

Mobile Laboratory to Measure Air Toxics in the Houston Ship Channel Area

Final Report

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The Environmental Protection Agency - Region 6

Local-Scale Air Toxics Ambient Monitoring

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Appendix A: Mobile Ambient Air Monitoring Laboratory (MAAML) Layout and Equipment Specifications

Appendix B: Standard Operating Procedure for TD-GC/FID/MS for Air Toxics Analysis in the MAAML

Appendix C: MAAML Data Records

1.0 Introduction

Houston, a major petrochemical processing area and one of the nation's largest ports, concentrates most of these petrochemical plants in the Houston Ship Channel (HSC) area. As a group, these facilities emit significant amounts of Hazardous Air Pollutants (HAPs) into the ambient environment. According to Texas Commission for Environmental Quality (TCEQ) inventories in 2007, Harris County (Houston's home county) had around 14242 permitted air pollutant emission points emitting 22748 tons of volatile organic compounds (VOCs) annually (Figures 1 and 2), with most emission points concentrated in the HSC area.

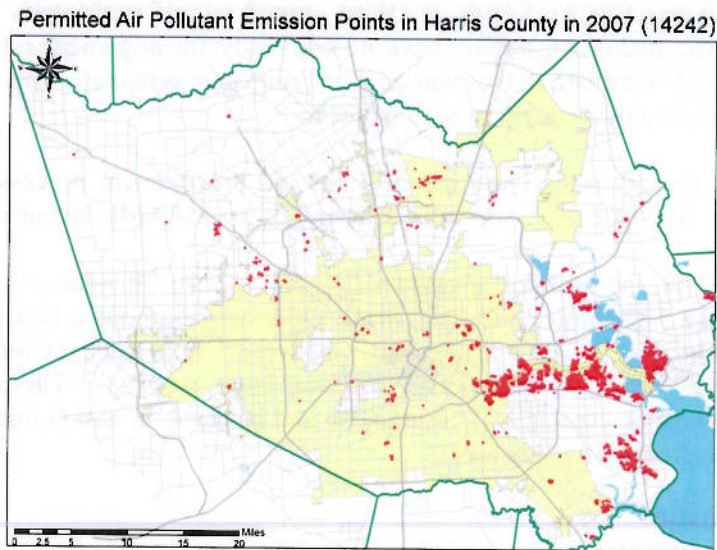


Figure 1: Permitted Air Pollution Emission Points – Harris County (2007)

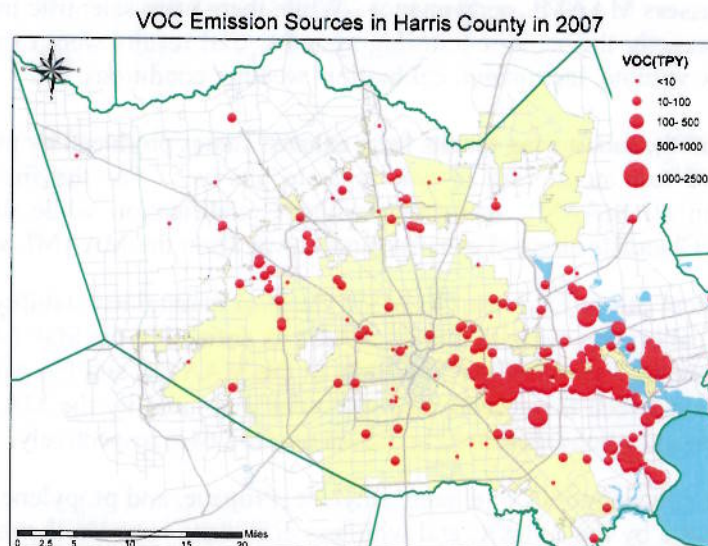


Figure 2: VOC Emission Sources – Harris County (2007)

Grants from the EPA and Houston Endowment Inc and matching funds from the City of Houston allowed the Houston Department of Health and Human Services (HDHHS) via the Bureau of Pollution Control and Prevention (BPCP, formerly the Bureau of Air Quality Control – BAQC) to construct a Mobile Ambient Air Quality Monitoring Laboratory (MAAML) that incorporates proven, best-in-class mobile laboratory monitoring technologies to determine the feasibility of a mobile platform

to identify and characterize point sources emissions in near real-time from petrochemical facilities adjacent to Houston neighborhoods. Specifically, the BPCP grant proposal indicated five major goals for the MAAML and the project as a whole with the five objectives delineated below.

The first objective lay in creating an analytical platform capable of identifying and characterizing 1,3-butadiene point source emissions from a local petrochemical industrial complex while the second focused on the identification and characterization of other compounds, such as styrene, to assist in the determination of the emissions source. The third, the attainment of lower detection levels (around 1 ppbv), initially calibrating the instrument platform for fewer compounds than current monitors, and greater accuracy in peak assignment, stem from the nature of the instrumentation on board the MAAML which sets it apart from monitors available at project onset. The fourth, mobility, stands as self-explanatory given the fact that comparable monitors found placed in fixed-base, tied-down trailers have no capability for alignment relative to every emissions plume. Lastly, this combination of goals will culminate in the final goal of bringing a systematic approach to compound identification and characterization to a geographic area desperately in need of such.

After rigorous project technology review, design and engineering, and procurement processes, the MAAML was built and delivered to BPCP for field trials in August 2007. Appendix A describes the MAAML layout and equipment specifications.

From August 2007 to December 2008, the Mobile Laboratory Program (MLP) Chemists of BPCP deployed the MAAML to monitor HAPs concentrations in the Manchester and Park Place super-neighborhoods, two areas in close proximity to four major petrochemical facilities, to wit: Houston Refining, Valero, Goodyear Tire & Rubber Company, and Texas Petrochemicals (TPC); the Houston Ship Channel; and the intersection of four large freeways. These geographical factors cause a disproportionate distribution of pollutants, especially 1,3-butadiene and benzene, in east Houston super-neighborhoods relative to other super-neighborhoods in the greater Houston area.

2.0 MLP Monitoring Activities

2.1 MAAML Initial Field Trials

From 10:00 08/13/07 through 15:00 08/16/07 (CST), MLP Chemists initiated the first field trials for the MAAML by deploying it at the City of Houston's Milby Park. MAAML siting adjacent to the TCEQ's Milby Park AutoGC trailer allowed the MLP team to perform test monitoring to assess MAAML performance. While there were scientific interest and value comparing data between these two similar but not exactly the same monitoring systems, trial results were expected to be somewhat different due to variations on samples, sample volume, instrument, calibration, weather conditions, etc.

To determine any potential impact on the monitoring results from exhaust fumes produced by the two diesel generators onboard the MAAML, the Chemists divided test monitoring in two separate phases. For the first phase (10:00 08/13/07~16:00 08/14/07 CST), MLP Chemists ran all MAAML equipment without modification while during the second phase (17:00 08/14/07~15:00 08/16/07 CST), the Chemists directed exhaust fumes away from the MAAML via flexible ducting.

Despite adverse weather from Tropical Storm Erin, the GC/MSD platform maintained stability throughout the MAAML field trials. All blank samples and daily calibration samples met all criteria as defined in the SOP (Appendix B). Concentrations of the 12 chemical compounds measured by both of TD-GC/FID/MS in the MAAML and the AutoGC showed good correlation. Figure 3 documents the correlations between the species concentrations measured by the MAAML and the AutoGC with the black and red symbols signifying concentrations measured in phases one and two, respectively.

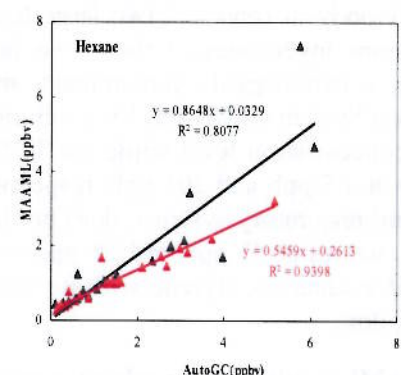
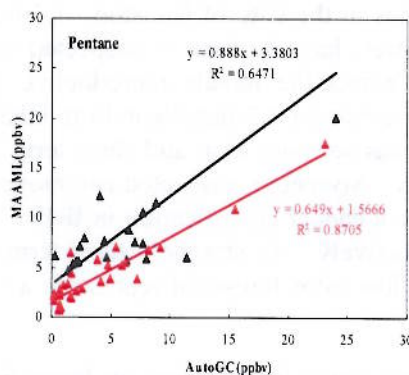
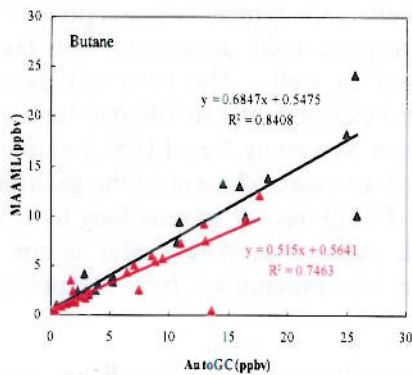
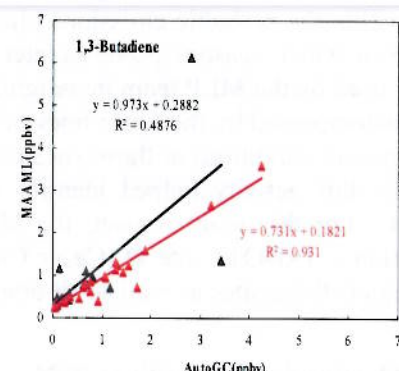
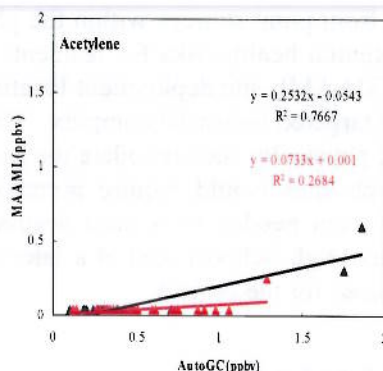
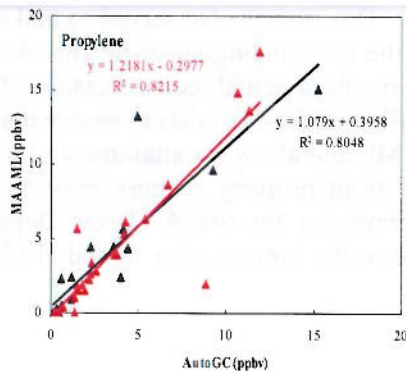
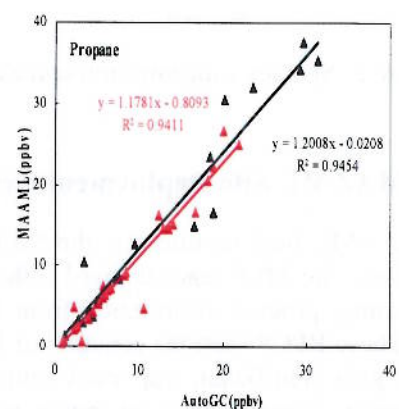
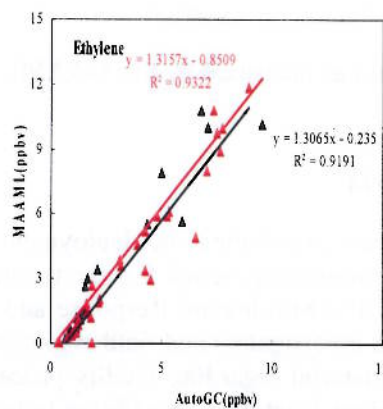
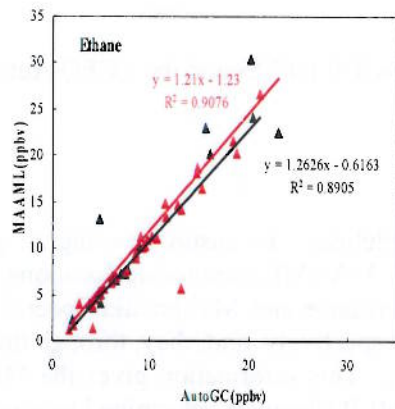
With the exception of acetylene, the concentrations of ethane, ethylene, propane, and propylene as analyzed using the MAAML FID correlate well with those measured by the AutoGC and with less difference between the results for each phase, suggesting negligible effects of the MAAML generator on the monitoring results for ethane, ethylene, propane and propylene. As most of acetylene concentrations measured by the MAAML ranged below the MDL, the Chemists could draw no definitive conclusions regarding the effects of generator emissions on acetylene concentrations.

MAAML and AutoGC measured concentrations for 1,3-butadiene, n-butane, n-pentane, n-hexane, benzene, toluene, and xylene did not correlate as well as those for ethane, ethylene, propane and propylene partly due to the difference in the detectors used by the MAAML (MSD) and the AutoGC (FID) to analyze the former compounds. MLP Chemists generate calibration curves for each compound analyzed via MSD to calculate concentrations. AutoGC operators use only two average response factors for

propane and benzene to calculate concentrations of C2-C5 and C6-C10, respectively, as their instrumentation utilizes only FID for their GC detectors.

During the monitoring run, the Chemists noted 1,3-butadiene concentrations at 2:00 and 3:00 08/14/07 (6.13 and 7.62 ppbv, respectively). At that time, calm winds prevented point source identification for the emissions event. Overall, comparison

monitoring results indicated the stability and reliability of the MAAML's TD-GC/FID/MS platform, and so, the MLP Chemists deemed the MAAML ready for field monitoring.



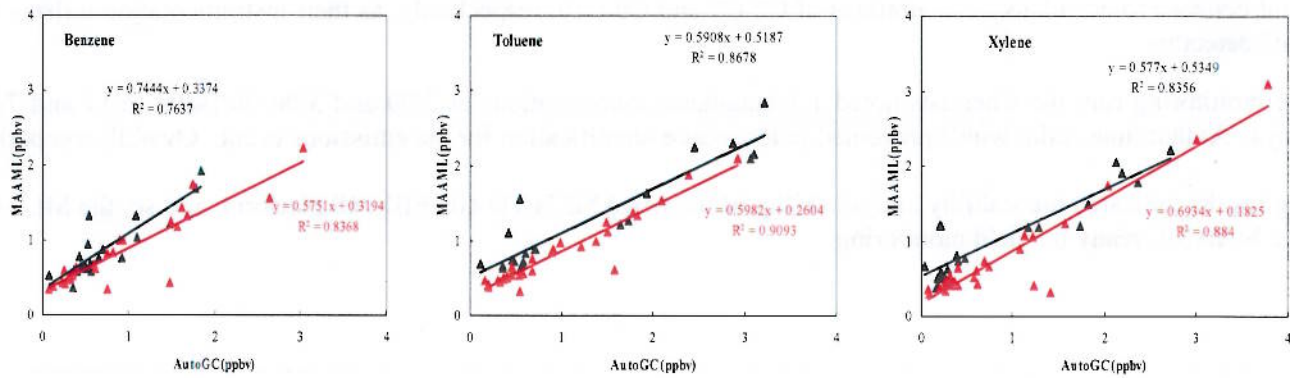


Figure 3: Species concentration correlations as measured by the MAAML TD-GC/FID/MS and the TCEQ AutoGC

2.2 MAAML Site Deployment Criteria

Prior to MAAML field monitoring, the MLP team established site deployment guidelines. To ensure meeting all grant goals and objectives, the MLP team devised a three-pronged approach for use to site all MAAML monitoring locations. The first involved getting process information from BPCP's Multimedia Response and Assistance and Multimedia Special Initiatives Sections. These BPCP sections contain our field investigators and field engineers, respectively, and, they, through the course of their work, gain significant, important source material regarding facility processes. This information gives the MLP team a starting point in determining point source emissions locations. In addition to this, MLP Chemists determined seasonal weather patterns from reviewing meteorological websites. This review, with its indication of seasonal prevailing winds, provided the team information vital in prioritizing which areas around the targeted facilities would more likely and more frequently place the MAAML within the probable emissions plume from point sources within the plant. This review also served to make the MLP team aware of which seasons posed greater potential health risks for residents in the surrounding super-neighborhoods. The third factor used by the MLP team in assigning MAAML site deployment locations involved actual reconnaissance of the entire perimeter encompassed by the fence lines of the targeted industrial complex. This allowed the Chemists to ensure that potential site locations and conditions at those sites could physically accommodate the MAAML and allow for attainment of grant goals. Additionally, this activity helped identify which sites would require permission from property owners prior to MAAML deployment. For this grant project, the MLP team needed to request access permission for site A (Texas Department of Transportation – TxDOT), site D (Cesar Chavez High School), and at a later time in the project, sites G and H (Goodyear). Figure 4 depicts these sites as well as all others used for the project.

2.3 Monitoring Activities - TPC and Goodyear

TPC and Goodyear represent two large facilities in the City of Houston. 1,3-butadiene and styrene, two compounds found in the emissions inventories of these two facilities, have known or suspected carcinogenic risks associated with them. 1,3-butadiene, a carcinogenic contaminant, may affect the female reproductive system as well. The EPA's Integrated Risk Information System (IRIS) sets the carcinogenic risk for 1,3-butadiene from inhalation exposure at 1 in 100,000 for a 0.14 ppbv ambient concentration level while the TCEQ has set long term and short term Effects Screening Level (ESL) values for 1,3-butadiene at 4.5 ppb and 203 ppb, respectively. Styrene, a suspected carcinogen and a suspected toxin to the gastrointestinal, kidney, and respiratory systems, does not have a cancer classification in IRIS. The TCEQ has set styrene long term and short term ESL values at 33 ppb and 25 ppb, respectively. As styrene's short term ESL values incorporate odor as one basis for compound evaluation, styrene with its rather low odor threshold represents a major air contaminant from the perspective of nuisance odors.

The MAAML's initial grant-related monitoring activities centered on fence line monitoring for 1,3-butadiene, styrene, and other VOCs for these two companies in order to fingerprint their fugitive emissions point sources. From August 2007 to December 2009, MLP Chemists deployed the MAAML at nine sites at TPC and Goodyear as shown in Figure 4 (Sites A through F) for ambient air monitoring while also marking the locations for two TCEQ AutoGCs in the general vicinity and three sites (G, H and I) deployed later during the course of the project.

