

**Standard Operating Procedure**

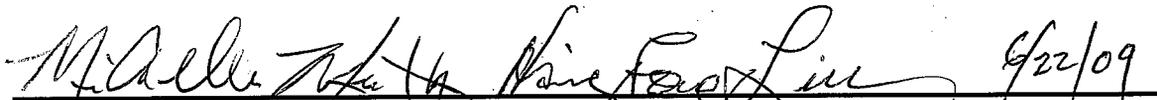
for

**LDEQ 1273 "GC/MS"**

**Determination of Target Toxic Compounds  
In Ambient Air by GC/MS**

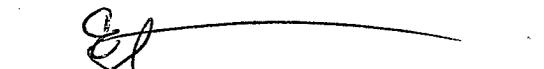
**Based on  
EPA Compendium Method TO-15**

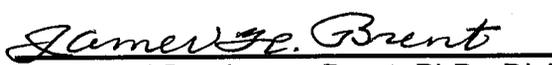
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Annual Document Reviews:

Changes made, if any:

1<sup>st</sup> Review: Added several tables and did some minor modifications on 08/02/06.

2<sup>nd</sup> Review: On 04/05/2007, added 13.4(Relative Retention Times Check), 13.5 (initial calibration verification); added more information in 11.1 for canister leak check; added more information in table 6 and added section 22.3 to reflect the traceability of canister ID for blanks and working standards; added more information in 18.0 for data out of the calibration ranges.

3<sup>rd</sup> Review: Made some minor modifications on 04/16/2008.

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4<sup>th</sup> Review: On 04/25/2009, inserted table 6, updated table 4,7 and 10; added more information in Quality Control and did modification of calibration curve fitting.

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1 <sup>st</sup>	_____	_____	_____	_____	_____
2 <sup>nd</sup>	_____	_____	_____	_____	_____
3 <sup>rd</sup>	_____	_____	_____	_____	_____
4 <sup>th</sup>	_____	_____	_____	_____	_____

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## 1.0 [Identification of Test Method](#)

This Standard Operating Procedure (SOP) has been developed based on EPA Compendium Method TO-15, "Determination of Volatile Organic Compounds in Air Collected in Specially-Prepared Canisters and Analyzed by Gas Chromatography/Mass Spectroscopy (GC/MS)".

## 2.0 [Applicable Matrices](#)

The applicable matrix is ambient air.

## 3.0 [Detection and Quantitation Limits](#)

### 3.1 Determination of the Method Detection Limit (MDL)

For ambient air analysis, the method detection limit 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.

MDLs in this lab are estimated by making seven replicate measurements of a standard mixture near (must be < 5 times) their expected MDLs. The lowest concentration, 0.5 ppbv, in the calibration is the standard used for this purpose. The estimated MDL for each compound is calculated by multiplying the standard deviation for the seven replicate measurements by the corresponding Student's t-value (3.14).

### 3.2 Expected Values of MDLs

TO-15 was developed to analyze ambient air with concentrations of volatile organic compounds (VOCs) above 0.50 ppbv. It requires the MDLs of 0.5 ppbv. In this lab, calculated MDLs of 0.20 ppbv have been achieved. However, for several polar compounds, their calculated MDLs could be over 0.20 ppbv occasionally but have never been and shall not be allowed to be over 0.5 ppbv. According to EPA guidance document 600-R-98/161, data below the calculated MDLs will be entered into LIMS and reported. This lab uses the criteria of the signal to noise ratios, helped by MS identification, for reporting any number below the calculated MDLs. The ratios have to be equal to or larger than 3:1.

### 3.3 Quantitation Limits

Quantitation limits are the lowest concentration in the calibration that is, 0.5 ppbv. Quantitation limits must be higher than the calculated MDL.

### 4.0 [Scope and Application](#)

EPA Method TO15 is applicable for the measurements of subset of the 97 VOCs that are included in the 189 hazardous air pollutants listed in Title III of the Clean Air Act Amendments of 1990. This lab identifies and quantifies 59 target compounds among these 97 VOCs. The 59 compounds are listed in Table 1.

In addition to determination of the compounds listed in Table 1, the SOP can also be used to tentatively identify certain untargeted VOCs by using library search or by interpreting fragmentation patterns of mass spectra. By comparing sizes of peaks of the untargeted compounds with those of a quantified target compound such as benzene, tentative semi-quantitative results can be estimated.

**Table 1 Toxic Compounds**

Freon-12®	1,1,2-trichloroethane	Chloromethane
Toluene	Freon 114®	1,2-dibromoethane
Vinyl chloride	Tetrachloroethylene	Bromomethane
Chlorobenzene	Chloroethane	Ethylbenzene
Freon 11®	m/p-xylene	1,1-dichloroethene
Styrene	Methylene chloride	o-xylene
Freon 113®	1,1,2,2-tetrachloroethane	1,1-dichloroethane
1,3,5-trimethylbenzene	cis-1,2-dichloroethylene	1,2,4-trimethylbenzene
Chloroform	m-dichlorobenzene	1,2-dichloroethane
Benzyl chloride	1,1,1-trichloroethane	p-dichlorobenzene
Benzene	o-dichlorobenzene	Carbon tetrachloride
1,2,4-trichlorobenzene	1,2-dichloropropane	Hexachlorobutadiene
Trichloroethylene	trans-1,3-dichloropropene	cis-1,3-dichloropropylene
1,3-butadiene	Acetonitrile	Acetone
Acrylonitrile	Diethyl ether	Allyl chloride
Carbon disulfide	MTBE	Methyl acrylate
Tetrahydrofuran	Nitrobenzene	Chlorobutane
Nitropropane	Methyl methacrylate	4-methyl-2-pentanone
Ethyl methacrylate	2-butanone	2-hexanone
Methacrylonitrile	Chloroacetonitrile	

## 5.0 [Summary of Method](#)

Air samples are collected using pressurized sampling, or “grabbed” by the canister vacuum in the cleaned pre-evacuated canisters (SUMMA, SILCOCAN or SILONITE). The canisters are then transported to the lab.

This lab uses an Entech 7100 pre-concentrator to concentrate samples, manage water, and remove carbon dioxide. The concentrator uses micro-scale purge & trap three-stage pre-concentration process. A sample of 400 ml together with 50 ml of the internal standard is trapped in Module 1 (glass bead trap) at  $-140^{\circ}\text{C}$  to concentrate the VOCs,  $\text{CO}_2$ , and  $\text{H}_2\text{O}$  into roughly a 0.50 ml sample. The glass bead trap is then heated to  $10^{\circ}\text{C}$  and is held there while 40 ml helium passes slowly through the trap to transfer the VOCs to Module 2. The Tenax trap in Module 2 is held at  $-30^{\circ}\text{C}$  to retain VOCs while letting  $\text{CO}_2$  purge through. Sweeping the VOCs from the first to the second trap with only 40 ml of sweep/purge gas transfers only the amount of water capable of saturating 40 ml of gas at room temperature. Bench-top mass spectrometers can handle this quantity of water quite easily ( $<0.3\mu\text{l}$ ). After the micro scale purging and trapping, the second trap is heated and back-flushed to the focusing trap to allow a rapid injection of the VOCs onto the GC/MS system that separates, identifies and quantifies the VOCs. All of these parameters of the pre-concentrator are saved in a method file named TO15t.mpt.

BFB target tune is used for data acquisition in MS. Before the sample analysis proceeds, the mass spectrometer must meet the performance criteria listed in Table 2. All the parameters for the GC and the mass spectrometer are saved in a method file named as TO15t.m.

