Standard Operating Procedure

for

LDEQ 1026 "GC/FID"

Determination of Ozone Precursors in Ambient Air

via

Gas Chromatography/ Flame Ionization Detector

Equipped with an Entech 7100 Cryogenic Concentrator

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Annual Document Reviews:

Changes made, if any:
1st Review: Made some minor modifications and added several tables on 08/02/06.
2nd Review: On 04/05/2007, modified the worksheet to contain information about the canister ID for working standards and blanks; added initial calibration verification using the second sources; added one more CCV (SRM) run in a sequence; added calculations (15.10); added more detailed information in sections 11.0,17.0,18.0, and 21.0 ; dropped the second retention time standard run in a sequence.
3rd Review: Made some minor modifications on 04/16/2008.

4th Review: On 5/12/2009 Removed signal to noise ratio requirements from section 3.3.Inclusion of o-ethyltoluene in section 7.1. Removal of section 12.8 and its corresponding table, (table 4), because the table is no longer in use. Updated data entry process in section 15. Added a statement to section 16.3 regarding acetylene recovery in quality control samples.

5thReview: On 06/23/2009 the number of samples in a batch was changed to 22, section 14.2.1.

Changes Reviewed and Approved by:

	Analyst	Supervisor	Manager	QAO	Date
1st	_____	_____	_____	_____	_____
2nd	_____	_____	_____	_____	_____
3rd	_____	_____	_____	_____	_____
4th	_____	_____	_____	_____	_____

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1.0 Identification of Test Method

This procedure is based on EPA guidance document 600-R-98/161, "Technical Assistance Document for Sampling and Analysis of Ozone Precursors".

2.0 Applicable Matrices

The applicable matrix is ambient air.

3.0 Detection and Quantitation Limits

3.1 For ambient air analysis, the method detection limit (MDL) is defined in 40 CFR Part 136 Appendix B. It is the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. The MDLs in this lab are determined by performing 7 replicate analyses of a standard mixture containing the target volatile organic compounds (VOCs) at 1-5 times their expected MDLs and multiplying the standard deviation for the seven replicate measurements by the corresponding students-t value (3.14).

3.2 The calculated MDL for all of the target compounds is 2 ppbC or less. The quantitation limit is 5 ppbC. The calibration range is from 5 to 500 ppbC.

3.3 According to EPA guidance document 600-R-98/161, data below the calculated MDLs will be entered into LIMS and reported. See section 12.2 for information pertaining to MDLs.

4.0 Scope and Application

This procedure is for the measurement of ozone precursors required in Section 182 of the Clean Air Act Amendments of 1990. The revised air quality regulations in Title 40 Part 58 of the Code of Federal Regulations outline the provisions for the monitoring of ozone, oxides of nitrogen, and volatile organic compounds.

5.0 Summary of Method

Air samples are collected using pressurized sampling, or "grabbed" by the canister vacuum in cleaned, pre-evacuated canisters (SUMMA, SILCOCAN or SILONITE). The canisters are then transported to the lab. A mass-flow controlled volume, 200 ml in this lab, is cryogenically concentrated; the water and carbon dioxide are subsequently separated; the remaining VOCs are then cryogenically focused and injected onto a capillary GC column that is equipped with a flame-ionization detector. For small pure hydrocarbons, the detector response, or peak area, is directly

proportional to number of carbons. The targeted compounds--pure hydrocarbons with number of carbons equal to or smaller than 11-- are reported as ppbC. The concentrations of the targeted compounds may be converted from ppbC into estimated ppbv for the purpose of comparing results from this method and GC/MS. The other non-methane hydrocarbons including partially oxidized hydrocarbons containing chlorine, sulfur and oxygen are also estimated as ppbC. The sum of the targeted ppbC and the untargeted ppbC is reported as total non-methane organic compounds (TNMOC). Table 1 lists the target ozone precursors.

Table 1 Ozone Precursors

Ethylene	2,3-dimethylbutane	n-octane
Acetylene	2-methylpentane	Ethylbenzene
Ethane	3-methylpentane	m/p-xylene
Propylene	1-hexene	Styrene
Propane	n-hexane	o-xylene
Isobutane	Methylcyclopentane	n-nonane
1-butene	2-4-dimethylpentane	Isopropylbenzene (cumene)
1,3-butadiene	Benzene	n-propylbenzene
n-butane	Cyclohexane	m-ethyltoluene
trans-2-butene (Z)	2-methylhexane	p-ethyltoluene
cis-2-butene (E)	2,3-dimethylpentane	1,3,5-trimethylbenzene
Isopentane (2-methylbutane)	3-methylhexane	o-ethyltoluene
1-pentene	2,2,4-trimethylpentane	1,2,4-trimethylbenzene
n-pentane	n-heptane	n-decane
Isoprene (2-methyl-1,3-butadiene)	Methylcyclohexane	1,2,3-trimethylbenzene
trans-2-pentene (z)	2,3,4-trimethylpentane	m-diethylbenzene
cis-2-pentene	Toluene	p-diethylbenzene
2,2-dimethylbutane	2-methylheptane	n-undecane
Cyclopentane	3-methylheptane	Total TNMOC

6.0 Definition of Terms

6.1 Absolute pressure – pressure measured with reference to absolute zero pressure, usually expressed in psia.

6.2 Gauge pressure – pressure measured with reference to the surrounding atmospheric pressure, usually expressed in inches in Hg if the pressure is under the surrounding atmospheric pressure, and in psig if the pressure is above the surrounding atmospheric pressure. Zero gauge pressure is equal to atmospheric (barometric) pressure.

6.3 Accuracy – the degree of agreement between an observed value and an accepted reference value. Accuracy is a data quality indicator and it

includes combination of random error (precision) and systematic error (bias) components.

6.4 Ambient air – the air occurring at a particular time and place outside of structures or facilities. Often used interchangeably with 'outdoor air'.

6.5 Chain of Custody – record that documents the possession of the samples from the time of collection to receipt in the laboratory.

6.6 Cryogen – a refrigerant used for obtaining sub-ambient temperatures in the VOC concentrator and/or on front of the analytical column. Liquid nitrogen is used in this lab.