It bears noting that the physical locations for the AutoGCs serve an important role for the TCEQ and coincidentally for the MLP team. These two sites represent the best available, publicly owned locations relative to seasonal weather patterns. The Milby Park AutoGC, located northwest of the industrial complex, addressing prevailing winds ranging from due southerly to due easterly. This placement allows for coverage for the vast majority of the summer weather pattern which for the Houston area actually encompasses most of the ozone season, i.e., March through November, with August and September typically the most likely for this pattern. The Cesar Chavez AutoGC, located on the grounds of Fire Station 29 (Houston Fire Department), represents the closest and most secure siting for winter seasonal patterns when the prevailing winds range from the northwest through due north to the north-northeast.



Figure 4: MAAML monitoring sites and AutoGC sites around TPC and Goodyear

2.3.1 Air Pollution Emissions – TPC

TPC separates C_4 olefin feedstocks to produce butadiene, methyl tert-butyl ether (MTBE), isobutylenes, and other C_4 products. A C_4 olefins mix represents a principal feedstock for TPC. TPC also purchases isobutane and methanol as primary feedstock. TPC mainly markets 7 major products: 1,3-butadiene (Bd), methyl tert-butyl ether (MTBE), butene-1, butene-2, isobutylene, isobutylene concentrate, diisobutylene (DIB), and polyisobutylene. Goodyear then purchases and utilizes the majority of the 1,3-butadiene that TPC makes to produce Styrene-Butadiene rubber (SBR). The information delineated below stems from public domain information submitted by TPC in support of their application for their most recent voluntary emission reduction permit (VERP).

Figure 5 depicts the production processing diagram at TPC. TPC produces 1,3-butadiene via two methods. The first method uses extractive distillation to remove butadiene from C_4 olefins mix while the second employs the OXO-dehydrogenation of normal butylenes. A series of distillation towers finish the 1,3-butadiene to a 99.5% purity level.

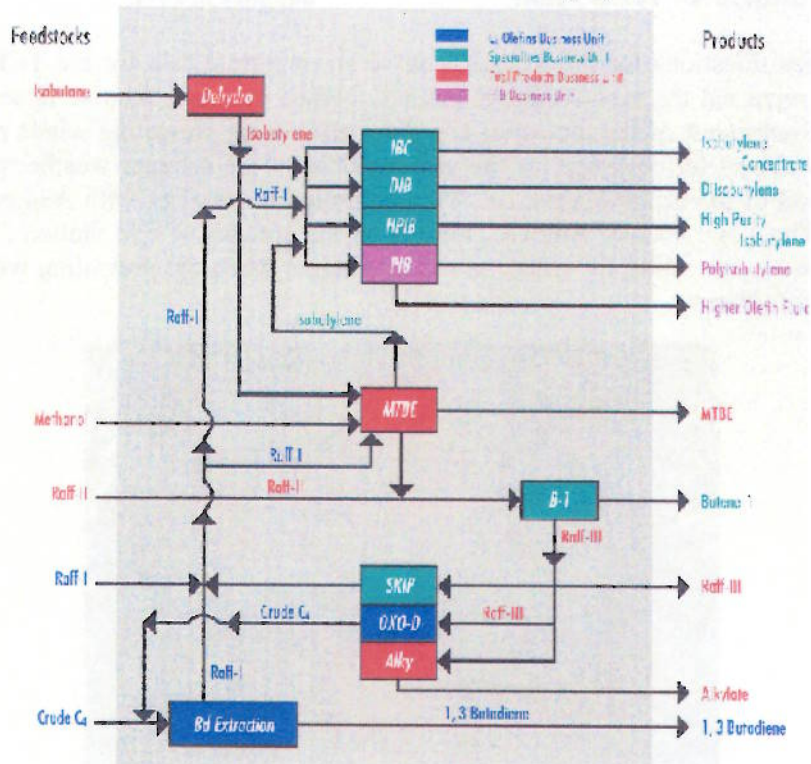


Figure 5: Production processing diagram at TPC

Grandfathered emissions sources represent the majority of air pollution sources at TPC, authorized by a VERP. TPC emits the following major air pollutants: NO_x, VOCs, CO, PM, and SO₂. Table 5 lists the annual emitting amounts of major air pollutants in 2007, according to the TCEQ’s emission inventories.

VOCs	CO	PM ₁₀	PM _{2.5}	SO ₂
495.9	188.3	126.8	52.6	4.9

Table 5: Major emission sources from TPC (tons/year)

In 2007, TPC emitted 390.8 tons of 39 different VOC species from 71 emission points with another 105.1 tons of VOCs emitted in Emissions Events, Maintenance, Startups and Shutdown activities (EESMSS). Of these VOCs, toluene, butene, 1,3-butadiene, isobutane, methyl tert-butyl ether, n-butane, vinyl cyclohexene, butyne, furfural, and dimethylformamide represent the top 10 VOC species emitted from TPC. Table 6 shows the annual and EESMSS emission amounts for these species.

	Toluene	Butene	1,3- Butadiene	Isobutane	MTBE
Annual	61.5	30.5	26.1	23.3	22.1
EESMSS	0.0	0.0	0.0	0.0	0.9
	n-Butane	Vinyl Cyclohexene	Butyne	Furfural	Dimethylformamide
Annual	20.3	20.2	19.3	12.2	9.0
EESMSS	0.9	0.0	0.0	0.0	0.0

Table 6: VOCs source emissions from TPC (tons/year)

TPC stands as a major 1,3-butadiene emission source for the City of Houston. In 2007, TPC had seventeen 1,3-butadiene emission points with about 26.1 tons of 1,3-butadiene emitted from these points. The major 1,3-butadiene emission points include 1C (fugitive), FUG-3 (fugitives fixed roof tank), FUG-4 (Tanks 71-4 & 80 fugitives), EP-5 (plant process flare), 2A (fugitive). Figure 6 depicts the locations for these 1,3-butadiene emission points at TPC as well as the 1,3-butadiene emission point in Goodyear.

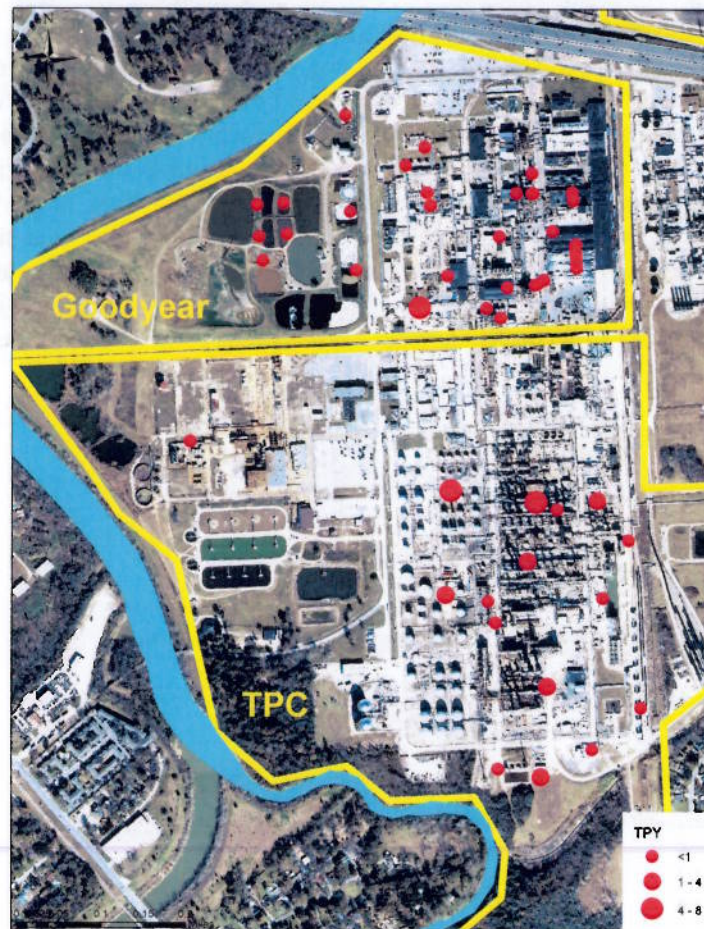


Figure 6: 1,3-butadiene emissions in TPC and Goodyear

2.3.2 Air Pollution Emissions – Goodyear

Goodyear Tire & Rubber Company uses two main raw materials, 1,3-butadiene and styrene, to produce latex and SBR rubber. TPC supplies Goodyear with 1,3-butadiene via pipeline. Goodyear stores it under pressure in tanks with relief valves vented to the plant flare, (EPN-Q4501). Goodyear has styrene delivered by tank truck, with the raw styrene, having a true vapor pressure of only 0.19 psia at 33 °C, stored in uncontrolled cone roof tanks. In addition, soaps and oils, necessary for synthetic rubber production, get processed in enclosed buildings with the soap solutions made with low rosin and fatty acids and used together with catalysts, activators, and a mercaptan modifier as a reactant media for the Styrene-Butadiene copolymerization reactions. Information about Goodyear process information stems from a BPCP internal engineering report which compiled the information with the subject matter presented not deemed confidential.

Figure 7 depicts the process flow diagram of SBR rubber at Goodyear. The Reactor Area produces synthetic rubber by cold and hot reaction processes. In the cold process, polymerization typically occurs at 50 F, while in the hot process, polymerization occurs at 122 F. In the reactor section styrene and 1,3-butadiene; combined with a modifier, soap solution activators, and catalyst; charged in a water-based solution initiates the conversion of monomers to polymer. Upon the achieving the desired degree of polymerization, i.e., the conversion of monomers to polymer, operators add a stopping agent (Short Stop) inline or in a mixing vessel, halting the polymerization by destroying the catalyst. For the reactor area, fugitives represent the major source of VOC air emissions.

In the Recovery Area, vacuum and steam distillation promotes the recovery of non-reacted monomers from the short stopped latex. 1,3-butadiene recovery occurs primarily via vacuum distillation in flash tanks and degassers with steam distillation in stripping columns under vacuum primarily accounts for styrene recovery. Goodyear reuses the recovered 1,3-butadiene and styrene in making latex by blending with raw incoming monomers. In the recovery area, fugitives represent the major source of VOC air emissions.

Prior to sending stripped SBR latex to the crumb rubber Finishing Areas, Goodyear stores it in tanks open to the atmosphere. Due to the low true vapor pressure of steam stripped latex at less than 0.01 psia at 150°F, uncontrolled VOC

emissions from these latex tanks do not contribute significantly. From the storage tanks, latex goes to the blend tanks to have an antioxidant mixture added. For oil extended SBR, operators add an emulsion of refined petroleum oils to the latex. Then, operators mix sulfuric acid, sodium chloride brine, and other coagulant aids with the blended latex, to dispel soap globules and to coagulate the latex. The rubber crumb then forms and placed on vibrating screens on vibrating screens for separation from the water whereupon the crumbs get washed and dewatered with the water discharged into the wastewater collection system. Operators send the wet crumb rubber to the rubber dryer where the crumb rubber driers, equipped with natural gas fired heaters, finish the drying process. Operators may add talcum powder to prevent crumbs from sticking to dryer components. The dry crumbs get compressed into bales, wrapped in plastic, and placed in containers for shipment. Finishing building VOC emissions occur as fugitives from the coagulation equipment in the crumb rubber finishing lines with fugitives emitted from either stacks or roof vents and as stack emissions from the crumb rubber dryers.

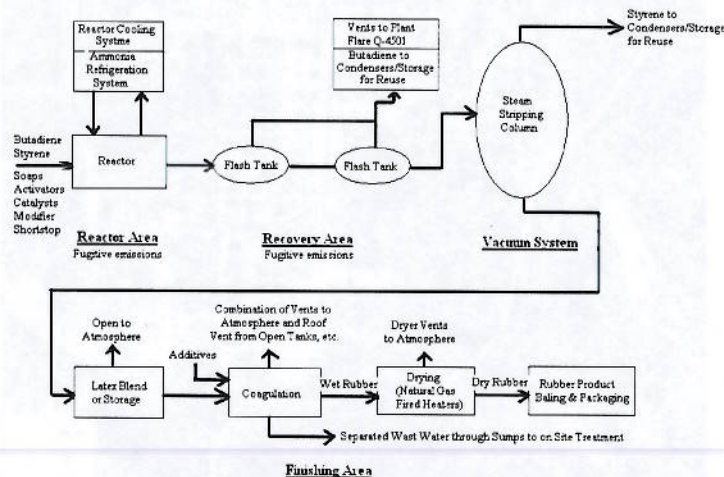


Figure 7: SBR rubber process flow chart

The D8 Latex Concentration Plant produces SBR latex while Figure 8 shows the process flow diagram. Operators steam strip the feedstock for D8 with unstripped high conversion SBR latex produced in the SBR polymerization area. This facility role involves removal water from the latex by vacuum distillation or "concentration". At D-8, a process of vacuum distillation of water from the latex, adjustment of the latex acidity and agglomeration of the latex particles to a standard size followed by a final heat and vacuum treatment causes the increase in the concentration of SBR latex from approximately 25% to 75% dry solids content. Operators blend and store this final SBR latex pending shipment by railcar and/or tank truck, or packaging in drums and/or various containers. The vacuum vent from the evaporation process connects to the thermal oxidizer (EPN Q-4502). Because the latex storage tanks operate at very low vapor pressures, uncontrolled VOC emissions, the major source of air emissions at the latex plant, do not contribute significantly.

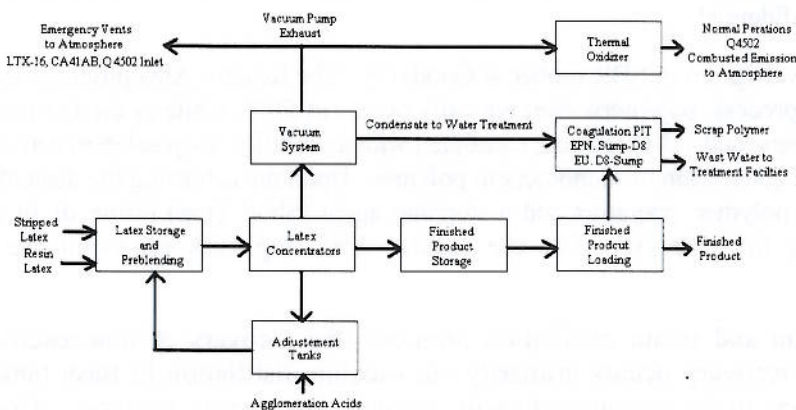


Figure 8: SBR Latex process flow diagram

A Flexible Air Permit serves as authorization for air pollution source emissions at Goodyear. According to 2007 TCEQ’s emission inventories, Goodyear had 251 emission points with thirty-one different airborne contaminants emitted into the ambient environment. From these emission points, NO_x, VOCs, CO, PM₁₀ and SO₂ represent Goodyear’s major emitted airborne species while Table 7 depicts their 2007 annual emitting amounts.

NO _x	VOCs	CO	PM ₁₀	PM _{2.5}	SO ₂
19.9	401.6	8.3	43.5	2.0	0.1

Table 7: Source emissions from Goodyear (tons/year)

In 2007, Goodyear emitted 401.2 tons of 27 different species of VOCs with another 0.4 ton of VOCs emitted in EESMSS. The top 10 species of VOCs emitted from Goodyear include styrene, paraffins cyclic-U, olefins-U, VOC-Unclassified, octane, trimethylbenzene, vinyl cyclohexene, 1,3-butadiene, ketones-U and carbon disulfide. Table 8 shows the 2007 annual and EESMSS emission amounts for these species.

	Styrene	Paraffins Cyclic-U	Olefins-U	VOC-Unclassified	Octane
Annual	185.4	80.1	52.2	26.2	12.2
EESMSS	0.0	0.0	0.0	0.0	0.0

	Trimethylbenzene	Vinyl Cyclohexene	1,3- Butadiene	Ketones-U	Carbon Disulfide
Annual	12.2	11.4	8.6	5.4	3.3
EESMSS	0.0	0.0	0.2	0.0	0.0

Table 8: VOCs source emissions from Goodyear (tons/year)

Goodyear, a major styrene emission source in Houston, emitted 185.4 tons of styrene from 200 points or areas in 2007, with most coming from the dryer process vent with other styrene emission points as follows: G-1 (G Dryer Exhaust), L1A (Aeration Basin), L2 (L Dryer Vent #2), K2 (K Dryer Vent #2), M2 (M Dryer Vent #2), J2 (J Dryer Vent # 2), and Q2 (Q Dryer Vent #2). Figure 9 shows all of the Goodyear and two TPC styrene emission points. In 2007, Goodyear also released a notable amount of 1,3-butadiene (annual emission amount - 8.6 tons). Figure 6 shows Goodyear’s 1,3-butadiene emission points.



Figure 9: Styrene emissions in Goodyear and TPC

2.3.3 Monitoring Results at Site A

Site A, located at the northeast corner of Goodyear, lies downwind for both TPC and Goodyear when winds come from the south to the south-southwest. From 08/27/07 to 08/28/07, 09/05/07 to 09/19/07, and 05/20/08 to 05/22/08, MLP Chemists deployed the MAAML here for ambient air quality monitoring. From 08/27/07~08/28/07, the MAAML collected and analyzed only two samples that met all QA/QC guidelines and, for those samples, MAAML data indicated concentrations for all target compounds. Figure 10 depicts the 1,3-butadiene concentrations as monitored by the MAAML from 09/05/07~09/19/07 along with the concentrations as measured by the AutoGCs at Milby Park and Cesar Chavez during the same period.

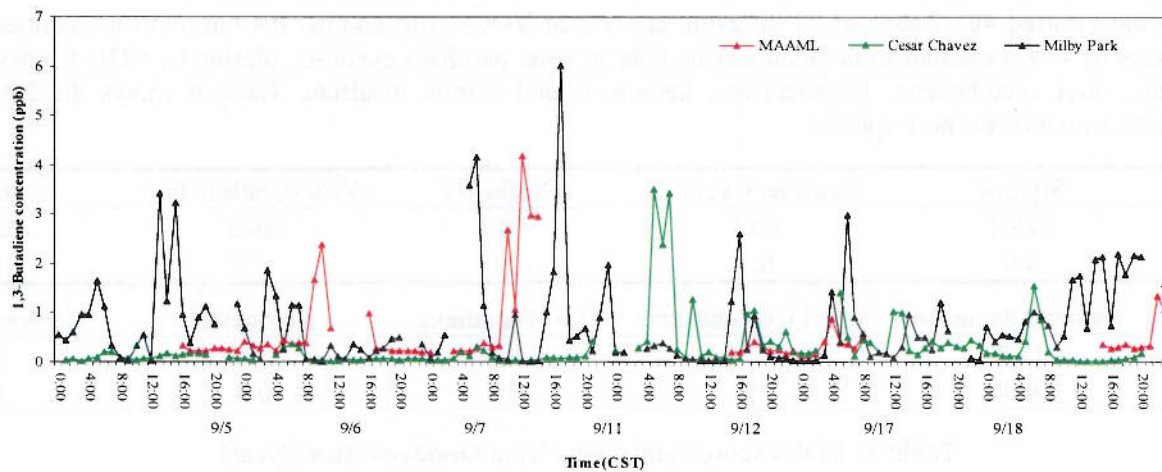


Figure 10: 1,3-butadiene time series graph - MAAML and AutoGCs at Milby Park and Cesar Chavez (09/05/07 to 09/07/07, 09/11/07 to 09/12/07, and 09/17/07 to 09/19/07)

At 12:00 on 09/07/07 (all times CST), the MAAML noted a 1,3-butadiene concentration spike of 4.2 ppbv with a prevailing south-southwesterly wind at 4.8 mph as measured by the MAAML, which did not correspond to the concentrations as measured by both the Milby Park and Cesar Chavez AutoGCs and the TPC north and south fence line monitors. Combining the MAAML data with the resultant wind direction plot (Figure 23), Goodyear seems the likely source for this concentration spike.



