs. A 6-port stream selection valve (SSV, VICI Valco, Houston, TX, model EMT2CSD6MWEPH) with 12-port actuator selects between air sample and standard, alternating between the two to produce a calibrated measurement, and directs the stream to a Nafion dryer (Permapure, LLC, Toms River, NJ, model MD-050-72S-1), which uses a countercurrent gas of zero air supplied by the pure air generator. The five micro-electric actuated valves contain purge housings to prevent introduction of ambient air during valve switching and utilize a flow of N₂ (that also flushes the FID columns) at 20 mL/min. Sample loops for the FID and ECD channels of 1.5 mL and 9 mL, respectively, are continuously flushed and filled with the sample for 45 seconds at 100 mL/min. At this time the SSV is closed and the sample is allowed to equilibrate with

ambient pressure for 30 seconds. A coiled length of tubing separates the two systems (FID and ECD) so that there is no possible backward mixing of CH_4 from the P-10 carrier gas into the FID system. Additionally a coiled length of tubing is placed at the end of the sample stream so there is no backwards diffusion of lab air into the sample loops. Zero air from the pure air generator is delivered through a 6L ballast volume to allow for air to be mixed prior to entering the FID in order to keep the flame steady.

Moisture traps were fitted on both the N_2 and P-10 gases (Agilent Technologies, Santa Clara, CA). Additionally, a heated gas purifier (Supelco, St. Louis, MO, model 23800-U) is used on the P-10 gas to remove trace amounts of O_2 . The purity of the gases with inclusion of these traps was determined to be of sufficient quality as it did not adversely impact instrument sensitivity or repeatability of the measured species.

Flow control for all carrier and fuel gases is achieved by the use of the electronic pneumatics control (EPC) units built into the GC. Flow control for the sample and standard are achieved using non-lubricated Viton seal micrometering valves (VICI Valco, Houston, TX, model ZBNV1-D).

A non-linear ‘memory’ effect exists for N_2O that results from doping of N_2O by CO_2 (in addition to doping by CH_4 from the P-10 carrier gas) but this effect is eliminated after ten consecutive, automated injections of air (or standard filled with air) every ten minutes. In the current chromatographic setup, CO_2 co-elutes with N_2O and variations in atmospheric CO_2 abundance could result in an artificial change in N_2O response. Furthermore, the molecular sieve column, which serves to reverse the order of N_2O and SF_6 elution, highly retains CO_2 . At the temperature that the column is held (180°C), CO_2 from a sample slowly bleeds off the column for about two hours. This property is exploited because ten automated injections accumulates enough CO_2 in the system to prevent small changes in ambient CO_2 in each sample from affecting N_2O response. The time to ‘equilibration’ was tested by sampling from a tank of air for a given number of runs and then injecting either a sample of zero air (no CO_2) or a $1000\text{ }\mu\text{mol mol}^{-1}$ (high concentration) CO_2 sample and re-sampling the tank of air. The number of runs was varied until no change (i.e. within instrumental repeatability) was noticed before and after the variable CO_2 sample was injected. Any time the instrument is switched off or sampling has been interrupted, the first four hours (as a overestimate) of data is thrown out.

Nonlinearity in the ECD was measured by exploiting the assumption that the FID is essentially linear over the range of concentrations of CH_4 that is being measured in the atmosphere. Beginning with this assumption, the non-linearity of the ECD was determined from seven samples containing CH_4 , N_2O , SF_6 in zero air that were made for the range of mole fractions measured at polluted AGAGE sites. The initial mixture was purchased from Linde LLC and diluted with zero air. Non-linearity analyses are plotted as the unitless ‘normalized sensitivity’ versus ‘normalized peak response’ in Figure 6. Normalized peak response, by either height or area depending on the substance, is analogous to the mole fraction of the sample normalized by a standard. Sensitivity is the detector ‘response per mole’ given the known concentrations of the samples.

