Optimizing a GC/FID for Analyzing Trace Levels of Non-methane Hydrocarbons at the Mount Bachelor Observatory in Oregon

Cassandra N. Sanders[1], B. T. Jobson[2], Brandon. D. Finley[3], D. A. Jaffe[3]

1. Environmental Science, Columbia Basin College 2. Laboratory for Atmospheric Research, Dept. of Civil & Environmental Engineering, Washington State University 3. Atmospheric Sciences, University of Washington

Introduction.

Anthropogenic pollution transported across the Pacific from Asia is well-documented (Reidmiller et al., 2009). The transport of non-methane hydrocarbons (NMHCs) to the Pacific Northwest is thought to have implications to local air quality (Jaffe and Ray 2007). Previous work on understanding the processes controlling transport of NMHCs has shown the transport of these pollutants is located in the mid- to upper-troposphere during May (Wang et al., 2006). To further understand these transport episodes, whole air samples were collected from the Mount Bachelor Observatory (MBO) and therefore represent clean "background" tropospheric air. The goal for this project involves using a gas chromatograph with a flame ionization detector (GC/FID) to analyze these air samples. The GC contains an Al_2O_3/KCl column and a sample handling system to cryogenically pre-concentrate hydrocarbons from a 800 ml sample.

Objectives:

-Establish retention times for C_2-C_6 hydrocarbons.
-Determine the cryogenic trapping efficiency of C_2-C_6 alkanes.
-Optimize the precision of the analysis (target 2%).

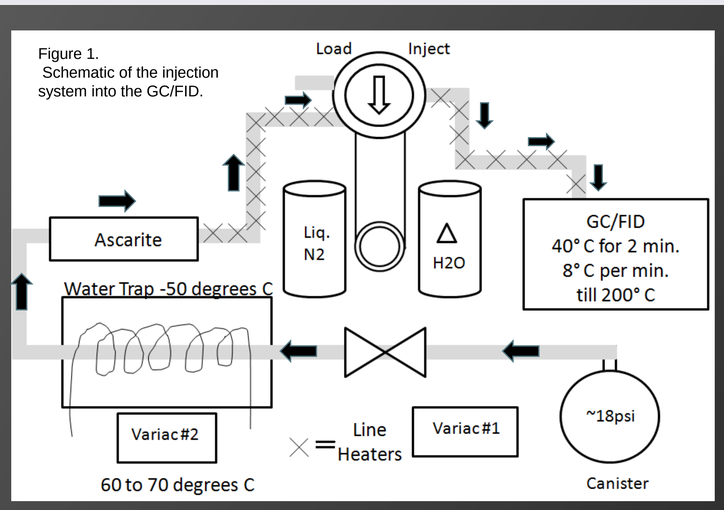

Figure 1.
Schematic of the injection system into the GC/FID.

Analysis Process.

A Hewlett Packard (HP) 5890 Series II Plus GC was used for the analyses.

-Sample from a stainless steel canister first passes through a water trap cooled to -50 C with dry ice. This removes water from the sample.

-Sample then passes through a teflon tube containing ascarite that scrubs the CO_2 from the sample.

-Then the sample passes through the sample loop which is immersed in liquid nitrogen to trap the hydrocarbons. The volume samples is between 374-504mL, which varies depending on whether a sample or standard is being analyzed.

Table 1. The gas flow setting for the GC/FID.

	Gas	Flow
CARRIER GAS	H2	15 cm³/min
MAKE UP	N2	250 cm³/min
FID	H2	100 cm³/min
FID	ZERO AIR	290 cm³/min

-Once enough sample is collected onto the sample loop, the sample loop is immersed in hot water and the sample is injected into the column of the GC and then to the flame ionization detector (FID).

-FIDs are only sensitive to compounds containing carbon, and the detector works by measuring an electrical current that is generated when hydrocarbons are burned in a hydrogen/air flame.

-After every injection, it is necessary to purge the sample line (heated for 15 minutes) to remove accumulated water.