6.7 Laboratory information management system (LIMS) – software that makes laboratory data management easy and concise. It is used for sample logging-in, sample batching, result entering, data validating, etc. This lab uses LABWORKS ES developed by Perkin Elmer, Inc.

6.8 Ozone precursors – organic compounds that undergo chemical reaction to help cause ozone formation in the troposphere.

6.9 Photochemical assessment monitoring station (PAMS) – monitoring sites required by the 1990 Clean Air ACT (CAA) and established by individual States for enhanced ozone monitoring. In these sites, in addition to ozone and nitrogen oxides, ozone precursors and meteorological parameters are also monitored.

6.10 ppbC (parts per billion Carbon) – a methane equivalent unit of measure of the concentration of hydrocarbon in air expressed as carbon atoms per billion parts of the air-gas mixture. The concentration in ppbC for a compound can be divided by the number of carbon atoms for that compound to estimate the concentration in ppbv.

6.11 ppbv (parts per billion by volume) – a unit of measure of the concentration of gases in air expressed as parts of the analyte gas by volume per billion (10^9) volume parts of total gas.

6.12 Response factor (RF) – also referred to as the multiplier in Agilent ChemStation software. It is the ratio of the concentration of a compound to the area counts of the instrument.

6.13 Relative percent difference (RPD) – the absolute value of the difference between duplicate analyses divided by their average value and expressed as a percentage.

6.14 Standard reference material (SRM) – a primary calibration standard referenced to a National Institute of Standards and Technology (NIST) standard. The SRM used in this lab is propane.

6.15 Volatile organic compounds (VOCs) – chemical substances containing hydrocarbons (hydrogen and carbon atoms) that evaporate into the atmosphere. EPA has limited the definition to those organic compounds

that participate in atmospheric photochemical reactions to produce ozone and ozone precursors.

6.16 Laboratory control standard (LCS) -- an uncontaminated sample matrix spiked with known amounts of analytes from a source independent from the calibration standard. It is generally used to establish intra-laboratory, or analyst-specific precision and bias, or to assess the performance of all, or a portion of the measurement system.

6.17 Zero air blank (ZAB) – a dry zero air blank prepared in a cleaned canister or directly from the in-house zero air.

6.18 Humidified zero air blank (HAB) –humidified zero air prepared in a cleaned and evacuated canister. For a 6-liter canister that is to be pressurized to 30psig, 110 μl of organic free water is added.

7.0 Interferences and Pretreatments

7.1 Interference with identification and quantitation mainly come from moisture and co-elution. Proper maintenance of the concentrator can minimize moisture problems. Co-elution problems this lab frequently experienced are toluene with 2,3,3-trimethyl-pentane, 1,2,4-trimethyl-benzne with a siloxane compound and 1,2,3-trimethyl-benzene with 2-ethyl-1-hexanol. Also, there have been occasions when o-ethyltoluene has co-eluted with an as yet unknown compound. Analysis via GC/MS will help resolve most co-elution problems.

7.2 Contaminations may also come from many other sources. The canisters might not be cleaned satisfactorily. A separate SOP (LDEQ LSD SOP#1120) for canister cleaning addresses both cleaning and certification. The glass bead trap in the concentrator might be contaminated and the chemicals in the Tenax trap might be deteriorated after many cycles of cooling and thermal desorption. They are replaced as necessary. All the routes in the concentrator might also be contaminated. A humidified blank will indicate this contamination if the blank is above the acceptance criteria. If this happens, run several humidified blanks to clean the system. Otherwise, it may be necessary to replace some of the tubing.

8.0 Safety

Safety glasses and lab coats are required in all laboratory operations. Liquid nitrogen “burn” is the biggest safety concern in this lab. No shorts or open-toed shoes are allowed. The proper gloves and eyewear shall be worn when a liquid nitrogen Dewar is filled or changed. The proper eyewear should also be worn when a column or tubing is cut off or changed. Precaution should be taken to prevent electrocution by

electronic equipment. Refer to LDEQ LSD Safety Manual SOP #1769 for more information.

9.0 Equipment and Supplies

9.1 Gas chromatograph (Agilent 6890N and7890N) equipped with a single flame ionization detector

9.2 Restek RTX-1(or its equivalent), capillary column 105m x 320um ID x 1.00um df (nominal)

9.3 Agilent ChemStation software

9.4 Entech Tower 7016CA-L 16-position loop-injection autosampler

9.5 Entech 7100 cryogenic concentrator

9.6 Vespel/graphite ferrules of appropriate sizes

9.7 Stainless steel tubing for helium and N_2 lines into the analytical system

9.8 Two 15-liter or 6-liter Summa polished canisters for standards

9.9 One 6-liter Summa canisters for humid air blank

9.10 Cryogenic 50-liter Dewar flask

10.0 Reagents and Standards

10.1 Helium (Ultra high grade purity - 99.999 grade or better)

10.2 Stock SRM propane: ~1.00 ppm

10.3 LCS: standard gas mixtures containing 18 to full list of target compounds

10.4 PAMS standard: a C2 –C12 hydrocarbon mixture; 20-60ppbC each

10.5 Liquid nitrogen for cryogenic operation

11.0 Sample Collection, Preservation, Shipment, Storage, and Sample Rejection Policy

11.1 The field operators collect samples in evacuated canisters in the field either over 25 minutes, 3 hours, 24 hours, or other periods, depending on the sample type needed. The canisters are then brought back to the laboratory for logging-in and analysis (refer to LSD SOP_1767). The canisters must be leak tested by the field operators before sampling. The canister pressures before and after sampling must be recorded in the chain of custody. The canister pressure before sampling must be <-28 inches in Hg. If not, the canister will be repaired and re-cleaned. After each sample is analyzed, the canister pressure is taken by the analyst and recorded on the chain of custody form.