**Table 2 Criteria of BFB for the Full Scan-Operating Mode**

<u>Mass</u>	<u>Abundance Ratio</u>
50	8.0 – 40.0% of mass 95
75	30.0 – 66.0% of mass 95
95	Base Peak, 100% relative abundance
96	5.0 – 9.0% of mass 95
173	Less than 2.0% of mass 174
174	50% to 120% of mass 95
175	4.0 – 9.0% of mass 174
176	93.0 – 101.0 % of mass 174
177	5.0 – 9.0% of mass 176

## 6.0 Definition of Terms

- 6.1 Laboratory Information Management System (LIMS) -- software that makes laboratory data management easy and concise. This lab uses LABWORKS ES developed by Perkin Elmer, Inc.
- 6.2 Continuous calibration verification (CCV) -- also called daily calibration that is the second highest standard in the initial calibration and analyzed in every sequence (within 24 hours) to verify the initial calibration still effective.
- 6.3 Absolute pressure -- pressure measured with reference to absolute zero pressure, usually expressed in psia.
- 6.4 Gauge pressure -- pressure measured with reference to 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.
- 6.5 Accuracy -- the degree of agreement between an observed value and an accepted reference value (so-called true value). Accuracy is determined as the value of the difference between the observed value and the true value divided by the true value and expressed as percentage.
- 6.6 Replicate precision -- precision determined from two canisters filled from the same air mass over the same time and determined as the absolute value of the difference between the analyses of canisters divided by their average value and expressed as percentage.
- 6.7 Duplicate precision -- precision determined from the analysis of two samples taken from the same canister. The duplicate precision is determined as the absolute value of the difference between the canister analyses divided by their average value and expressed as percentage.
- 6.8 Ambient air -- the air occurring at a particular time and place outside of structures or facilities. Often used interchangeably with 'outdoor air'.
- 6.9 Cryogen -- a refrigerant for obtaining sub-ambient temperatures in the VOC concentrator and/or on front of the analytical column. Liquid nitrogen is used in this lab.
- 6.10 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.

- 6.11 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 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. TO-15 classifies a substance to be a VOC based on its vapor pressure: an organic compound with a vapor pressure equal to or greater than 0.1 mm Hg under standard conditions.
- 6.13 Zero air blank (ZAB) —a dry zero air blank prepared in a cleaned canister or directly from the in-house zero air.
- 6.14 Humidified zero air blank (HAB) – a humidified zero air prepared in a cleaned canister. For a 6-liter canister, 110  $\mu$ l water is added.

## 7.0 [Interferences and Pretreatments](#)

Interferences and contaminations come from many sources. The canisters might not be cleaned satisfactorily. A separate SOP (# 1120) for canister cleaning addresses both cleaning and certification. Artifacts in the ion source of mass spectrometers may form after a certain time of operation. This will become evident as the MS sensitivity decreases, the reproducibility is poor, or BFB tune fails. When these conditions occur, the ion source should generally be cleaned. Other parts might also need to be replaced. The class bead trap might be contaminated and the chemicals in the Tenax trap might be deteriorating 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 acceptance criteria. If this happens, several humidified blank runs will normally clean the system. Otherwise, some tubing might need to be replaced.

## 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 and 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 shall also be worn when a column or tubing is cut off or changed. Precaution should be taken to prevent electrocution by electronic equipment.

Use care and follow standard safety procedures when handling compressed gas cylinders. See LDEQ Safety Manual (SOP#1769), as amended. See handling procedures for cryogenic liquids.

## 9.0 [Equipment and Supplies](#)

- 9.1 Agilent 6890 Gas Chromatograph
- 9.2 Agilent 5973N and 5975C quadrupole mass selective detector with a capillary direct Interface
- 9.3 Restek RTX-1, capillary 105m x 320um x 0.50um nominal
- 9.4 PC [Dell, Pentium 4] - Microsoft 2000 Professional
- 9.5 Entech 7016CA tower autosampler (9" W x 18" H x 21" D)
- 9.6 Entech 7100 Preconcentrator with two high volume cryotrap, filled with glass beads and with Tenax sorbent (P/N 04-01710, 04-01720)], and a cryofocusing trap (P/N 04-01730). The preconcentrator was configured for micro-scale purge & trap
- 9.7 Entech Smart Lab™ software
- 9.8 Four 15-liter Summa polished canisters for standards
- 9.9 Printer (e.g. Hewlett Packard Laser Jet, or similar)
- 9.10 50-liter cryogenic Dewar flask

## 10.0 [Reagents and Standards](#)

- 10.1 Helium (Research Grade Purity 6.0-99.9999%)
- 10.2 Nitrogen (Ultra High Purity)
- 10.3 Zero air (Ultra Zero)
- 10.4 Perfluorotributylamine (FC-43) for MS calibration
- 10.5 Chemical standards for preparation of calibration mixture
- 10.6 Liquid nitrogen for cryogenic operations
- 10.7 Bromofluorobenzene (BFB) and internal standards (1.0 ppmv of BFB and three internal standards: p-bromochloromethane, 1,4-difluorobenzene, and d5-chlorobenzene in nitrogen)
- 10.8 Laboratory control standard: standard gas mixtures containing 18 target to full list of target compounds

## 11.0 [Sample Collection, Preservation, Shipment, Storage, and Sample Rejection Policy](#)

- 11.1 The field operators collect samples in evacuated stainless steel Summa SilcoCan, or Silonite 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 of 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 Lab Services Internal Auditing

Guidelines for quality control are detailed in Lab Services Quality Manual. The Lab Services QA officer will schedule bench auditing and proficiency test (PT) sample analyses.

## 12.2 Demonstration of Capability

A demonstration of capability (DOC) consists of four consecutive CCVs, all within acceptable limits. Each of four CCVs and the mean of the four CCVs must meet the criteria in 12.4. DOC is required for each analyst before analysis of samples.

## 12.3 Frequency of MDL Determination

MDL 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. The supervisor and the analysts will decide if MDL studies need to be performed after certain maintenance. Each instrument's current MDLs are located at that instrument's workstation.

## 12.4 Accuracy of CCVs

For each sample sequence run, the second highest standard. ~7.5 ppbv, in the calibration is used as a daily calibration or CCV standard. Two runs of this standard bracket the samples. The first run is coded as \$I\_TO15; the second run is coded as \$C\_TO15. For both runs, the accuracy should be 100 +/-30%. Random two compounds are allowed to vary greater than 100+/-30%, but must be less than 100+/-40%; if failed, both allow running second time only. Table 3 shows an example of CCVs in a sequence. Column 2 lists the true values and column 5 shows RPD. 2-nitropropane and nitrobenzene may vary by ±55%.

## 12.5 Accuracy of LCS

A LCS standard contains 59 target compounds. The accuracy of LCS should be 100+/- 30%. Random two compounds are allowed to vary greater than 100+/-30%, but must be less than 100+/-40%. 2-nitropropane and nitrobenzene may vary by ±55%. One LCS standard (coded as \$L1TO15 and humidified) will be analyzed once in each batch; if failed, it allows running second time only. Table 4 shows an example of LCS analytical results in one sequence.

