VOC Measurements at T1 Using PIT-MS and GC-FID: Emissions Characterization

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Instrumentation

GC-FID

The NOAA GC/FID instrument acquired 5-minute integrated samples every 15 minutes continuously throughout the campaign beginning at 21:00 (UTC) on 11 March, 2006. The sample stream passed through an Ascarite trap for CO_2 removal followed by a -40°C water trap before sample cryo-collection at -165°C. A 50-meter Alumina PLOT column, divided in half to allow backflushing, was used for species separation. Seventeen VOCs in the C2-C6 range were quantified with a detection limit of ~5 pptv with the accuracy stated as ± 15%.

Species Measured:

acetylene	1-butene
propane	trans-2-butene
i-butane	cis-2-butene
n-butane	2-methyl propene
n-pentane	1-pentene
i-pentane	trans-2-pentene
n-hexane	cis-2-pentene
ethylene	2-methyl 1-butene
propylene	3-methyl 1-butene

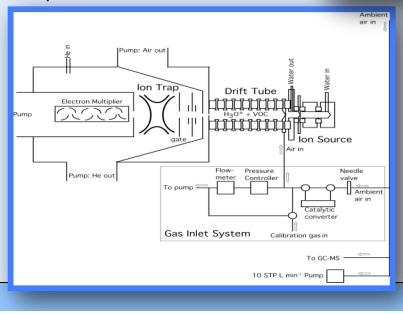
PIT-MS

Proton-Transfer **Ion Trap** Mass Spectrometry

The PIT-MS instrument is based on PTR-MS (proton-transfer-reaction mass spectrometry). VOCs are ionized using proton transfer reactions. The PIT-MS is a fast instrument measuring a full mass spectrum (30-240 amu) in about 10s. It provides online measurements of oxygenated VOCs as well as aromatic species. In order to distinguish compounds with the same m/z, a GC pre-separation method was used on several occasions during the MILAGRO campaign. Currently the detection limit of the PIT-MS is about 1 ppbv for most compounds measured.

Species Measured:

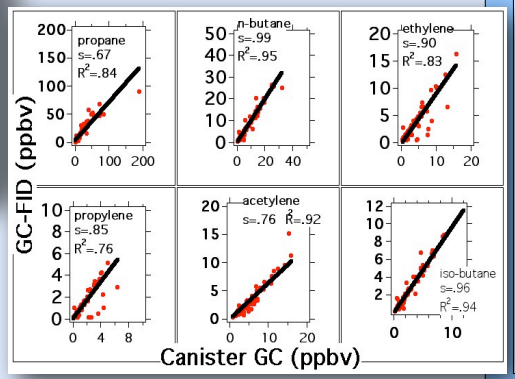
methanol
acetonitrile
acetaldehyde
acetone
acetic acid
methyl ethyl ketone
benzene
toluene
ΣC8 benzenes
ΣC9 benzenes
ΣC10 benzenes
ΣC11 benzenes



Intercomparisons

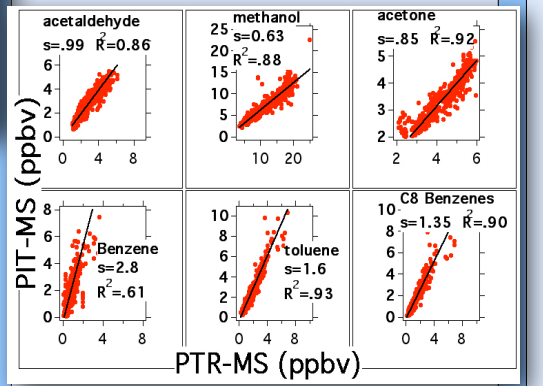
GC-FID

The Milagro campaign provided several opportunities for instrument intercomparison. Canisters were filled every three hours and analyzed afterwards by gas chromatography [Blake et. al]. These results compared well with GC-FID measurements as shown below.