Figure 11: Resultant wind direction plot at 12:00 09/07/07 (CST)

At 06:00 and 17:00 on 09/07/07, the Milby Park AutoGC noted two 1,3-butadiene concentration spikes (4.2 and 6.0 ppbv, respectively) which did not correspond to the concentrations as measured by the MAAML and the Cesar Chavez AutoGC. The prevailing winds suggest that the two concentration spikes came from TPC.

Figures 12 and 13, respectively, depict the time series graphs for 1,3-butadiene and styrene as measured by the MAAML from 05/20/08 to 05/22/08 as well as those measured by the Milby Park AutoGC and the TPC north fence line monitor. The MAAML detected 1,3-butadiene concentrations from 12:00 on 05/20/08 to 08:00 on 05/21/08 with prevailing south-southeasterly winds which did not correspond to the 1,3-butadiene concentrations from the Milby Park AutoGC. However, the TPC north fence line monitor did detect 1,3-butadiene concentration that matched the MAAML’s for the 19:00 reading of 05/20/09. The MAAML-measured 1,3-butadiene concentration decreased over time as the prevailing wind direction shifted from south-southeast to due southeast. This contrasted to the Milby Park AutoGC 1,3-butadiene concentrations as the AutoGC became downwind of TPC with the change in wind direction. This strongly suggests TPC as the point of origin.

The MAAML noted styrene concentrations from 15:00 on 05/20/08 to 01:00 on 05/21/08 with prevailing south-southeasterly winds which did not correspond to styrene concentrations measured by the TPC north fence line monitor. TPC and Goodyear emissions representations and process descriptions strongly suggest Goodyear as the point of origin.

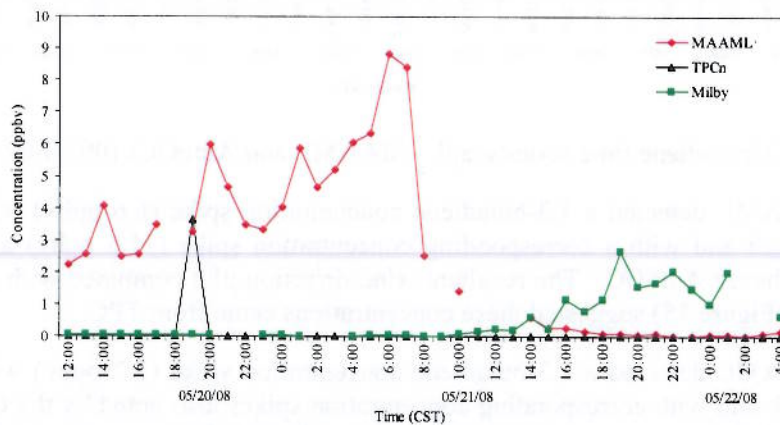


Figure 12: 1,3-butadiene time series graph – MAAML, Milby Park AutoGC, and TPC north fence line monitor (05/20/08 - 05/22/08)

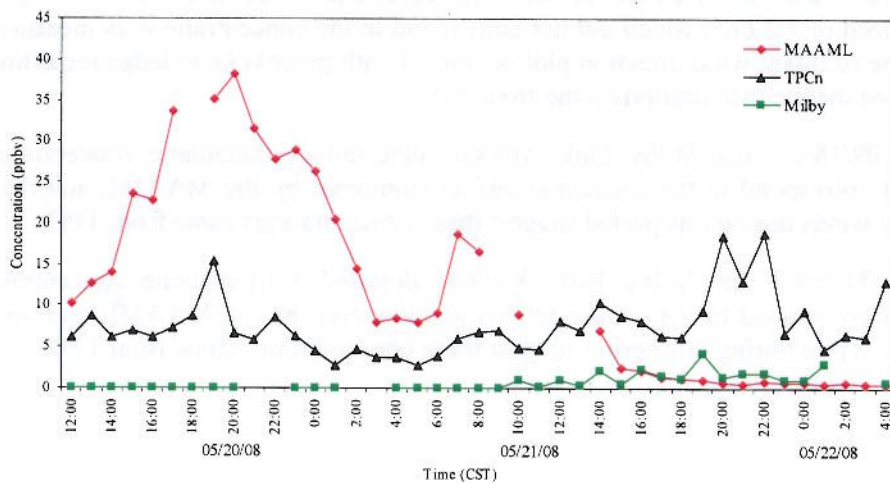


Figure 13: Styrene time series graph – MAAML, Milby Park AutoGC, and TPC north fence line monitor (05/20/08 - 05/22/08)

2.3.4 Monitoring Results at Site B

Site B, located on the west side of TPC and Goodyear, lies downwind of TPC with winds from the east-southeast to the south-southeast and downwind of Goodyear with winds from the northeast to the east. From 09/19/07 to 10/12/07, the chemists

deployed MAAML here for ambient air quality monitoring. Figure 14 shows the 1,3-butadiene concentrations as monitored by the MAAML and the AutoGCs at Milby Park and Cesar Chavez during this period.

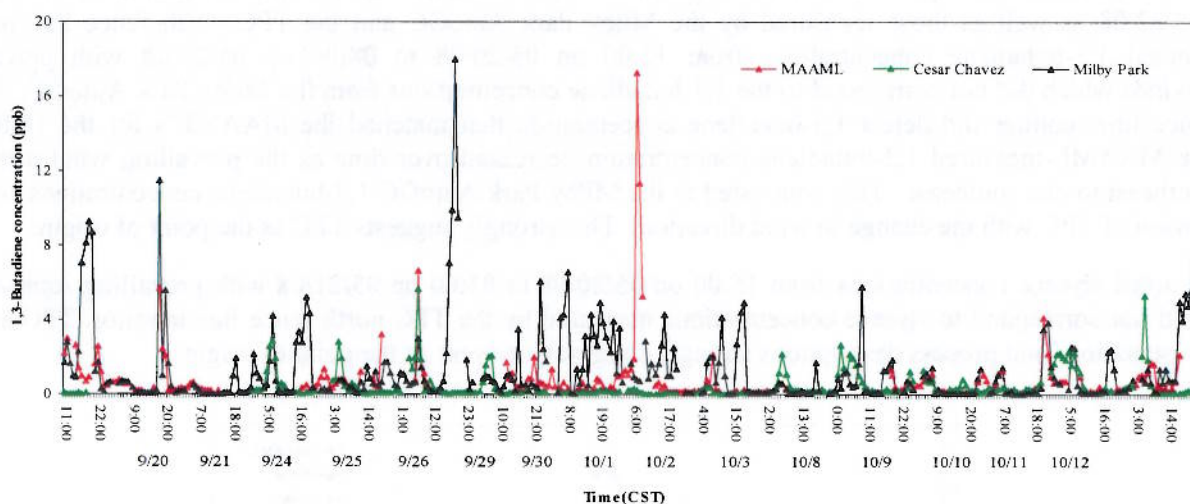


Figure 14: 1,3-butadiene time series graph - MAAML and AutoGCs (09/19/07~10/12/07)

At 18:00 on 09/20/07, the MAAML detected a 1,3-butadiene concentration spike (6.6 ppbv) with a prevailing northeasterly wind and wind speed of 4.5 mph and with a corresponding concentration spike (11.5 ppbv) also noted by the Milby Park AutoGC but not by the Cesar Chavez AutoGC. The resultant wind direction plot combined with process knowledge regarding emissions points in the vicinity (Figure 15) suggested these concentrations came from TPC.

At 07:00 on 09/26/07, the MAAML detected a 1,3-butadiene concentration spike (5.7 ppbv) with a prevailing northeasterly wind and wind speed of 3.3 mph and with corresponding concentration spikes also noted by the Cesar Chavez and Milby Park AutoGCs. The resultant wind direction plot combined with process knowledge regarding emissions points in the vicinity suggested these concentrations came from TPC.

From 07:00 to 09:00 on 10/01/07, the MAAML detected 1,3-butadiene concentrations (5.3~17.3 ppbv) with a prevailing southerly wind and wind speed of 5.2 mph which did not correspond to the concentrations as measured by the Milby Park and Cesar Chavez AutoGCs. The resultant wind direction plot combined with process knowledge regarding emissions points in the vicinity (Figure 16) suggested these concentrations came from TPC.

From 20:00 to 21:00 on 09/18/07, the Milby Park AutoGC detected 1,3-butadiene concentrations (7.4 and 5.9 ppbv, respectively) which did not correspond to the concentrations as monitored by the MAAML and the Cesar Chavez AutoGC. The prevailing southeasterly winds during this period suggest these concentrations came from TPC.

From 17:00 to 20:00 on 09/26/07, the Milby Park AutoGC detected 1,3-butadiene concentrations (7.1 ~ 19.0 ppbv, respectively) which did not correspond to the concentrations as monitored by the MAAML and the Cesar Chavez AutoGC. The prevailing southeasterly winds during this period suggest these concentrations came from TPC.



Figure 15: Resultant wind direction plot for Site B at 18:00 09/20/07 (CST)



Figure 16: Resultant wind direction plot for Site B at 07:00 10/01/07 (CST)

2.3.5 Monitoring Results at Site C

Site C, located at the southwest corner of TPC, lies downwind of Goodyear and TPC with prevailing winds from the north-northeast to the northeast. With east-northeasterly winds, site C lies downwind of TPC only. From 10/29/07 to 11/03/07, MLP Chemists deployed the MAAML here for ambient air quality monitoring. Figure 17 shows the 1,3-butadiene concentrations as measured by the MAAML and the Milby Park and Cesar Chavez AutoGCs for this period.

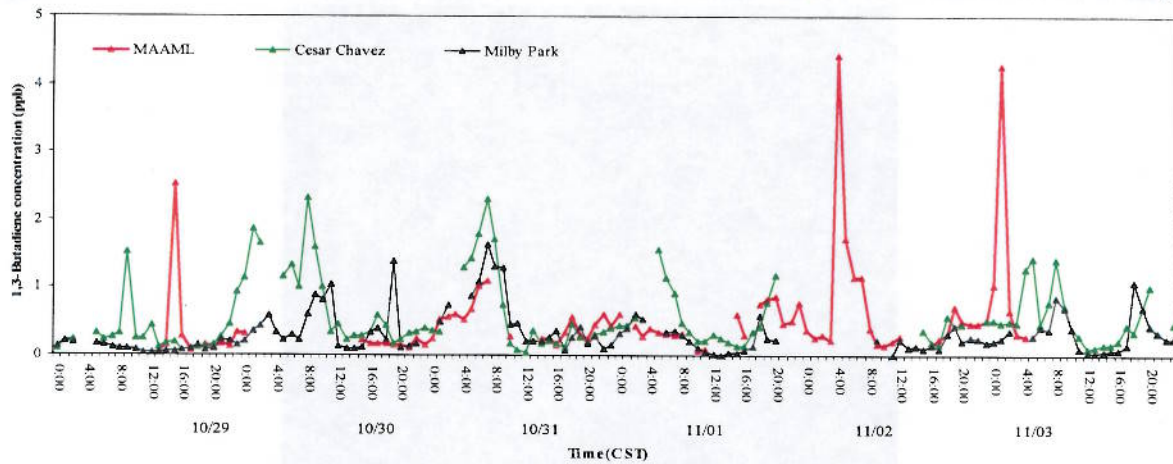


Figure 17: Time series of 1,3-butadiene measured by MAAML and AutoGCs in periods of 10/29/07~11/03/07.

At 04:00 on 11/02/07 and at 01:00 on 11/03/07 (CST), the MAAML detected two 1,3-butadiene concentration spikes (4.4 ppbv and 4.3 ppbv, respectively) with a prevailing north-northeasterly wind for the 04:00, 11/02/07 reading and calm winds for the 01:00, 11/03/07 reading. The Milby Park and Cesar Chavez AutoGCs did not correspond with the MAAML readings, which when combined with the resultant wind direction plot and process knowledge regarding emissions points in the vicinity (Figure 18), suggested these concentrations came from TPC.



Figure 18: Resultant wind direction plot for Site B at 04:00 11/02/07 (CST)

2.3.6 Monitoring Results at Site D

Site D, located south of TPC, lies downwind of Goodyear and TPC with north-northwesterly to north-northeasterly winds. From 12/11/07 to 12/14/07, MLP Chemists deployed the MAAML at Site D for ambient air quality monitoring. Figure 19 depicts 1,3-butadiene concentrations as monitored by the MAAML and the Milby Park AutoGC with the data from the Cesar Chavez AutoGC unavailable for that time period.

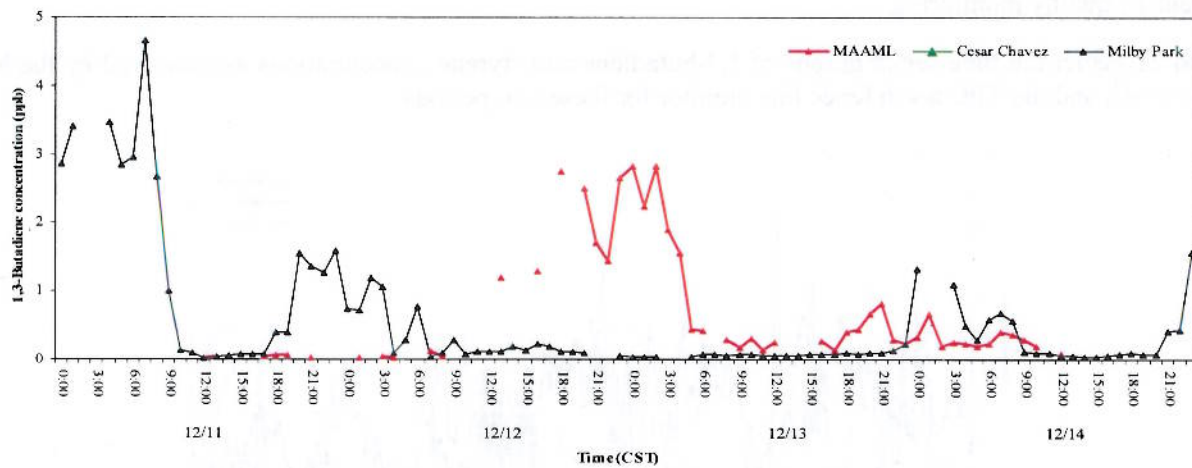


Figure 19: Time series of 1,3-butadiene measured by MAAML and AutoGCs in periods of 12/01/07~12/04/07

The MAAML detected no confirmed 1,3-butadiene concentration spikes. However, at 07:00 on 12/11/07 (CST), the Milby Park AutoGC noted a spike 1,3-butadiene concentration with a prevailing southeasterly wind. This suggests that this spike originated from TPC.

2.3.7 Monitoring Results at Site E

Site E, located southeast of TPC, lies downwind of Goodyear and TPC with northwesterly to north-northwesterly winds. From 12/17/07 to 12/21/07, MLP Chemists deployed the MAAML at Site E for ambient air quality monitoring. Figure 20 depicts the 1,3-butadiene concentrations monitored by MAAML and the Milby Park and Cesar Chavez AutoGCs with no concentrations of significance detected by the MAAML.

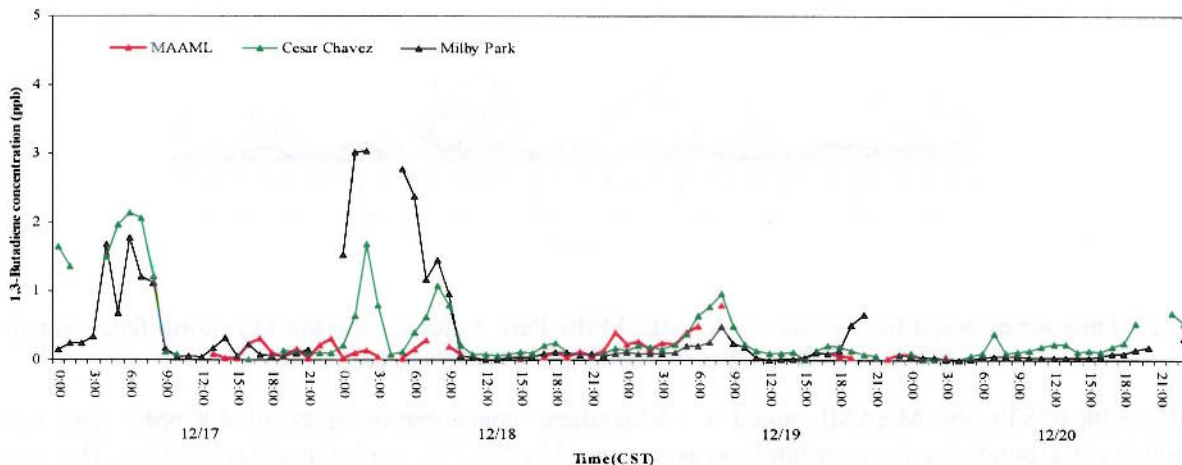


Figure 20: Time series graph - 1,3-butadiene as measured by MAAML and AutoGCs from 12/01/07 to 12/04/07

2.3.8 Monitoring Results at Site F

Site F, located east of Goodyear, lies downwind of Goodyear with winds from west-southwesterly to west-northwesterly and downwind of TPC with southwesterly winds. From 09/03/08 to 09/05/08, MLP Chemists deployed the MAAML at Site F for ambient air quality monitoring finding 1,3-butadiene and styrene concentrations during this period.