**Table 3 An Example of CCV Analyses in a Sequence**

Batch #: \$TO15-131082		QA#: AJ11407				
Compound Name	TO15-2	\$I TO15	\$C TO15	RPD (\$I/\$C)	DEV (\$I)	DEV (\$C)
	ppbv	ppbv	ppbv	%	%	%
Freon-12	7.13	6.45	6.45	0.0	-9.5	-9.5
Chloromethane	7.58	6.93	6.69	3.5	-8.6	-11.7
Freon-114	6.90	6.19	6.23	0.6	-10.3	-9.7
Vinyl Chloride	7.28	6.67	6.4	4.1	-8.4	-12.1
1,3-butadiene	7.13	6.57	6.45	1.8	-7.9	-9.5
bromomethane	7.05	6.24	6.21	0.5	-11.5	-11.9
chloroethane	7.13	6.39	6.22	2.7	-10.4	-12.8
Acetonitrile	6.77	6.83	5.78	16.7	0.9	-14.6
Acetone	7.67	7.58	6.58	14.1	-1.2	-14.2
Freon-11	7.13	6.3	6.54	3.7	-11.6	-8.3
Acrylonitrile	7.01	8.51	6.82	22.0	21.4	-2.7
Diethylether	7.67	8.89	7.13	22.0	15.9	-7.0
1,1-dichloroethene	8.10	7.69	7.68	0.1	-5.1	-5.2
Methylene Chloride	7.43	6.78	6.79	0.1	-8.7	-8.6
Allyl Chloride	7.43	7.17	7.00	2.4	-3.5	-5.8
Carbondisulfide	8.09	7.3	7.3	0.0	-9.8	-9.8
Freon-113	7.50	6.61	6.65	0.6	-11.9	-11.3
1,1-dichloroethane	7.58	6.9	6.71	2.8	-9.0	-11.5
MTBE	7.67	9.33	7.52	21.5	21.6	-2.0
Methacrylonitrile	7.67	8.86	7.24	20.1	15.5	-5.6
2-Butanone	7.51	8.36	7.13	15.9	11.3	-5.1
cis-1,2-dichloroethene	7.58	7.28	7.07	2.9	-4.0	-6.7
Methyl Acrylate	7.10	8.28	7	16.8	16.6	-1.4
Chloroform	7.58	6.89	6.59	4.5	-9.1	-13.1
Tetrahydrofuran	7.51	8.58	7.14	18.3	14.2	-4.9
1,2-dichloroethane	7.50	7.07	6.6	6.9	-5.7	-12.0
Chloroacetonitrile	7.10	7.65	6.68	13.5	7.7	-5.9
1,1,1-trichloroethane	7.43	6.77	6.78	0.1	-8.9	-8.7
Chlorobutane	7.34	7.3	6.72	8.3	-0.5	-8.4
Benzene	7.50	7.34	6.83	7.2	-2.1	-8.9
Carbon Tetrachloride	7.28	6.62	6.68	0.9	-9.1	-8.2
Nitropropane	7.34	8.1	7.24	11.2	10.4	-1.4
1,2-dichloropropane	7.50	7.23	6.62	8.8	-3.6	-11.7
Trichloroethylene	7.43	6.9	7.04	2.0	-7.1	-5.2
Methylmethacrylate	7.51	8.99	7.98	11.9	19.7	6.3
cis-1,3-dichloropropene	7.20	7.72	7.17	7.4	7.2	-0.4
4-methyl-2-pentanone	7.43	9.06	8.42	7.3	21.9	13.3
trans-1,3-dichloropropene	7.43	8.13	7.39	9.5	9.4	-0.5
1,1,2-trichloroethane	7.43	7.44	6.88	7.8	0.1	-7.4
Toluene	7.05	7.56	6.76	11.2	7.2	-4.1
Ethyl methacrylate	7.34	9.44	8.42	11.4	28.6	14.7
2-Hexanone	7.34	9.09	8.65	5.0	23.8	17.8
1,2-dibromoethane	7.50	7.46	7.09	5.1	-0.5	-5.5
Tetrachloroethylene	7.35	6.88	6.85	0.4	-6.4	-6.8
Chlorobenzene	7.43	7.12	6.73	5.6	-4.2	-9.4
Ethylbenzene	7.58	8.27	7.5	9.8	9.1	-1.1
m/p Xylene	7.65	8.43	7.64	9.8	10.2	-0.1
Styrene	7.43	8.38	7.66	9.0	12.8	3.1
o Xylene	7.43	8.11	7.48	8.1	9.2	0.7
1,1,2,2-tetrachloroethane	7.43	7.33	7.01	4.5	-1.3	-5.7
1,3,5-trimethylbenzene	7.43	8.18	7.63	7.0	10.1	2.7
1,2,4-trimethylbenzene	7.35	8.21	7.74	5.9	11.7	5.3
m-dichlorobenzene	7.43	8.51	8.22	3.5	14.5	10.6
Benzylchloride	7.43	7.43	7.3	1.8	0.0	-1.7
p-dichlorobenzene	7.50	7.71	7.45	3.4	2.8	-0.7
o-dichlorobenzene	7.43	7.94	7.77	2.2	6.9	4.6
Nitrobenzene	6.85	9.06	8.67	4.4	32.3	26.6
1,2,4-trichlorobenzene	7.65	8.79	8.84	0.6	14.9	15.6
1,3-hexachlorobutadiene	7.65	7.96	7.9	0.8	4.1	3.3

**Table 4 An Example of a LCS Analysis**

Batch #: \$TO15-201308 QA#: AM04662

Compound Name	True Value ppbv	Measured Value ppbv	DEV (\$L1) %
Freon-12	6.55	6.17	-5.7
Chloromethane	6.95	6.16	-11.4
Freon-114	6.89	6.18	-10.3
Vinyl Chloride	6.95	6.51	-6.4
1,3-butadiene	7.16	6.83	-4.6
bromomethane	6.82	6.43	-5.7
chloroethane	6.41	6.20	-3.3
Acetonitrile	7.23	7.82	8.2
Acetone	7.23	7.39	2.3
Freon-11	6.61	5.65	-14.6
Acrylonitrile	7.23	7.76	7.4
Diethylether	7.16	7.53	5.2
1,1-dichloroethene	6.95	6.42	-7.7
Methylene Chloride	7.16	6.54	-8.6
Allyl Chloride	7.23	6.93	-4.1
Carbondisulfide	6.89	6.17	-10.4
Freon-113	7.16	6.67	-6.8
1,1-dichloroethane	6.95	6.48	-6.8
MTBE	7.16	7.81	9.1
Methacrylonitrile	7.16	8.10	13.1
2-Butanone	7.16	7.76	8.4
cis-1,2-dichloroethene	7.09	6.86	-3.3
Methyl Acrylate	7.23	8.03	11.1
Chloroform	7.02	6.49	-7.6
Tetrahydrofuran	7.16	7.70	7.6
1,2-dichloroethane	6.89	6.68	-3.0
Chloroacetonitrile	7.23	8.22	13.7
1,1,1,-trichloroethane	6.95	6.53	-6.1
Chlorobutane	7.16	7.17	0.2
Benzene	7.09	7.00	-1.3
Carbon Tetrachloride	5.73	6.52	13.8
Nitropropane	7.16	8.32	16.2
1,2-dichloropropane	6.95	7.13	2.5
Trichloroethylene	6.89	6.52	-5.3
Methylmethacrylate	7.16	8.15	13.8
cis-1,3-dichloropropene	6.61	8.03	21.4
4-methyl-2-pentanone	7.16	7.86	9.8
trans-1,3-dichloropropene	6.61	7.05	6.6
1,1,2-trichloroethane	6.82	6.85	0.5
Toluene	6.89	7.21	4.7
Ethyl methacrylate	7.16	8.12	13.4
2-Hexanone	7.16	7.89	10.2
1,2-dibromoethane	6.89	7.05	2.4
Tetrachloroethylene	6.95	6.67	-4.1
Chlorobenzene	6.95	6.92	-0.5
Ethylbenzene	6.89	7.14	3.7
m/p Xylene	6.95	7.21	3.7
Styrene	6.41	6.62	3.3
o Xylene	6.89	6.84	-0.7
1,1,2,2-tetrachloroethane	6.95	6.58	-5.4
1,3,5-trimethylbenzene	6.75	6.86	1.6
1,2,4-trimethylbenzene	6.82	6.99	2.5
Benzylchloride	6.89	7.74	12.4
m-dichlorobenzene	6.89	6.91	0.3
p-dichlorobenzene	7.09	7.02	-1.0
o-dichlorobenzene	7.09	6.76	-4.7
Nitrobenzene	7.16	7.31	2.1
1,2,4-trichlorobenzene	7.02	6.87	-2.2
1,3-hexachlorobutadiene	6.75	5.73	-15.1

## 12.6 Precision of Replicate or Duplicate Runs

The field unit occasionally collects replicate samples to verify the effectiveness of the sampling system. For each sample sequence, one sample is randomly selected as a duplicate sample. For replicate or duplicate samples and duplicate CCV standard, the precision (RPD) for the compounds should be better than 25% within the calibration range. Random three compounds are allowed over 25% but must be under 35%. If it fails, repeat the duplicate. If it fails again, trouble-shoot the instrument and re-run the entire sequence.

