REQUEST FOR INFORMATION (RFI)

"Air Analysis and Consulting Services"

LOUISIANA DEPARTMENT OF ENVIRONMENTAL QUALITY

RFI #: 3000025696
Date Posted: 11/25/2025

Response Due Date/Time: 12/17/2025, 10:00 AM CT

I. Purpose of this RFI

The purpose of this Request for Information (RFI) is to gather general information from bona fide, qualified Respondents who are interested in providing Air Analysis and Consulting Services for the Louisiana Department of Environmental Quality (LDEQ or the Department), as detailed in the Scope.

LDEQ is seeking information about laboratories able to provide air analysis and consulting services as described in this RFI and are already accredited, or interested in becoming accredited, by the Louisiana Department of Environmental Quality, Louisiana Environmental Laboratory Accreditation Program (LELAP) in accordance with Louisiana Administrative Code (LAC) 33:I.Chapters 45-59, using either the LAC or TNI standard.

Respondents should be highly-familiar with services and requirements described in this RFI.

II. Background

LDEQ is committed to the assessment and monitoring of environmental conditions, as well as the investigation of sites of known, suspected, or potential contamination throughout the State by providing the analytical data needed to make Agency decisions. LDEQ must obtain quality, legally defensible analytical data to support the Department's monitoring, assessment, and remediation activities. The analytical data must be of a quality such that it may be admissible and defensible if presented in litigation as evidence. The project may include air samples from any source.

The in-house LDEQ laboratory was closed in 2009, and the Department privatized all laboratory functions. This decision necessitates contracting with outside laboratories in order for the mission of the Department to be fulfilled. Since 2009, LDEQ has maintained multiple contracts with commercial laboratories to fulfill the analytical needs of the Department, with one of these contracts having a primary focus on air analysis.

The following historical data is provided for reference only. The Department shall not guarantee a minimum or maximum amount of work to be performed:

Method	Quantity Completed in 2023	Quantity Completed in 2024
TO-12	3158	3244
TO-13A	0*	14*
TO-15	1246	1320

* = TO-13A PAHs restarted in late 2024. Anticipated 40-60 per year as grant funding allows.

III. Administrative Information

All communications relating to this RFI must be directed to the RFI Coordinator named below. All communications between Respondents and LDEQ staff members concerning this RFI will be strictly prohibited.

A. RFI Written Inquires

Respondents may submit written inquiries to the RFI Coordinator via email according to the Schedule of Events provided herein.

LDEQ shall provide responses to all written inquiries, according to the Schedule of Events, in the form of an RFI addendum, posted to the LaPAC at:
https://wwwcfprd.doa.louisiana.gov/osp/lapac/pubMain.cfm

B. RFI Responses

Respondents interested in providing information requested by this RFI must submit responses containing the specified information no later than the Deadline for Receipt of RFI Responses specified in the Schedule of Events. **Submissions are accepted via email only.** All responses must be received by the due date and time indicated on the Schedule of Events. Responses received after the due date and time may not be considered. It is the sole responsibility of each Respondent to assure that its response is delivered by email prior to the deadline.

C. RFI Coordinator

Written questions and RFI Responses for this RFI must be submitted to Robyn Geddes via e-mail at Robyn.Geddes@LA.GOV

1. Subject Line of all e-mails pertaining to this RFI should be:

   - Questions for Air Analysis and Consulting Services RFI
     or
   - Response to Air Analysis and Consulting Services RFI

IV. Schedule of Events

	Date	Time
RFI posted to LaPac	11/25/2025	
Deadline for Respondent Inquires	12/8/2025	10:00 AM CT
Deadline for LDEQ Response to Inquiries	12/10/2025	
Deadline for Receipt of RFI Responses	12/17/2025	10:00 AM CT

LDEQ reserves the right to revise this schedule. Revisions, if any, before the Deadline for Receipt of RFI Responses will be formalized by the issuance of an addendum to the RFI which will be posted at: https://wwwcfprd.doa.louisiana.gov/osp/lapac/pubMain.cfm

V. Scope

Respondent should be able to serve as an analytical resource for the analyses listed in **Exhibit 1, Air Analysis Analyte List and Analytical Requirements for Testing**. The Respondent, either as a prime contractor, sister laboratory or via subcontractor combined, should have the capability to perform 100% of the method/analytes. For the purposes of this RFI, sister laboratories are considered subcontractors.

Any laboratory (Respondent and/or subcontractor) providing analytical services to the Department shall be accredited by the LDEQ, Louisiana Environmental Laboratory Accreditation Program (LELAP) in accordance with LAC 33:I Chapters 45-59, using either the LAC or the National Environmental Laboratory Accreditation Conference (NELAC) Institute (TNI) standard.

Respondent should be able to provide all personnel, equipment, materials, reagents, and facilities necessary to conduct the required analyses on all samples received by the laboratory. All instruments must be in good working condition and calibrated prior to use.

Respondent and any subcontractors should be able to meet the Laboratory Facilities and Equipment and Supplies requirements in LAC 33:I Chapters 45-59. For data consistency, instrumentation for any subcontractor(s) shall be identical to instrumentation for the Respondent.

A. LELAP Accreditation

The Respondent and any subcontractor should be able to acquire LELAP accreditation for all of the analyses listed in Exhibit 1 before any work begins and maintain LELAP accreditation for the duration of the project. The Respondent should be able to comply with LAC 33:I.5307.D: "Whenever samples are subcontracted to another environmental testing laboratory, the original laboratory shall maintain a verifiable copy of results with a Chain of Custody (COC). This procedure may not be used to circumvent proper accreditation or any State requirements. The original laboratory is responsible for ensuring that the secondary laboratory used is properly accredited for the scope of testing performed."

The Respondent should be able to perform all proposed analyses in-house or should be able to use subcontractor arrangements. The Respondent and/or their subcontractor's LELAP accreditation should be able to cover all Department required methodologies for each test category per field of testing.

B. Sample Quantitation Limits

The Respondent should have the capability to achieve the sample quantitation/reporting limits using the analytical methods specified in **Exhibit 1**.

The estimated detection limit for specific target Volatile Organic Compounds (VOCs) of the Photochemical Assessment Monitoring Station (PAMS) analysis shall be 2 ppbC or better and the estimated detection limit for Toxic Organics (TO)-15 analysis shall be 0.2 ppbV or better.

For all air analyses, the Department and EPA require that all data shall be reported down to 0.01 ppbC or 0.01 ppbV, even if considered estimated data with a qualifier. Gas Chromatogram/Flame Ionization Detector (GC/FID) data shall have a quantitation/reporting limit of 5.0 ppbC. Gas Chromatogram/Mass Spectrometer (GC/MS) (TO-15) data shall have a quantitation/reporting limit of 0.50 ppbV. The quantitation limit for Polycyclic Aromatics Hydrocarbons (PAH) compounds on the TO-13A list shall be 0.1 ng/uL. The quantitation limit for the non-standard compounds added to the list shall be determined by the Respondent after the estimated detection limit has been identified and in accordance with LAC 33:I.5301.H.1.d as detailed below.

The Respondent should have documentation of instrument Detection Limits (DL) (established annually) to support its ability to achieve the method-specified sample quantitation limits. Method Detection Limit (MDL) studies shall be determined as required by the method or as required by LELAP in LAC 33:I.5301.H.1.d.