11.2 After they are logged-in, the canisters are stored in the sample room at 25°C. The sample holding time is 30 days.

11.3 An analysis request may be halted for reconsideration if any of the following conditions exist:

- The data sheet does not contain all of the pertinent information.
- The canister has an obvious physical defect.
- The pressure in the canister is below -5 inches in Hg.
- The pressure is equal to or close to the pressure threshold of the sampler. Generally, the pressure threshold of a sampler is 25 psig. The canister pressure should be at least 2 psig less than the pressure threshold.
- The sample was collected in an expired canister.
- The sample is beyond the prescribed holding time.
- During ozone seasons, a decision is made by AQO whether or not the lab performs the requested analyses for some samples. If not, the supervisor or the designee will remove the analyses "test codes" with the reasons entered in LIMS and then assign "clean" test code. The canisters are sent for cleaning. The chain of custody and the e-mail from AQO are filed in the data files.

Note: The sample collectors must be contacted to resolve the matter of incomplete or incorrect sampling information. The supervisor or the manager in the lab will make the decision whether or not to proceed with the analysis. In most of cases, the analysis shall proceed with appropriate flagging of the result.

12.0 Quality Control

12.1 Demonstration of Capability

A demonstration of capability (DOC) consists of analysis of four consecutive LCS standards in one sequence or in separate sequences annually or before a new analyst starts to analyze samples. Each of the four LCS analyses and the mean of the four analyses must meet the criteria listed in 12.5.

12.2 Frequency of MDL Determination

In this laboratory, MDLs refer to the method detection limits of our target analytes, (see table 1). Each instrument's current MDLs are located at that instrument's workstation. MDLs must be performed annually or after certain system maintenance that may change the sensitivity of the

instrument to the extent that the sensitivity will not meet the requirement for the method. For example, if after maintenance, area counts of the CCV vary more than ten percent, it will be necessary to determine whether the instrument's sensitivity has also been affected. The supervisor and the analysts will decide if MDL studies need to be performed after system maintenance. The concentration requirements for the MDL standard are specified in 3.1. The formula to prepare this MDL standard is given in 15.9.5. See 40CFR Part 136 appendix B for the MDL calculation procedure.

12.3 PAMS Standard

A humidified working PAMS standard is used as a retention time standard (the PAMS standard provided by EPA doesn't contain 1,3-butadiene). In each batch, one PAMS standard (coded as $I_PPFID) will be analyzed). The retention times must be within ±0.1 min. This standard also helps monitor the recoveries of the target compounds. The target compounds should have recoveries from 80-120%. As the PAMS standard ages, the recoveries for many of the compounds, including 1,3-butadiene and undecane, will decrease and may not meet the quality control criteria. Table 2 shows an example of PAMS standard results in a sequence. The humidified preparation is given in 15.10.4.

12.4 Precision for Duplicate Analysis

For each sample sequence, at least one sample is randomly selected as a duplicate sample ($D_PPFID). For duplicate sample runs, the precision (RPD) for the targeted compounds must be within 25% in the calibration range. If it fails, repeat the duplicate. If it fails again, trouble-shoot the instrument and re-run the entire batch. See section 15.10.3 for the relative percent difference equation.

12.5 Accuracy of LCS

A LCS standard (coded as $L1PPFID and humidified) contains at least 16 target compounds and at least one compound in each carbon group. However, all the target compounds will be included in LCS over a 2-year period. One LCS will be analyzed once in each batch. At least one compound from each carbon group must have the recovery of 80-120%. All compounds must have a recovery of 70-130%. Table 3 shows an example of the LCS results in a sequence.

12.6 Accuracy of Continuous Calibration Verification (CCV)

A canister that contains ~100 ppbC of propane (SRM) will be used as a continuous calibration verification standard. Two runs (coded as $I_SRM and $C_SRM) in each sequence will bracket the samples. The response factors (RF) of both CCVs must be within 90-110% of the RF obtained in the initial calibration. If either fails, run the second time. If either fails again, troubleshoot the instrument and re-run the sequence.

12.7 Blank Analyses

For each batch, a dry zero-air blank (coded as $B_PPFID) directly from a zero air cylinder and a humidified zero air blank (coded as $HBPPFID) are analyzed. The criteria for both zero air blanks must contain <20 ppbC total non-methane organic carbon (TNMOC). All target compounds must be <2 ppbC. If background contamination is found, investigate the source of contamination. This can be done by running the bake-out cycle for both the concentrator and GC, followed by running a dry zero blank and a humidified zero blank from another cleaned canister filled with humidified zero air.

Table 2 An Example of PAMS Standard Results

DATE:8/24/2006	QC NO:AJ25216		BATCH NO:140424
COMPONENTS	True Value (ppbc)	Test Value (ppbc)	Recovery (%)
Ethylene	22.9	24.32	106.2
Actetylene	24.8	24.49	98.8
Ethane	24.9	27.17	109.1
Propylene	22.7	22.84	100.6
Propane	40.9	41.05	100.4
Isobutane	25.8	25.63	99.3
1-Butene	30.2	31.17	103.2
n-Butane	41.1	41.21	100.3
t2-butene	26.8	25.34	94.6
c2-butene	33.2	36.28	109.3
Isopentane	42	40.25	95.8
1-Pentene	24.5	24.72	100.9
n-Pentane	25.4	25.20	99.2
Isoprene	37.8	37.21	98.4
t2-Pentene	31.9	24.89	78.0
c2-Pentene	32.1	33.00	102.8
2,2-Dimethylbutane	42.3	40.25	95.1
Cyclopentane	20.3	17.18	84.7
2,3-Dimethylbutane	53.9	53.21	98.7
2-Methylpentane	22.1	21.15	95.7
3-Methylpentane	42	40.03	95.3
1-Hexene	56	57.70	103.0
1-Hexane	32.1	30.00	93.5
Methylcyclopentane	26.5	25.14	94.9
2,4-Dimethylpentane	41.5	39.24	94.6
Benzene	30.6	29.55	96.6
Cyclohexane	42.5	40.36	95.0
2-Methylhexane	25.1	24.71	98.4
2,3-Dimethylpentane	54.1	50.94	94.2
3-Methylhexane	26	24.94	95.9
2,2,4-Trimethylpentane	31	29.55	95.3
n-Heptane	26.1	24.75	94.8
Methylcyclohexane	31.6	30.06	95.1
2,3,4-Trimethylpentane	25.4	24.33	95.8
Toluene	40	38.75	96.9
2-Methylheptane	25.7	24.29	94.5
3-Methylheptane	26.1	24.86	95.3
n-Octane	30.8	29.34	95.3
Ethylbenzne	25	24.21	96.8
m/p-Xylene	39.3	38.79	98.7
Styrene	34.9	33.35	95.6
o Xylene	24.8	23.86	96.2
n-Nonane	25.3	23.97	94.7
Cumene	39.8	38.02	95.5
n-Propylbenzene	29.6	28.14	95.1
m-Ethyltoluene	25.6	24.46	95.5
p-Ethyltoluene	40.8	38.29	93.8
1,3,5-Trimethylbenzene	24.8	23.66	95.4
o-Ethyltouene	29.9	28.39	94.9
1,2,4-trimethylbenzene	38.4	36.76	95.7
n-Decane	30.8	28.60	92.8
1,2,3-Trimethylbenzene	24.3	23.31	95.9
m-Diethylbenzene	39.7	36.50	91.9
p-Diethylbenzene	25.1	22.88	91.1
n-Undecane	31.1	27.31	87.8