Figure 2. GC/FID used for the analysis of non-methane hydrocarbons from MBO samples

COMPOUNDS	
ETHANE	I-PENTANE
ETHYLENE	N-PENTANE
PROPANE	PROPYNE
PROPENE	2,2-DIMETHYLBUTANE
I-BUTANE	2-METHYLPENTANE
N-BUTANE	3-METHYLPENTANE
ACETYLENE	I-BUTYNE
ISOBUTANE	N-HEXANE
2,2-DIMETHYLPROPANE	2-BUTYNE

Table 2.
List of known compounds analyzed by the GC/FID. The compounds in red are alkanes, green are alkenes, and blue are alkynes.

GC Efficiency.

Trapping efficiencies for C_2-C_6 alkanes were determined for the analytical system. As shown in Figure 3, ethane (C_2) and propane (C_3) both were biased high, perhaps due to contamination in the diluent air. The other compounds displayed a constant response per carbon atom, indicating efficient trapping in the cryo loop.

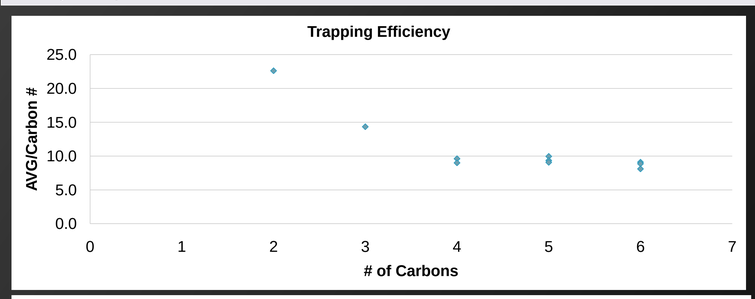

Figure 3.
This is a table of the trapping efficiency. The response ppbC should be consistent for all compounds regardless of the number of carbons.

Standards.

- A series of standards were created to determine when each compound elutes, or the retention time.

-The standards contained n-alkanes, iso-alkanes, and alkynes.

#	COMPOUND	#	Compound
1	ETHANE	7	2,2-DYMETHYLPROPANE
2	ETHYLENE	8	I-PENTANE
3	PROPANE	9	N-PENTANE
4	I-BUTANE	10	2,2-DIMETHYLBUTANE
5	N-BUTANE	11	2-METHYLPENTANE
6	ACETYLENE	12	2-METHYLPENTANE

Table 3.Compounds included in the standard and their respective retention time (minutes).

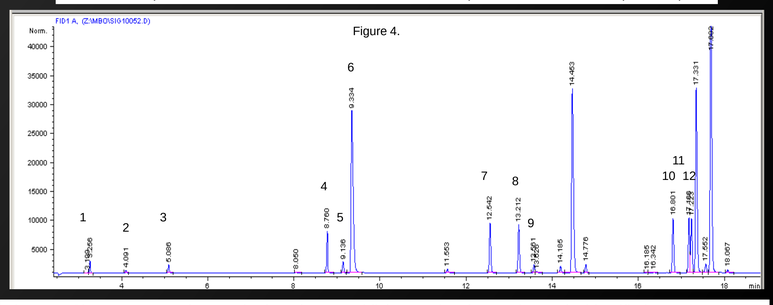

Figure 4.

Figure 4. Chromatogram of a standard made to establish retention times. The peaks identified as 1-6 corresponds to those listed in Table 3.

	AVG	SD	RSD
ETHYLENE	459.9	14.3	3.1
NEOHEXANE	1147.3	24.6	2.1

Table 4.
A certified can of ethylene (10.06 ppmv)and neohexane (10.01 ppmv) was diluted with liquid nitrogen blow off to 1sccm. Neohexane is a stable compound often used in finding the sensitivity of the GC/FID.

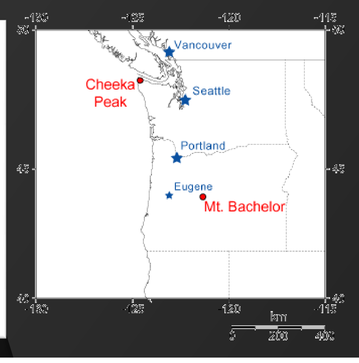

Figure 5 and 6: Mt. Bachelor is an isolated volcanic peak with a summit at 2.7 km (9,000ft) above sea level (asl) and is a choice location for an atmospheric observatory. At this altitude, the observatory receives mostly free tropospheric air and sometimes stratospheric air, enabling us to sample air which has been relatively undisturbed during transport from Asia.
http://research.uwb.edu/jaffegroup/modules/MBO/ (7/2/10).