Dilutions amount to approximately 5% of the samples. Duplicate frequency is specified in **Exhibit 2 – LDEQ Standard Operating Procedure for Air Analysis (PAMS SOP #1026)** and **Exhibit 3 – LDEQ Standard Operating Procedure for Air Analysis (TO-15 SOP #1273).**

C. Quality Assurance/Quality Control (QA/QC) Requirements

Data is primarily used to determine if the ambient air at a monitoring site complies with the Department air toxics ambient air standards. A statistical analysis performs that determination. However, for that analysis to be valid, the data shall meet certain accuracy, precision and confidence levels as described in the Data Quality Objectives (DQOs) outlined in **EPA Technical Assistance Document for Sampling and Analysis of Ozone Precursors** (link provided in Section VIII, Resources and Reference Documents), and the DQOs outlined in **Exhibit 5 - LDEQ PAMS Quality Assurance Project Plan (QAPP) #1003 R19**. Meeting these DQOs ensures that the data is of adequate quality to perform statistical analysis. All data shall meet the QA/QC requirements of the laboratory SOPs and Quality Assurance Manual (QAM) as required by LELAP. If data does not comply with EPA's air quality data model, the laboratory shall be required to reanalyze and/or reassess the data.

The Respondent and any subcontractor should be able to maintain a QA/QC Plan that meets or exceeds all LELAP requirements. The QA/QC plan at a minimum shall meet the requirements of LAC 33:I.5301, including but not limited to having protocols in place to evaluate test performance such as accuracy and precision and annual review of the quality

system. All data, including QA/QC, generated for the Department shall be subject to inspection and review at any time by the Department and/or its authorized representatives.

D. Internal Laboratory Verification

The Respondent and any subcontractor should have Standard Operating Procedures (SOPs) that detail the appropriate level of laboratory review.

E. Data Packages

The Respondent should have the capability of producing summary or fully-supported data packages. For both types of deliverables, two separate Electronic Data Deliverable (EDD) formats are required, one in Louisiana Environmental Analytical Data Management System (LEADMS) format and one in Air Quality System (AQS) format.

- **Summary Reports**
  Summary reports must include at a minimum all requirements of the Louisiana Administrative Code (LAC) 33:I:5313 for reporting. Copies of the chain of custodies must also be included. The data deliverable package shall be one complete document, paginated, with reproduction quality such that all pages are legible. The EDD shall be checked with the EQUIS® EDP and be free of errors. The report must include the laboratory certification number, the date of report preparation, and a cross-reference between the Department sample identifications and the laboratory identifications. The report must define any data qualifiers contained in the analytical results. Associated QC data must be included in the analytical report and the EDD. The AQS format shall also be included.

  Summary reports shall not require attaching raw data.

- **Fully-Supported Data Packages**
  Fully-supported data packages must contain all of the required information as the summary report with the additional Contract Laboratory Program (CLP) or equivalent forms and all supporting raw and calculated data. Supporting raw data shall include, but shall not be limited to, extraction logs, preparation/digestion logs, quantitation reports, chromatograms, instrument analysis reports, analysis/sequence run logs, percent moisture logs, weight logs, bench sheets, standard and reagent logs, and sample receipt checklist(s). Raw data for all samples (including any and all dilutions) and any associated method or batch QC samples must be included. The Contractor shall refer to the resources available on the EPA Superfund Contract Laboratory Program (CLP) webpage for more detailed descriptions of the required forms https://www.epa.gov/clp/superfund-analytical-methods-sfam011). Custom forms equivalent to the CLP forms shall be acceptable.

  Fully-supported data packages shall require submitting all raw data and the associated CLP or equivalent summary forms.

The narrative of both the summary and fully-supported data reports must address any issues with chain-of-custody, condition of the sample upon receipt by laboratory personnel, unacceptable QA/QC, and any other notable concerns or issues with the sample and its analytical results. Preparation methods, as well as any clean up procedures, must be identified in the final report. When revisions/corrections are requested, the narrative must be revised to describe the reason for change.

F. Analytical Methods and Procedures

The Respondent should be able to provide analysis consistent with the methodology provided in **Exhibit 1** and the documents referenced in Section VII.

The SOPs of the Respondent and any subcontractors shall meet all SOP requirements of LAC 33:I Chapters 45-59, Laboratory Accreditation.

Multiple methods may be listed for the same analytes, but shall not be used interchangeably. Methods shown in **Exhibit 1** document shall not be substituted with other accredited methods

Updates to analytical methods must be followed when approved by the Department. All laboratory procedures shall be performed in accordance with the appropriate analytical method. Any deviations, variances or modifications must be equivalent or superior to the requirements of the analytical method and approved by the Department as required in LAC 33:I.5105.B.

Instrumentation identified in the Department SOPs has been demonstrated to meet the requirements of the Department. For data consistency, instrumentation for subcontractor(s) shall be identical to instrumentation for the Respondent. Alternative instrumentation shall be capable of meeting Department method requirements. The Respondent should be able to meet blank criteria, blank residuals effect on the initial calibration (ICAL), handling high humidity ambient samples, and analyses from canisters at -0.2”Hg (grab samples). The majority of samples received will be in pressurized canisters.

The analyte list may vary for each sample location, and may potentially change on a project-by-project basis. Additional analytes may also be required as needed.

Regulation holding times for samples as specified in the analytical method must be met.

G. Special Conditions

The Respondent shall have an inventory of **at least 1000 summa canisters** dedicated to this project.

The Respondent should be able to comply with the following documents for performance of the work:

- **Exhibit 2 - LDEQ SOP for Air Analysis (PAMS SOP #1026)**
- **Exhibit 3 - LDEQ SOP for Air Analysis (TO-15 SOP #1273)**
- **Exhibit 4 - LDEQ SOP for Canister Cleaning (SOP #1120)**
- **Exhibit 5 - LDEQ PAMS QAPP #1003 R19**
- **EPA Method TO-13A**

The Respondent should be able to clean and certify canisters according to a Department approved method based on EPA's Technical Assistance Document for Sampling and Analysis of Ozone Precursors and EPA Method TO-15. One canister per cleaning apparatus batch shall be certified by GC/FID. The canister to be certified per batch shall be the one with the highest original Total Non-Methane Organic Carbon (TNMOC) concentration. Canisters shall be certified to less than 10 ppbC TNMOC, using a heated procedure, with no individual analyte concentrations higher than the quantitation limit. Certification shall be by GC/FID. Canisters shall be pressurized to no greater than -28 mmHg. Canisters not meeting these criteria shall be returned to the Respondent at no cost to the Department.

H. Sampling Supplies

The Respondent should be able to provide:

1. Summa and fused silica lined canisters with a capacity of six liters (gauges optional). Gauged canisters are required for grab samples.

   The Respondent should be able to provide routine delivery/shipment of canisters to all Department regional offices or other designated Department facilities within three (3) calendar days of notice. If requested by the Department, the Respondent should be able to provide overnight or two (2) calendar day canister delivery. See Section M. Timelines, Locations, and Hours of Operation for shipping/delivery location information.

   Each time a canister is sent by the Department for analysis or cleaning, the Respondent should be able to ship a replacement canister to the appropriate regional office unless otherwise directed by the Department.

   The Respondent should have facilities for cleaning 15 liter canisters provided by the Department for cleaning.

2. The Respondent should be able to supply the Department with gas standards for TO-15 in six liter, fused silica lined canisters with gauges as needed.
   - 10 ppbv initial calibration/continuing calibration verification,
   - 5 ppbv initial calibration/continuing calibration verification, and
   - 10 ppbv laboratory control samples.

3. The Respondent should be able to supply the Department with clean cartridges for TO-13A samples. The cartridge must contain PUF/XAD2resin/PUF, fit a Tisch semi

volatile high volume sampler and meet all requirements in reference EPA Method TO-13A.

4. The Respondent should be able manage and track canister inventory including sample/clean status, location, etc.

I. COC/Sample Receipt

All samples are submitted to the laboratory with a Department COC form.

The Respondent should be able to secure the field samples under strict chain-of-custody procedures. The laboratory shall follow Federal Department of Transportation (DOT) Hazardous Materials Regulations, Louisiana and other applicable states regulations on the transport of hazardous materials. The laboratory shall be responsible for any damages to samples once custody has been accepted, including transport to subcontractors.