Table 3 An Example of the LCS Results in a Sequence

LABORATORY CONTROL STANDARD FID # 5

DATE:	2/6/2009	QC NO:	AM02414	BATCH NO:	199574
Initial Calibration	$I_SRM: 0.5375	$C_SRM: 0.5340			
COMPONENTS	STD (ppbc)	$I (ppbc)	REC%		
Ethylene	50.00	48.56	97.1		
Actetylene	50.00	24.91	49.8		
Ethane	50.00	48.88	97.8		
Propylene	50.00	46.77	93.5		
Propane	50.00	48.64	97.3		
n-Butane	50.00				
Isobutane	45.45	46.26	101.8		
1-Butene	50.00	46.98	94.0		
1,3-Butadiene	50.00	44.15	88.3		
n-Butane	50.00	48.01	96.0		
t2-butene	50.00	46.55	93.1		
c2-butene	50.00	46.50	93.0		
Isopentane	50.00	43.20	86.4		
1-Pentene	50.00	42.65	85.3		
n-Pentane	50.00	43.26	86.5		
Isoprene	50.00	41.82	83.6		
t2-Pentene	50.00	42.09	84.2		
c2-Pentene	50.00	42.71	85.4		
2,2-Dimethylbuta	50.00	43.93	87.9		
Cyclopentane	50.00	45.18	90.4		
2,3-Dimethylbuta	45.45	43.76	96.3		
2-Methylpentane	50.00	45.83	91.7		
3-Methylpentane	45.45	43.92	96.6		
1-Hexene	50.00	42.46	84.9		
1-Hexane	45.45	43.94	96.7		
Methylcyclopenta	50.00	44.27	88.5		
2,4-Dimethylpent	47.14	43.28	91.8		
Benzene	45.45	42.68	93.9		
Cyclohexane	45.45	43.90	96.6		
2-Methylhexane	45.45	43.88	96.6		
2,3-Dimethylpent	49.27	44.89	91.1		
3-Methylhexane	45.00	44.09	98.0		
2,2,4-Trimethylp	44.55	44.70	100.3		
n-Heptane	45.45	42.51	93.5		
Methylcyclohexa	45.45	44.10	97.0		
2,3,4-Trimethylp	43.64	43.26	99.1		
Toluene	45.55	44.29	97.2		
2-Methylheptane	43.64	42.25	96.8		
3-Methylheptane	43.64	42.34	97.0		
n-Octane	43.64	41.67	95.5		
Ethylbenzne	43.64	42.79	98.1		
m/p-Xylene	43.64	44.40	101.8		
Styrene	43.18	39.70	91.9		
o Xylene	43.64	44.18	101.2		
n-Nonane	42.73	40.51	94.8		
Cumene	43.18	42.49	98.4		
n-Propylbenzene	43.64	42.12	96.5		
m-Ethyltoluene	43.18	43.20	100.0		
p-Ethyltoluene	39.55	40.67	102.9		
1,3,5-Trimethylbe	42.73	42.31	99.0		
o-Ethyltouene	50.00	42.99	86.0		
1,2,4-trimethylbe	44.09	43.27	98.1		
n-Decane	45.45	40.96	90.1		
1,2,3-Trimethylbe	43.64	39.08	89.6		
m-Diethylbenzene	45.45	42.11	92.6		
p-Diethylbenzene	41.82	40.23	96.2		
n-Undecane	42.73	38.85	90.9		
		2509.12			

13.0 Calibration

13.1 Multi-point calibration of propane is performed annually to establish the linear range, quantitation limit and RF in terms of ppbC. At least, five calibration points must be used for linear curves. The lowest point must be 5 ppbC and the highest point must be 500 ppbC. Least square is favored over the average of response factors since the slope—the first derivative for a linear curve—is independent of any possible contamination. Area regression vs. concentration is performed. To be linear in this range, a correlation coefficient >0.995 is required. The reverse of the slope is the response factor (RF)

13.2 After the above initial calibration, a second source standard that contains all the targeted compounds must verify the initial calibration. All the targeted compounds must have recovery of 70-130%. At least one compound in each carbon group must have a recovery of 80-120%.

13.3 Annually, a multi-point calibration for one compound in each carbon group, C2 through C11, is performed to confirm the analytical efficiency in certain concentration ranges. RF in each carbon group must be within 80-120% of the RF obtained in 13.1. At least five different concentrations for each selected compound are analyzed. The LCS standard is used for this purpose. A plot of area vs. concentration is evaluated for each selected compound. A correlation coefficient of >0.990 is required to be linear.

14.0 Procedure

14.1 QC Sample Number

For each sample sequence, log into the LIMS and generate a QC batch and the corresponding QC number (refer to appendix A). This number is assigned to data files of blanks and QC standards. Obtain this number from LIMS before the sample sequence is created.

14.2 Create an Analytical Batch

14.2.1 An analytical batch containing all applicable QC (SRM, PAMS, Duplicate, Blanks, LCS) with as many as 22 samples including duplicate run. This number maximizes the number of samples run in a batch based on the number of samples received on a chain of custody, which is in multiples of four, plus one twenty four hour sample and a duplicate. This also allows all samples on a chain of custody to be analyzed on the same instrument, eliminating variations in response between different instruments.