2.3.9 Monitoring Results at Site G

Site G, an employee parking lot just north of the Goodyear plant, sits downwind Goodyear and TPC with east-southeasterly to west-southwesterly wind directions. From 05/22/08–06/12/08 and 07/30/08–08/01/08, MLP Chemists deployed the MAAML here for ambient air quality monitoring.

Figures 21 and 22 depict the time series graphs of 1,3-butadiene and styrene concentrations as measured by the MAAML, the Milby Park AutoGC, and the TPC north fence line monitor for these two periods.

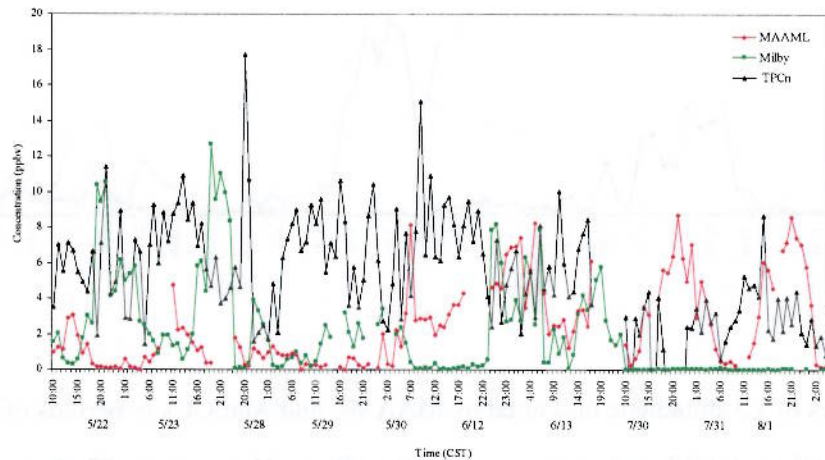


Figure 21: Time series graph for 1,3-butadiene - MAAML, Milby Park AutoGC, and the TPC north fence line monitor from 05/022/08 to 06/13/08 and 07/30/08 to 08/01/08

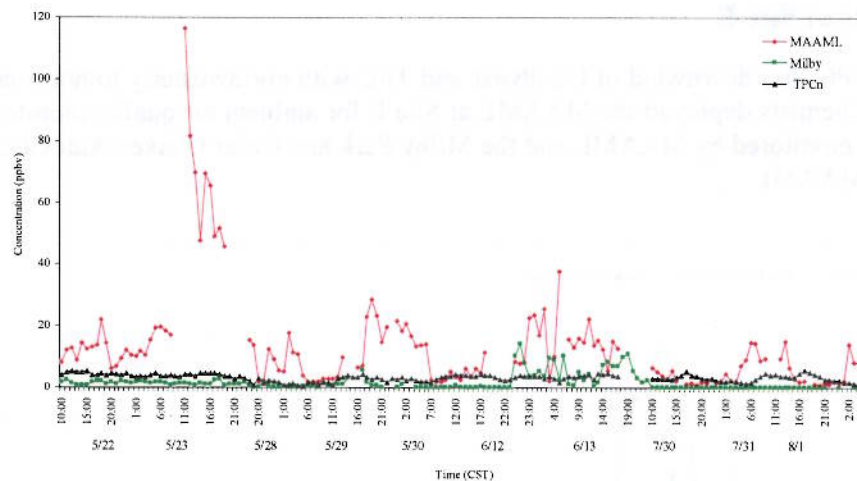


Figure 22: Time series graph for styrene - MAAML, Milby Park AutoGC, and the TPC north fence line monitor from 05/022/08 to 06/13/08 and 07/30/08 to 08/01/08

At 11:00 on 05/23/08 (CST), the MAAML noted a 1,3-butadiene concentration spike of 4.8 ppbv with winds prevailing southeasterly which corresponded to the concentration as measured by the TPC north fence line monitor. This strongly suggests that this spike originated from TPC.

At 7:00 on 05/30/08 (CST), the MAAML noted a 1,3-butadiene concentration spike of 8.2 ppbv with winds prevailing southeasterly which did not correspond to the concentration as measured by the TPC north fence line monitor. This strongly suggests that this spike originated from Goodyear.

From 20:00 on 06/12/08 to 7:00 on 06/13/08 (CST), the MAAML noted 1,3-butadiene concentrations with winds from southeasterly to south-southeasterly which corresponded to the concentration as measured by the TPC north fence line monitor and the Milby Park AutoGC. This strongly suggests that this spike originated from TPC.

From 18:00 on 07/30/08 to 02:00 on 07/31/08 and from 15:00 on 07/31/08 to 00:00 on 08/01/08 (CST), the MAAML noted 1,3-butadiene concentrations with southerly to south-southwesterly winds which did not correspond to the concentrations as measured by the TPC north fence line monitor and the Milby Park AutoGC. This strongly suggests that the concentrations originated from Goodyear.

From 19:00 on 05/22/08 to 03:00 on 05/23/08, from 16:00 to 23:00 on 05/23/08, from 20:00 to 22:00 on 06/12/08, from 03:00 to 06:00 on 06/13/08, and from 18:00 to 19:00 on 06/13/08 (CST), both the MAAML and the Milby Park AutoGC detected 1,3-butadiene concentrations with southeasterly to south-southeasterly winds. This strongly suggests that the concentrations originated from TPC.

The MAAML detected styrene concentrations from 11:00 to 19:00 on 05/23/08 (CST) with southeasterly winds. At the same time, both the Milby Park AutoGC and the TPC north fence line monitor measured much lower styrene concentrations. This strongly suggests that the concentrations originated from Goodyear.

2.3.10 Monitoring Results at Site I

From 12/28/08 – 12/31/08, BPCP received seventeen complaints of chemical odors around TPC and Goodyear, especially predominant in a residential area located south-southwest of TPC. The complainants alleged that they suffered from severe nausea, headaches, and vomiting as a result of the odors, and, in some cases, they had to leave their homes and sleep elsewhere due to the effects from the odors. As a part of the investigation, BPCP staff took a routine ambient air sample in a SUMMA container and sent it to an independent subcontract laboratory for analysis via EPA Method TO-15.

In response to these resident complaints, MLP Chemists deployed the MAAML at Site I to monitor ambient air quality from 11:00 12/30/08 to 12:00 12/31/08 (CST). Two unknown peaks of noteworthy size appeared in the chromatograms for the samples taken from 01:00~09:00 on 12/31/08. An MSD library search performed by the MLP team tentatively identified the two peaks as 4-vinyl-1-cyclohexene (VCH) and 2,4,4-trimethylpentene (TMP), respectively. VCH, as a known air toxic, has a TCEQ Short-Term Health Effects Screening Level (ESL) of 1 ppbv. Since VCH and TMP do not frequently occur as Houston area HAPS, the MLP team did not have them on the list of target compounds for the MAAML. As a result, the MLP Chemists had to estimate the concentrations of VCH and TMP by using the calibration curves for n-hexane. Figure 23 reflects the time series graph for VCH, TMP, 1,3-butadiene, and styrene as measured by MAAML.

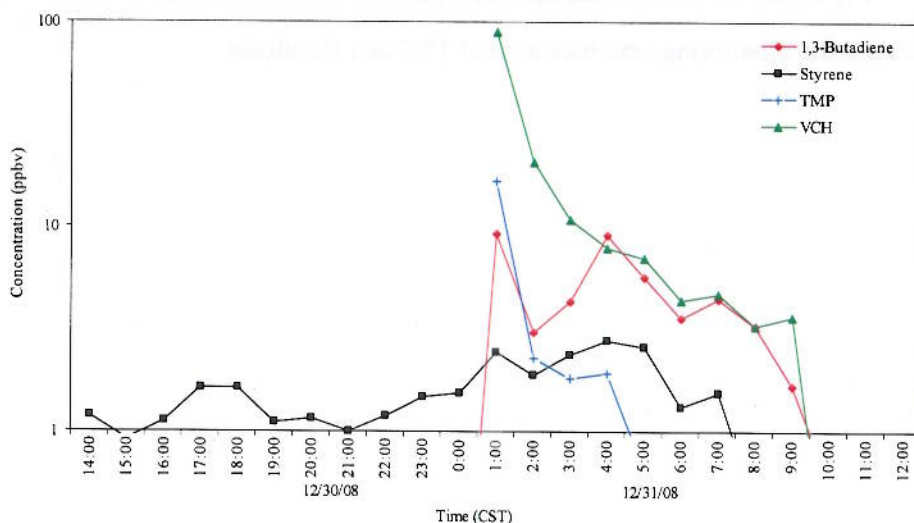


Figure 23: Time series graph - VCH, TMP, 1,3-butadiene, and styrene (MAAML: 11:00 on 12/30/08 to 12:00 on 12/31/08)

The MAAML detected concentrations of VCH from 01:00~09:00 12/31/08 as northerly winds prevailed. Additionally, the MAAML also concurrently noted 1,3-butadiene concentrations with values ranging from 1.7~9.1 ppbv. The resultant wind direction plot for 1:30 12/31/08 (Figure 24) indicated that peak concentrations for 1,3-butadiene, VCH, and TMP came from the waste water treatment areas for TPC and Goodyear.

TPC did not admit having had an upset in the API Separator until the BPCP staff began a full-scale investigation into the incident to address citizen complaints. A malfunction caused TPC to discharge absorber oil (also called lean oil) to the API

Separator. On 12/28/2008 at about 15:00, TPC released lean oil from the 3F-105 Suction Drum to the API to prevent it from entering the compressor suction line where Suction Drum 3F-105 normally collects liquid from the process off-gasser that feeds one of the compressors. The high-level indicator on this drum alerted that the drum was filling with liquid. TPC immediately started the manual pump to remove the liquid from 3F-105 and pump it to 3F-1521, the oil separator associated with the wastewater system. The investigation performed by BPCP staff in conjunction with TPC environmental liaisons confirmed that concentrations of VCH, TMP and 1,3-butadiene came from the TPC wastewater treatment area. In addition, the independent subcontract laboratory reported VCH as a tentatively identified compound (TIC) via their GC/MS analysis of the SUMMA canister ambient air sample as taken by BPCP staff as the time of the initial complaint investigation.

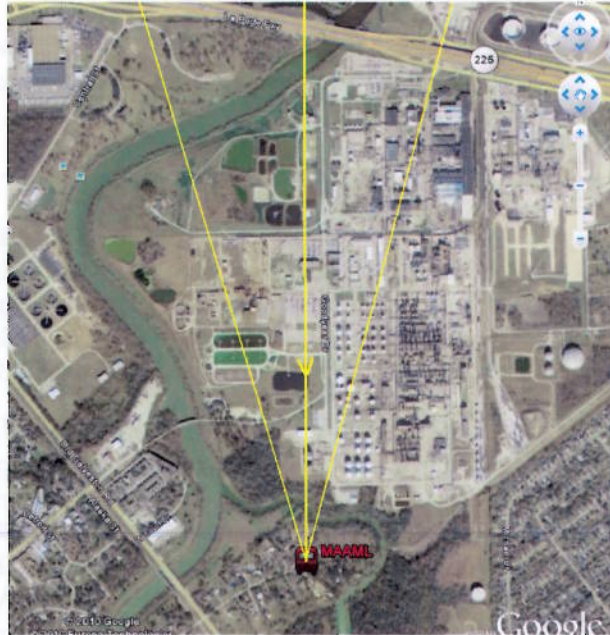


Figure 24: Resultant wind direction plot for Site I at 01:30 12/31/08

Appendix C contains all data for the monitoring activities around TPC and Goodyear.

3.0 Conclusions and Recommendations

A thorough review of the work performed by the MLP team reveals that the MAAML as a mobile analytical platform and the MLP as a whole met and well exceeded the goals and objectives as contained in the original EPA grant proposal. The ability to collect data based upon downwind site deployment relative to prevailing winds allows analysts to determine the seasonal aspects of point source emissions and the impact of these variations on the communities adjacent to the sources of air toxics emissions. Fixed-base monitors, while excellent for the acquisition of continuous and nearly uninterrupted air quality data, do not have the capability to relocate relative to the cones of point source emissions. In addition, the presence of Chemists monitoring the data as it becomes available without having to confirm its validity allows for more immediate response when exceedances occur, two other shortcomings associated with fixed-base monitors. The MAAML as a mobile field base of operations also provides the Chemists the chance to expand upon the field investigation through the collection of upwind air samples, IR camera footage, and PID readings both to bracket the targeted facility and to gather strong supporting evidence in further demonstrating and assigning sourcing for an emissions event. This all falls under the heading of identification and characterization of point source emissions, the core objective of the EPA grant.

The mobility aspect of the MAAML has played a vital role in the success of the MLP as a way to determine ambient air toxics concentrations in the communities adjacent to facilities. The work performed by the MLP team at Site I as described above stands as a case study on the ways in which the MAAML can enhance local-scale air toxics monitoring. As both official confirmation of the emissions and corrective actions to contain the emissions within the plant fence lines did not occur promptly, without the capabilities provided by the MAAML, no other means existed to obtain as quickly the necessary information to determine the severity of the emissions event. In addition, the high quality data collected by the MAAML ensured that other BPCP field investigators had the type of evidence they needed to aggressively pursue their investigations. This feature of the MAAML, combined with the first-hand knowledge about potential “bad actors” that local environmental agencies have at their disposal, makes the MAAML a vital front-line tool in the realm of local-scale air toxics ambient monitoring.

Another aspect of the MLP and its feasibility for implementation regards the financial commitment involved in both the construction of the MAAML and the ongoing costs associated with the MLP. Obviously, not every municipality will have access to the necessary resources (\$450,000 - 500,000) for construction of a mobile laboratory with comparable instrumentation to the MAAML. However, not every municipality requires instrumentation like that in the MAAML to address their specific local-scale monitoring activities. In fact, many agencies have taken the concept initiated by the MAAML and modified it to suit their individual areas of concern. While agencies so incorporating the mobile laboratory concept have reflected county- or state-level environmental agencies to date, the concept has validity for larger metropolitan areas with air quality challenges. Considering the flexibility in analytical platforms and the ability to monitor more areas than traditional fixed-based monitors, the mobile laboratory approach can have far-reaching consequences for environmental agencies across the country.

Although the MAAML did perform quite well in its role as a means for local-scale air toxics ambient monitoring platform, this does not mean that no problems occurred during the course of the grant period. The vast majority of issues that happened entailed downtime for equipment maintenance and repairs. Given the complexities involved with an analytical platform such as the MAAML, this outcome did not come as a surprise to the MLP team. Field operations in general tend to center as much on the challenges of keeping the equipment operating at acceptable levels as on the completion of the actual field investigations themselves. Despite the occasional downtime that resulted from the amount of usage seen by the onboard MAAML instrumentation, the MLP team continued to persevere in their mission of achieving all grant goals and objectives.

Appendix A: MAAML Layout and Equipment Specifications

MAAML

MAAML, built on a 2006 Ford E-450 van chassis, contains two diesel generators, two air conditioners, four leveling jacks, and a telescopic mast to raise the meteorological sensors to a height of 10 meters (Figures 1 to 3). The truck runs on diesel fuel with a 55 gallon fuel tank.



Figure 1: The MAAML in field deployment at Milby Park

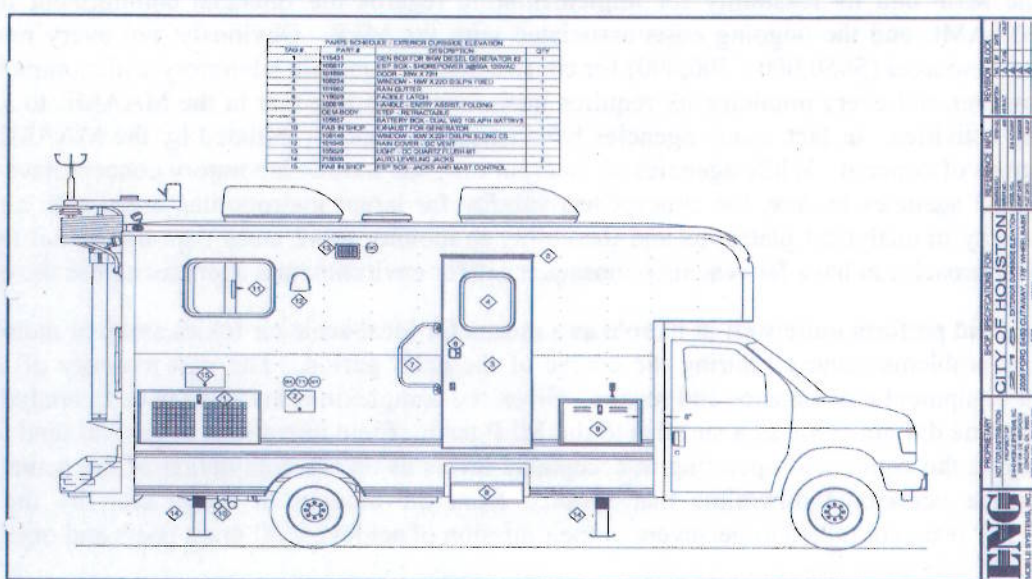


Figure 2: Side draft view of the MAAML

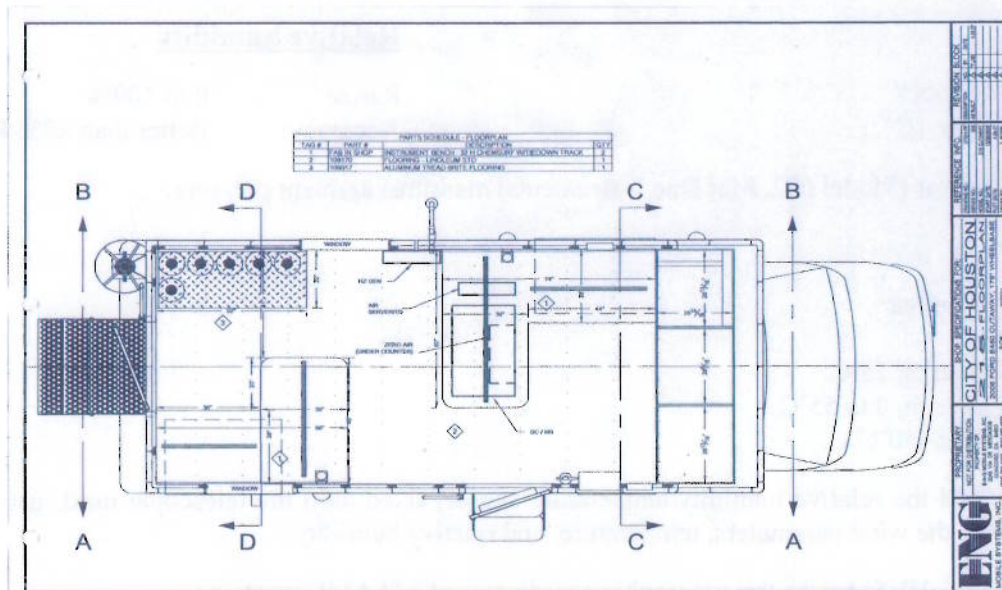


Figure 3: Top cutaway draft view of the MAAML

The MAAML derives its electrical power from one of two methods: two 50 amp 120V shore power lines or two onboard 7.5 KW generators, diesel fueled and sharing the same fuel tank with the van base.