The Respondent should be able to report any anomalies or incidents associated with the Department samples that occur after initial sample receipt to the Department P within 48 hours of occurrence.

J. Library Searches

The Respondent should be able to perform library searches for non-target sample components and the tentative identification of these compounds on all TO-13A and TO-15 samples at no additional cost to the Department. The Department shall require the 10 highest concentration Tentatively Identified Compounds (TIC's) to be reported. The TIC and estimated concentration must be included in the reports.

K. Sample Storage and Disposal

The Respondent should be able to store samples in a designated, secure, climate controlled location and its access limited to authorized personnel only.

After all analyses are completed, the field samples and associated dilutions shall be retained in the event that any shall need reanalysis. They shall be placed in appropriate storage until either 14 calendar days after report is issued or sample holding time expiration, whichever is sooner, unless (a) otherwise notified in writing by the Department that the samples must be retained longer or (b) the samples were submitted for criminal investigations as described in the paragraph below. At the end of the storage period, the Respondent may send the canisters/cartridges for cleaning and reuse.

The Respondent should be able to store samples submitted to the laboratory for criminal investigations, as identified on individual COC forms, at the laboratory in a separate, secured location. Such samples shall be stored until picked up by the Department or its designee or until the laboratory is directed in writing by the Department to dispose of the samples. Criminal investigation samples must be stored for at least four months. At the

end of the four months, the laboratory must contact the Department in writing to request disposition of the criminal investigation samples.

L. Consultation and Expert Testimony

The Respondent should be able to provide analytical consulting services not otherwise defined in this Scope on an "as needed" basis. Consulting meetings shall primarily involve discussions concerning analytical methodology and the resulting data for samples analyzed for the Department. The Respondent should be able to prepare documents and provide background information within its areas of expertise.

The Respondent should be able to provide technical assistance regarding sample collection, analysis, and reporting as a routine part of this Scope and as specifically requested by the Department.

The Respondent should be able to provide qualified expert witnesses for court testimony concerning analytical methodology and the resulting data for samples analyzed for the Department. The Respondent would be required to prepare documents, assist in the finding of fact, and provide background information within its areas of expertise. The Respondent should be able to provide representation and organized reports, calculations, and any other documentation necessary to defend the data in question.

M. Timelines, Locations, and Hours of Operation

The Respondent should be able to conduct all analyses in their own facilities and/or those belonging to subcontractors.

The Respondent should be able to report all analytical results to the Department as soon as the data are available, but no later than 30 calendar days from sample receipt from the Department. Turnaround Times (TAT) shall commence with the laboratory's acceptance of the samples as noted by the time and date of the signature on the COC form.

If the Department finds it necessary to obtain analytical results in less than the 30 calendar days, then the Department will notify the laboratory of the required accelerated TAT prior to sample receipt or as soon as possible.

The Respondent should be able to provide personnel and means of transport to pick up samples and deliver certified clean canisters to Department Headquarters, all of the Department Regional Offices, or other designated locations as directed within the following timeline:

- Same day sample pickup if laboratory is notified before 2:00 PM Central Time (CT);
- Following business day sample pickup (no later than 10:00 AM CT) if laboratory is notified at 2:00 PM CT or later.

When necessary, the Respondent should be able to pick up/receive samples from locations mentioned below on late Friday afternoons, weekends, or holidays to meet holding time requirements or if samples require a quick TAT. If samples are routine and holding times allow, the samples should be picked up by the Respondent no later than 10:00 AM Central Time (CT) the following Monday. The Respondent should be able to coordinate pickup to meet short holding times.

During peak ozone sampling, the Department may require daily weekday pickup at DEQ offices in Baton Rouge.

The Respondent should be able to provide a local courier service for pickup and delivery, whether by direct employment or a subcontracted service provider. Common carrier (e.g. UPS, FedEx) is not an acceptable arrangement for routine performance of the project, but may be allowed on a case-by-case basis as approved by the Department. The Department reserves the right to require alternative courier services if project timelines are consistently not met. If requested by the Department under unusual circumstances, i.e., hurricane response activities or major incidents, the laboratory shall pick up samples on weekends and holidays. The Respondent should be able to provide emergency contact information in such incidents.

Physical addresses of all current locations are provided below:

Dept. of Agriculture and Forestry
(DEQ Offices at this location)
5825 Florida Blvd Suite, Warehouse #5
Baton Rouge, LA 70806

Bayou Lafourche Regional Office (BLRO)
125 Barataria St.
Lockport, LA 70374

Dept. of Environmental Quality
(Headquarters/Capital Regional Office (CRO))
602 N. Fifth St.
Baton Rouge, LA 70802

Kisatchie Central Regional Office (KCRO)
2800 S. MacArthur Drive, Suite A
Alexandria, LA 71301

Northeast Regional Office (NERO)
508 Downing Pines Road
West Monroe, LA 71292

Acadiana Regional Office (ARO)
111 New Center Drive
Lafayette, LA 70508

Northwest Regional Office (NWRO)
1525 Fairfield, Room 520
Shreveport, LA 71101-4388

Southeast Regional Office (SERO)
990 N. Corporate Drive Suite 102
New Orleans, LA 70123

Southwest Regional Office (SWRO)
1301 Gadwall Street
Lake Charles, LA 70615

LDEQ Warehouse
1824 Commercial Drive
Port Allen, LA 70767

The Respondent should be able to furnish shipping containers (e.g. tote boxes or equivalent for air canisters or ice chests for TO-13A cartridges) for the purpose of transporting collected samples between the Department and the laboratory.

N. Laboratory Personnel

The Respondent should be able to provide and maintain a qualified staff of personnel, including non-supervisory, to perform and accomplish the required tasks. The Respondent's key personnel including Laboratory Manager, Laboratory Technical Directory, Project Manager, Quality Assurance Manager, and Supervisor, should have relevant experience in PAMS, TO-15, and TO-13A air analytical methods and analytical consulting services. **All personnel, including non-supervisory personnel, shall meet education and experience requirements of LAC 33:I Chapters 45-59, Laboratory Accreditation.**

VI. RFI Requirements

This RFI is issued as a means of technical discovery and information gathering. This RFI is for planning purposes only and should not be construed as a solicitation, nor should it be construed as an obligation on the part of the LDEQ or any other agency of Louisiana to make any purchases or enter into any agreement. LDEQ may utilize the results of this RFI in drafting a competitive solicitation through a request for proposal (RFP) for similar services.

A. Response submissions should include the following:

1. Company Information – Respondents should include Company Name, Division/Location, Business Address, and Contact Name with Title, email address, and phone number

2. List of Qualifications – Respondents should include a description of their company including brief company history, corporate structure and organization, relevant expertise, and proof of experience as such pertains to the project.

3. Questions by Category – Respondents should provide responses to the questions provided in Section IX of this RFI.

Response be prepared simply, providing straightforward language and descriptions. Responses should be in at least 12-point font and no longer than 45 pages. Responses that do not meet these specifications may be rejected. Any submitted addenda shall not be counted in the page limit.

**No cost information, resumes, or LELAP accreditation scopes shall be included in this RFI response.*

VII. Additional Information

A. Liabilities of Agency

This RFI is only a request for information about potential products/services and no obligation on behalf of the LDEQ or any other Louisiana state agency whatsoever shall arise from the RFI process.

Participation in this RFI is voluntary, and all costs incurred are at the expense of the Respondent. This RFI does not commit the LDEQ or any other Louisiana state agency to pay any cost incurred in the preparation or submission of any response to the RFI.

B. RFI Ownership

All submissions in response to this RFI shall become the property of the LDEQ and will not be returned. Selection or rejection of a response shall not affect this right.