14.2.2 Load canisters you want to analyze in a batch onto the auto-sampler.

14.2.3 Fill out the FID worksheet shown in table 4.

14.2.4 Create an analytical batch such as in Table 5 and record this in your lab logbook. In Table 5, data file names in column 1 are for bookkeeping in the air lab. H refers to FID2 (F, K, J, L refer to FID1, FID3, FID4, FID5, respectively); the second letter refers to months of the year (e.g., C here refers to March); 09 refers to date; 05 refers to the year 2005; the final two digits refer to data file number. Column 2 refers to Inlet # in the concentrator. Column 3 refers to port # in the auto sampler. Column 4 refers to canister serial #. Column 5 refers to LIMS # computer generated when the canisters are logged-in. Column 6 refers to analysis codes. Column 7 briefly explains sample/site information.

14.3 Concentrator Sample Sequence Setup

14.3.1 Create the Entech sequence by editing an existing sequence. The sequence table can contain up to 30 different entries. The old sequence table is retrieved by clicking on **Open** button, followed by clicking on the desired sequence. To edit the sequence, highlight the desired line and then that highlighted line will appear in the top of the table. Make the desire entry in that top line, followed by clicking on **REPLC** button and then the old line will be replaced. The pre-concentrator sequence must match the batch in Table 5. Table 6 is an example of the pre-concentrator sample sequence.

14.3.2 Click on **SAVE** button and enter a different sequence name such as sq030905 to save the sequence. The file will be saved automatically with the extension “seq” in the C:\SMART subdirectory. To print a hard copy of the sequence, click on **SQTBL** button. A copy of the sequence will appear in the screen, where the sequence can be viewed and checked for errors. Double-click the screen to exit it and then click on **PRINT** button.

Table 4

GC/FID Daily Worksheet FID__

Date _____ **Operator** _____
Batch #_____ **QC #** _____

Working Gases and Quality Control Standards:

Carrier Gas Helium Pressure _____ Pulse Gas Pressure _____
Zero Air: Pressure____; Preparation Date____; Canister ID_____
Hum Zero Air: Pressure _____; Preparation date___; Canister ID___
Combustion Air Pressure _____ Hydrogen Pressure _____
Nitrogen Pressure for dewar _____
LCS: Std ID__; Preparation Date___; Pressure___; Canister ID___
PAMS: Std ID___; Preparation Date__; Pressure___; Canister ID___
SRM: Std ID___; Preparation Date___; Pressure___; Canister ID_____

Entech Setup:

Name of Sequence: _____
Sequence Saved? _____ Sequence Printed? _____
Leak Check Performed? _____

GC/FID Chemstation Setup:

Name of Sequence: _____
Sequence Saved? _____ Sequence Printed? _____
Bakeout.M Loaded at End? _____

Acquisition Startup:

Do Both Sequences Match? _____ Canister Valves Open? _____
Entech Sequence Started? _____ Chemstation Sequence Started? ___

Total Runs in the sequences:

Number of Std: _____
Number of Blanks: _____
Number of Samples _____
Number of Duplicates: _____
Number of Sys Blanks: _____
Number of Cert Cans: _____
Total Runs in the sequences: _____

Date and Time Sequence Started: _____ /____
Comments:

14.4 Concentrator Leak Check

14.4.1 Initially, leak check all ports using the automatic leak check.

14.4.2 To do leak check for the auto sampler, highlight the first line of the sequence table and click on **Leak** button, followed by clicking on **Go** in the next screen. All the lines in the sequence will be automatically leak-checked and a hard copy of the leak-checking report will be printed.

14.4.3 Check the report to see if the **START** and **END** pressures are less than 1.5psig and the difference between the **START** and **END** pressures are less than 0.4 psi/min. If yes, the leak check passed. If not, troubleshoot the auto sampler and the pre-concentrator and perform the leak check again. It may be necessary to manually leak check ports that fail the automatic leak check.

14.5 GC/FID Sample Sequence Setup

14.5.1 In **Method & Run Control** screen, select **Sequence Parameters** under **Sequence** menu.

14.5.2 In the field of Operator Name, type analyst's two-letter initials.

14.5.3 In **Data File** section, check the box for **Prefix/Counter**. In the field of Signal **1**, type part of data file name, in this case,

HC0905 for **Prefix** and type 01 for **Counter**. This will set up the computer to start to collect data by HC090501.

14.5.4 In the field of methods to run, select **According to Runtime Checklist**.

14.5.5 In the field of **Sequence Comment**, type necessary information for the sequence. Then exit **Sequence Parameter** screen by clicking on **OK**.

14.5.6 Select **Sequence Table** from **Sequence** menu.

In the **GC/FID Sequence Table**, shown in Table 7, **Line** lists the number of runs. Entry in the **Location** column is optional. Information for **Sample Name** is the same as column one in Table 6. **Method Name** refers to GC/FID method name: **PAMS** for the first 17; **Bakeout** for the last line.

Enter 1 in the **Inj/Location** column. Preview the sequence, save the sequence such as sq030905 and print a hard copy of the sequence.

Table 5 An Example of an Analytical Batch

Data File #	Sample Inlet #	Auto Port #	Can. #	LIMS #	Code #	Comments
HC090501	3	-	S1369	AH07088	$HBPPFID	H ZAB
HC090502	1	-	G1018	AH07088	$I_SRM	Cal std
HC090503	2	-	G1153	AH07088	$I_PPFID	RT std
HC090504	3	-	S1369	AH07088	$HBPPFID	H ZAB
HC090505	4	-	S1398	AH07088	$B_PPFID	ZAB
HC090507	1	16	S1469	AH07088	$L1PPFID	LCS
HC090508	1	1	S1435	AH06887	$PPFID	BAP/24 hrs.
HC090509	1	2	S1433	AH06888	$PPFID	BAP/3 hrs.
HC090510	1	3	TS3177	AH06889	$PPFID	BAP/3 hrs.
HC090511	1	4	5108	AH06890	$PPFID	BAP/3 hrs.
HC090512	1	5	7033	AH06891	$PPFID	BAP/3 hrs.
HC090513	1	6	1472	AH06892	$PPFID	BAP/3 hrs.
HC090514	1	7	5057	AH06893	$PPFID	BAP/3 hrs.
HC090515	1	8	6998	AH06894	$PPFID	BAP/3 hrs.
HC090516	1	9	5096	AH06895	$PPFID	BAP/3 hrs.
HC090517	1	1	S1435	AH06887	$D_PPFID	BAP/24 hrs
HC090518	1	-	G1018	AH07088	$C_SRM	Cal std