## 12.7 Blank Analysis Check

For each sample sequence run, dry zero-air blank (coded as \$B\_TO15) directly from a zero air cylinder or a zero air generator and humidified zero-air blank (coded as \$HBTO15) from a cleaned canister filled with humidified zero air must be run to check the analytical system and the canister for background contamination. Each blank analysis, with the exception of acetone (it could be up to 1 ppbv), must show that each target compound has less than 0.20 ppbv. An exception for acetone is being made because it is frequently enhanced by uncontrollable contamination. 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.

## 12.8 Internal Standard

The internal standard retention time (RT) must be within  $\pm 0.33$  minutes of the mean RT and the internal standard (IS) area must be  $\pm 40\%$  of the mean area of the 5 calibration points in the last multi-point calibration.

## 12.9 Frequency of Initial Calibration

A new and full calibration must be run if the CCV criteria are not met, or when instrument maintenance is performed. It may also be run at operator's discretion.

## 12.10 Surrogate Compound

TO15 doesn't require surrogates but BFB is used as a surrogate in this lab. Its recovery should be between 80 to 120% and must be between 70 to 130%

### 12.11 Checklist

A check is available for assistance in data review. The checklist contains information from both PAMS and TO15 analyses. Table 5 shows an example of the checklist of PAMS and TO15 analyses for a sample collected in Kenner.

## 13.0 [Calibration](#)

### 13.1 Internal Standards and Calibration Range

The calibrations are based upon the internal standard calibration method. Three compounds, p-bromochloromethane, 1,4-difluorobenzene, and d5-chlorobenzene, are used as internal standards. BFB is used as a surrogate and a BFB tune performance-checking standard. Most of our samples are under 10 ppbv. Therefore, the instrument is calibrated in the range from 0.50 to 10 ppbv. The 10.0-ppbv working calibration mixture is prepared. The five calibration points of 0.5, 2.5, 5.0, 7.5 and 10.0 ppv are made by concentrating different volumes from the 10.0 ppbv working standard (refer to Table 6).

### 13.2 Preparation of Internal and Calibration Standards

Working internal and calibration standards are prepared by dynamic diluting the stock standards with nitrogen into 15-litre RESTEK T.O.-Can canisters (refer to SOP 1686 for standards preparation procedures). The standards are humidified.

**Table 5 Checklist for Sample Analysis and Data Review**

Air Organics, Lab Services Division, LDEQ

Sample LIMS ID: *AJ11393*  
Sample Collection Date: *04/05/2006*

Sample Location: *Kenner*  
Sample Type: *24 hours*

Method/ SOP	PAMS/1026 R04	TO15/1273 R06
Instrument/analyst	<i>FID5/HFL</i>	<i>HP4/HFL</i>
Batch number	<i>\$PPFID-131071</i>	<i>\$TO15-131272</i>
QC number for the batch	<i>AJ11390</i>	<i>AJ11674</i>
Sample analysis date	<i>04/11/2006</i>	<i>04/12/2006</i>
Data file number	<i>LD100624</i>	<i>MD120610</i>
PAMS STD prepared within last 30 days?	<i>YES</i>	<i>N/A</i>
SRM STD prepared within last 30 days?	<i>YES</i>	<i>N/A</i>
GC/MS cal std prepared within last 30 days?	<i>N/A</i>	<i>YES</i>
LCS std prepared within last 30 days?	<i>YES</i>	<i>YES</i>
Did BFB check pass the criteria?	<i>N/A</i>	<i>YES</i>
New initial calibration?	<i>NO</i>	<i>YES</i>
Did GC/MS CCV pass the criteria?	<i>N/A</i>	<i>YES</i>
Initial cal SRM RF/CCV RF	<i>0.5100/0.4914</i>	<i>N/A</i>
Did the retention time STD pass the criteria?	<i>YES</i>	<i>YES</i>
Did LSC pass the criteria?	<i>YES</i>	<i>YES</i>
Did the zero air blank pass the criteria?	<i>YES</i>	<i>YES</i>
Did the hum zero air blank pass the criteria?	<i>YES</i>	<i>YES</i>
Did the duplicate pass the criteria?	<i>YES</i>	<i>YES</i>
Manual integrations printed, coded and initialed ?	<i>YES</i>	<i>YES</i>
Data reviewed, initialed and dated?	<i>YES</i>	<i>YES</i>
Report generated from LIMS?	<i>YES</i>	<i>YES</i>
The canister pressure after analysis recorded?	<i>YES</i>	<i>YES</i>
Batch QC measures documented?	<i>YES</i>	<i>YES</i>

Comments:

2<sup>nd</sup> reviewer:

3<sup>rd</sup> reviewer

**Table 6 An Example of the Standard Preparation for TO15 Calibration**

	Scott cyl.	Working Stand	T1 400ml	T2 300ml	T3 200ml	T4 100ml	T5 20ml
	ppm	ppbv	ppbv	ppbv	ppbv	ppbv	ppbv
Freon-12	0.98	8.91	8.91	6.68	4.45	2.23	0.45
Chloromethane	1.05	9.55	9.55	7.16	4.77	2.39	0.48
Freon-114	1.03	9.36	9.36	7.02	4.68	2.34	0.47
Vinyl Chloride	1.04	9.45	9.45	7.09	4.73	2.36	0.47
1,3-butadiene	1.05	9.55	9.55	7.16	4.77	2.39	0.48
bromomethane	1.03	9.36	9.36	7.02	4.68	2.34	0.47
chloroethane	1	9.09	9.09	6.82	4.55	2.27	0.45
Acetonitrile	1.06	9.64	9.64	7.23	4.82	2.41	0.48
Acetone	1.04	9.45	9.45	7.09	4.73	2.36	0.47
Freon-11	0.93	8.45	8.45	6.34	4.23	2.11	0.42
Acrylonitrile	1.06	9.64	9.64	7.23	4.82	2.41	0.48
Diethylether	1.04	9.45	9.45	7.09	4.73	2.36	0.47
1,1-dichloroethene	1.01	9.18	9.18	6.89	4.59	2.30	0.46
Methylene Chloride	1.05	9.55	9.55	7.16	4.77	2.39	0.48
Allyl Chloride	1.07	9.73	9.73	7.30	4.86	2.43	0.49
Carbon disulfide	0.98	8.91	8.91	6.68	4.45	2.23	0.45
Freon-113	1.05	9.55	9.55	7.16	4.77	2.39	0.48
1,1-dichloroethane	1.01	9.18	9.18	6.89	4.59	2.30	0.46
MTBE	1.05	9.55	9.55	7.16	4.77	2.39	0.48
Methacrylonitrile	1.05	9.55	9.55	7.16	4.77	2.39	0.48
2-Butanone	1.05	9.55	9.55	7.16	4.77	2.39	0.48
cis-1,2-dichloroethene	1.02	9.27	9.27	6.95	4.64	2.32	0.46
Methyl Acrylate	1.06	9.64	9.64	7.23	4.82	2.41	0.48
Chloroform	1.02	9.27	9.27	6.95	4.64	2.32	0.46
Tetrahydrofuran	1.06	9.64	9.64	7.23	4.82	2.41	0.48
1,2-dichloroethane	1	9.09	9.09	6.82	4.55	2.27	0.45
Chloroacetonitrile	1.07	9.73	9.73	7.30	4.86	2.43	0.49
1,1,1,-trichloroethane	1.01	9.18	9.18	6.89	4.59	2.30	0.46
1-Chlorobutane	1.05	9.55	9.55	7.16	4.77	2.39	0.48
Benzene	1.01	9.18	9.18	6.89	4.59	2.30	0.46
Carbon Tetrachloride	1.01	9.18	9.18	6.89	4.59	2.30	0.46
2-Nitropropane	1.06	9.64	9.64	7.23	4.82	2.41	0.48
1,2-dichloropropane	1.01	9.18	9.18	6.89	4.59	2.30	0.46
Trichloroethylene	1	9.09	9.09	6.82	4.55	2.27	0.45
Methylmethacrylate	1.05	9.55	9.55	7.16	4.77	2.39	0.48
cis-1,3-dichloropropene	1.1	10.00	10.00	7.50	5.00	2.50	0.50
4-methyl-2-pentanone	1.05	9.55	9.55	7.16	4.77	2.39	0.48
trans-1,3-dichloropropene	0.95	8.64	8.64	6.48	4.32	2.16	0.43
1,1,2-trichloroethane	0.98	8.91	8.91	6.68	4.45	2.23	0.45
Toluene	0.99	9.00	9.00	6.75	4.50	2.25	0.45
Ethyl methacrylate	1.05	9.55	9.55	7.16	4.77	2.39	0.48
2-Hexanone	1.05	9.55	9.55	7.16	4.77	2.39	0.48
1,2-dibromoethane	0.96	8.73	8.73	6.55	4.36	2.18	0.44
Tetrachloroethylene	1.01	9.18	9.18	6.89	4.59	2.30	0.46
Chlorobenzene	1.01	9.18	9.18	6.89	4.59	2.30	0.46
Ethylbenzene	0.98	8.91	8.91	6.68	4.45	2.23	0.45
m/p Xylene	0.98	8.91	8.91	6.68	4.45	2.23	0.45
Styrene	0.88	8.00	8.00	6.00	4.00	2.00	0.40
o Xylene	0.96	8.73	8.73	6.55	4.36	2.18	0.44
1,1,2,2-tetrachloroethane	0.97	8.82	8.82	6.61	4.41	2.20	0.44
1,3,5-trimethylbenzene	0.94	8.55	8.55	6.41	4.27	2.14	0.43
1,2,4-trimethylbenzene	0.94	8.55	8.55	6.41	4.27	2.14	0.43
Benzylchloride	1	9.09	9.09	6.82	4.55	2.27	0.45
m-dichlorobenzene	0.96	8.73	8.73	6.55	4.36	2.18	0.44
p-dichlorobenzene	0.95	8.64	8.64	6.48	4.32	2.16	0.43
o-dichlorobenzene	0.94	8.55	8.55	6.41	4.27	2.14	0.43
Nitrobenzene	0.97	8.82	8.82	6.61	4.41	2.20	0.44
1,2,4-trichlorobenzene	0.85	7.73	7.73	5.80	3.86	1.93	0.39
1,3-hexachlorobutadiene	0.84	7.64	7.64	5.73	3.82	1.91	0.38

### 13.3 Calibration Curve Fitting

Internal studies have shown that the instrument responses are linear over the above-mentioned calibration range. Five calibration points must be used for linear curves. . Except the slight contamination of acetone (suspected from the environmental air in our laboratory), the concentrations of the rest 58-target compounds in the system background are clean, they are negligible compared with those in the lowest calibration level. Since the system blank is clean, the average response factor (ARF) curve fit can be used. The advantage of ARF curve fit is that it treats every calibration point equally and hence the more complicated weighted curve fit will not be an issue. However, a few compounds such as 2-nitropropane and nitrobenzene have a tendency to fit the other curves the best. In this case, these types of curves should be used. As a general rule, the analyst should use the best curve by checking with the verification of the criteria of Accuracies of CCVs and LCS. The  $r^2$  value (coefficient of determination) must be greater than 0.99. The use of a quadratic regression requires the use of six calibration points.

The percent relative standard deviation (%RSD) of the average response factor curve fit should be within 30% (not applicable to the analytes using the different curve fittings). However, two target compounds are allowed to have %RSD greater than 30% but must be less than 40% (see EPA Compendium Method TO15, 10.5.4.3 for the equations). The %RSD acceptance criteria for 2-nitropropane and nitrobenzene is 55%.

### 13.4 Relative Retention Times (RRT) for Initial Calibrations

Relative retention time for each target compound is the ratio of the absolute retention time of a target compound to the absolute retention time of the related internal standard. The mean of RRT for each target compound in the calibrations is the average of RRTs of all calibration levels. The RRT for each target compound at each calibration level must be within 0.06 RRT units of the mean RRT for that compound. In our case, this 0.06 RRT deviation is equivalent to the absolute average retention time +/- 1.0 min. The absolute retention time windows for most target compounds will be set to the absolute average retention time +/- 0.50 min. For several polar compounds, it will be set to the absolute average retention time +/- 1.0 min. The detailed RRT studies will be done yearly when MDL studies are performed. The biggest deviation of RRT in this lab has been 0.02 units.

### 13.5 Initial Calibration Verification

After initial calibrations, a second source standard that contains all the target compounds at the middle level of the calibration shall verify the initial calibration. The criteria in 12.4 must be met.

## 14.0 [Procedure](#)

### 14.1 QC Sample Number and Worksheet

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. Fill out the worksheet shown in table 7.

### 14.2 GC/MS Procedure

#### 14.2.1 Autotune

- 14.2.1.1 The purpose of autotune is to optimize the mass spectrometer operation to maximize the sensitivity across the scan mass range. An autotune is conducted after the ion source is cleaned. Auto tune is a starting point for BFB tune.
- 14.2.1.2 If any valves have been opened or closed in the concentrator, load the method **Bakeout.M** by selecting **Load/Bakeout.m** from **Method** menu. Wait for 30 minutes to permit any water present to escape from the MS detector.
- 14.2.1.3 From **view** menu in **Instrument Control** screen, select **manual tune**. In the following screen, select **Autotune** to load auto-tune file under **File** menu.
- 14.2.1.4 From **Tune** menu, select **Autotune**. The program will automatically conduct the autotune and print a hard copy of the tuning report, save, and update the autotune file as C:\HPchem\1\5973n\atune.u.
- 14.2.1.5 Check the hard copy to ensure that peaks of 69, 219, and 502 are smooth and symmetric; their peak widths are 0.55-0.65; their mass assignments vary no more than  $\pm 0.1$ ; the total peak number is less than 250; the relative abundance of nitrogen to 69 is less than 10% (normally less than 5%); the relative abundance of 219 is larger than 50%; the relative abundance of 502 to 69 larger than 3.2%. If all these criteria are met, place the hard copy of the autotune report in the

maintenance book and proceed to the **BFB target tune procedure.**

**Table 7 GC/MS Daily Worksheet HP3 or 4**

**Date:** \_\_\_\_\_ **Operator:** \_\_\_\_\_

**Batch #: DOC \$TO15-** \_\_\_\_\_ **QC #:** \_\_\_\_\_

**MS Source:** Source cleaned on \_\_\_\_\_

**MS Tuning:** Auto and BFB tuning (or Profile Repeating) performed on \_\_\_\_\_

Abundance at 69: \_\_\_\_\_; EM Volts: \_\_\_\_\_

Filament: \_\_\_\_\_

Mass 69: Exact Mass: \_\_\_\_\_ PW: \_\_\_\_\_

Mass 219: Exact Mass: \_\_\_\_\_ PW: \_\_\_\_\_

Mass 502: Exact Mass: \_\_\_\_\_ PW: \_\_\_\_\_

**MS Calibration:** New five point standard calibration performed on \_\_\_\_\_

**Working Gases and Quality Control Standards at Current Reading:**

Carrier Gas Helium Pressure: \_\_\_\_\_; Pulse Gas Pressure: \_\_\_\_\_;