C. Confidential Information, Trade Secrets, and Proprietary Information

For the purposes of this RFI, the provisions of the Louisiana Public Records Act (La. R.S. 44.1 et. seq.) shall be in effect. Pursuant to this Act, all proceedings, records, contracts, and other public documents relating to this RFI shall be open to public inspection. Respondents are reminded that while trade secrets and other proprietary information they submit in conjunction with this RFI may not be subject to public disclosure, protections must be claimed by the Respondent at the time of submission of its response. Respondents should refer to the Louisiana Public Records Act for further clarification.

Any response copyrighted or marked as confidential or proprietary in its entirety may be rejected without further consideration or recourse.

If the Respondent is claiming any portion of its submittal as confidential, proprietary, or protected, Respondent must clearly designate the part of the response that contains a trade secret and/or privileged or confidential proprietary information as “confidential” in order to claim protection, if any, from disclosure. The Respondent must submit a redacted copy of their response along with their original. The redacted copy of the response will be the copy produced by the Department if a person seeks review or copies of the Respondent’s response. **If the Respondent does not submit a redacted copy, it will be assumed that any claim to keep information confidential is waived.**

If a Respondent wishes to secure nondisclosure of information contained in its response, the Respondent must also submit a written request to the Secretary of the Department in accordance with LAC 33:I. Chapter 5 and applicable laws. Upon review of the written request, the Secretary of the Department will determine if the information requires confidentiality.

Respondent must be prepared to defend the reasons why the material should be held confidential. By submitting a proposal with data, information, or material designated as containing trade secrets and/or privileged or confidential proprietary information, or otherwise designated as "confidential", the Respondent agrees to indemnify and defend (including attorney's fees) the State and hold the State harmless against all actions or court proceedings that may ensue which seek to order the State to disclose the information.

VIII. Resources and Reference Documents

1. Exhibit 1 - Air Analysis Analyte List and Analytical Requirements for Testing

2. Exhibit 2 - LDEQ Standard Operating Procedures for Air Analysis (PAMS SOP#1026)

3. Exhibit 3 - LDEQ Standard Operating Procedures for Air Analysis (TO-15 SOP#1273)

4. Exhibit 4 - LDEQ Standard Operating Procedure for Canister Cleaning (SOP#1120)

5. Exhibit 5 - LDEQ PAMS QAPP #1003 R19

6. Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air (TO-12, TO-13A, and TO-15)
   https://www.epa.gov/amtic/compendium-methods-determination-toxic-organic-compounds-ambient-air

7. LDEQ EDD Submittal Requirements Manual and List of Valid Values
   http://deq.louisiana.gov/page/leadms-resource-page

8. Louisiana Administrative Code Title 33
   - Louisiana Environmental Laboratory Accreditation Program (LELAP) (LAC 33:I, Chapters 45-59
     http://deq.louisiana.gov/assets/docs/Legal_Affairs/ERC/33v01OSEC.docx
   - Louisiana Department of Environmental Quality Confidential Information Regulations (LAC 33:I),
     http://deq.louisiana.gov/assets/docs/Legal_Affairs/ERC/33v01OSEC.docx
   - Ambient Air Quality – (LAC 33:III.701)
     http://deq.louisiana.gov/assets/docs/Legal_Affairs/ERC/33v03Air.docx

9. CLP Analytical Methods Statement of Work http://www.epa.gov/clp

10. LELAP Information and Regulations http://deq.louisiana.gov/page/la-lab-accreditation

11. 2016 TNI standard http://www.nelac-institute.org/content/CSDP/standards.php

12. Code of Federal Regulations (CFR), Title 40 Part 50, the most current revision
    https://www.ecfr.gov/current/title-40/chapter-I/subchapter-C/part-50?toc=1

13. EPA AQS User's Guide https://www.epa.gov/aqs

14. EPA Technical Assistance Document for Sampling and Analysis of Ozone Precursors https://www.epa.gov/system/files/documents/2023-05/TAD%20R3%20May%202023.pdf

IX. Questions by Category

1. Would your organization be interested in proposing on a future Request for Proposals (RFP) for services substantially similar to those described in this RFI?

2. Does your organization currently have all personnel, equipment, materials, reagents, and facilities, including all instruments in good working condition and calibrated prior to use, necessary to conduct the required analyses on all samples received by the Department?

a. If not, please explain the qualifications your organization already has.

3. If your organization plans to use a subcontractor or sister laboratory, is their instrumentation identical to instrumentation to your organization?

4. Does your organization and any subcontractor(s) meet the Laboratory Facilities and Equipment and Supplies requirements in LAC 33:I Chapters 45-59?

5. Is your organization able to provide the required analyses listed in Exhibit 1 **in the volumes** comparable to the historical data listed in Section II, Background?

A. LELAP Accreditation

6. Does **your organization currently** have the required LELAP accreditation for **all of the methods and analytes listed in Exhibit 1**?

If no:

a. Please list any methods and/or analytes from Exhibit 1 where **your organization does not have LELAP accreditation**.

b. Does **your organization have interest**, capability, equipment, personnel, facilities, etc. to become LELAP accredited for these methods and/or analytes?

c. Do you anticipate **your organization** could acquire the necessary equipment, personnel, facility, etc. to apply for and obtain LELAP accreditation within approximately 60 days?

d. Has your organization submitted an application to LELAP for accreditation for the missing methods and/or analytes in the past?

i. If no, please provide additional information on why your organization has not sought accreditation for these methods and/or analytes (i.e. equipment needed, under staffed, no previous clients needed these tests, etc.)

ii. If yes, please provide additional information on why your organization is not currently accredited for these methods and/or analytes (i.e. lapse in accreditation, accreditation was not granted for previous application, etc.)

7. Does your organization intend to use **a subcontractor or sister laboratory** to meet **the required LELAP accreditation <u>for 100%</u>** of the methods and/or analytes listed in Exhibit 1?

If yes:

a. Please list any methods and/or analytes from Exhibit 1 where **your subcontractor or sister laboratory <u>currently has</u> LELAP accreditation**.

b. Has your **subcontractor or sister laboratory** submitted an application to LELAP for accreditation for the missing methods and/or analytes?

i. If yes, please provide the date the application(s) submittal and the current status.

8. Does the **combined** LELAP accreditation of your organization and any subcontractor or sister laboratory **cover 100% methods and analytes listed in Exhibit 1**?

B. Sample Quantitation Limits

9. Does your organization have the capability to achieve the required sample quantitation/reporting limits using the analytical methods described in Section V. Scope, B. Sample Quantitation Limits, and Exhibit 1?

10. Does your organization have documentation of instrument Detection Limits (DL) to support its ability to achieve the method-specified sample quantitation limits as described in Section V. Scope, B. Sample Quantitation Limits, and Exhibit 1?

C. QA/QC

11. Does your organization and any subcontractor(s) maintain QA/QC plan that meets/exceeds all LELAP Requirements as described in Section V. Scope, C. Quality Assurance/Quality Control? *Do not provide the full QA/QC documents.*

D. Internal Lab Verification

12. Does your organization and any subcontractor(s) have SOPs for internal lab review as described in Section V. Scope, D. Internal Laboratory Verification? *Do not provide the full SOP documents.*

E. Data Packages

13. Describe your organization's capability of producing summary or fully-supported data packages as described in Section V. Scope, E. Data Packages.

F. Analytical Methods and Procedures

14. Describe your organization's capability to provide analysis consistent with the methodology provided in Exhibit 1 and the documents referenced in Section VIII, Resources and Reference Documents. *Do not provide the full LELAP accreditation scope.*

15. Describe your organization's capability to add additional analytes, if needed.

G. Special Conditions

16. Does your organization have an inventory of at least 1000 summa canisters that could be **dedicated** to this project?