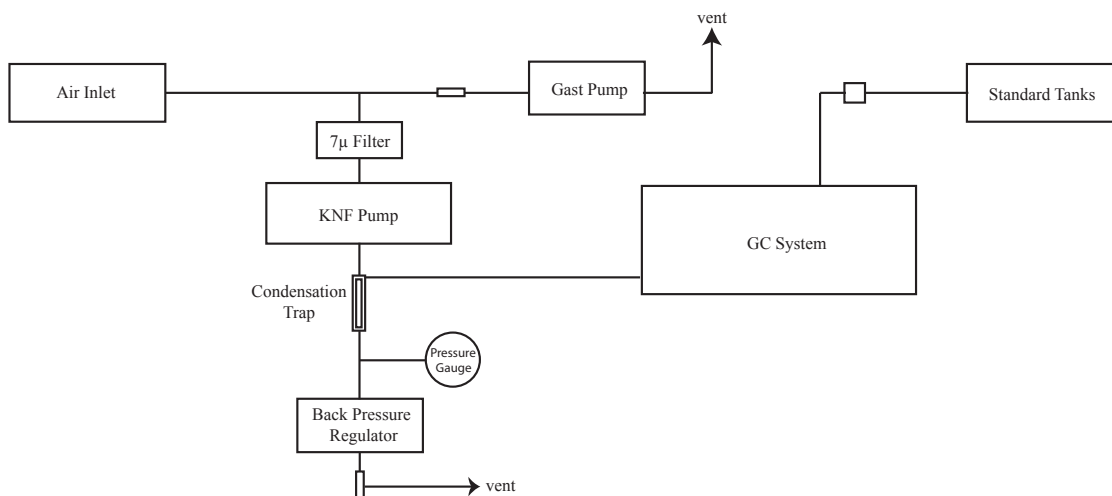


Figure 1: Flow diagram of the air and standard intake system, including the configuration of the pump module. The Gast pump continuously flushes the line, while the non-contaminating KNF pump draws air into the instrument for analysis for 45 seconds every 20 minutes.