A hydraulic leveling system with four jacks ensures that the MAAML remains level and stable.

Meteorological Equipment, GPS, and Datalogger

A sonic wind sensor (Model 50.5, Met One Instrument) measures wind speed and wind direction (Figure 6):

Wind speed

Range: 0 to 50 m/s
 Accuracy: $\pm 0.2 \text{ m/s} \leq 11.3 \text{ m/s}$ or $\pm 2\% \geq 11.3 \text{ m/s}$
 Resolution: 0.1 m/s

Wind direction

Range: 0 to 360°
 Accuracy: $\pm 3^\circ$
 Resolution: 1°



Figure 4: Wind, temperature, and relative humidity sensors

A relative humidity/temperature sensor (Model 083D, Met One Instruments) measures ambient temperature and relative humidity.

Temperature

Range: -20°C to +60°C
Coefficient: $\pm 0.04\%$ per 1°C

Relative humidity

Range: 0 to 100%
Accuracy: Better than $\pm 2\%$ RH

A Barometric Pressure sensor (Model 092, Met One Instruments) measures ambient pressure:

Barometric Pressure

Range: 600~1100 mbar
Resolution: 0.1 mbar
Accuracy: ± 0.35 mbar @ 25°C
 ± 0.75 mbar @ 0 to 55°C
 ± 1 mbar @ -40°C

The sonic wind sensor and the relative humidity/temperature sensor, fixed atop the telescopic mast, get raised to a standard height of 10 m to measure the wind parameters, temperature, and relative humidity.

A GPS receiver (Garmin 16-HVS) tracks the geographic coordinates of MAAML locations.

A scientific datalogger (CR1000 Measurement and Control System, Campbell Scientific) collects and stores all GPS and meteorological data.

TD-GC/FID/MS System

Markes CIA8 Air Server and Markes UNITY2 Thermal Desorber (Figure 5) process on-line ambient air samples as well as blank or calibration samples and inject them into the GC analytical platform. Typically, the instrumentation draws 500cc aliquots in the system over 40 minutes at a flow rate of 12.5 cc/min with excess moisture in the sample removed by a heated sample line and a Nafion[®] based drying membrane. The dry sample, collected by an electrically cooled cold trap in the thermal desorber becomes concentrated on the cold trap to achieve high sensitivity for very low concentrations of air toxics. Then, the preconcentrator, rapidly heated to thermally desorb the sample gets back-flushed into the GC analytical platform via a reversal in the carrier gas flow.



Figure 5: Markes CIA8 Air Server and Markes UNITY2 Thermal Desorber

Figure 6 shows the operation cycles for TD and GC. MLP Chemists use Agilent's Model 6890N network GC with Flame Ionization Detector (FID 210), dual EPA split/splitless inlets (112), a microfluid Dean's switch (888), pneumatics control module (309), LAN and 7683 interface and Agilent Model 5975C Inert Mass Selective Detector (MS) performance turbo EI mainframe with G3397A ion gauge controller (Figure 7) to analyze samples. Due to the wide boiling point range of the VOCs, the GC has dual columns: a plot column for light compounds and a BP1 column for heavier compounds. Hydrocarbons from C2 through C3 elute early from the BP1 column with the programming switching flow thereafter to the Plot column by a Dean's switch. The FID analyzes hydrocarbons from C2 through C3. The high boiling point materials from C4 through C10 elute later from the BP-1 column for analysis via the MS. Figure 8 depicts the sample path overview for the air server, desorber and GC/FID/MSD. MLP Chemists have developed a set of sampling and analyzing methods to control and operate the TD-GC/FID/MS system found in Appendix B as the Standard Operating Procedure (SOP) for TD-GC/FID/MS for Air Toxics Analysis in the Mobile Ambient Air Monitoring Laboratory.

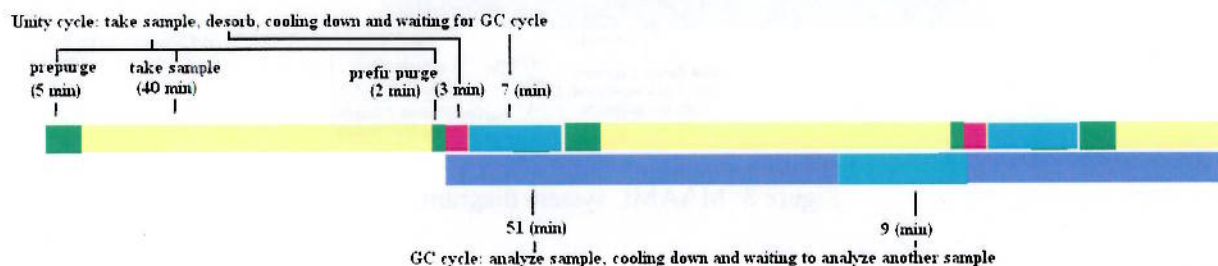


Figure 6: GS/MS and TD cycles chart



Figure 7: Agilent Model 6890N GC and Agilent 5975C MS

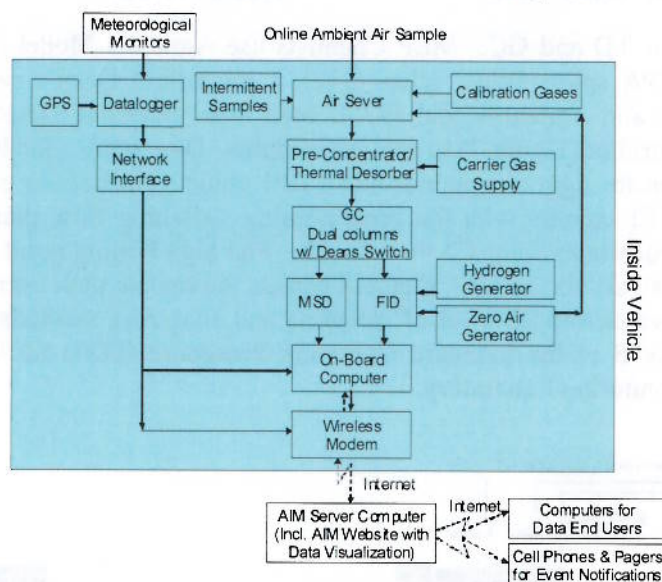


Figure 8: MAAML system diagram

A Matheson Hydrogen generator (Model NM Series 2 provides hydrogen for the FID.

A Matheson Zero Air Generator combined with an air compressor provides zero-grade air for the TD-GC/FID/MS.

From August 2007 to February 2008, the MAAML targeted fourteen chemical compounds with the TD-GC/FID/MS system: ethane, ethylene, propane, propylene, acetylene, 1,3-butadiene, butane, pentane, 2-methylpentane, 1-hexene, n-hexane, benzene, toluene, and xylene. From March 2008 to July 2008, MLP Chemists added styrene and ethylbenzene as target chemical compounds. Since August 2008, MLP Chemists have devised a fifty-one chemical compounds target list for the MAAML. Among these target compounds, 1,3-butadiene and benzene represent definite risk pollutants in Houston's ambient air. Vinyl chloride, carbon tetrachloride, and 1,1,2,2-tetrachloroethane represent probable risk pollutants (Table 2).

AIM data management

The meteorological data, GPS location and MAAML monitor results goes to a remote server via a wireless module with all data available at the AIM website. The AIM can plot time series graphs for chemical compounds, wind speed, wind direction, and other parameters (Figure 9). It can also evaluate all targeted compounds for an ambient sample (Figure 10). Also, the AIM website provides functions to plot back and forward trajectories. MLP chemists can trace the emissions source upon identification of concentrations of a chemical compound. Additionally, MLP Chemists may estimate the possible affected area(s) as well, such as when the MAAML detected high benzene concentrations at 14:00 on March 7, 2008. The backtrajectory suggested that it came from a ground flare for the tank area (Figure 11).

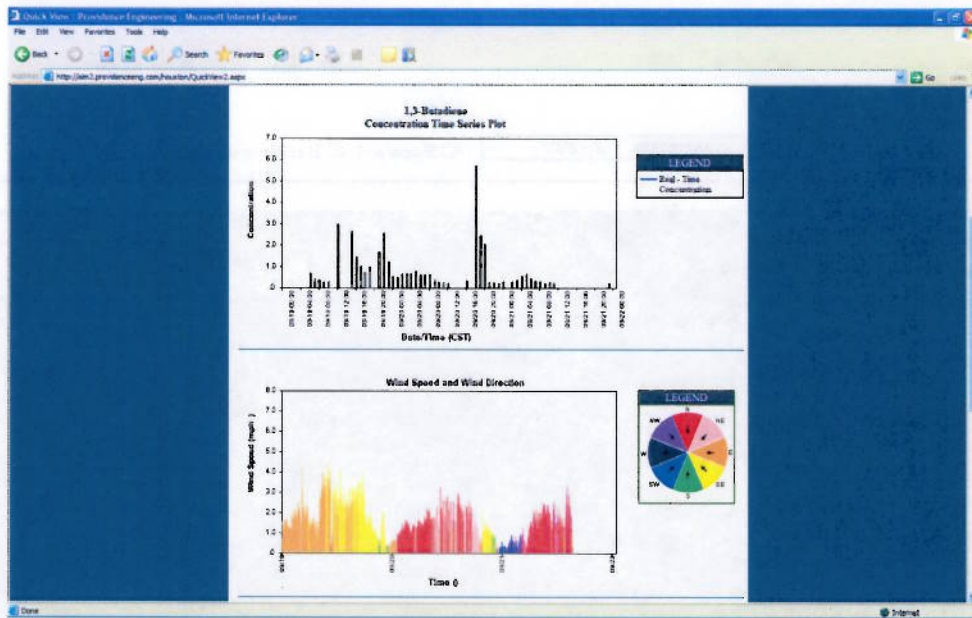


Figure 9: Time series graphs for 1,3-butadiene, wind speed, and wind direction

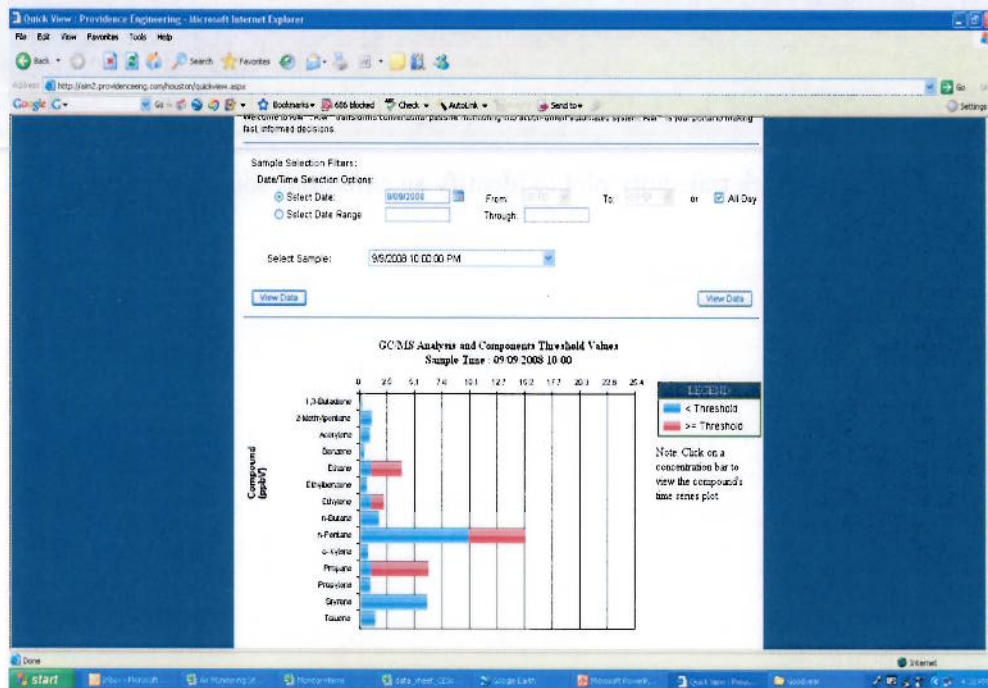


Figure 10: Bar chart to evaluate concentrations of chemical compounds

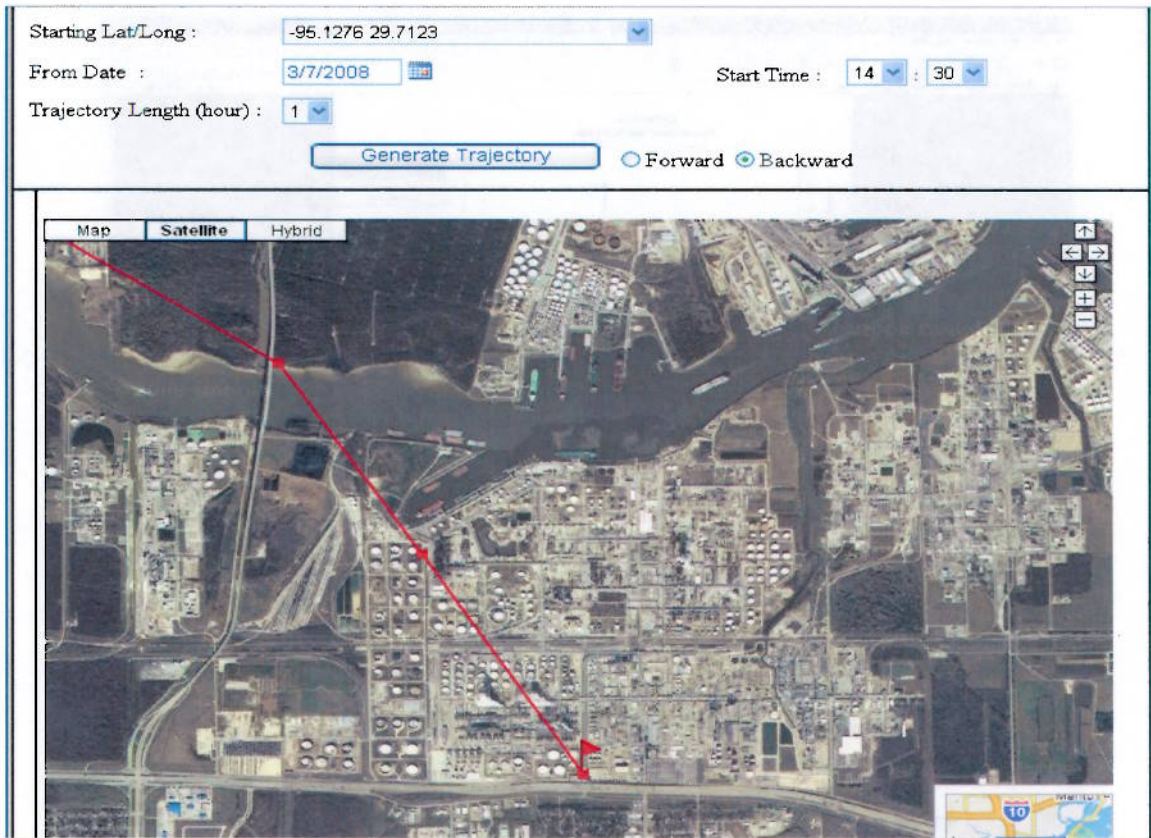


Figure 11: Back trajectory plot to identify an emissions source location

Appendix B: Standard Operating Procedure for TD-GC/FID/MS for Air Toxics Analysis in the MAAML

Bureau of Pollution Control and Prevention Standard Operating Procedure TD-GC/FID/MS for Air Toxics Analysis in the Mobile Ambient Air Monitoring Laboratory (MAAML)

Revised by:

Dr. Youjun Qin – Chemist IV Date

Approved by:

James Rhubottom – Chemist IV/Operations Leader Date

Dr. Peter Chen – Chemist IV Date

Dr. Wei-Yeong Wang – Quality Assurance Manager Date

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1.0 Purpose

This SOP documents the analytical procedure and protocols for the measurement of volatile organic air toxics using the TD-GC/FID/MS in the Mobile Ambient Air Monitoring Laboratory (MAAML). The data will provide an air quality database that will assist in tracking and monitoring emissions from industrial facility sources and automobile sources. The air toxics that represent the primary focus of the MAAML's investigations, volatile organic compounds (VOCs) such as 1,3-butadiene and benzene, can cause serious health effects and include ozone precursors. This document covers system performance checks, sample loading, sample analysis, data acquisition, and data verification of the TD-GC/FID/MS.

2.0 Scope and Applicability

Instruments include the Agilent 6890N/5975C Gas Chromatograph/Mass Spectrometer with a Flame-Ionization Detector, the Markes CIA Air Server and UNITY2 Thermal Desorber. The primary focus of this SOP, namely the quantitation of organic air toxics such as 1,3-butadiene, benzene, etc. follows with the quantitation limits and standard analyte list provided in Table 1 and Table 3, respectively.

This document covers system performance checks, sample loading, sample analysis, data acquisition, and data verification and documentary. This procedure will allow for continuous measurements of ambient air samples, as well as analysis of collected samples in SUMMA[®] canisters and sample bags.

3.0 Personnel Qualification and Training

This document stands as a reference guide intended for Chemists and Environmental Investigators working for the City of Houston Bureau of Pollution Control and Prevention in the Mobile Ambient Air Monitoring Laboratory. For the purposes of this document, qualified personnel will have the designation Operators. Operators require no certification but working knowledge of analytical instruments, basic chromatography, and mass spectrometry. All MAAML personnel must receive hands-on training with the MAAML equipment and related analytical instruments. All MAAML personnel must demonstrate working knowledge of the instrumentation through the completion of a Demonstration of Capability (DOC), administered by the Technical Services manager. The MAAML team must receive training in field sampling, defensive driving, first aid, and emergency procedures

4.0 Definitions

Calibration – A process of determining a mathematical response ratio to a set of known concentrations.