Table 6 An Example of the Pre-concentrator Sequence

Sample Name	Sample Inlet	Auto Port	Sample Vol	Cal Std Vol	Method
AH07088 $HBPPFID	3	-	200		C:\Smart\PAMS.MPT
AH07088 $I_SRM	-	-	0	200	C:\Smart\PAMS.MPT
AH07088 $I_PPFID	2	-	200	0	C:\Smart\PAMS.MPT
AH07088 $HBPPFID	3	-	200	0	C:\Smart\PAMS.MPT
AH07088 $B_PPFID	4	-	200	0	C:\Smart\PAMS.MPT
AH07088 $L1PPFID	1	16	150	0	C:\Smart\PAMS.MPT
AH06887 $PPFID	1	1	200	0	C:\Smart\PAMS.MPT
AH06887 $PPFID	1	2	200	0	C:\Smart\PAMS.MPT
AH06887 $PPFID	1	3	200	0	C:\Smart\PAMS.MPT
AH06887 $PPFID	1	4	200	0	C:\Smart\PAMS.MPT
AH06887 $PPFID	1	5	200	0	C:\Smart\PAMS.MPT
AH06887 $PPFID	1	6	200	0	C:\Smart\PAMS.MPT
AH06887 $PPFID	1	7	200	0	C:\Smart\PAMS.MPT
AH06887 $PPFID	1	8	200	0	C:\Smart\PAMS.MPT
AH06887 $PPFID	1	9	200	0	C:\Smart\PAMS.MPT
AH06887 $D_PPFID	1	1	200	0	C:\Smart\PAMS.MPT
AH07088 $C_SRM	-	-	0	200	C:\Smart\PAMS.MPT

14.6 Run and Synchronize GC/FID and Pre-concentrator Sequences

14.6.1 Set HPCHEM to **Standby** and move on to Entech sequence table. From the sequence table, start concentrator by clicking on **Go Start**. Click on **View** to switch to microscale purge and trap and wait until event number 10 to start the GC. Click back to HPCHEM online to start GC. From HPCHEM, select **Run Control** from pull down menu and click on **Run Sequence**.

14.6.2 Answer yes to the query that follows.

14.6.3 Make sure that the correct method/file number is displayed.

Table 7 An Example of GC/FID Sequence

Line	Location	Sample Name	Method Name	Inj/Location
1	-	AF07088 $HPPPFID	PAMS	1
2	-	AF07088 $I_SRMD	PAMS	1
3	-	AF07088 $I_PPFID	PAMS	1
4	-	AF07088 $HBPPFID	PAMS	1
5	-	AF07088 $B_PPFID	PAMS	1
6	-	AF07088 $L1PPFID	PAMS	1
7	1	AH06887 $PPFID	PAMS	1
8	2	AH06887 $PPFID	PAMS	1
9	3	AH06887 $PPFID	PAMS	1
10	4	AH06887 $PPFID	PAMS	1
11	5	AH06887 $PPFID	PAMS	1
12	6	AH06887 $PPFID	PAMS	1
13	7	AH06887 $PPFID	PAMS	1
14	8	AH06887 $PPFID	PAMS	1
15	9	AH06887 $PPFID	PAMS	1
16	1	AH06887 $D_PPFID	PAMS	1
17	-	AF07088 $C_SRM	PAMS	1
18	-	Bakeout	Bakeout	1

15.0 Evaluation of Data, Reporting Results and Calculations

15.1 After run is complete, review data by clicking on **HPChem Offline**, and then **File/Load Signal** to select the desired run file.

15.2 Examine each chromatographic peak for correct identification by referring to current retention time standard. Peaks for target analytes should be sharp and Gaussian (bell-shaped).

15.3 Examine each peak for correct integration, manually integrating as necessary according to the manual integration policy in Appendix B. Pay close attention to merged peaks and polar-compound co-elution. For assistance, consult an experienced analyst and/or the HPChem software tutorial. Note: the peaks for m/p-xylene should be considered as one peak and not split into two.

15.4 The canister numbers for the standards and blanks shall be either handwritten or digitally added to the data reports of each.

15.5 Upon completion, click on **Report/Specify Report**. Select **File** and **Screen**.

15.6 Click on **Report/Print Report**. This saves the processed data.

15.7 To transfer data to the LIMS after it has been processed and checked, follow these steps:

15.7.1 Open Excel file hpchem\1\data\fid_6890. Click on **Enable macros**. Press **Ctrl plus A**. Type the data file number and press **Enter**. Continue until all files have been transferred. **Save**. Insure that all results have the correct analysis code and LIMS number.

15.7.2 Check to see that the correct data files are copied. Copy and paste from the Excel sheet to the disk containing FID csv file.A/FIDDAT2. Note: Do not save file as .exe file.

15.7.3 Log on to the LIMS with correct ID and insert disk with .csv file.

15.7.4 Under Results menu, choose **Instrument Conversion**. Make sure that DEQ Air Lab CSV format has been selected as the instrument result file type.

15.7.5 Select the file e.g. FIDDAT. Click "**OK**". (This only gives the list of files to be transferred). Print a copy of the GRF files. Click **Exit** and go back to the **Results** menu.

15.7.6 Under **Results** menu, choose **Multi-Component Transfer**. Select Result file mode. In the window that comes up, make sure that **Generic Results File** is selected. Then click on **Add Files to List**.

15.7.7 Choose drive L and the path: L:\labworks6\lwdata6\interface\ladeqair.

15.7.8 Then click on **Find Samples**. A list of files will be added to the larger sheet.

15.7.9 Select **Load Results**. This will show all the files to be added to the result list for sample and test code. Check the list for any missing files or any duplicates. Check the appropriate box if a previous result needs to be overridden. Then click **Save the Results**. The screen will turn gray for a moment until it finishes uploading the sample results. When the screen is completely gray, exit the results screen. .