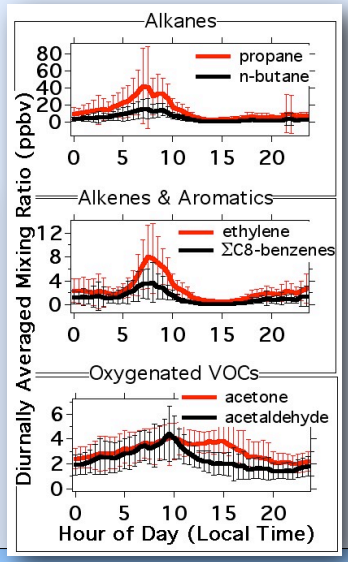


PIT-MS

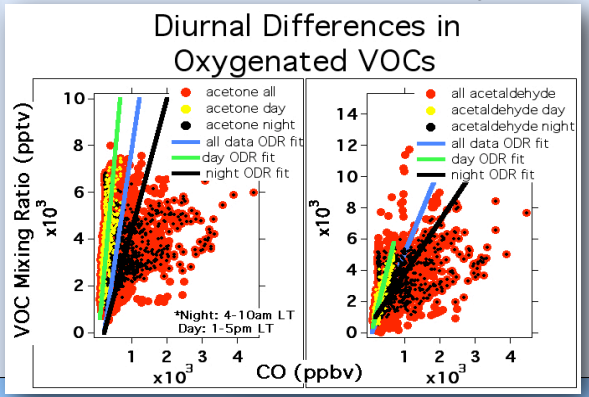
The Aerodyne Mobile Lab was equipped with a PTR-MS and spent two days sampling at T1. This provided an intercomparison with the PIT-MS [Knighton, et. al]. Oxygenated species compared well. Poor comparisons for aromatic species were seen between the two instruments probably due to calibration issues with the PIT-MS.



VOC Diurnal Variation



At T1, most VOCs peaked at about 6 to 8 am local time and dropped off significantly after sunrise. Both alkanes and more reactive alkenes like ethylene showed strong diurnal variation. Oxygenated species showed weaker diurnal variation and generally reach maximum mixing ratios during daylight hours. Oxygenated species also showed diurnal differences in enhancement ratios with higher afternoon (local time) CO correlations than at other times of day.



T1 Enhancement Ratios

Preliminary enhancement ratios were calculated using carbon monoxide measurements. Enhancement ratios showed reasonable agreement with US cities. Significantly elevated ratios were found for propane, butane and some oxygenated species versus US cities. Correlations with CO were best for species with primarily automotive sources. Weaker correlations with CO may be indicative of evaporative sources for species like toluene and C8 Benzenes like xylene. Poor correlation with CO was found for many oxygenated species, probably due to photo-chemical production.

Compound	New England (2004) pptv [ppbv CO]⁻¹	Milagro 2006 All Data	R²	Day	R²	Night	R²
		pptv [ppbv CO]⁻¹					
ALKANES							
n-butane	1.688	**11.0**	0.52	-		-	
propane	7.733	**29.0**	0.46	-		-	
i_butane	1.012	**3.9**	0.53	-		-	
i_pentane	3.991	**2.6**	0.78	-		-	
n-butane	1.688	**12**	0.53	-		-	
t-2-butene	0.053	**0.19**	0.81	-		-	
t-2-pentene	0.097	**0.19**	0.85	-		-	
ALKENES							
1-butene	0.139	**0.3**	0.85	-		-	
1-pentene	0.112	**0.2**	0.84	-		-	
c-2-butene	0.059	**0.2**	0.81	-		-	
c-2-pentene	0.05	**0.1**	0.84	-		-	
ethylene	4.564	**6.3**	0.88	-		-	
propylene	1.363	**2.5**	0.83	-		-	
acetylene	3.6	**5.7**	0.87	-		-	
AROMATICS							
benzene	0.617	**2.2**	0.50	-		-	
toluene	2.622	**3.4**	0.75	-		-	
Σ(Xylenes+Ethyl Benzene)	1.932			-		-	
C8_Benzenes		**3.4**	0.77	-		-	
OXY-VOCs							
Acetone	2.88±1.8	**10.0**	0.08	**16.0**	0.46	**5.6**	0.08
MEK	0.828±0.04	**22.0**	0.15	**41.5**	0.80	**12.0**	0.16
Acetaldehyde	0.684±0.25	**5.5**	0.31	**8.9**	0.75	**3.4**	0.30
Methanol	3.96±0.25	**15.0**	0.28	**15.7**	0.66	**13.7**	0.14