If not,

a. How many does your organization currently have?
b. What is the approximate timeline to purchase the additional canisters needed?

17. Does your organization currently have the capability to clean and certify canisters to DEQ/EPA methods?

H. Sampling Supplies

18. Describe your organization's capability to provide the requirements as described in Section V. Scope, H. Sampling Supplies, including:

- Summa and fused silica lined canisters with a capacity of six liters;
- Gauged canisters for grab samples;
- Shipment of a replacement canister to the appropriate location each time a canister is sent by the Department;
- Cleaning of 15 L canisters provided by the Department;
- TO-15 gas standards to the Department;
- TO13A clean cartridges to the Department; and
- Any other relevant services your organization can provide.

19. Describe your organization's canister management and tracking system.

I. COC Sample Receipt

20. Can your organization receive samples under strict chain of custody and send notification to the Department of any discrepancies within 48 hours?

21. Describe your organization's capability to secure the field samples and chain-of-custody procedures.

J. Library Searches

22. Can your organization provide library searches, for non-target sample components and the tentative identification of these compounds on all samples analyzed by TO-13A and TO-15?

K. Sample Storage and Disposal

23. Can your organization and any subcontractor(s) comply with Section V. Scope, K. Sample Storage and Disposal including:

- retain field samples in the event that any need to reanalysis;
- sample storage and disposal requirements;
- store samples for 4 months for criminal investigations?

24. Can your organization meet the regulation holding times?

L. Consultation and Expert Testimony

25. Describe your organization's capability to provide consultation and expert testimony as described in Section V. Scope, L. Consultation and Expert Testimony.

M. Timelines, Locations and Hours of Operation

26. Can your organization meet the analytical requirements and holding times with respect to sample pickup, transport, and TAT?

27. Describe your organization's capability to provide personnel and means of transport to pick up samples and deliver certified clean canisters to Department Headquarters, all of the Department Regional Offices, or other designated locations, as directed.

28. Can your organization furnish shipping containers (e.g. tote boxes or equivalent for air canisters or ice chests for TO-13A cartridges) for the purpose of transporting collected samples between the Department and the laboratory?

N. Lab Personnel

29. Can your organization provide and maintain a qualified staff of personnel, including non-supervisory, to perform and accomplish the required tasks as described in Section V. Scope and in the volumes comparable to the historical data listed in Section II, Background?

Exhibit 1
Air Analysis Analyte List and Analytical Requirements for Testing

Table 1. Air Analysis Analyte List

LDEQ requires additional analytes not included in the original EPA Method TO15.

CASRN	Analyte/Parameter	GC/FID Quantitation Limit (ppbc)	GC/MS Quantitation Limit (ppbV)	TO-13A(Modified) Quantitation Limit(ng/uL)
71-55-6	1,1,1-Trichloroethane	---	0.5	---
79-34-5	1,1,2,2-Tetrachloroethane	---	0.5	---
79-00-5	1,1,2-Trichloroethane	---	0.5	---
75-34-3	1,1-Dichloroethane	---	0.5	---
75-35-4	1,1-Dichloroethene	---	0.5	---
120-82-1	1,2,4-Trichlorobenzene	---	0.5	---
95-63-6	1,2,4-Trimethylbenzene	5	0.5	---
106-93-4	1,2-Dibromoethane	---	0.5	---
95-50-1	1,2-Dichlorobenzene	---	0.5	---
107-06-2	1,2-Dichloroethane	---	0.5	---
78-87-5	1,2-Dichloropropane	---	0.5	---
108-67-8	1,3,5-Trimethylbenzene	---	0.5	---
106-99-0	1,3-Butadiene	5	0.5	---
541-73-1	1,3-Dichlorobenzene	---	0.5	---
87-68-3	1,3-Hexachlorobutadiene	---	0.5	---
106-46-7	1,4-Dichlorobenzene	---	0.5	---
78-93-3	2-Butanone	---	0.5	---
591-78-6	2-Hexanone	---	0.5	---
108-10-1	4-methyl-2-pentanone	---	0.5	---
67-64-1	Acetone	---	0.5	---
75-05-8	Acetonitrile	---	0.5	---
107-13-1	Acrylonitrile	---	0.5	---
107-05-1	Allyl chloride	---	0.5	---
71-43-2	Benzene	5	0.5	---
100-44-7	Benzylchloride	---	0.5	---
74-83-9	Bromomethane	---	0.5	---
56-23-5	Carbon Tetrachloride	---	0.5	---
75-15-0	Carbon disulfide	---	0.5	---
107-14-2	Chloroacetonitrile	---	0.5	---
108-90-7	Chlorobenzene	---	0.5	---
109-69-3	1-Chlorobutane	---	0.5	---
75-00-3	Chloroethane	---	0.5	---

67-66-3	Chloroform	---	0.5	---
74-87-3	Chloromethane	---	0.5	---
156-59-2	cis-1,2-Dichloroethene	---	0.5	---
10061-01-5	cis-1,3-Dichloropropene	---	0.5	---
60-29-7	Diethyl ether	---	0.5	---
97-63-2	Ethyl methacrylate	---	0.5	---
100-41-4	Ethylbenzene	5	0.5	---
75-69-4	Freon-11	---	0.5	---
76-13-1	Freon-113	---	0.5	---
76-14-2	Freon-114	---	0.5	---
75-71-8	Freon-12	---	0.5	---
XYLENESMP	m/p Xylenes	5	0.5	---
1634-04-4	Methyl-t-butyl ether	---	0.5	---
126-98-7	Methacrylonitrile	---	0.5	---
96-33-3	Methyl Acrylate	---	0.5	---
80-62-6	Methyl methacrylate	---	0.5	---
75-09-2	Methylene chloride	---	0.5	---
95-47-6	o Xylene	5	0.5	---
98-95-3	Nitrobenzene	---	0.5	---
25322-01-4	Nitropropane	---	0.5	---
100-42-5	Styrene	5	0.5	---
127-18-4	Tetrachloroethylene	---	0.5	---
109-99-9	Tetrahydrofuran	---	0.5	---
108-88-3	Toluene	5	0.5	---
10061-02-6	trans-1,3-Dichloropropene	---	0.5	---
79-01-6	Trichloroethylene	---	0.5	---
75-01-4	Vinyl Chloride	---	0.5	---
526-73-8	1,2,3-Trimethylbenzene	5	---	---
106-98-9	1-Butene	5	---	---
540-84-1	2,2,4-Trimethylpentane	5	---	---
74-86-2	Acetylene	5	---	---
74-84-0	Ethane	5	---	---
74-85-1	Ethylene	5	---	---
75-28-5	Isobutane	5	---	---
78-79-5	Isoprene	5	---	---
78-78-4	Isopentane	5	---	---
74-98-6	Propane	5	---	---
115-07-1	Propylene	5	---	---
TNMOC	Total NMOC	N/A	---	---
590-18-1	cis-2-Butene	5	---	---
620-14-4	m-Ethyltoluene	5	---	---
106-97-8	n-Butane	5	---	---
110-54-3	n-Hexane	5	---	---