15.8 After all data have been transferred to the LIMS, delete the generic files created from the LIMS directory by following these steps:

15.8.1 Go to the Windows Explorer and delete the conversion files under the directory, L://LWDAT6/Interface/LADEQAir.

15.8.2 Do not delete the file folder.

15.9 The procedure for printing a sample report

In LIMS, go to reports/can_1report/type in sample numbers or batch number/view selections/enter selections Enable all macros and select the Air Lab FID report in ppbv. Print the reports and add to appropriate sample folders.

15.10 Calculations and standard preparations

15.10.1 Response Factor (RF)

RF= Std Concentration/Area Counts

15.10.2 Recovery (100%)

Recovery (%) = 100 x Measured Value/Certified Value

15.10.3 Relative Percent Difference (PRD)

$$\text{RPD}=\frac{|\text{Sample 1}-\text{Sample 2}|}{(\text{Sample 1}+\text{Sample 2})/2}*100$$

15.10.4 Humidified PAMS standard preparation

A cleaned canister is attached to the certified PAMS standard cylinder. Flush the lines for several minutes using PAMS standard from the cylinder. Close the cylinder, open the canister and inject 110 µl of high purity water (for a 6-liter canister) using Hamilton

micro-syringe into the canister. Then open the cylinder again and let the canister filled up to 30psig.

15.10.5 Working standard preparations by dynamic dilution

Calibration Standards, CCV, LCS and MDL standards are prepared using an Entech 4500A dynamic diluter. The following is the formula for calculation:

Ct = Cs*Fs/(Fs+Fd)

where : Ct = targeted concentration

Cs = Concentration of the stock standard

Fs = the flow rate of the stock standard

Fd = the flow rate of the balance gas (nitrogen)

16.0 Method Performance

16.1 For all targeted compounds, MDLs must be 2 ppbc or better.

16.2 For duplicate runs, RPD must be 25% or better in the calibration range of 5-500 ppbC.

16.3 At least one compound in each carbon group in LCS must have the recovery of 80-120%. However, as the LCS and PAMS standards age, the acetylene recovery for each decreases and may not meet this criterion. PT or audit samples must have the recovery of 80-120%.

17.0 Pollution Prevention

Refer to LSD's Lab Waste Disposal SOP_1197.

18.0 Data Assessment and Acceptance Criteria

For the data of a sample to be acceptable, blanks, duplicates, SRM, PAMS, and LCS standards, in the batch associated with the sample, must meet the criteria set in Section 12.0.

Any data out of the calibration range of 5 –500 ppbC are estimated. For those data below the quantitation limit of 5 ppbC, LIMS will automatically put a qualifier "J". If any data are larger than 500 ppbC, the sampler may be re-analyzed with proper dilution to bring them into the calibration range, qualifier "DC" will be used. If the sample is not re-analyzed with dilution, the qualifier "J" will be used.

Data are reviewed by the analyst, the supervisor, and the manager or QA Officer and must meet the criteria in Section 12.0.

The chromatograms, quantitation, and custom reports are enclosed in the sample folders. After analysts finish analysis, the first-line supervisor will

initially check the data and reports, and then the manager will finally approve the analysis, sign and release the report.

19.0 Corrective Action for Out of Control Data

If quality control criteria are not met, as outlined in Section 12.0, trouble shoot the instrument and re-run the batch, or let another GC/FID run the samples.

20.0 Contingencies for Handling Unacceptable Data

If quality control results, i.e., blanks, standards, duplicates, do not meet the criteria mentioned in Sections 12 and 13 and corrective action is unable to be taken, the sample data are considered unacceptable and must be reported in LIMS with a flag indicating the nature of the problem. These events must be reported to the lab supervisor and a corrective action form completed.

21.0 Waste Management

Refer to LSD's Lab Waste Disposal Sop_1197_r04.

22.0 Data and Records Management

22.1 Logbook Documentation

Record all the analytical activities in the logbook. Whiteouts are prohibited.

22.2 Batch QC Documentation

The batch QC documentation includes: 1.) the worksheet (table 5); 2.) printouts of Entech and GC/FID sequences, (table 7 and 8), plus Entech leak check report; 3.) quantification reports from both the dry and humidified zero air blanks; 4.) two CCVs' quantitation reports; 5.) LCS quantification report plus table 3; 6.) PAMS quantification reports plus table 2. All this is stabled together and filed in a designated binder and a cabinet

22.3 Sample Analysis Documentation

Sample analysis documentation includes: 1chain-of-custody; 2. quantitation reports plus manually integrated printouts; 3. hard copies generated from LIMS.

23.0 Tables, Diagrams, Flowcharts, and Validation Data

The tables and diagrams are inserted into the context of this SOP.

24.0 References

24.1 Technical Assistance Document for Sampling and Analysis of Ozone Precursors. EPA/600-R-98/161. Research Triangle Park, NC: U.S. Environmental Protection Agency. 1998.

24.2 Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air. Compendium Method TO-12. Method for the Determination of Non-Methane Organic Compounds (NMOC) in Ambient Air Using Cryogenic Preconcentration and Direct Flame Ionization Detection (PDFID), EPA-600/4-89/017. Research Triangle Park, NC: U.S. Environmental Protection Agency. 1998

24.3 Compendium Method TO-15, Determination of Volatile Organic Compounds (VOCs) In Air Collected in Specially-Prepared Canisters and Analyzed by Gas Chromatography/ Mass Spectroscopy, Second Edition.

24.4 Quality Assurance Project Plan QAPP, for PAMS and Air Toxics Sampling Network. LA DEQ.

24.5 Federal Register vol.49, no. 209. Octorber 26,1984.

Appendix A Batching Samples into LIMS

Go to next Appendix

A.1 Log on to LIMS.

A.2 Select **QA Batching** from **QA/QC** menu. In the coming screen, click on **New Batches**, followed by clicking on **Batch By Analysis** in the next screen.

A.3 The following screen will show a list of analysis codes such as $TO15 and $PPFID. Select **$PPFID** or **$TO15** from the list, followed by clicking on **OK** and then **OK** again in the next screen.