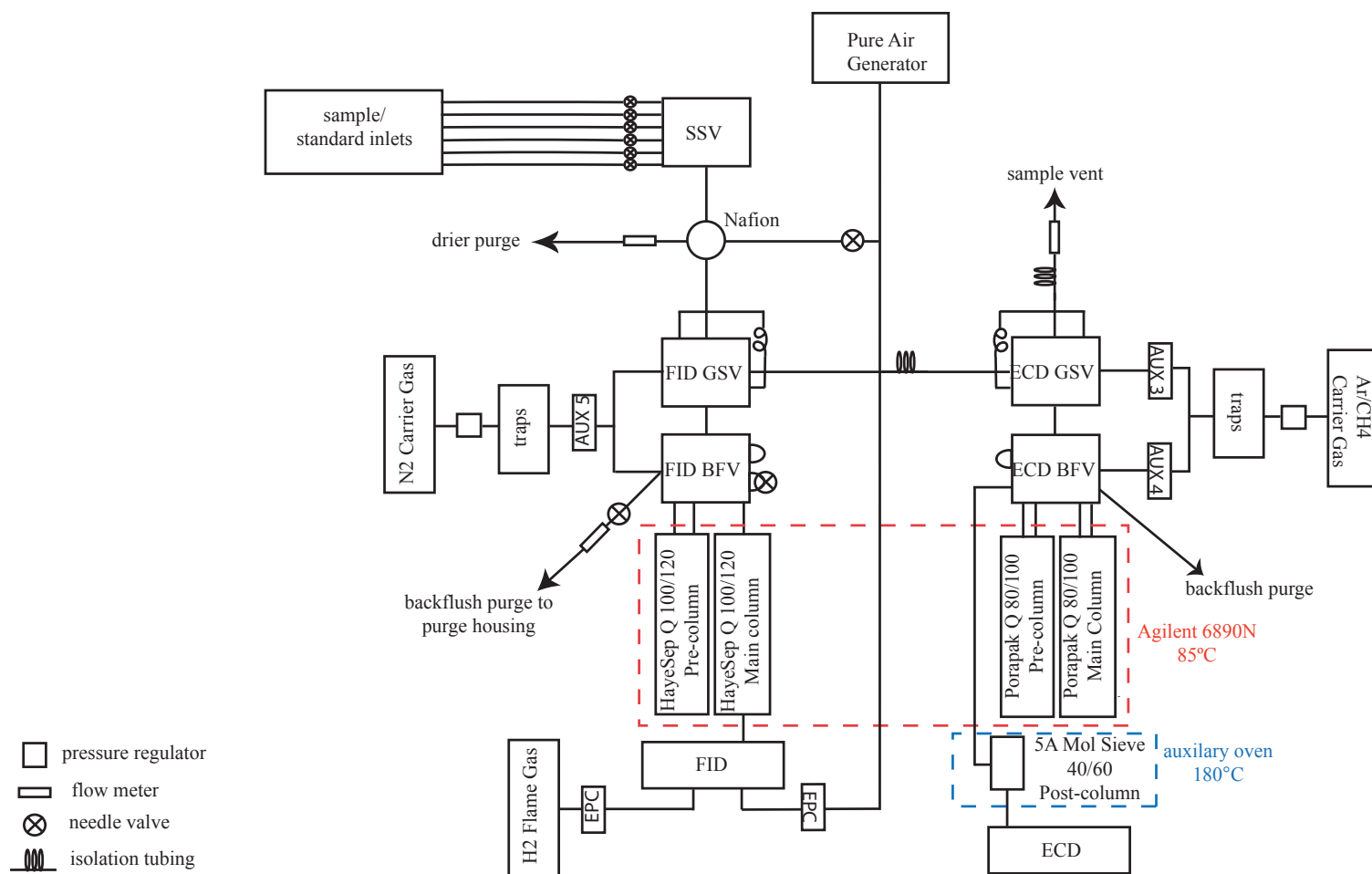


Figure 2: Flow diagram containing components and connections of the GC-FID/ECD system. Air or standard is selected using a stream selector valve (SSV) which fills each sample loop. Each system contains a gas sampling valve (GSV) and a backflush valve (BFV) to control the chromatographic separation. The red box shows which columns are contained within the GC, held isothermally at 85°C and the blue box represents a custom-built column oven held at 180°C.