109-66-0	n-Pentane	5	---	---
98-82-8	Isopropylbenzene	5	---	---
1120-21-4	n-Undecane	5	---	---
611-14-3	o-Ethyltoluene	5	---	---
622-96-8	p-Ethyltoluene	5	---	---
624-64-6	trans-2-Butene	5	---	---
95-48-7	2-Methylphenol	---	---	0.1
MEPH34	3&4-Methylphenol	---	---	0.1
108-95-2	Phenol	---	---	0.1
83-32-9	Acenaphthene	---	---	0.1
208-96-8	Acenaphthylene	---	---	0.1
120-12-7	Anthracene	---	---	0.1
56-55-3	Benzo(a)anthracene	---	---	0.1
50-32-8	Benzo(a)pyrene	---	---	0.1
205-99-2	Benzo(b)fluoranthene	---	---	0.1
191-24-2	Benzo(g,h,i)perylene	---	---	0.1
207-08-9	Benzo(k)fluoranthene	---	---	0.1
92-52-4	1,1’-Biphenyl	---	---	0.1
218-01-9	Chrysene	---	---	0.1
53-70-3	Dibenzo(a,h)anthracene	---	---	0.1
132-64-9	Dibenzofuran	---	---	0.1
206-44-0	Fluoranthene	---	---	0.1
86-73-7	Fluorene	---	---	0.1
193-39-5	Indeno(1,2,3-cd)pyrene	---	---	0.1
90-12-0	1-Methylnaphthalene	---	---	0.1
91-57-6	2-Methylnaphthalene	---	---	0.1
91-20-3	Naphthalene	---	---	0.1
85-01-8	Phenanthrene	---	---	0.1
129-00-0	Pyrene	---	---	0.1

Table 2. Analytical Requirements for Testing

Parameter	Quantitation Limit	Reporting Limit	Method
Photochemical Precursors (PAMS) by GC/FID (see Table 1 for analyte list)	5.0 ppbC	0.01 ppbC	Department Approved PAMS Method
Air Toxics Analysis by GC/MS (see Table 1 for analyte list)	0.5 ppbV	0.01 ppbV	Department Approved TO-15 Method
Canister Cleaning and Certification **6 Liter**			Department Approved Cleaning Method
Canister Cleaning and Certification **15 Liter**			Department Approved Cleaning Method
Standards 10 ppbv ICAL/CCV	NA	NA	Contract Laboratory SOP
Standards 5 ppbv ICAL/CCV	NA	NA	Contract Laboratory SOP
Standards 10 ppbv ICV/LCS	NA	NA	Contract Laboratory SOP
Polynuclear Aromatic Hydrocarbons Analysis by GC/MS (see Exhibit 1 for analyte list)	0.1 ng/uL	0.01 ng/uL	EPA TO-13A (Modified)
Polynuclear Aromatic Hydrocarbons Cartridge and Cartridge Cleaning			EPA TO-13A

Exhibit 2

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

Please Note: The official version of this document is maintained on the LDEQ Intranet and on the Laboratory Information Management System. Copies, whether in electronic or printed form (unless issued by the LSD QAO and stamped controlled), are not official and should be verified by the LSD QAO. The Control Header of the SOP will be used for comparison to the official document.

Amy A. Knight 6-24-9

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6-24-9

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Approved By: Elaine Sorbet, Quality Assurance Officer. — Date

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Approved By: James Brent, PhD, Division Administrator — Date

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)

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

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.

Exhibit 3

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**

Please Note: The official version of this document is maintained on the LDEQ Intranet and on the Laboratory Information System. Copies, whether in electronic or printed form (unless issued by the LSD QAO and stamped controlled), are not official and should be verified by the LSD QAO. The Control Header of the SOP will be used for comparison to the official document.

6/22/09
Document Owners: Michelle McCarthy and Hsing-Fong Liu, Env. Scientists 3 Date

6-22-9
Process Owner: Randy Creighton, Env. Scientist Supervisor Date

6-22-09
Approved By: Leonard Killmer, Env. Scientist Manager Date

6-24-09
Approved By: Elaine Sorbet, Quality Assurance Officer Date

6/24/09
Approved By: James Brent, PhD, Division Administrator Date

Annual Document Reviews:

Changes made, if any:

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

2nd 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.

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

_____

4th 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.

_____

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 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-cichloropropylene
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^{0}C to concentrate the VOCs, CO_2, and H_2O into roughly a 0.50 ml sample. The glass bead trap is then heated to 10$^°$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^{0}C to retain VOCs while letting 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 (<0.3μl). 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

Mass	Abundance Ratio
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 μl 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 cryotraps, 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	Measured Value	DEV ($L1)
	ppbv	ppbv	%
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 ±0.33 minutes of the mean RT and the internal standard (IS) area must be ±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 to120% 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 Location: *Kenner*
Sample Collection Date: *04/05/2006* Sample Type: *24 hours*

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

Comments:

2nd reviewer: 3rd 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 ±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 ±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 tp 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

Bromochloromethane

LEVEL	Xi	(Xi-Ave.)/Ave	Status
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**

Average = 399260
Avg-40%= 239556
Avg+40%= 558964

1,4-diflourobenzene

LEVEL		(Xi-Ave.)/Ave	Status
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**

AVG= 823564
Avg-40%= 494138
Avg+40%= 1152989

d5-Chlorobenzene

LEVEL	Xi	(Xi-Ave.)/Ave	Status
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**

Average = 571450
Avg-40%= 342870
Avg+40%= 800030

Surrogate QC Check

LEVEL	Xi	% Recovery	Status
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**	

Level	Data File
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:

$$X = Aut * Cb/Ab$$

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 fileTOX_99 in drive A and click on **OK**. Print a copy of GRF files generated and then exit **Instrument Converson**.

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 Bacthing** 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 Manaul 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.

Standard Operating Procedure

for

Cleaning Regular and Silico-Canisters Using Xontech 960

Please Note: The official version of this document is maintained on the LDEQ Intranet and on the Laboratory Information Management System. Copies, whether in electronic or printed form (unless issued by the LSD QAO and stamped controlled), are not official and should be verified by the LSD QAO. The Control Header of the SOP will be used for comparison to the official document.

Document Owners: Manfredo Giaccio and Jerry Knight, Env. Sci. 3 — Date: 10/1/2009

Process Owner: Randy Creighton, Env. Scientist Supervisor — Date: 10-1-9

Approved By: Leonard Killmer, Env. Scientist Manager — Date: 10-1-2009

Approved By: Elaine Sorbet, Quality Assurance Officer — Date: 10-1-09

Approved By: James H. Brent PhD, Division Administrator — Date: 10-1-09

Annual Document Reviews:

Changes made, if any:

1st Review: Corrected errors; added the sub-section of batching on 08/15/2005.

_____

2nd Review : Made some minor modification on 08/22/2006.

_____

3rd Review : Added a Notepad file to help batching; added a summery of canister cleaning history table for better record keeping; added contents in 2.0, 7.0, 11.0, 17.0 and 21.9; made some other minor modifications on 08 /22/2007.

_____

4th Review : Reviewed on 09/15/2008. No change has been made.

5 th Review : Section 22.1, clarified documentation requirements.

Changes Reviewed and Approved by:

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

Table of Contents

1.0 Identification of Test Method

This standard operating procedure has been developed for cleaning regular and silico-canisters using Environmental System Inc's (previous name is Xontech) eight and twelve canister cleaning systems based on EPA 600-R-98/161: Technical Assistance--Documentaton for Sampling and Analysis of Ozone Precursors.

2.0 Applicable Matrices

VOC free zero air or nitrogen.

3.0 Detection and Quantitation Limits

The analysis on the control sample is done with LDEQ 1026 "GC/FID" for ozone precursor analysis. The method detection limit (MDL) for the method is determined according to Title 40CFR, Part 136. MDLs for the target ozone precursors are typically 1 ppbC with several compounds probably over 1 ppbC but under 2 ppbC. The quantitation limits are 5 ppbC.

4.0 Scope and Application

This procedure is applicable to 6 liter and 15 liter regular (SUMMA and Silonite) or silico–canisters. A 6 liter canister containing 1000 ppmC of VOCs has been satisfactorily cleaned using this procedure.

5.0 Summary of Method

The systems clean canisters using three cycles. Each cycle consists of evacuating and filling the canisters with clean air or nitrogen depending on type of canisters. The final evacuation, high vacuum finish (HVF), vacuums canisters down to 35 mtorr to prepare the canisters for sampling. The dirtiest canister in a batch is selected as a control sample. The canister is filled with clean air and submitted for FID analysis. If the analytical results meet the criteria for total non-methane organic compounds left, the batch is validated and the canisters are released.