Calibration Verification Standard and Duplicate (CVS/CVSD) – A quantitative sample consisting of known concentrations of standard analytes, ex. propane, 1,3-butadiene and benzene. Analysis used to verify analytical system accuracy

Dilution Factor – A measure comparing the amount of a sample or standard and its diluent in a solution

Flame Ionization Detector – Gas chromatographic detector used for hydrocarbon analysis

Linearity Range – The acceptable range of response for quantitation of results with the upper acceptance for this range represents the highest calibration point.

Method Blank – A sample consisting of zero air used to assess potential contamination within an analytical system

Method Detection Limit (MDL) – An analysis consisting of a series of known concentrations used to mathematically determine the threshold concentration for the minimum response representing the minimum concentration of an analyte measurable and reported with a 99% confidence that the analyte concentration is greater than zero

Percent Recovery – A calculation of a measure value compared to a theoretical value. The amount of a component which is recovered and detected from a known standard

Precision – The measure of the reproducibility of a measured value

Response Factors (RF) – A measure which indicates a system's response to a known value, the ratio of the detector response to the amount of analyte in the calibration standard used for calibration in flame ionization detector and mass spectrometry

Retention Time (RT) – The amount of time a specific compound resides in a chromatographic system before reaching the analytical detector

Retention Time Verification Standard (RTS) – A sample with a blend of known compounds used to verify the location of those compounds in a chromatographic column

Standard Deviation (STD) – A measure of the average distance of individual observations from the mean

Relative Standard Deviation (RSD) – A measure of variability adjusted for the magnitude of observations involved

Tentatively Identified Compounds (TICs) – Compounds detected in a sample not reflecting a target compound, internal standard, or surrogate compounds and tentatively identified by mass spectral library searches, typically reported with estimated concentrations

5.0 Safety

Operators must perform all work in accordance with the appropriate health and safety procedures specified in the Houston Department of Health and Human Services Safety and Health Manual (May 2003).

5.1 Personal Protective Equipment

Operators and visitors must wear appropriate personal protective equipment, including but not necessarily limited to eye protection, Nomex[®] suits, steel-toed shoes, gloves, and hearing protection as specified by HDHHS Safety and Health Manual to include all within the working scope of the MAAML.

5.2 Specific Safety Concerns or Requirements

Operators can obtain health and safety information from the Material Safety Data Sheets (MSDSs) maintained by the laboratory. The MAAML presents potential electrical, physical, and chemical hazards. The following represent known specific concerns or hazards:

Chemicals used: methanol, acetone, methylene chloride, hydrogen, zero air, helium.

Compressed gas cylinders, often heavy and hard to handle physically, must have tight, secure fittings (strap or chain) to a sturdy, fixed structure. Never remove the safety cap on a cylinder while moving it. Transport cylinders using a cylinder dolly only. Clearly mark empty and full cylinders. When attaching a regulator to a cylinder, use the appropriate CGA fitting. Check gas lines and fittings for leaks after cylinder or regulator replacement.

Always unplug a heat traced line before maintenance and when disconnecting gas lines. Check for frayed or missing insulation before turning the power on.

Operators must check electrical systems periodically for frayed wires, loose connections, or missing components. Never use electrical tape to repair frayed wires, or to join a spliced wire.

If a circuit breaker throws, Operators must power down all instruments on that circuit before restoring power. Only then may Operators turn on instruments one at a time to determine which instrument caused the breaker to throw.

The Thermal Desorber and analytical instruments have extreme heat and cold zones. The Thermal Desorber uses an electrically cooled trap which can reach a temperature of -35°C during sample collection. The trap may climb to 325 °C during desorption. The gas chromatograph oven and FID may reach temperatures of up to 250°C. Avoid contact with the internal components of the instruments to avoid injury and burns. Cryogenic burn zones include the thermal desorber. Heated zones include the thermal desorber, GC oven, FID, and transfer lines.

The enclosed space of the MAAML makes trip hazards present in the form of electrical and sampling lines. Operators must secure all such lines out of the main walkways or cover them with protective strips.

The zero air and hydrogen gas generators producing gas on a continuous basis. Flammable hydrogen gas can accumulate in a confined area. Do not allow hydrogen gas to collect in one area, and always maintain adequate ventilation.

Operators must have a posted list of emergency phone numbers, contacts, and personal protective equipment including gloves, safety glasses, and have a first aid kit available inside the MAAML and in the garage.

5.3 Materials Used

The following table represents a list of the primary materials used in this procedure, which have a serious or significant hazard rating. This does not include all materials used in the sampling effort, or the sample matrices. Employees must review the information in the MSDS for each material before using it for the first time.

Material	Hazards	Signs or Symptoms of Exposure
Methanol	Flammable, Poison, Irritant	Slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure may include headache, drowsiness and dizziness. Methanol, a defatting agent, may cause skin to become dry and cracked. Skin absorption can occur; symptoms may parallel inhalation exposure. Irritant to the eyes.
Methylene chloride	Carcinogen, Irritant	Causes irritation to respiratory tract, gastrointestinal tract. Strong narcotic effects with mental confusion, fatigue, nausea, vomiting and headache. Causes formation of CO in blood which effects cardio and central nervous system. Continued exposure may cause unconsciousness and death. Causes redness and pain on skin contact; liquid degreases the skin. May be absorbed thru the skin.
Acetone	Flammable, Irritant	Inhalation may irritate respiratory tract. May cause coughing, dizziness, and headache. Irritating due to defatting action on skin; causes redness, pain, drying and cracking of the skin. Long term exposure may produce central nervous system depressions, narcosis, and unconsciousness.

6.0 Equipment and Supplies

6.1 Markes Air Collection System

Markes CIA8 Air Server

Markes UNITY2 Thermal Desorber

6.2 Agilent GC/FID/MS System

Agilent Model 6890N network gas chromatograph with flame ionization detector (FID 210), dual EPA split/splitless inlets (112), a microfluid Dean's switch (888), pneumatics control module (309), LAN and 7683 interface

Agilent Model 5975C Inert Mass Selective Detector (MSD) performance turbo EI mainframe with G3397A ion gauge controller

7.0 Reagents and Standards

GC Carrier Gas – GC grade helium (He) or equivalent

MS Instrument Performance Check Compound – 4-Bromofluorobenzene (BFB)

MS Tuning Compound – Perfluorotributylamine (PFTBA)

Calibration Standards – 100 ppbv of standards containing compounds listed in Table 3

8.0 Quality Control

Quality control (QC) samples ensure that the data produced from a particular analytical source meet acceptability and show consistent quality throughout the analytical procedure. QC samples, analyzed to assess precision and accuracy, include method blanks, calibration samples and duplicates, laboratory control samples and duplicates, sample duplicates, surrogates, and internal standards. Table 1 lists a summary of these criteria.

8.1 Method Blank

The method blank (MB), a control sample prepared using a well-characterized blank matrix (e.g. zero air), uses the same reagents used for sampling. As part of a QC batch, the method blank accompanies the samples through all steps of the analytical process. The MB monitors the level of contamination introduced to a batch of samples as a result of handling in the laboratory. Operators must process one MB within an analytical batch, normally analyzed daily before any samples are analyzed. The MB should not contain any confirmed analytes of interest > 2ppbc for FID, and >1.0 ppbv for MS. The sum of all target compounds must be < 20.0 ppbc. See Table 1 for a list of QC criteria.

Corrective Action for Blanks:

If a target analyte in the method blank exceeds the reporting limit, Operators must reanalyze the method blank. If the reanalysis still fails the acceptance criteria, Operators must resample all samples analyzed within the batch if possible. With re-sampling not possible, Operators must flag all associated samples with a “B” flag on the appropriate analyte of interest, and possible invalidation of the data after review and add a narrative to the data for further documentation.

The following special situations may allow the reporting of qualified data without reanalysis, but will require a non-conformance memo (NCM).

With no analyte greater than the reporting limit in the samples associated with an unacceptable MB, Operators may report the data with qualifiers.

With the analyte concentration in the samples greater than 10 times the MB concentration, Operators may report the data with qualifiers.

With blank contamination less than the concentration present in the samples and less than 1/10th of the regulatory limit, Operators may report the data with qualifiers.

Any surrogates in the method blank must pass acceptance criteria. If the surrogates fail acceptance criteria, Operators must review the data to determine whether the MB has accurately demonstrated the analysis free of contamination; or if the MB matrix creates a matrix effect altering surrogate recoveries.

8.2 Calibration Verification Standard and Duplicate (CVS/CVSD)

The calibration verification standard (CVS), prepared by obtaining the known concentrations of target compounds, assesses instrument accuracy. Operators analyze the CVS daily with an acceptable recovery criterion of 70-130% and routinely (weekly) analyzed in duplicate (CVSD) to assess instrument precision from run to run with the acceptable precision criterion an RPD of ≤ 25%. See Table 1 for a list of QC criteria.

Corrective Action for CVS/CVSD Recovery Failure:

If one or more analytes lie outside the established control limits, Operators should check instrument performance and reanalyze the CVS or CVSD. If the reanalysis does not resolve the failures, replace the CVS standard and reanalyze. If still unresolved, contact the Technical Services manager to assess whether a need exists for re-sampling of any samples associated with the failing CVS. With no re-sampling, flag the data with the appropriate flag.

The following special situations may allow qualified data to be reported without reanalysis, but will require an NCM.

With CVSD recovery high and no analytes detected in the sample, Operators may report the data with qualifiers.

With low analyte concentrations, RPD calculations may reach a statistical limit of precision. In such cases, Operators may use surrogate recoveries to provide evidence of accuracy control.

With all compounds of interest within control, but non-target compounds out of control, Operators may consider the CVS acceptable for reporting.

Corrective Action for CVS Precision Failure:

With no established control limits for precision met, check instrument performance. With the RPD out of control, but both accuracy recoveries within acceptance criteria, prepare an NCM and qualify the data.

8.3 Surrogates

Surrogates represent organic compounds similar in chemical nature and behavior to target analytes but not normally found in environmental samples. 4-Bromofluorobenzene stands as the surrogate for this procedure.

Operators spike all samples in a batch with the surrogate to monitor the effects of both the matrix and the analytical process on accuracy. Operators must evaluate surrogate spike recoveries evaluated by determining whether the concentration (measured as percent recovery) falls within the required recovery limits. Operators must ensure surrogate recoveries within established control limits and document any failure on the final data reports.

Corrective Action for Surrogates:

Operators must ensure that the surrogate recoveries lie within established control limits for the CVS and method blank and check all calculations to ensure that no errors occurred. Check surrogate spiking solution for degradation, contamination, etc.

With no source of spiking failure discovered, reanalyze the QC sample. If reanalysis does not confirm the original analysis, and lies within acceptance criteria, then the problem stayed within the analyst's control and the operator should only report the reanalyzed data. If the surrogate recovery still fails, reanalyze batch if samples remain available.

If the surrogate fails acceptance criteria in a field sample, reanalyze the field sample if possible to check for matrix interference, i.e. humidity, interfering compounds, or interference from a prior analysis. Document the failure and note it on the final data report.

8.4 Internal Standards

Internal standards, added to each analytical standard, sample, and blank sample see use only used the mass spectrometric detector. Operators set the acceptance criteria for each internal standard at $\pm 50\%$ recovery of the internal standard area from the calibration verification standard (CVS) with the acceptance criteria for each internal standard's retention time in every analysis within ± 20 seconds of the internal standard retention time from the continuing calibration standard.

Corrective Action for Internal Standards:

With the internal standard outside acceptance criteria, check instrument performance and the internal standard spiking standard for degradation. If unresolved, search for possible matrix effects, including co-elutions, interferences, excess moisture, et al. Reanalyze the sample, and if still outside of control limits, issue an NCM with suspected interference.

8.5 Retention Time Verification Standard (RTS)

The RTS, used to assess the qualitative ability of the analytical platform to identify peaks in a chromatogram with FID detector, has a composition of FID targeted compounds of FID spiked near the mid-point concentration of the calibration range. Operators should analyze the RTS after installation of a new column and then as needed based on performance. Failure of the system to correctly identify these RTS compounds will require instrument optimization by the operator.

9.0 Calibration and Standardization

9.1 Initial Calibration Verification and Curve Fits

9.1.1 GC/FID

An initial calibration curve (ICAL-FID) consists of a minimum of three concentration levels analyzed to determine a working linear range of the analytical system for each compound. The concentration of the lowest point should lie at or below the reporting limit.

The calibration curve correlation coefficient (r) must have a value ≥ 0.995 or an RSD of RFs $< 20\%$. If any curve fits fail the acceptance criteria, check the system performance, and repeat analysis of outlying points.

9.1.2 GC/MS

An initial calibration curve (ICAL-MS) consists of five concentration levels (1, 5, 10, 20 and 40 ppbv) analyzed to determine a working linear range of the analytical system for each compound. The concentration of the low point should lie at or below the reporting limit.

The calibration curve correlation coefficient (r) must have a value ≥ 0.995 or RSD of RFs $< 30\%$, with only two exceptions allowed where this value lies at $< 40\%$. If any curve fits fail the acceptance criteria, check the system performance, and repeat analysis of outlying points.

Initial Calibration Verification:

The initial calibration verification (ICV), a secondary source standard, contains target analytes analyzed immediately after the initial calibration. For each analyte, a percent recovery is calculated using the average response factor. The guidance acceptance criterion stands at $\pm 35\%$. If the ICV fails acceptance criteria, reanalyze ICV and check instrument performance. If the ICV still fails, check ICAL analyses for problems or statistical anomalies.

9.2 Daily Calibration Verification (CVS)

Every 24 hours of operation, Operators must analyze a calibration verification standard (CVS) to assess instrument performance and to verify the response factors generated from the ICAL. The CVS represents a standard containing known amounts of target analytes routinely spiked in the mid-range of the calibration linearity range. Operators then calculate the percent difference (%D) between the CVS RF from the ICAL average RF where in general, %D must lie within $\pm 30\%$.

Calibration Verification Standard Failure:

As long as less than 10% of all analytes in the CVS fail the acceptance criteria, continue the analysis with the failing compounds flagged appropriately. If more than 10% of all analytes fail the acceptance criteria, check instrument performance and reanalyze the CVS. If the CVS still fails, Operators must perform corrective maintenance.

10.0 Procedure

10.1 Method Summary

Operators analyze VOCs using the Markes Thermal Desorber, and Agilent GC/FID/MS system. The instruments consist of a gas chromatograph equipped with flame ionization and mass spectrometry detectors. The system uses a Markes U-AIRSV to collect the ambient air samples or induce the standard samples.

The system draws ambient air into the Markes Thermal Desorber at a specified rate where a Nafion[®] based drying membrane removes excess moisture in the sample. The dry sample, collected in an electrically cooled cold trap in the thermal desorber, becomes concentrated on the cold trap to achieve a high sensitivity for very low concentrations of air toxics. The preconcentrator then gets rapidly heated to thermally desorb the sample with the carrier gas flow reversed to back flush the VOCs into the gas chromatograph. Due to the wide boiling point range of the VOCs, the GC has dual columns; a Plot column for light compounds and a BP1 column for heavier compounds. The hydrocarbons from C_1 through C_3 get eluted from the BP1 column early with the sample flow switched to the Plot column by a heated Dean's switch with the hydrocarbons from C_1 through C_3 get detected by the flame ionization detector. The high boiling point materials from C_4 through C_{10} eluted late from BP-1 column see detection via using mass spectrometry. Figure 1 depicts an overview of the sample path for the system.

10.2 Instrument Preparation

10.2.1 GC/FID

Each new column used for this method must undergo a 72-hour retention time study. Operators must calculate a retention time windows for each analyte on each GC column. Operators make three injections of standard throughout the course of a 72-hour period and then calculate the standard deviation of the three absolute retention times for each single component. With the

standard deviation for a particular compound at zero, or less than 1.8 seconds, Operators will use the default of 1.8 seconds per SW-846 as the retention time window.

The retention time of each analyte, as established by the daily calibration check standard, plus or minus three times the standard deviation of the absolute retention times of the 72-hour retention time window study, defines the daily retention time window.

Operators use the ratio of six times the standard deviation for instruments with electronic pressure control (EPC). Retention time windows greater than 1.5% indicate a problem with the system with corrective action necessary.

Check for ignition of the FID by condensation on metal object held above the FID chimney. With the FID unlit, Operators can use either the instrument's auto-igniter or a coil lighter.

Verify communication to the computer, and create an analytical sequence in the ChemStation software, sure to use the current methods and correct report formats. Include all QC and samples for analysis.

Download the sequence to the data interface or data logger. Ensure downloading the next sample for analysis.

10.2.2 GC/MS

Operators may use an autotune as a diagnostic tool for troubleshooting the mass spectrometer (MS), and it also establishes the optimal voltages in the ion source. Operators must perform an autotune after major maintenance to the mass spectrometer with the settings compared to the most recently performed autotune. Significant difference may indicate a problem with the mass spectrometer. Upon completing the autotune, Operators store it named for the date performed, e.g. Jan0107.u with the resulting tune report reviewed and compared to previous reports. Significant differences may require recalibration of the GC/MS.

Operators evaluate the filament current by ramping the repeller using different filament current settings. The curves generated represent an acceptable filament current when good separation of the peak maxima for all three masses (69,219, 502) exists from the tuning compound, PFTBA.

Operators may adjust the sensitivity of the mass spectrometer by increasing the voltage on the electron multiplier with the need to perform this task determined by examining the area of the internal standards and comparing them with those generated during the last detection limit study. With areas less than 50% of those found in the detection limit study, Operators may add voltage to the multiplier to correct for the loss of sensitivity.

Operators perform a daily check of the instrument tune by evaluating the 4-bromofluorobenzene (BFB) from the first QC sample that passes its acceptance criteria at the beginning of the sequence and then average the spectrum of the full BFB with a background scan subtracted before evaluation. Operators select the header "tuner" and the select the task of "evaluate BFB to screen". The resulting report contains the tune acceptance criteria necessary to begin sample analysis. See Table 2.

Operators need to verify communication to the computer, and create an analytical sequence in the ChemStation software, being sure to use the current methods and correct report formats. Include all QC and samples for analysis.