Zero Air:

Pressure: \_\_\_\_\_ Preparation Date: \_\_\_\_\_ Canister ID: \_\_\_\_\_

Hum Zero Air:

Pressure: \_\_\_\_\_ Preparation Date: \_\_\_\_\_ Canister ID: \_\_\_\_\_

Internal Std. (ID: \_\_\_\_\_):

Pressure: \_\_\_\_\_ Preparation Date: \_\_\_\_\_ Canister ID: \_\_\_\_\_

Lab Control Std. (ID: \_\_\_\_\_):

Pressure: \_\_\_\_\_ Preparation Date: \_\_\_\_\_ Canister ID: \_\_\_\_\_

Calibration Std. (ID: \_\_\_\_\_):

Pressure: \_\_\_\_\_ Preparation Date: \_\_\_\_\_ Canister ID: \_\_\_\_\_

Initial Calibration Verification Std. (ID: \_\_\_\_\_):

Pressure: \_\_\_\_\_ Preparation Date: \_\_\_\_\_ Canister ID: \_\_\_\_\_

**Entech Setup:**

Name of Sequence: \_\_\_\_\_; Sequence Saved? \_\_\_\_\_

Sequence Printed? Yes; Leak Check Performed? \_\_\_\_\_

**GC/MS Chemstation Setup:**

Name of Sequence: \_\_\_\_\_; Sequence Saved? \_\_\_\_\_

Sequence Simulated? \_\_\_\_\_; Sequence Printed? \_\_\_\_\_

Bake out Method Loaded at End? \_\_\_\_\_

**Acquisition Startup:**

Do Both Sequences Match? \_\_\_\_\_; Canister Valves Open? \_\_\_\_\_

Entech Sequence Started? \_\_\_\_\_; Chemstation Sequence Started? \_\_\_\_\_

**Total Run in the Sequence:** \_\_\_\_\_

Number of Standards: \_\_\_\_\_

Number of Sample Blanks: \_\_\_\_\_ Number of Sys. Blanks: \_\_\_\_\_

Number of Samples: \_\_\_\_\_ Number of Duplicates: \_\_\_\_\_  
**Date and Time Sequence started:** \_\_\_\_\_ / \_\_\_\_\_  
**Comments:**

#### 14.2.2 BFB Tune

- 14.2.2.1 BFB tune must be done after autotune. The purpose of BFB tune is to calibrate the mass spectrometer to meet the criteria listed in Table 2.
- 14.2.2.2 Load **Bakeout** method. Wait about 30 min.
- 14.2.2.3 In **Instrument Control** screen, select **manual tune** from **View** menu. In the following screen, select **Load Tune** from **File** menu to load BFB tune file. Then select **BFB Tune** from **Tune** menu. The program will automatically conduct the BFB tune and print a hard copy of the tuning report, save, and update the tune file as C:\HPchem\1\5973\BFB.U. Check the hard copy to make sure that peaks of 69, 219 and 502 are smooth and symmetric; their peak widths are from 0.45-0.55; their mass assignments vary no more than  $\pm 0.1$ ; the total peak number is less than 250; the absolute abundance of ion 69 is between 500,000 to 700,000; the relative abundance of ion 28 to 69 is less than 10% (normally less than 5%); the target relative abundances of the other ions specified in BFB file are also achieved. If all these criteria are met, the mass spectrometer is ready for data acquisition.

#### 14.2.3 Creating GC/MS Sample Sequence

- 14.2.3.1 You can usually create the GC/MS sample sequence by editing an existing sequence. Each sequence must be finished within 24 hours.
- 14.2.3.2 In **Top** screen, select **Load Sequence** from **Sequence** menu and then select an existing sequence you want to edit.
- 14.2.3.3 Choose **Edit Sample Log Table** from **Sequence** menu to edit the sequence. Table 8 is an example of the GC/MS sample sequence.
- 14.2.3.4 In table 8, data file names in column 4 are for bookkeeping in the air lab. S refers to HP3 (M refers to HP4); the second letter refers to months of the year (e.g., A here refers to January); 24 refers to date; 05 refers to year 2005; the final two digits refers to data file number.

- 14.2.3.5 Choose **Simulate** from **Sequence** menu and then **Run Sequence**. A report will appear in the screen. It will indicate whether there are any duplicate file names and how much space the MSD data files need.
- 14.2.3.6 Save the sequence by selecting **Save** from **Sequence** menu. Save the sequence as a different name from the current sequence such as SEQ0124205. Then print a hard copy of the sequence (brief format). Proceed to Entech procedure.

### 14.3 Procedure for Entech Pre-Concentrator

#### 14.3.1 Pre-Concentrator Sample Sequence Setup

- 14.3.1.1. 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 desired entry in that top line, followed by clicking on **REPLC** button and then the old line will be replaced. The volume of the internal standard to be concentrated will be 50 ml that is entered in the box for internal standard. The 50 ml will be applicable to all lines in the sequence once it is entered. The pre-concentrator sample sequence must match the GC/MS sample sequence. Table 9 is an example of the pre-concentrator sample sequence.
- 14.3.1.2. Click on **SAVE** button and enter a different sequence name such as sq012405 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 8 An Example of the GC/MS Sample Sequence**

Line	Type	Vial	Data File	Method	Sample Name
1)	Blank	1	SA240501	TO15T	BFB/012405
2)	Cal	1	SA240502	TO15T	TO15-5
3)	Cal	2	SA240503	TO15T	TO15-5
4)	Cal	1	SA240504	TO15T	TO15-4
5)	Cal	1	SA240505	TO15T	TO15-3
6)	Cal	1	SA240506	TO15T	AH02148 \$I_TO15
7)	Cal	1	SA240507	TO15T	TO15-1
8)	Cal	1	SA240508	TO15T	AH02148 ICV
9)	Cal	1	SA240509	TO15T	AH02148 \$HBTO15
10)	Blank	1	SA240510	TO15T	AH01625 \$TO15
11)	Sample	1	SA240511	TO15T	AH01601 \$TO15
12)	Sample	1	SA240512	TO15T	AH00728 \$TO15
13)	Sample	1	SA240513	TO15T	AH01646 \$TO15
14)	Sample	1	SA240514	TO15T	AH01748 \$TO15
15)	Sample	1	SA240515	TO15T	AH02148 \$L1TO15
16)	Sample	1	SA240516	TO15T	AH01655 \$TO15
17)	Sample	1	SA240517	TO15T	AH01746 \$TO15
18)	Sample	1	SA240518	TO15T	AH01666 \$TO15
19)	Sample	1	SA240519	TO15T	AH00986 \$TO15
20)	Sample	2	SA240520	TO15T	AH01625 \$D_TO15
21)	Cal	3	SA240521	TO15T	AH02148 \$C_TO15
22)	Blank	3	SA240522	TO15T	AH02148 \$B_TO15