Results.

-MBO canister T-2 was collected on 5/15/10 at 5 am. T-2 is a free troposheric air sample. Figure 7 shows the concentration (ppbC) for multiple compounds. The can was analyzed 3 times (500mL was pre-concentrated) to determine precision of the analysis. The statistics of the analysis are shown in table 5. The precision at the 2 ppbC range (ethane) was 3%. At 0.05 ppbC (isobutane) it was 11%, corresponding to the level of quantitation for this analysis

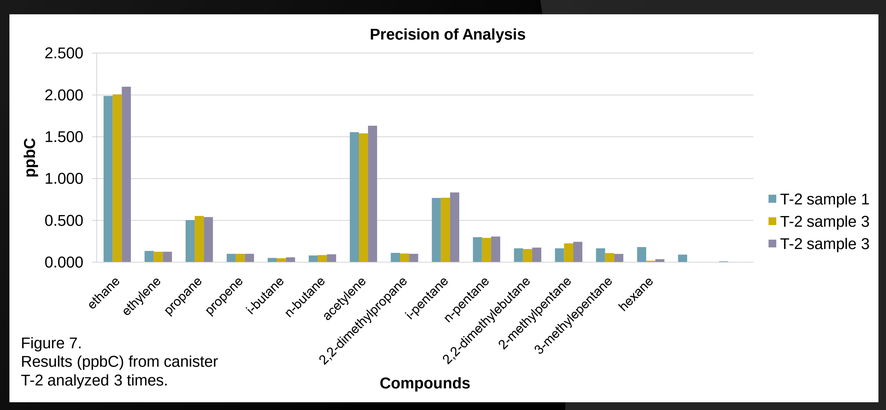

Figure 7.
Results (ppbC) from canister T-2 analyzed 3 times.

Table 5. List of compounds identified for the MBO canister T-2 and their precision

Compounds	AVG. RT(min)	AVG (ppbC)	SD (ppbC)	RSD (%)
ETHANE	3.27	2.031	0.059	2.91
ETHYLENE	4.16	0.128	0.005	4.11
PROPANE	5.15	0.532	0.026	4.82
PROPENE	7.30	0.100	0.001	0.60
I-BUTANE	8.05	0.052	0.006	10.91
N-BUTANE	8.20	0.087	0.006	7.37
ACETYLENE	9.24	1.576	0.049	3.12
2,2-DYMETHYLPROPANE	12.68	0.105	0.006	5.32
I-PENTANE	13.33	0.791	0.037	4.71
N-PENTANE	13.67	0.299	0.008	2.66
2,2-DIMETHYLBUTANE	16.81	0.166	0.009	5.28
2-METHYLPENTANE	17.30	0.216	0.033	15.09
2-METHYLPENTANE	17.35	0.009	0.009	9.23
HEXANE	17.98	0.021	0.013	62.67

Conclusion and Future Work.

-The retention time of 17 compounds have been established for this method.

-The trapping efficiency has shown to be unbiased except for two compounds ethane and propane. Since these compounds are higher, this could indicate that the gas (zero air) chosen to dilute the standard contained ethane and propane. The test will be repeated with a more pure dilutent gas.

-Precision has been established for the neohexane standard at about 2%. Manual integration of the MBO samples was required to improve analysis precision.

-Ethylene was observed in both the MBO free tropospheric air samples and in the laboratory prepared mixture of n-alkanes. The presence of ethylene is likely an artifact produced by the canister and is a known problem with trace gas sampling using canisters.

References.

Jaffe, D. et al.. "Six 'new' episodes of trans-Pacific transport of air pollutants". Atmosphere Environment. 9 Oct. 2002.

Reidmiller D. R. el al.. "Interannual variability of long-range transport as seen at the Mount Bachelor Observatory". Atmospheric Chemistry and Physics. 27 Jan. 2009.

Wang, Y. el al.. "Late-spring increase of trans-Pacific pollution transport in the upper troposphere". Geophysical Research Letters. 2006.

Acknowledgments.

We would like to thank Will Wallace of WSU for his help in this research and Dan Jaffe for funding

This work was supported by the National Science Foundation's REU program under grant number ATM-0754990.