10.2.3 Instrument Settings

The table following shows the Markes U-AIRSV and Agilent GC/MS/FID settings for use in the ozone precursor analysis:

GC Function Key	GC Parameter	Default Method
Oven Programming	Temp 1	45 °C
	Time 1	15.0 min
	Rate 1	6 °C/min
	Temp 2	170 °C
	Time 2	0.0 min
	Rate 2	15.0 °C/min
	Temp 3	200 °C
	Time 3	6.0 min
	Rate 3	END
TD Programming (ambient sample)	Sample rate	12.5 mL/min
	Sample time	40.0 min
	Trap temp	-15 °C
	Purge	2.0 min
	Purge rate	10 mL/min
	Desorb time	3.0 min

10.2.4 Sequences

A sequence file represents a table of instructions used by the Markes U-AIRSV or GC/FID/MS system to control collection, analysis, and interpretation parameters. For routine analysis, Operators must create the sequence files for the Markes U-AIRSV and GC/FID/MS system separately, and then correlate the files with each other to maintain sample and data integrity. Before sample desorption into the GC the instrumentation adds an internal standard to an ambient (calibration, blank, etc) sample. Each row in the sequence for Markes U-AIRSV (Figure 4) corresponds to one set of instructions for a sample to be collected, including the number of sample, the type of sample, the instrument method (Figure 5) used for the sample collection and channel of sample.

Sample Type	Channel	Method Name
Blank	3	Airserver_method_blank(500c).mth
45 compounds standard	1	Airserver_50cc(10ppb_mod).mth
16 compounds standard	6	Airserver_50cc(10ppb_mod).mth
Internal standard	2	Airserver_Intenalstand(IS_5ppb).mth
Ambient	4	Airserver_500c(sample_mod).mth
Canister or bag	5, 7 & 8	Airserver_500c(sample_mod).mth

Each row in the sequence for GC/FID/MS (Figure 6) corresponds to one set of instructions for a sample up for analysis to include sample type, process method used for interpretation of the raw data, and the filename for the raw data files and analysis result files.

10.2.5 Process Methods

Parameters that define the kind of sample (ambient air, standard or blank) collected and the interpretation of raw data lie contained in the analytical systems' process methods. Since the analytical system in the MAAML represents a dual column sampler with a separate collection instrument, Operators require three process methods. EnviroQuant, ChemStation, and the Markes U-AIRSV use these methods to take ambient air samples or standard samples, define integration principles, identify peaks, and calculate compound concentration from peak area.

10.2.6 Data File Nomenclature

During analysis, the instrumentation continually stores information in a raw file (*.raw). This file contains information such as sample acquisition time, FID response, and MS response. Upon completion of the sample run, the software closes the raw file. ChemStation can use the information to process the data into result (*.rst), or text, (*.txt) files. ChemStation uses the data stored in the raw files to analyze information and create results, or text files. The result files yield interpreted information such as component name, concentration, and elution time. The text files represent the same information in an easily transferable electronic format, e.g. ASCII or Excel.

Filenames have two parts: the file extension which defines the presentation of the information, and the root file name. The root file name gives each analysis a unique identifier which provides information as to its origin. See table below for file nomenclature.

Example: TSYYMMDDHH

T = Sample Type	B C D M Q A T X	Method Blank (MB) Daily Calibration Verification Standard (CVS) Method Detection Limit (MDL) Initial Calibration Verification (CAL) Retention Time Study (RTS) Ambient Air Sample Audit Sample Bad or Test Sample
S = Site ID	X	Garage
YY = Year	#	2008 = 08
MM = Month	#	Jan. = 01
DD = Date	#	1 st = 01
HH = Hour	#	0:00 = 00

10.3 Sample Analysis

Create a short sequence in both the Markes and Agilent systems. A method blank, a calibration and a calibration duplicate represent the three top samples for each short sequence. Use appropriate sample methods for various samples in the sequence.

Attach the appropriate QC standards to the sample ports on the Markes air server. Open all canister or cylinder valves and check all pressure gauges.

Start Markes and Agilent systems via the sequences. Close standard containers or cylinder after calibration sample desorbs.

After completion of the calibration verifications and method blanks, run the “qedit” program in ChemStation to ensure correct identification of the peaks and to ensure the drawing of all baselines. Save any changes made and regenerate the summary report. Then quantify the calibration and blank samples.

If QC meets all acceptance criteria, the GC platform will analyze ambient samples, canister samples or bag samples with an additional blank sample and calibration sample required after every 23 ambient samples.

Check all instruments and create a summary sequence for field sampling and record it in the instrument logbooks. Include sample specific information such as location, field ID, injection volume, and raw data file name. Include daily CVS and Blank sample in the sequence for field sampling.

11.0 Data Analysis, Qualifiers, and Calculations

11.1 Data Analysis

A trained analyst may perform manual changes in the instrument data. The mathematical algorithms used to automatically integrate the sample peaks may not entirely accurately represent the peaks. Operators may perform manual integrations to change those misshapen integrations into an optimized interpretation. Operators must save the altered data with a different file extension to demonstrate performance of a manual integration. For mass spectrometry data integrations using ChemStation, Operators must have the audit trail function turned on at all times. Operators must transfer all data to a secure location for storage and/or immediate public display. Operators must redistribute data in which manual integrations were performed through an approved storage location for permanent storage.

11.2 Qualifiers

While reviewing the data, the operators and reviewer may flag any data that does not comply with the appropriate quality specifications with the appropriate qualifiers. The following flags include but do not remain limited to the ones listed below, and Operators may apply them to the data.

Flag	Definition
B	Analyte detected in method blank above 0.5 ppbv and analysis result <10 times the value in the method blank
I	Interference or co-elution suspected
NA	Not analyzed/Not available
C	Daily calibration sample does not meet the criteria
D	Duplicate calibration sample does not meet the criteria
ND	Not detected
Q	Result does not meet specification
U	Result less than sample specific method detection limit (MDL)
J	Result higher than or equal to MDL and less than the reporting limit (the lowest concentration for initial calibrations – 1 ppbv)

11.3 Calculations

Relative Percent Difference (RPD):

$$RPD = \frac{|x_1 - x_2|}{\left(\frac{x_1 + x_2}{2}\right)} * 100$$

Where:

x_1 = analytical % recovery

x_2 = replicate % recovery

Percent Recovery:

$$\%R = \frac{[MeasuredConcentration]}{[TheoreticalConcentration]} * 100$$

Response Factor for MS:

$$RF = \frac{(A_x C_{is})}{(A_{is} C_x)}$$

Where:

A_x = area of the characteristic ion for the compound being measured

A_{is} = area of the characteristic ion for the specific internal standard

C_{is} = concentration of the specific internal standard ($\mu\text{g/mL}$)

C_x = concentration of the compound being measured ($\mu\text{g/mL}$)

Average Response Factor for MS:

$$\overline{RF} = \frac{\sum (RF_1 + RF_2 + \dots + RF_n)}{n}$$

Where:

RF_1 = response factor for first calibration point of a compound

RF_2 = response factor for second calibration point of a compound

RF_n = response factor for last calibration point of a compound

n = total number of calibration points

Standard Deviation:

$$s = \sqrt{\frac{\sum_{i=1}^n (x_i - \bar{x})^2}{n-1}}$$

Where:

n = total number of measurements in the set

x = individual measurements

\bar{x} = measured mean for the set

Canister Dilution Factor:

$$CanisterDF = \frac{PF - PI}{PT + 14.7(\text{psig})}$$

Where:

PF = canister pressure after sampling (psig)

PI = canister pressure before sampling (psig)

PT = canister pressure after pressurization with diluent gas (psig)

Concentration of Analyte in a Sample Using Average Response Factor for MS:

$$\text{Concentration} = \frac{(A_x)(C_{is})(DF)}{(A_{is})RF}$$

Where:

A_x = area counts of characteristic ion for compound being measured

C_{is} = concentration of internal standard injected ($\mu\text{g/L}$)

A_{is} = area counts of characteristic ion for the internal standard.

Calibration Factor (CF) for FID:

$$CF = \frac{\text{PeakArea}}{\text{Concentration}}$$

Sample Concentration for FID:

$$\text{PeakConcentration} = \frac{\text{PeakArea}}{\text{CalibrationFactor}}$$

Method Detection Limit:

$$MDL = (S)(t)$$

Where:

S = standard deviation of the replicate analyses

t = students' t value for 99% confidence level and a standard deviation estimate with n-1 degrees of freedom

12.0 Method Performance**12.1 Training**

The analyst must complete the laboratory safety orientation training that includes, but not solely comprising, chemicals, PPE requirements, and electrical safety.

The analyst must read and understand this SOP.

The analyst must have a completed training record approved by the technical services chief.

12.2 Responsibilities**12.2.1 Operator**

The operator shall:

Daily:

- Verify proper system operating status,
- Verify the operation of the modem and data logger,
- Ensure that the analytical systems are functioning and collecting data,
- Review the daily calibration verification standard and method blank results,
- Check the peak identification, integration, and general chromatography of all samples collected,
- Optimize the methods if necessary,
- Verify BFB tuning requirements,
- Update electronic and written logbooks,

Weekly:

- Analyze the second source laboratory control standard (LCS) in duplicate (LCSD),

Bi-weekly

- Review and update sequence files,

- Check gas generation stations

Monthly:

- Verify all data archival,
- Routine data backup to CD/R/RW,
- Perform any computer or instrument maintenance as necessary.

12.2.2 Lab/Technical Manager

The lab/technical manager shall:

Certify the meeting of the project specification,

Ensure that each operator has been properly trained in its use and has the required experience to perform this procedure,

Ensure documentation of all training/experience,

Periodically review all logs and logbooks documenting this review.

13.0 Waste Management

Waste generated during the performance of this procedure must see disposal in accordance with the City of Houston Waste Management Plan. Contact the waste management coordinator for additional information.

Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices of the City of Houston. They must have training on the hazardous waste disposal practices upon initial assignment to these tasks, followed by annual refresher training.

14.0 References, Deviations and Clarifications**14.1 References**

TCEQ. Revision 12, May 2003. PAMS Network Quality Assurance Project Plan for Monitoring Texas. TCEQ. Austin, TX

TCEQ, May 2005. Standard Operating Procedure, Perkin-Elmer Auto Gas Chromatography for VOC Ozone Precursor Analysis

EPA, October 2003. Compendium Method TO15, "The Determination of Volatile Organic Compounds (VOCs) in Air Collected in SUMMA® Canisters and Analyzed by Gas Chromatography/Mass Spectrometry (GC/MS)"

40 Code of Federal Regulations, Part 136, Appendix B.

15.0 Tables and Figures

Table 1: Summary of Calibration and QC Analyses

Table 2: BFB Key Ions and Abundance Criteria

Table 3: Analyte Lists and Quality Control

Figure 1: Sample Path

Figure 2: GS/MS and Unity2 cycle chart

Figure 3: Elution sequences for FID and MS

Table 1: Summary of Calibration and QC Analyses

Calibration & QC Analyses	Description	Frequency	Acceptance Criteria	Corrective Action
Initial Calibration (ICAL)	FID: 5-point calibration MS: 5-point calibration	Minimum annually or when calibration verification fails to meet acceptance criteria	FID: a calibration curve correlation coefficient ($r \geq 0.995$) or an RSD of RFs < 20%. MSD: a calibration curve correlation coefficient ($r \geq 0.995$) or an RSD of RFs < 30%, with two exceptions of < 40%.	1. Reanalyze concentration not meeting criteria 2. Troubleshoot instrument
Demonstration of Capability (DOC)	Quadruplicate analysis of second source standard	1. Initial method setup 2. For each new analyst prior to analysis of any samples	Mean Accuracy: % Recovery +/- 35%	1. Verify calibration with second source standard 2. Troubleshoot instrument.
Calibration Verification Standard (CVS)	Standard for assessment of instrument accuracy containing analytes of interest	Daily	70%-130% recovery	1. Repeat CVS 2. Troubleshoot 3. Recalibrate
Method Blank (MB)	Canister containing humidified UHP air to assess background	Daily	FID: 1. Target compound concentrations ≤ 2.0 ppbc 2. TNMHC values ≤ 20.0 ppbc MS: Target compounds ≤ 0.5 ppbv	1. Reanalyze MB 2. If not resolved, reanalyze all samples 3. If reanalysis not possible, flag all data <ul style="list-style-type: none"> • If no analyte > RL in samples, data may be reported without flags • If analyte concentration in sample is > 10 times the MB concentration, may be reported with qualifiers 4. Troubleshoot instrument.

Calibration & QC Analyses	Description	Frequency	Acceptance Criteria	Corrective Action
Calibration verification Standard Duplicate (CVSD) for Precision	Standard containing analytes of interest analyzed in duplicate	Weekly	Precision: <25%	<ol style="list-style-type: none"> 1. Reanalyze CVSD 2. Reprep CVS standard and analyze 3. Troubleshoot instrument.
Retention Time Standard (RTS)	Standard containing target compounds identified by FID.	Initial study after installation of a new column and then bi-weekly or as needed based on performance	Retention time window is set at plus or minus three times the standard deviation of the absolute retention times for the 72-hour study	<ol style="list-style-type: none"> 1. Identify and correct source of problem. 2. Repeat study.
BFB Tuning Check	Evaluation of 4-bromofluorobenzene (BFB) peak in the calibration verification.	At the beginning of each analytical sequence	Must meet ion abundance criteria listed in Table 2.	<ol style="list-style-type: none"> 1. Evaluate BFB in method blank 2. Re-tune and reanalyze BFB 3. Troubleshoot, retune if necessary.
Internal Standards	Three internal standard added to each sample, standard, and blank	All samples, standards, and blanks	Measured area must be $\pm 50\%$ of internal standard area from the calibration verification standard (CVS)	<ol style="list-style-type: none"> 1. Reanalyze sample if out of specification 2. Identify and correct problem 3. Recalibrate
Analytical Surrogate	One surrogate compounds are added to each sample, standard, and blank	All samples, standards, and blanks	Accuracy: 50%-150% recovery	<ol style="list-style-type: none"> 1. Reanalyze sample for matrix effect evaluation 2. If matrix specific, flag data 3. Troubleshoot instrument

Table 2: BFB Key Ions and Abundance Criteria

Mass	Ion Abundance Criteria
50	8.0 to 40% of mass 95
75	30 to 66% of mass 95
95	Base peak, 100% relative abundance
96	5.0 to 9.0% of mass 95
173	<2% of mass 174
174	50 to 120% of mass 95
175	4.0 to 9.0% of mass 174
176	93 to 101% of mass 174
177	5.0 to 9.0% of mass 176

Table 3: Analyte Lists and Quality Control - Expanded Analyte List

Name	CAS No.	MDL (ppbv)	Name	CAS No.	MDL (ppbv)
Ethane	74-84-0	0.1	1,1,1-Trichloroethane	71-55-6	0.6
Ethylene	74-85-1	0.1	Benzene	71-43-2	0.2
Propane	74-98-6	0.1	Carbon Tetrachloride	56-23-5	0.8
Dichlorodifluoromethane	75-71-8	0.8	1,2-Dichloropropane	78-87-5	0.5
Propylene	115-07-1	0.1	Trichloroethylene	79-01-6	0.2
Acetylene	74-86-2	0.1	Cis-1,3-dichloropropene	10061-01-5	0.4
Methyl chloride	74-87-3	0.3	Trans-1,3-Dichloropropene	10061-02-6	0.2
1,2-Dichlorotetrafluoroethane	76-14-2	0.4	1,1,2-Trichloroethane	79-00-5	0.3
Vinyl chloride	75-01-4	0.2	Toluene	108-88-3	0.2
1,3-Butadiene	106-99-0	0.4	1,2-Dibromoethane	106-93-4	0.2
n-Butane	106-97-8	0.2	Tetrachloroethylene	127-18-4	0.3
Bromomethane	74-83-9	0.2	1,1,1,2-Tetrachloroethane	630-20-6	0.2
Ethyl chloride	75-00-3	0.3	Chlorobenzene	108-90-7	0.1
Trichlorofluoromethane	75-69-4	0.1	Ethylbenzene	100-41-4	0.1
n-Pentane	109-66-0	0.1	m/p-Xylene	108-38-3 & 106-42-3	0.3
1,1-Dichloroethylene	75-35-4	0.1	Styrene	100-42-5	0.1
Methylene Chloride	75-09-2	0.3	o-Xylene	95-47-6	0.1
1,1,2-Trichlorotrifluoroethane	76-13-1	0.3	1,1,2,2-Tetrachloroethane	79-34-5	0.3
1,1-Dichloroethane	75-34-3	0.2	Cumene	98-82-8	0.2
2-methylpentane	107-83-5	0.1	1,3,5-Trimethylbenzene	108-67-8	0.1
1-Hexene	592-41-6	0.1	1,2,4-Trimethylbenzene	95-63-6	0.1
Cis-1,2-Dichloroethylene	156-59-2	0.3	1,3-Dichlorobenzene	541-73-1	0.1
Hexane	110-54-3	0.1	1,4-Dichlorobenzene	106-46-7	0.1
Chloroform	67-66-3	0.5	1,2-Dichlorobenzene	95-50-1	0.2
1,2-Dichloroethane	107-06-2	0.4	1,2,4-Trichlorobenzene	120-82-1	0.4
1,1,1-Trichloroethane	71-55-6	0.6	Hexachloro-1,3-butadiene	87-68-3	0.3
1,2-Dichloroethane	107-06-2	0.4			

Surrogate

- Bromofluorobenzene (BFB)