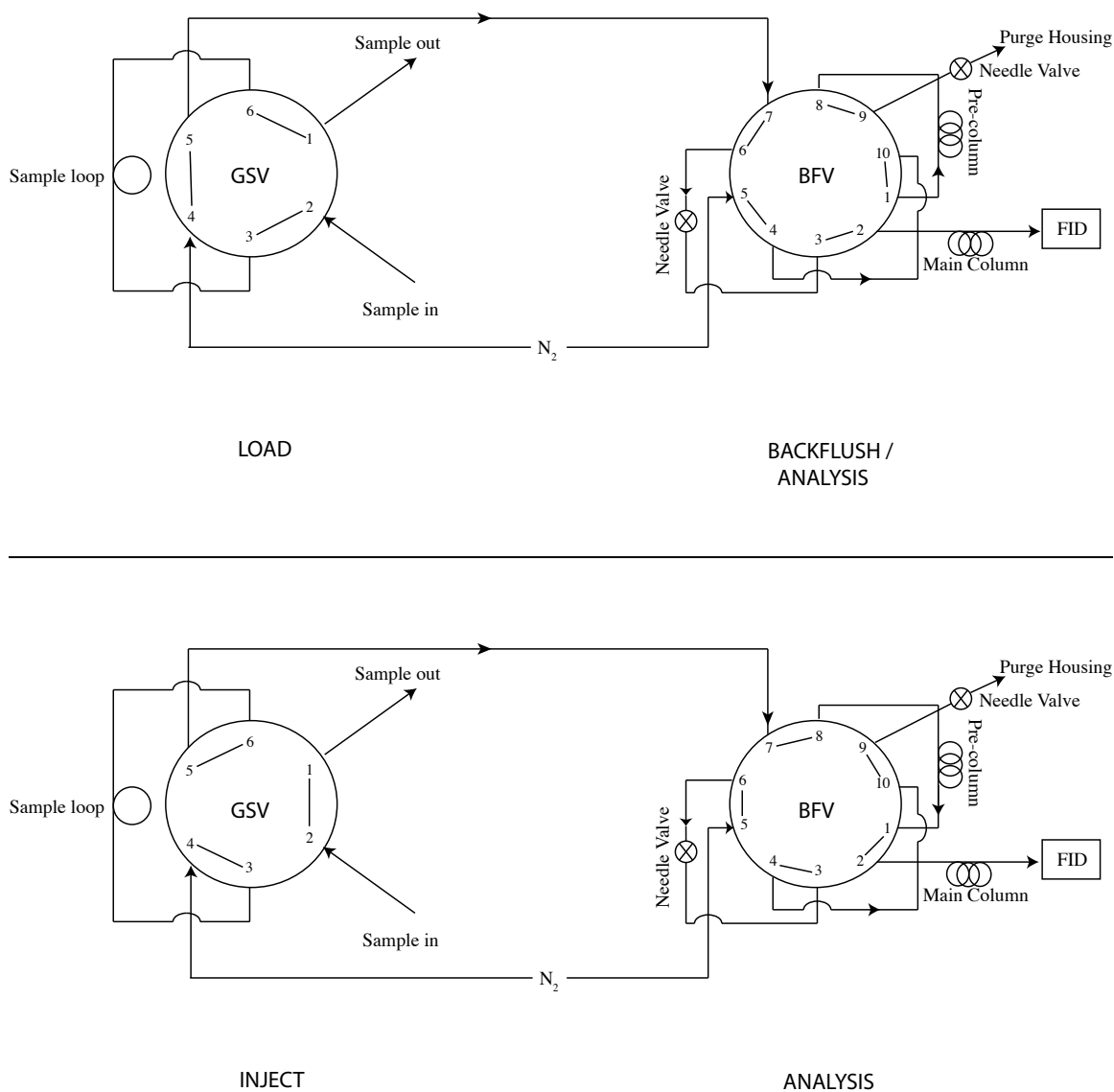


Figure 3: FID valve configurations in the load/inject and backflush/analysis positions. During 'load' the sample loop is filled. The GSV then switches to 'inject', while the BFV is in 'analysis'. After CH_4 has passed through the pre-column, the BFV switches to 'backflush/analysis' and CH_4 proceeds to the main column and FID while the pre-column is backflushed. Needle valves control flow rates through the GSV and BFV since only one auxiliary EPC is used in this setup.

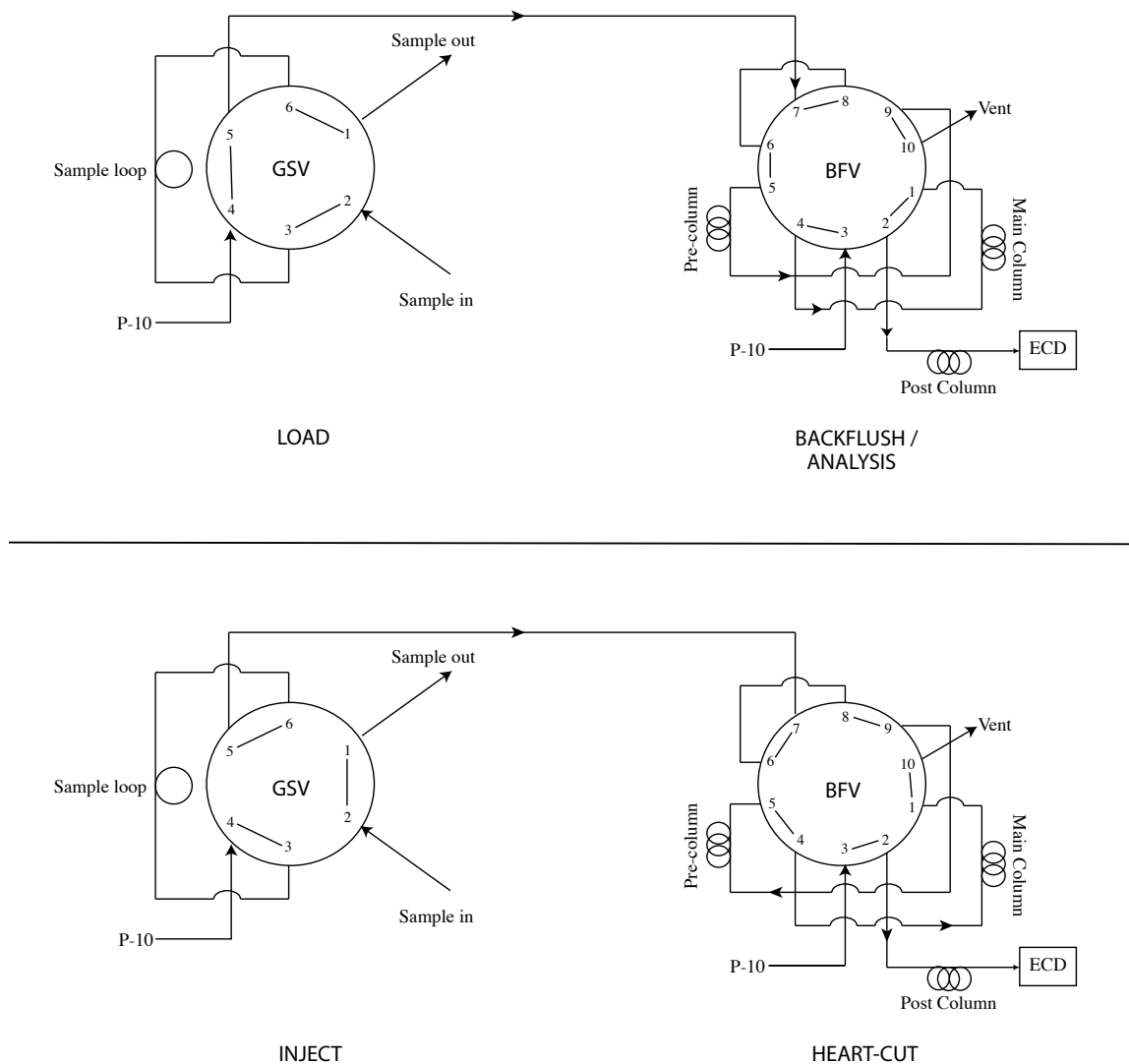
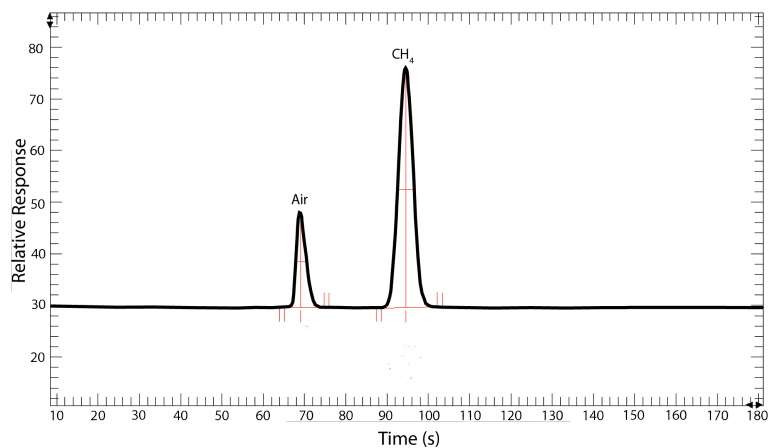
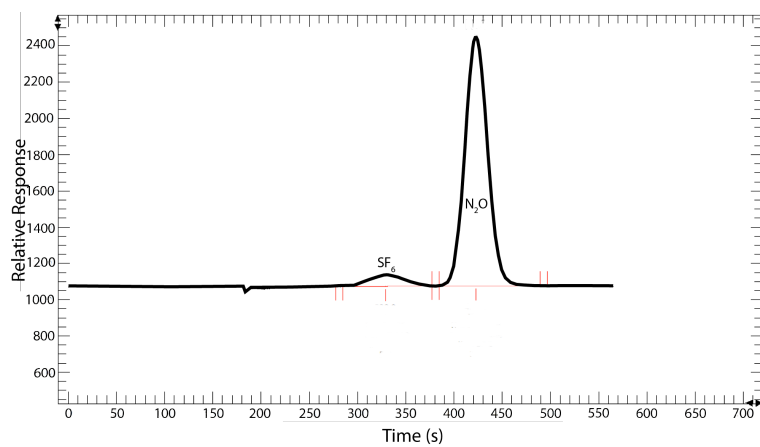