6.0 Definition of Terms

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

6.2 Total non-methane organic compounds (TNMOC) –- the sum of ppbC of the targeted and untargeted compounds quantified.

6.3 Acceptance criteria -- specified limits placed on the amounts of hydrocarbons left in the canister being cleaned. Target ozone precursors: </=2 ppbC; TNMOC: </=20 ppbC.

6.4 Laboratory information management system (LIMS) -- software that makes laboratory data management easy and concise. This lab uses LABWORKS ES developed by Perkin Elmer, Inc.

6.5 Milliohm (mohm) – 1/1000 of an ohm. An ohm is a SI unit of resistance to the flow of an electrical current through a substance (e.g: distilled water. The mohm value is directly proportional to the purity of the water.) Highly pure water will have a resistivity in the mega ohm, not the milli ohm, range.

7.0 Interferences and Pretreatments

Interferences come from water, in-house zero air or nitrogen. High quality VOC free water must be used and also replaced regularly. Purity of In-house nitrogen or zero air will be tested by GC/FID or GC/MS.

8.0 Safety

8.1 For Lab Services Division's general policy, see SOP#1769.

8.2 Safety glasses and lab coats are required in all laboratory areas.

8.3 Canisters with pressures above 20 psig should be partially vented in a hood before processing.

8.4 Gloves should be worn when removing canisters and other hot items after the end of a run.

8.5 Standard precautions must be taken to prevent electrical shock.

8.6 Standard safety procedures must be followed when handling compressed cylinders.

8.7 Warning! Don't place a canister containing liquid in any system manifold. At 120 °C, we risk rapid boiling and development of excessive pressure. If the canister valve is closed, the system's relief valve cannot function risking an explosion.

9.0 Equipment and Supplies

9.1 Barcode readers "Symbol LS4278".

9.2 Zebra TLP2844 printer.

9.3 ONE XONTECH MODEL 960 Canister Cleaning Command Unit for 8 or 12 canister systems. It features:

9.3.1 A manifold with four canister connections immersed in an oven with a temperature controller in degrees Celsius set at 120 °C.

9.3.2 A rough pump and a high vacuum pump system.

Command Unit

9.3.3 A dial gauge pressure is measured with reference to atmospheric pressure. Zero gauge pressure is equal to atmospheric (barometric) pressure. If the pressure is positive, the scale of 0 to 30 psig is used; if the pressure is negative, the scale of 0 to 30 inches in Hg is used.

9.3.4 A Hastings vacuum gauge with a range from 0 to 1000 mtorr. Millitorr (mtorr) are defined as 1/1000 of a torr. A torr is a pressure unit used chiefly in vacuum technology being the pressure required to support one mm Hg (mercury) at 0°C.

9.3.5 The “Time Remaining” window displays the minutes left to completion.

9.3.6 The “Cycle Number” window displays the number of ongoing cycles

9.3.7 The “Start – Continuous” toggle switch allows the selection of automatic run vs. continuous run.

9.3.8 The “AIR – H_20” programming push wheel is used to set the first number of wet cycles.

9.3.9 The” DRY AIR” push wheel is used to set the following number of dry cycles.

9.3.10 The “MANUAL FILL – EVACUATE” toggle switch operates the MANUAL FILL MODE or the MANUAL EVACUATION MODE.

9.3.11 The “HIGH VACUUM FINISH” switch commands the high vacuum pump activation in the “DRY AIR” mode. When the system is operating, this switch must be ON (Red).

9.3.12 The” “POWER” switch turns the unit ON.

9.3.13 The humidifier trap provides the required moisture for the wet cycles. It must be checked at the beginning of the run.

9.4 MODEL 960 Canister Cleaning Auxiliary Units - additional units under control of the command unit. Each Auxiliary Unit holds four canisters. The twelve-canister system uses two auxiliary units. The eight-canister system uses one auxiliary unit. They feature the following items:

9.4.1 A manifold with four (4) canister connections immersed in an oven with a thermo – regulator in degrees Celsius set at 120 °C.

9.4.2 A “POWER” switch used to turn the unit ON.

9.5 One RM Environmental Systems, Inc. Canister Cleaning Unit for 8 and 12-canister systems.

9.6 Temperature controller AEOmega CN 9000A °F.

9.7 Brass and stainless steel ferrules of appropriate size.

9.8 Plastic tubing to fit canister’s connections.

10.0 Reagents and Standards

10.1 Gases

10.1.1 Air UHP Ultra Zero Grade from the gas network

10.1.2 Nitrogen UHP Ultra Zero Grade from the gas network

10.2 Reagent Water 18 Mohm

Auxiliary Unit

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

The cleaned canisters are stored in a designated room air conditioned at 25 °C. Whenever a canister is checked out, the canister inventory form (Table 3) must be filled out. 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 is leaking. The canister will be fixed and re-cleaned.

12.0 Quality Control

For each batch, the dirtiest canister is selected as a control sample. The canister is filled with dry clean air and submitted for FID analysis. If all the targeted compounds are less than or equal to 2 ppbC and TNMOC is less than or equal to 20 ppbC, the batch is validated and the canisters can be

released. If not, the second dirtiest canister is analyzed again. If the second fails again, troubleshoot the system and re-clean the batch.

13.0 Calibration

This section is deliberately left blank for reason of inapplicability.

14.0 Procedure

14.1 Create a Batch for Canisters to Be Cleaned

14.1.1 Verify that all of canisters for a batch are properly labeled with LIMS #.

14.1.2 Create a Notepad file that contains all LIMS # of the canisters in the batch (entering LIMS # either using a barcode reader or manually inputting). The file is saved as **Reservoir** in the local computer.

14.1.3 Select the dirtiest canister as a control sample. To do this, input the Notepad file **Reservoir** into LIMS to find the dirtiest canister. Double click on CR_Canister **in Folder View** in LABWORKS. In the next screen, select **External File** and click on **Browse**. Select file **Reservoir** from your local computer and then click on **View Selection**, followed by clicking on **Enter Selection**. **Canister Cleaning Report** will appear on the screen. This report lists total NMOC for all the canisters in the batch. The canister with the largest number of total NMOC will be the control canister. Note: if there is more than one canister that has the same total NMOC or the canisters in the batch are process canisters, simply randomly select one canister as the control sample.

14.1.4 Verify that all the canisters in the batch have finished with the assigned tests and are assigned with test code $Clean. To do this, input the Notepad file **Reservoir** into LIMS again. Select **Modify/Delete Sample** from **Maintenance** menu in LABWORKS. In the next screen, select **External File** and click on **Browse**. Select file **Reservoir** from your local computer and then click on **View Selection**, followed by clicking on **Enter Selection,** icon for **Modify selected samples, Multisample spreadsheets** and **Analysis order.** A spreadsheet will show the information whether or not the assigned tests are completed and the test code $Clean is assigned. If not, consult with the supervisor.

14.1.5 Select QA **Batching** from **QA/QC** menu in LIMS.

14.1.6 Click on the icon for **Specify new batches by sample**.

14.1.7 Select **External File** and click on **Browse.**

14.1.8 Select file **Reservoir** from your local computer.

14.1.9 Click **Enter Selections**, followed by clicking on **Enter Selection.**

14.1.10 Click on **…** for **All analyses assigned to samples.**

14.1.11 Click on test code **$Clean.**

14.1.12 Click on icon **Create new batches,** followed by clicking on **OK**.

14.1.13 Ensure that **Batch size #** is not smaller than **Number Samples** and then click on **OK**.

14.1.14 Point to the dirtiest sample and left click on it. This sample will appear in the cell of **QA Sample**. This sample will be automatically assigned with additional test code $CLTNMOC.