**Table 9 An Example of the Pre-Concentrator Sample Sequence**

Sample Name	Sample Inlet	Auto Port	Sample Vol	Cal Std Vol	Method
BFB/012405	3	1	400	0	C:\Smart\TO15T.MPT
TO15-5 \$TO15	1	1	0	20	C:\Smart\TO15T.MPT
TO15-5 \$TO15	1	1	0	20	C:\Smart\TO15T.MPT
TO15-4 \$TO15	1	1	0	100	C:\Smart\TO15T.MPT
TO15-3 \$TO15	1	1	0	200	C:\Smart\TO15T.MPT
AH02418 \$I_TO15	1	1	0	300	C:\Smart\TO15T.MPT
TO15-1 \$TO15	1	1	0	400	C:\Smart\TO15T.MPT
AH02418 ICV	1	11	400		C:\Smart\TO15T.MPT
AH02418 \$HBTO15	3	1	400	0	C:\Smart\TO15T.MPT
AH01625 \$TO15		1	400	0	C:\Smart\TO15T.MPT
AH01601 \$TO15	1	2	400	0	C:\Smart\TO15T.MPT
AH00728 \$TO15	1	3	400	0	C:\Smart\TO15T.MPT
AH01646 \$TO15	1	4	400	0	C:\Smart\TO15T.MPT
AH01748 \$TO15	1	5	400	0	C:\Smart\TO15T.MPT
AH02418 \$L1TO15	1	6	400	0	C:\Smart\TO15T.MPT
AH01655 \$TO15	1	7	400	0	C:\Smart\TO15T.MPT
AH01746 \$TO15	1	8	400	0	C:\Smart\TO15T.MPT
AH01666 \$TO15	1	9	400	0	C:\Smart\TO15T.MPT
AH00986 \$TO15	1	10	400	0	C:\Smart\TO15T.MPT
AH01625 \$D_TO15	1	1	400	0	C:\Smart\TO15T.MPT
AH02418 \$C_TO15	1	1	0	300	C:\Smart\TO15T.MPT
AH02418 \$B_TO15	4	1	400	0	C:\Smart\TO15T.MPT

#### 14.3.2 Pre-Concentrator Leak Check

- 14.3.2.1 Place canisters in the auto sampler rack and connect them to the sample line.
- 14.3.2.2 Leak-check for the inlets of the internal standard, the calibration standard, and the humidified zero air will be done manually. Leak check for the inlets of the auto sampler can be done automatically.
- 14.3.2.3 To do leak check for the auto sampler, highlight the first line of the auto sampler in the sequence table and click on **Leak** button, followed by clicking on **Go** in the next screen. All the auto sampler lines in the sequence will be automatically leak-checked and a hard copy of the leak-checking report will be printed.
- 14.3.2.4 Check the report to see if the **START** and **END** pressures are less than 1.5 psig and the difference between the **Start** and **End** pressures are less than 1.5 psi/min. If yes, the leak check passed. If not, trouble shoot the auto sampler and the pre-concentrator and do the leak check again.

#### 14.4 Run and Synchronize GC/MS and Pre-concentrator Sequences

- 14.4.1 Open all canisters and the liquid nitrogen Dewar.
- 14.4.2 In the screen of the pre-concentrator Entech sequence table, click **Start** button. At the prompt of saving or not, click **No**. The pre-concentrator will start to run the sequence.
- 14.4.3 In top screen of GC/MS, select **Run** from **Sequence** menu, followed by clicking **Run the Sequence** in the next screen. The GC/MS sequence must be started after the starting of the concentrator sequence but before the 13th step of the concentrating process in the pre-concentrator.

#### 14.5 Instrument Performance Check

- 14.5.1 Before the sample sequence can proceed, the mass spectrometer must meet the criteria of BFB for the full scan-operating mode listed in Table 2. Compound BFB with other

three internal standards is spiked into each sample. Absolute amount of spiked BFB is about 13 ng.

- 14.5.2 At the end of the first run in the sequence, load the data file by selecting **Load Data File** from **File** menu in Environmental Data Analysis screen.
- 14.5.3 Select **Evaluate BFB** from **Tuner** menu, followed by selecting **Autofind BFB to Printer** and clicking on **OK**. The report will be printed. Check the report to see if the criteria listed in Table 2 are met. If not, stop both sequences of the GC/MS and the concentrator. Modify the parameters in BFB tune file and re-run BFB tune. Run the sequences again. If the criteria are still not met, the mass spectrometer ion source may be dirty and need cleaning.

## 15.0 [Evaluation of Data, Reporting Results and Calculations](#)

### 15.1 Create Calibration Curves

- 15.1.1 The new calibration curve is created by updating the existing calibration table.
- 15.1.2 Load method TO15T.m from **File** menu.
- 15.1.3 Load a calibration standard data file from **File** menu.
- 15.1.4 Calculate and generate a report to screen by selecting **Calculate/Generate Report** from **Quant** menu.
- 15.1.5 All the target compounds must be looked at one by one for correct identification and integration. Go to the edit menu by selecting **Qedit Quant Results** from **Quant** menu. Four windows will appear in the screen. Window **Quick Qedit** shows all target compounds and internal standards. Window [1] shows mass spectrum of a target compound selected from **Quick Qedit** window. Window # 6 shows integration. Window [7] shows the retention times, the concentration and the absolute response of the target ion used for quantification and the relative responses of the qualifier ions. Click any compound in window **Qedit** results to see if the integration in window # 6, the mass spectrum in window [1], the retention time and the responses in window [7] are satisfactory. Do appropriate manual integrations (refer to Appendix B for manual integration policy). Print a hard copy of the custom report by selecting **Print Report** from **Cust Rpt** menu.
- 15.1.6 To update the current calibration level in the calibration table, select **Update Levels** from **Init Cal** menu. In the following

screen, select the level of the current calibration standard for **Levels ID; Recalibration for Using Calib; Replace** for retention times and responses. Then click **Do Update**.

- 15.1.7 Load another calibration standard. Repeat the 15.1.4-15.1.6 except that **Average** is selected for the retention times.
- 15.1.8 After all calibration levels in the calibration table are updated, evaluate the calibration curves to see if the criteria specified in 13.2 are met. If yes, save the method by overwriting current method and proceed to 15.1.9. If not, troubleshoot the instrument and rerun calibration standards and samples.
- 15.1.9 In order that the calibration is valid, the internal standard QC check criteria in 12.8 must also be met. For surrogate BFB internal standard, the recovery for each calibration level must be in the range of 70% to 130%. Table 10 shows an example of internal QC checks. If the criteria are met, proceed to data processing. If not, troubleshoot the instrument, and rerun the calibration and samples.

## 15.2 Data Processing

- 15.2.1 For all samples, blanks, CCV and LCS standards in a sequence, internal standard QC check criteria specified in 15.1.9 must be met.
- 15.2.2 Load data files of blanks and follow the 15.1.4 and 15.1.5 to process the data. If all target compounds except acetone in the humidified blank are less than 0.20 ppbv, transfer the data to database by selecting **Update Database** from **CustRpt** menu. Proceed to 15.2.3. If not, the instrument was probably contaminated and the data in the entire sequence will be invalid. Troubleshoot the instrument and rerun the entire sequence.
- 15.2.3 Load the CCV standards and follow 15.1.4 and 15.1.5 to process the data. If the criteria in 12.4 and 12.6 are met, transfer the data to database by selecting **Update Database** from **CustRpt**. Proceed to the next step to data-process the samples. If not, stop here. Recalibrate the instrument and rerun the samples.
- 15.2.4 Load LCS standard and follow 15.1.4 and 15.1.5 to process the data. If the criteria in 12.5 are met, transfer the data to database by selecting **Update Database** from **CustRpt.**,

**Table 10 HP4 Internal Standard QC Check**

**4/15/2009**

<b>Bromochloromethane</b>			
<b>LEVEL</b>	<b>Xi</b>	<b>(Xi-Ave.)/Ave</b>	<b>Status</b>
1	391938	-1.8%	Pass
2	415041	4.0%	Pass
3	397188	-0.5%	Pass
4	404577	1.3%	Pass
5	387555	-2.9%	Pass

<b>Average = 399260</b> <b>Avg-40%= 239556</b> <b>Avg+40%= 558964</b>
---

<b>1,4-diflourobenzene</b>			
<b>LEVEL</b>	<b>Xi</b>	<b>(Xi-Ave.)/Ave</b>	<b>Status</b>
1	837707	1.7%	Pass
2	835994	1.5%	Pass
3	829219	0.7%	Pass
4	846350	2.8%	Pass
5	768548	-6.7%	Pass

<b>AVG= 823564</b> <b>Avg-40%= 494138</b> <b>Avg+40%= 1152989</b>
---

<b>d5-Chlorobenzene</b>			
<b>LEVEL</b>	<b>Xi</b>	<b>(Xi-Ave.)/Ave</b>	<b>Status</b>
1	578740	1.3%	Pass
2	598452	4.7%	Pass
3	572905	0.3%	Pass
4	588785	3.0%	Pass
5	518367	-9.3%	Pass

<b>Average = 571450</b> <b>Avg-40%= 342870</b> <b>Avg+40%= 800030</b>
---

<b>Surrogate QC Check</b>			
<b>LEVEL</b>	<b>Xi</b>	<b>% Recovery</b>	<b>Status</b>
1	409727	102.19	Pass
2	423268	102.09	Pass
3	395090	99.54	Pass
4	402136	98.59	Pass
5	349248	97.25	Pass
SD	28090	2.18%	Pass
AVG	395893.8	% RSD	

<b>Level</b>	<b>Data File</b>
Level1	MD140909
Level2	MD140908
Level3	MD140907
Level4	MD140906
Level5	MD140905

proceed to the next step to data-process the samples. If not, stop here. Recalibrate the instrument and rerun the samples.