Internal Standards

- Bromochloromethane
- 1,4-Difluorobenzene
- Chlorobenzene-d5

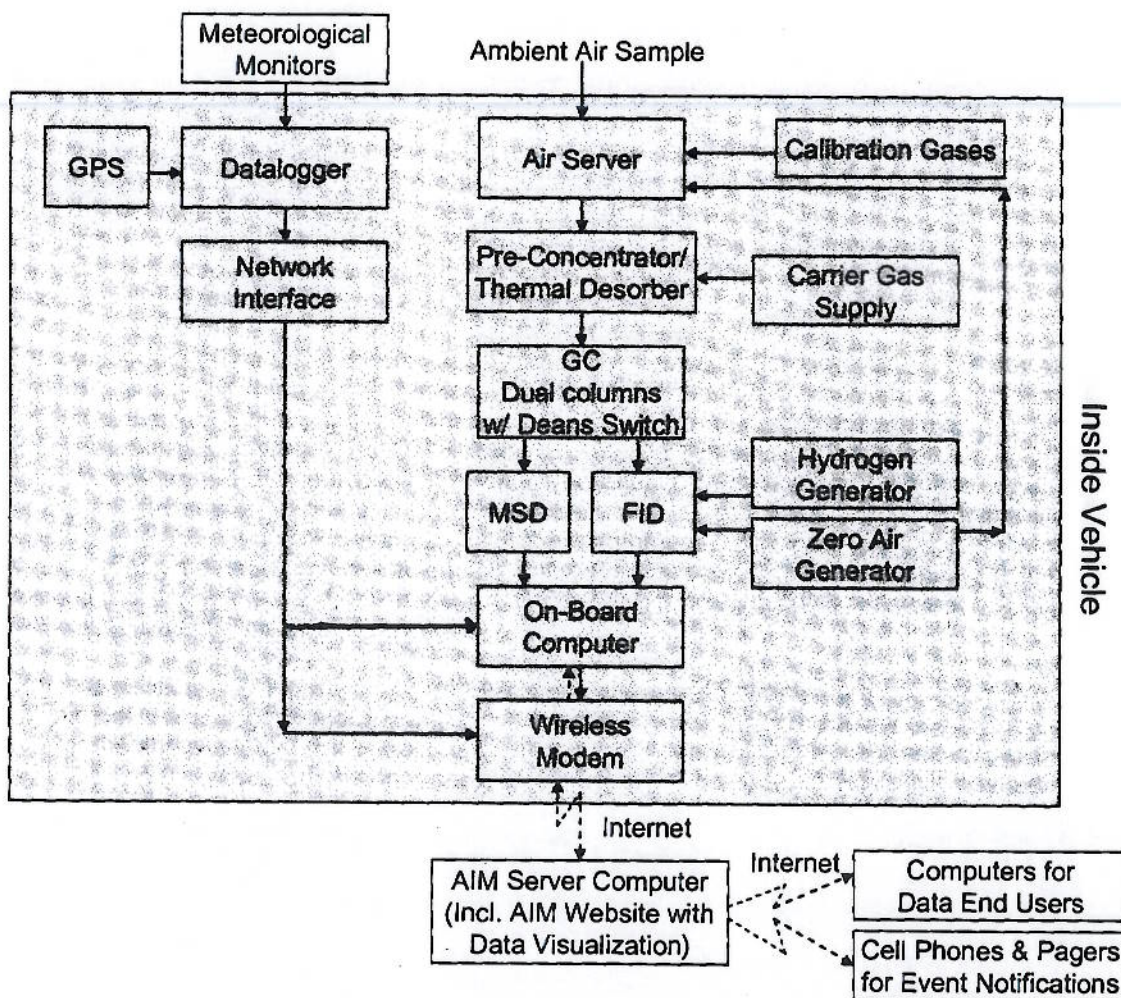


Figure 1: Sample Path

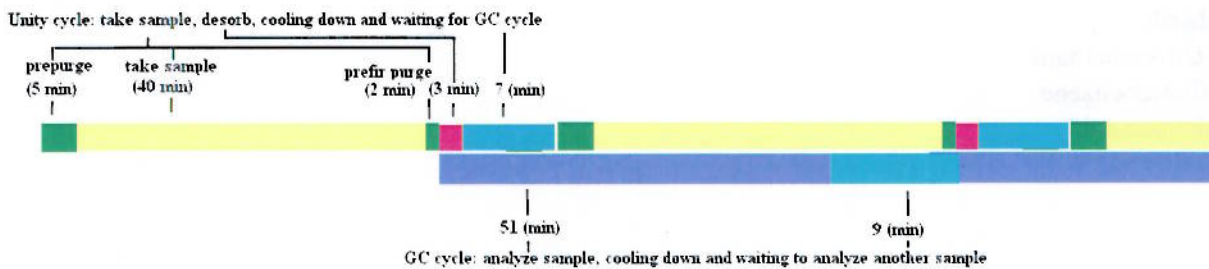
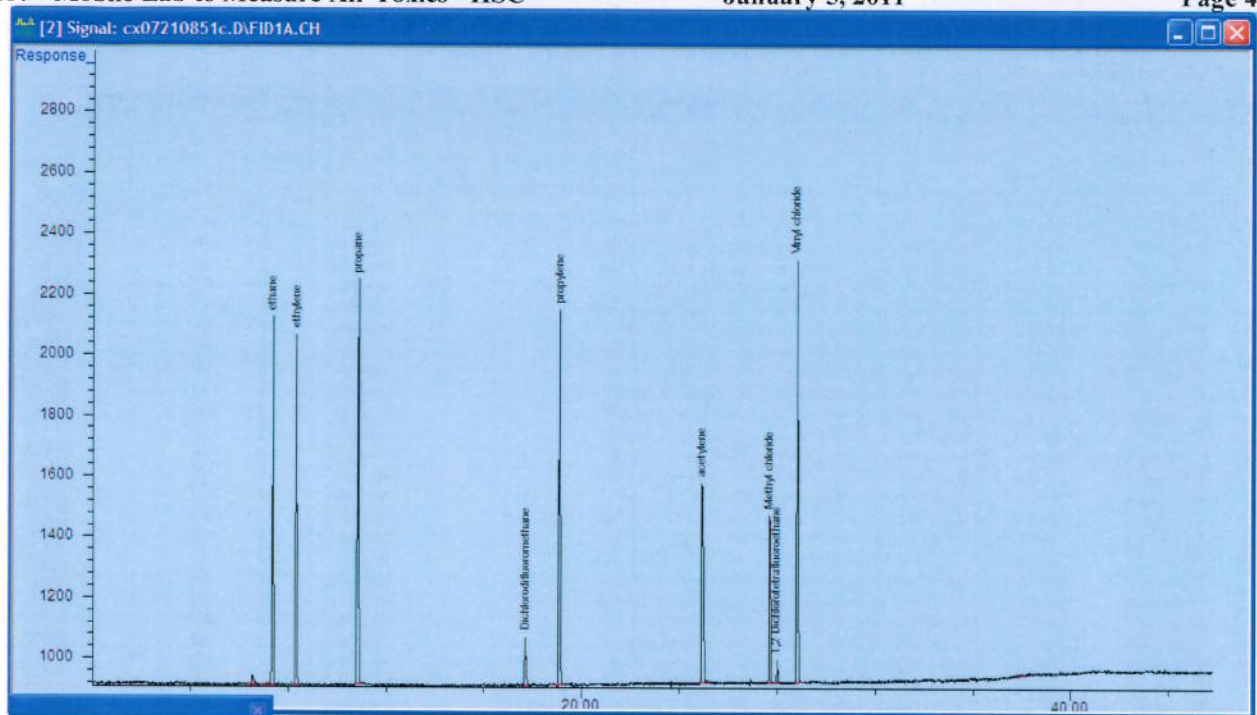
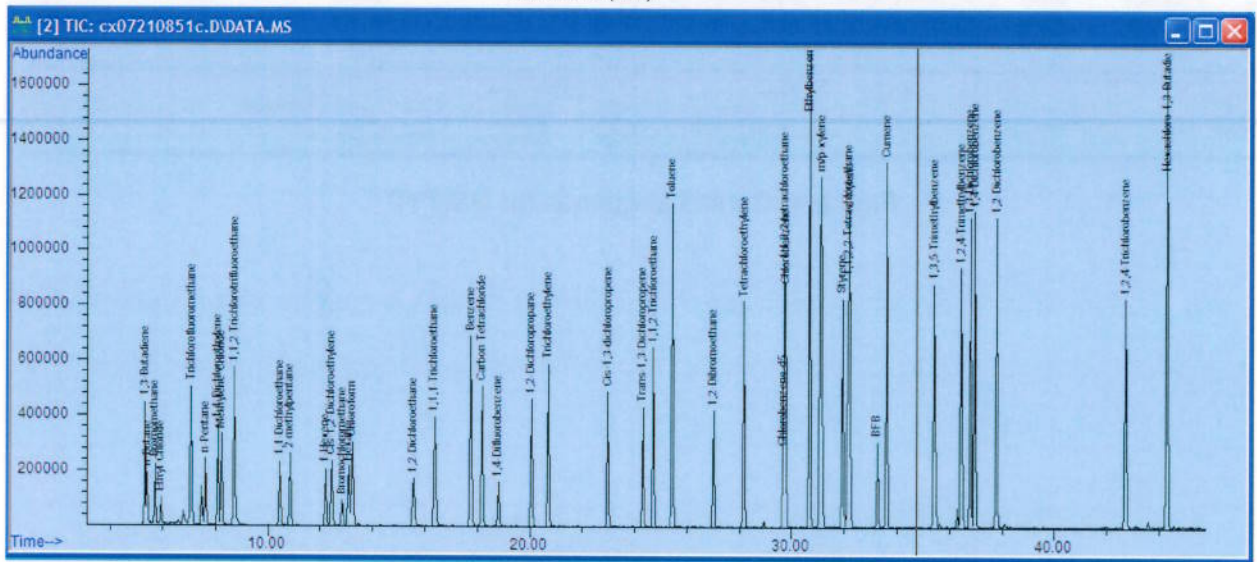


Figure 2: GS/MS and Unity2 cycle chart



Plot Column (FID)



BP1 Column (MS)

Figure 3: Elution sequences for FID and MS

The screenshot shows the Unity software interface. The main window is titled 'Unity' and contains a 'Sequence Builder' window. The 'Sequence Builder' window has a table with columns: Set, TYPE, Method, Start Time, Channel, Gas, and Injection. The table lists 27 steps, including 'Set_Mon', 'Sample01' through 'Sample27', and 'Sample28'. The steps alternate between 'Blank', 'Calibration', and 'SAMPLE' types. The 'Method' column contains file paths like 'C:\Program Files\Unity\methods\airserver_method_blank(500cc).mth'. The 'Start Time' is 'Immediate' for all. The 'Channel' and 'Gas' columns show values like 3 AIR, 2 N2, 1 N2, 2 N2, 4 AIR, 2 N2, 4 AIR, 2 N2, 4 AIR, 2 N2, 4 AIR, 2 N2, 4 AIR, 2 N2, 4 AIR, 2 N2, 4 AIR, 2 N2, 4 AIR, 2 N2, 4 AIR, 2 N2, 4 AIR, 2 N2, 4 AIR. The 'Injection' column is '1' for all. At the bottom of the interface, there is a status bar with 'Standby' indicators for 'Unity' and 'AirServer', a pressure reading of '40.1 psi', and a 'GC' status of 'Not Ready'.

Set	TYPE	Method	Start Time	Channel	Gas	Injection
Set_Mon	Various					1
Sample01	Blank	C:\Program Files\Unity\methods\airserver_method_blank(500cc).mth	Immediate	3	AIR	1
Sample02	Calibration	C:\Program Files\Unity\methods\airserver_internalstand(S_5ppb).mth	Immediate	2	N2	1
Sample03	Calibration	C:\Program Files\Unity\methods\airserver_500cc(10ppb_mod).mth	Immediate	1	N2	1
Sample04	Calibration	C:\Program Files\Unity\methods\airserver_internalstand(S_5ppb).mth	Immediate	2	N2	1
Sample05	Calibration	C:\Program Files\Unity\methods\airserver_500cc(10ppb_mod).mth	Immediate	1	N2	1
Sample06	Calibration	C:\Program Files\Unity\methods\airserver_internalstand(S_5ppb).mth	Immediate	2	N2	1
Sample07	SAMPLE	C:\Program Files\Unity\methods\airserver_500cc(sample_mod).mth	Immediate	4	AIR	1
Sample08	Calibration	C:\Program Files\Unity\methods\airserver_internalstand(S_5ppb).mth	Immediate	2	N2	1
Sample09	SAMPLE	C:\Program Files\Unity\methods\airserver_500cc(sample_mod).mth	Immediate	4	AIR	1
Sample10	Calibration	C:\Program Files\Unity\methods\airserver_internalstand(S_5ppb).mth	Immediate	2	N2	1
Sample11	SAMPLE	C:\Program Files\Unity\methods\airserver_500cc(sample_mod).mth	Immediate	4	AIR	1
Sample12	Calibration	C:\Program Files\Unity\methods\airserver_internalstand(S_5ppb).mth	Immediate	2	N2	1
Sample13	SAMPLE	C:\Program Files\Unity\methods\airserver_500cc(sample_mod).mth	Immediate	4	AIR	1
Sample14	Calibration	C:\Program Files\Unity\methods\airserver_internalstand(S_5ppb).mth	Immediate	2	N2	1
Sample15	SAMPLE	C:\Program Files\Unity\methods\airserver_500cc(sample_mod).mth	Immediate	4	AIR	1
Sample16	Calibration	C:\Program Files\Unity\methods\airserver_internalstand(S_5ppb).mth	Immediate	2	N2	1
Sample17	SAMPLE	C:\Program Files\Unity\methods\airserver_500cc(sample_mod).mth	Immediate	4	AIR	1
Sample18	Calibration	C:\Program Files\Unity\methods\airserver_internalstand(S_5ppb).mth	Immediate	2	N2	1
Sample19	SAMPLE	C:\Program Files\Unity\methods\airserver_500cc(sample_mod).mth	Immediate	4	AIR	1
Sample20	Calibration	C:\Program Files\Unity\methods\airserver_internalstand(S_5ppb).mth	Immediate	2	N2	1
Sample21	SAMPLE	C:\Program Files\Unity\methods\airserver_500cc(sample_mod).mth	Immediate	4	AIR	1
Sample22	Calibration	C:\Program Files\Unity\methods\airserver_internalstand(S_5ppb).mth	Immediate	2	N2	1
Sample23	SAMPLE	C:\Program Files\Unity\methods\airserver_500cc(sample_mod).mth	Immediate	4	AIR	1
Sample24	Calibration	C:\Program Files\Unity\methods\airserver_internalstand(S_5ppb).mth	Immediate	2	N2	1
Sample25	SAMPLE	C:\Program Files\Unity\methods\airserver_500cc(sample_mod).mth	Immediate	4	AIR	1
Sample26	Calibration	C:\Program Files\Unity\methods\airserver_internalstand(S_5ppb).mth	Immediate	2	N2	1
Sample27	SAMPLE	C:\Program Files\Unity\methods\airserver_500cc(sample_mod).mth	Immediate	4	AIR	1
Sample28	Calibration	C:\Program Files\Unity\methods\airserver_internalstand(S_5ppb).mth	Immediate	2	N2	1

Standby Unity: Standby
AirServer: Standby
0.0 40.1 psi
Unity: Trap temperature -15/15°C, Transfer line tempera... 150/150°C, HV temperature 151/150°C
AirServer: Gas type He, Channel no. n/a, Standby flow 10/10 ml/min
GC: Not Ready

Figure 4: Control sequence for UNITY2

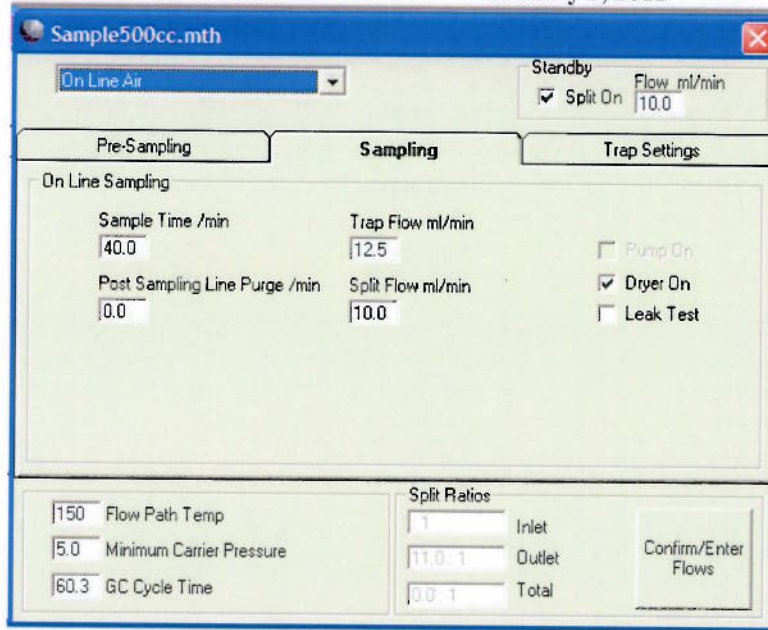


Figure 5: Sample Method for UNITY2

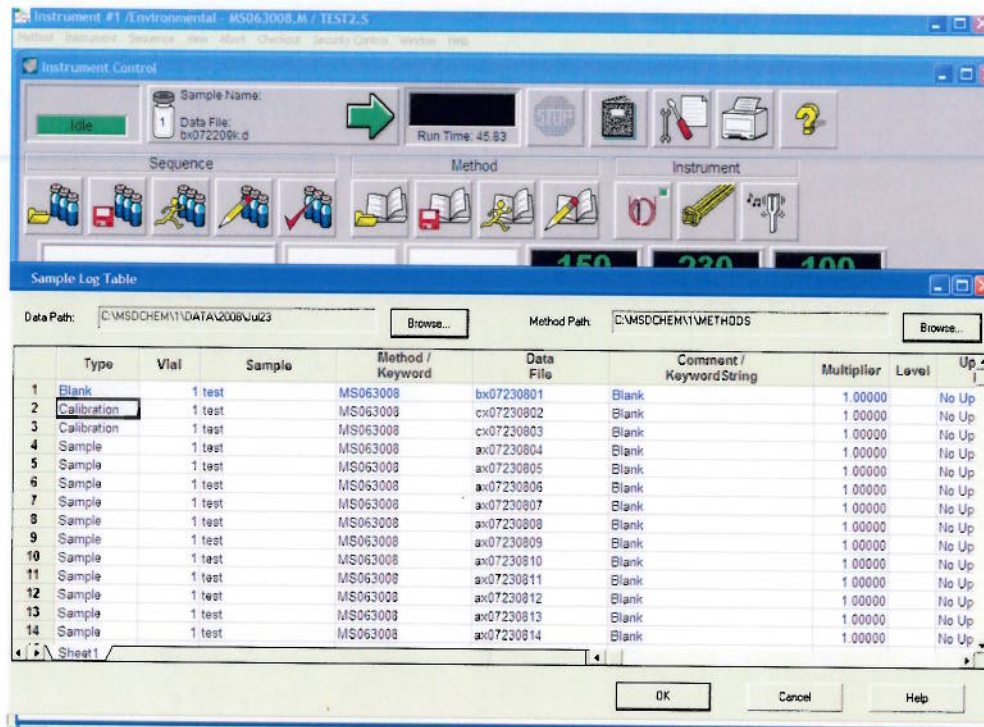


Figure 6: Control sequence for GC/MS