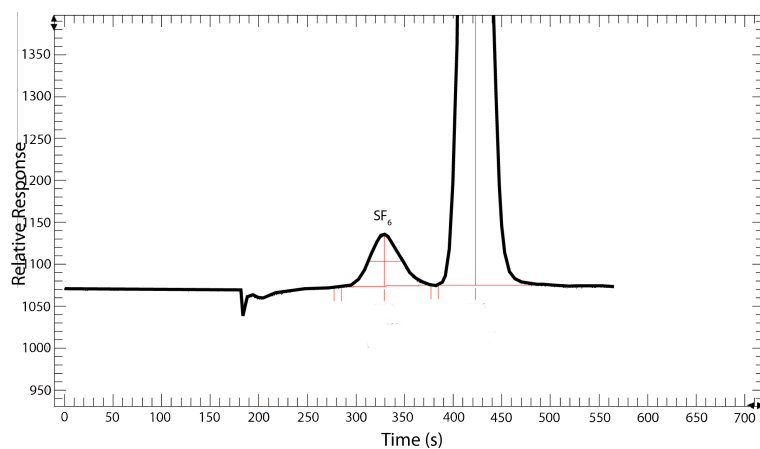
Figure 4: ECD valve configurations in the load/inject and backflush/heart-cut positions. During 'load' the sample loop is filled. The GSV then switches to 'inject', while the BFV is in 'heart-cut' to vent out O_2 . After all O_2 has been removed, the BFV switches to 'backflush/analysis', at which time N_2O and SF_6 proceed to the main/post columns and ECD and the pre-column is backflushed.