A.4 In the following screen of **Batch Selections**, deselect all the samples by clicking on the box next to **Batch** in the top line of the screen. Then select all the samples (up to 21) you want to batch by clicking the box next to **Pending** of each sample, followed by clicking on **OK**.

A.5 The following screen will allow you to control the size of your batch. The default batch size is 10. If you have selected more than 10 samples in step A.4, you must change **Batch size** number from 10 to the number you have batched. After you adjust Batch size number, click on **OK**.

A.6 In the following screen of **Batch QA Sample Specification**, LIMS will assign **Batch Name** and **Batch Number** for your batch. Record the name and the number in your Logbook.

A.7 To select a sample for duplicate run in your batch, click on that sample and the sample will appear in the field of **QA Sample ID**.

A.8 To obtain a QA sample ID for the batch, place your cursor at the field of **Batch Name** and right-click to select **Clone batch**. Another column will appear. Scroll down to the bottom of the list and right-click on the field of **Special Samp** to select **Login special QA sample**. A QA sample ID will appear in the field of **QA Sample ID** in the second column.

A.9 To assign test codes to the duplicate run and QA samples, left-click on the fields of **QA Test Added** and select test codes in the following screen, followed by clicking on **OK**.

A.10 To assign Instrument to the batch, right-click on the fields of **Assigned Instr** and select **Assign instrument for batch**. In the following screen, select an instrument code such as **HP-FID4**, followed by clicking on **OK**.

A.11 When you are back at the screen of **Batch QA Sample Specification**, click on **OK** and then click on **Exit**. Now you have created a batch.

Appendix B Manual Integration Policy

B.1.0 Scope

B.1.1 Manual integration is a common practice used in quantitative analyses. Manual integration must not be used to accomplish the following:

I. To bring the data below the regulatory limits.
II. To meet the quality control criteria to avoid trouble shooting the instrument or to avoid re-analyzing samples.
III. To be overconfident in personal professional judgment.

B.1.2 This manual integration policy has been written to ensure the integrity of the data produced in Air Organics Lab.

B.2.0 Improper Manual Integration

B.2.1 To manipulate data willfully by improper manual integration to meet the regulatory requirements is considered laboratory fraud.

B 2.2 Auto integration parameters have been selected for optimized auto integration of the target compounds overall. For a few compounds, these auto integrations might not be optimized. Auto integration provides consistency; therefore use the auto integrations rather than personal judgment unless the integration is incorrect for other reasons such as incorrect baselines.

B.2.3 If auto integration results are on the borderlines of meeting QC criteria, data might still be acceptable without re-analyzing samples. Document these situations. Don't suppose that slight manipulation by manual integration will be acceptable.

B.2.4 Adjusting auto integration parameters might be acceptable, but must be adjusted before the full calibration. It is not permitted to adjust auto integration parameters in individual samples after a full calibration.

B.2.5 Other forms of improper manual integration include, but are not limited to, manipulating internal standard integrations, changing baselines, or changing the start/stop points for peaks.

B.3.0 Acceptable Reasons for Manual Integration

B.3.1 Incorrect Identification

There are mainly two cases leading to a peak's incorrect identification: the retention time window of a target compound might cover other compounds; or mass spectra of isomers are very similar. For FID, referring to CCV in the same sequence for the adjacent identified target compounds, and for the peak shape will help correctly identify the incorrectly identified compound. For MS, it is much easier to solve misidentification problems. For incorrect

identifications because of isomers, the retention times will help; and for incorrect identifications because of retention time windows, MS spectra will help.

B.3.2 Poor Chromatograms

For poor chromatograms, the computer integration software might not know how to integrate or integrate correctly. In this case, manual integration is necessary using best personal professional judgment. This best judgment comes not only from general knowledge about integration but also from knowledge of how auto integration parameters were set up in the software and how target compounds in the standard are auto-integrated. Those poor chromatograms could lead to, but are not limited to, the following situations:

I. Peaks are split by software.
II. A target compound is a rider on the shoulder of another large peak.
III. There are rising or falling baselines or negative baselines.

There are many reasons for poor chromatograms: instruments might have malfunctioned momentarily, there might be too much moisture in GC columns, and/or matrix of a sample might be very dirty.

B.4.0 Documentation

B.4.1 GC/FID

B.4.1.1 Hard copies of the text quantitation reports before and after manual integration shall be printed. In the text report after manual integration, a code **mm** indicates manual integration. Code **mm** will allow the supervisors, the manager or auditors to track all manual integrations. The hard copies will be stapled together. Analysts shall initial and date the first page of the hard copies of the quantitation text report after manual integration.

B.4.1.2 If a manually integrated peak is equal to or larger than 2 ppbC, print hard copies of chromatograms before and after manual integration. Write the reasons for manual integration, initial and date the manually integrated chromatogram.

B.4.2 GC/MS

B.4.2.1 Print hard copies of quantitation reports before and after manual integration. In the quantitation report after manual integration, manually integrated compounds are denoted by

an **m** appearing to the right of the compound response and deleted compounds are denoted by a **d** appearing to the right of the concentration. Codes **m** and **d** will allow the supervisor, the manager or auditors to track which compounds were manually integrated or deleted. Print a hard copy of the custom report that reflects manual integration. Initial and date the custom report.

B.4.2.2 If a manually integrated peak is equal to or larger than 0.20 ppbv, print hard copies of chromatograms and mass spectra before and after manual integration. Write the reasons for manual integration, initial and date the hard copy of chromatogram and spectrum.

B.5.0 Secondary Review

The supervisor shall review, initial and date all manual integrations. The manager or QA officers may also randomly select some manual integrations for review. The analysts who perform manual integrations shall be required to give solid scientific reasons for manual integrations.

B.6.0 Codes for the Reasons for Manual Integration

ID-----Incorrect Identification
MI-----Missed Identification
ND----Under MDL (signal to noise ratio less than 3:1, but the peak was automatically integrated)
CI-----Combining Isomers such as m/p-xylenes
IB-----Incorrect Baseline (including using tangent skim and changing the starting and ending points of the baseline)
CE----Co-Elution (only apply to those splittable peaks that have obvious valleys, sometimes shoulders)

For the situations that are not listed above, use narratives.