- 15.2.5 Load sample data files and follow 15.1.4 and 15.1.5 to process the data. Print a hard copy of the custom report and transfer the data to the database.
- 15.2.6 Examine chromatograms for any significant TIC peaks of untargeted VOCs. Tentatively identify 10 largest untargeted compounds which have over 10% of the peak of adjacent internal standard by library search. If requested, tentatively estimate the amount of untargeted compounds. From **Int** menu, click on **Integrate**. The software will integrate all peaks in the chromatogram. From **Int** menu, click on **Integration Results**. Integration results including retention times and areas for all the peaks will appear on screen. Print a hard copy. Use the following equation to calculate tentative semi-quantitative concentration of the untargeted compound:

$$X = \text{Aut} * \text{Cb}/\text{Ab}$$

Where

- X concentration of the untargeted compound (ppbv)  
Aut: area of the untargeted compound.  
Cb: quantified concentration (ppbv) of benzene that should be present in every sample.  
Ab: area of benzene.

*The semi-quantitative concentration obtained using this equation is tentative, since the relation between TIC and concentration is different from compound to compound. For those large peaks that are easily correlated between chromatograms of GC/FID and GC/MS, it is more accurate to use data (ppbC) from GC/FID for estimation.*

## 16.0 [Method Performance](#)

- 16.1 For all targeted compounds, MDLs must be 0.50 or better (should be 0.20 ppbv or better).
- 16.2 For duplicate runs, RPD must be 35% or better in the calibration range of 0.5-0 ppbv (should be 25 % or better).

16.3 The accuracy of LCS and CCV standards or PT and audit samples should be 100+/- 30%. Two of them are allowed to vary greater than 100+/-30%, but must be less than 100+/-40%.

#### 17.0 [Pollution Prevention](#)

Refer to LSD's Lab Waste Disposal SOP\_1197.

#### 18.0 [Data Assessment and Acceptance Criteria](#)

The policy of data review by analyst, the supervisor, and the manager or QA Officer is detailed in the data view SOP 1826 and must be followed.

For the data of a sample to be acceptable, BFB performance check, internal standard abundance and retention times, surrogate BFB recovery, the CCV, the LCS, the blanks in the sequence associated with the sample and the internal standard must meet the criteria set in 12.0.

Any data out of the calibration range of 0.5 ppbv –10 ppbv are estimated. For those data below the quantitation limit of 0.5 ppbv, LIMS will automatically put a qualifier "J". If any data are larger than 10 ppbv, the sample may be re-analyzed with proper dilution to bring them into the calibration range and qualifier "DC" will be used. If the sample is not re-analyzed with dilution, the qualifier "J" will be used.

#### 19.0 [Corrective Action for Out of Control Data](#)

- 19.1 Determine the source of the problem.
- 19.2 Notify the lab management of the problem.
- 19.3 Reanalyze all affected samples if necessary.
- 19.4 Use data qualifiers to flag the data, if they are unable to be rerun.
- 19.5 Document the event in the instrument log.

#### 20.0 [Contingencies for Handling Unacceptable Data](#)

All data, including any out of control events, or non-compliant data, must be documented and reported for actual analyses performed.

All appropriate personnel must be notified. Data must be flagged with appropriate data qualifiers with explanation in narratives if necessary.

#### 21.0 [Waste Management](#)

Refer to LSD's Lab Waste Disposal SOP\_1197.

## 22.0 [Data and Records Management](#)

- 22.1 Record all daily activities in the logbook. Whiteouts are prohibited.
- 22.2 The batch QC documentation includes: 1, the worksheet--table 7; 2, printouts of Entech and GC/MS sequences—table 8 and 9 plus Entech leak check report; 3, printouts of BFB performance checks, response factors and table 10; 4, quantification reports from both zero blanks; 5, LCS quantification report plus table 4; 6, CCV quantification reports plus table 3. All this is stapled together and filed in a designed binder and a cabinet.
- 22.3 The canister numbers for the standards and blanks shall be either handwritten or digitally on the quantitation reports.
- 22.4 Prepare a folder for each sample. Include the Canister Sampling Field Data Sheet, the GC/MS custom report, the data report generated from LIMS, and summary reports of before-and-after manual integration in the report folder, chromatograms before and after manual integration, tentatively identified untargeted compounds. If necessary, include the checklist (table 5).
- 22.5 Transfer data to the LIMS from MS database after the data have been validated.
  - 22.5.1 To enter MS database, click on **Custom Reports** from the **CustRpt** menu In **Environmental Data Analysis** screen.
  - 22.5.2 In column 2, enter proper analysis codes: \$TO15; \$HBTO15; \$B\_TO15; \$I\_TO15; \$C\_TO15; \$L1TO15; \$D\_TO15.
  - 22.5.3 Transfer the data from MS database to a floppy disk by using **Copy and Paste**. The disk contains an Excel TOX\_99.csv file. Paste the data into this file and save it as the same name by overwriting it.
  - 22.5.4 Log on to LIMS and ensure that Instrument has been assigned for the data to be transferred.
  - 22.5.5 Insert the disk. Choose **Instrument Result Conversion** under **Results** menu. Ensure that **DEQ air Lab CSV Format** and **Generic Result files** are checked. Then select the file TOX\_99 in drive A and click on **OK**. Print a copy of GRF files generated and then exit **Instrument Conversion**.

- 22.5.6 Under **Results** menu, select **Multicomponent Transfer**. In the following screens, select **Result File Mode** and **Add files to list** and go to L:/LWDATA5/Interface/LADEQAir.
- 22.5.7 In the screen that follows, click on **Find samples**. The list of files will be added to the left of the sheet. Then select **Load Results**. All the files will be added to the right of the sheet. Check the appropriate boxes if previous results need to be overwritten. Check to see if there is any violation. Click on **Save the Results**. Wait for the screen to turn gray to finish uploading the sample results. **Exit** LIMS.
- 22.5.8 Go to Windows Explorer™ and delete the generic files created from L:/LWDATA5/Interface/LADEQAir.

### 23.0 [Tables, Diagrams, Flowcharts, and Validation Data](#)

The tables and diagrams are inserted in the context of this SOP. The chromatograms, mass spectra and 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.

### 24.0 [References](#)

- 24.1 HP MS ChemStation and Instrument Operation Course Number H4043A Student Manual. Hewlett-Packard Company, 1998.
- 24.2 Entech 7100 Operators Manual, Version 2.0, Entech Instruments, Inc. 2001
- 24.3 Technical Assistance Document for Sampling and Analysis of Ozone Precursors, EPA/600-R98/161, October 31, 1999.
- 24.4 HP 5973N Mass Selective Detector Hardware Manual, February 1999.

## [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 **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 19) 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 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.