(a) CH_4

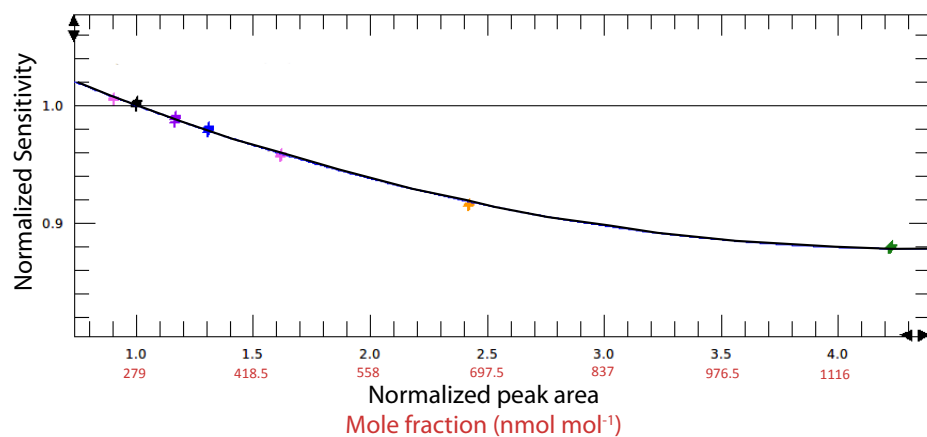


(b) N_2O

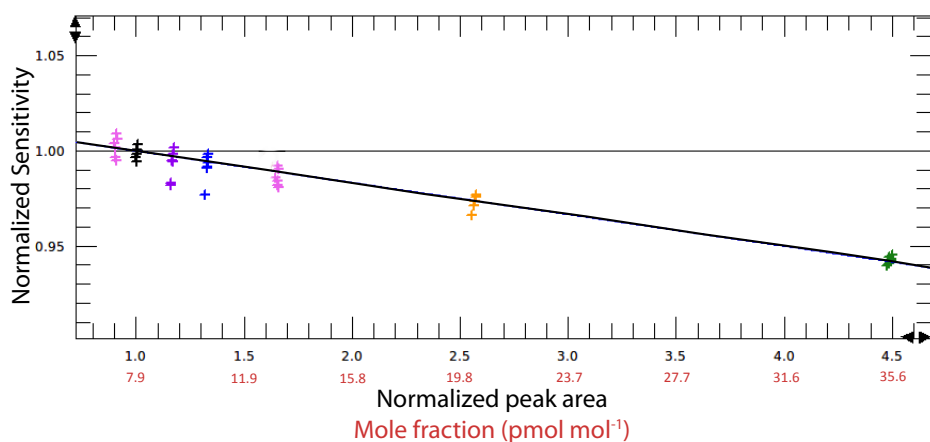


(c) SF_6

Figure 5: Typical chromatograms with units in relative response on the y-axis and time in seconds on the x-axis. (a) CH_4 elutes as a narrow peak at 95 s after a small air peak. (b) N_2O elutes at 422 s after oxygen is vented out and SF_6 elutes from the molecular sieve column. (c) SF_6 elutes at 329 s, prior to the much larger N_2O peak.



(a) N₂O



(b) SF₆

Figure 6: Non-linearity analysis, showing normalized sensitivity on the y-axis and normalized peak response (height or area) of the instrument on the x-axis. Mole fractions calculated using dilution factors that were derived from FID measurements of CH₄ in each sample are shown in red. (a) N₂O (b) SF₆

Meteorological Measurements

Meteorological measurements were collected for air temperature, barometric pressure, wind speed and direction, solar radiation and precipitation using sensors that were implemented by the Bose Institute in 2010. Components of the meteorological station are listed in Table 1.

Table 1: Components, make and model of the sensors used in the meteorological station at the Bose Institute, Darjeeling.

Component	Make	Model
Wind speed and direction monitor	Campbell Scientific	05103
Temperature and relative humidity probe	Campbell Scientific	HC-S3
Barometric pressure sensor	Campbell Scientific	61302V
Solar radiation	Campbell Scientific	SP LITE
Rain gauge	Campbell Scientific	TE525
Data logger	Campbell Scientific	CR1000