14.1.15 Click on **OK.** Now you have created a batch for canister cleaning. Print a hard copy of the batch and check for accuracy. Record the batch information in the **Canister Cleaning Worksheet** shown in Table 1.

14.2 Operation

14.2.1 Fill the worksheet shown in Table 1 beginning with the analyst initials, the date. Circle the system used and the number of canisters processed. Select the gas used and cross the one not in use.

14.2.2 Verify that the pressure in the line is 40 to 50 psig and the lines are appropriately open.

14.2.3 Verify that the humidifier contains enough water, up to the **fill line**. System 1 allows removal of the humidifier and therefore water can be filled directly. Systems 2, 3 and 4 require a siphon to change the water as necessary for maintenance.

14.2.4 Verify that the HIGH VAC FINISH switch is ON (red).

14.2.5 If the batch contains only regular canisters, use air and a setting: 2 Air-H2O, 1 Dry Air cycles.

14.2.6 If the batch contains regular and silico-canisters, use the same gas and settings but do not heat the silico-canisters.

14.2.7 If the batch contains only silico-canisters, use nitrogen with settings: 0 Air-H2O cycles and 3 Dry Air cycles.

14.2.8 Connect all canisters to the pressure hoses. Do not over tighten the fittings.

14.2.9 Close the ovens to be heated, top with the insulating covers and wrap the insulating “socks” around the gaps.

14.2.10 Pressure leak test: with the power still off, close all canister valves. Pressurize the system by opening the valve of a pressurized canister with a gauge reading of at least 15 psig and

then close the canister's valve. Wait 2 minutes and note the gauge reading again. Record the reading in the worksheet (Table 1). Any pressure drop of more than 0.5 psig should require troubleshooting guidelines.

14.2.11 Vacuum leak test:

- Set the push-wheel of the AIR/H_2O cycle to 0.
- Set the push-wheel of the DRY AIR to 0.
- Ser the HIGH VAC FINISH switch ON (Red).
- Turn the power ON. Leave all the canister valves closed.
- Press the the "evacuate button" ON. This will start a 30 minutes evacuation procedure.
- Wait until 22 minutes before the end of the cycle and take the reading in the Hastings vacuum gauge. Record the reading in the worksheet (Table 1).
- A final pressure should be less than 35 mtorr and must be less than 50 mtorr.

14.2.12 Once the system has been found leak proof, open all canisters.

14.2.13 Turn the heaters ON.

14.2.14 Turn the start switch ON.

14.2.15 After 2 hrs 58 min (2 min before the end of the process) the system will attain final vacuum. Record the pressure from Hastings Manometer in the worksheet.

14.2.16 Close all the canisters.

14.2.17 Remove the canisters from the ovens.

14.2.18 Fill the control canister with dry zero air and submit it for FID analysis.

14.3 Troubleshooting Guidelines

14.3.1 Check that all line connections are tight. If any are loose, retighten, and then retest. In pressure testing, SNOOP™ can be used to detect a leak by applying it on individual fittings. Bubbles will show at the leaking site when the system is pressurized. SNOOP should not be used on canisters due to the risk of contaminating them during the vacuum cycle.

14.3.2 From all the auxiliary units, choose the most remote auxiliary unit from the Command Unit. Disconnect the unit from the manifold line and cap manifold line. THEN, test the system again.

TABLE 1 CANISTER CLEANING WORKSHEET

Air Organics, LSD, LOUISIANA DEQ

Analyst	
Run Time, Date	
System	1 , 2 , 3 or 4
Gas/Pressure	Air, Nitrogen/
Settings (WetCyc/DryCyc)	2 /1 or 0/3
Trap	
HVFnsh	
Batch Number	$Clean-
Number of the Canisters Batched	8 or 12
Leak Check/Starting–Ending Pressure	
Vaccum Leak Check: mTorr/min left	
FinalVac (mtorr)	
The first Canister for Certification (LIMS #/Canister #)	
TNMOC of the first Certified Canister	
Certified by FID/Analyst	
Data File:	
The second Canister for Certification (LIMS#/Canister#)	
TNMOC of the second Certified Canister	
Certified by FID/Analyst	
Data File:	
Date of Canisters-Releasing	

Comments:

Reviewed by: Date:

14.3.3 If no leaks are found, the problem is isolated to Auxiliary Unit 2.

14.3.4 If the leak persists, it could be either Auxiliary Unit 1 or the Command Unit. (NOTE: Leaks can also be found in the valves of canisters. If the leak cannot be found, disconnect all canisters one by one; plug the lines, and then retest.)

14.3.5 Proceed as above closing the connection between the Command Unit and Auxiliary Unit 1 by first disconnecting the two units and capping the main manifold line. Retest for leaking. (EXCEPTION: It has been noticed on several occasions that all lines passed leak tests, but pressure would not stabilize. This problem was due to the vacuum pumps' valves incorrectly sealing. By starting the vacuum cycle and letting the pump motor run several minutes, then ending the cycle, the system probably sealed itself without any further leaks.).

14.3.6 By following a leak will be quickly isolated. This will indicate which auxiliary unit, or possibly the command unit, is leaking. When the leaking unit is isolated, leak test the individual lines. Remove the individual line from the manifold, plug the connection, and retest the unit.

15.0 Evaluation of Data, Reporting Results and Calculations

15.1 The FID results for the control sample in a batch must meet the criteria specified in 12.0. Record the analytical results in the worksheet (Table 1).

15.2 If the control sample doesn't meet the criteria in 12.0, select the second dirtiest sample in the batch and submit it for FID analysis. Record the result in the worksheet. If the FID meets the criteria, modify the batch, that is, remove the first control sample from the batch and designate the second dirtiest canister as the control sample.

15.3 If the second dirtiest control doesn't pass the criteria, trouble instruments and re-clean the batch.

15.4 Enter Results into LIMS

15.4.1 From **Results** menu in LIMS, select **Results Entry** and click on **Batch Numbers**. Enter manually the batch number.

15.4.2 Click on **Find** and **Check All**.

15.4.3 Click on **View Selections.** Verify that the batch corresponds to the Worksheet and then click on **Enter Selection**.

15.4.4 A window **Results Entry** opens. Right click on the first sample cell in $CLEAN column and select **Enter or load results** from the coming menu.

15.4.5 A new dialog box shows the headings: **Component Result Entry** for the given sample at the given location.

- Start date is to be changed only in the first sample of the batch.
- Start Time is to be changed only in the first sample of the batch.
- End date is automatically set by the computer. However there is a small discrepancy that can be corrected directly. Also this correction holds for the first sample of the batch. The rest of the batch is automatically dated.

15.4.6 Manually enter the TNMOC and LIMS # for the control sample. The results can also be entered automatically using a barcode reader. To do so, create two barcodes for TNMOC and LIMS# by going to **Create Bar Code List** in **Utilities** menu. Save the entries by clicking on **Store Results**. Continue this process for each sample in the batch to completion.

15.4.7 On the **Results Entry** form, there is a second column **$CLTMNOC**. There is only one entry (TNMOC) in this cell. Manually or automatically enter the number.

15.4.8 Stamp the canister tags with the cleaning date and release canisters.

16.0 Method Performance

Refer to 18.0.

17.0 Pollution Prevention

Refer to LSD's Lab Waste Disposal SOP_1197.

18.0 Data Assessment and Acceptance Criteria

The final absolute pressure in the canisters must be less than 50 mTorr.

The FID results for the control sample in a batch must meet the criteria specified in 12.0.

19.0 Corrective Action for Out of Control Data

Should the concentration be at or above the limit, a second canister from the batch will be analyzed by FID. If the second canister passes the criteria, release the canisters in the batch except the first canister that was selected for certification. Re-clean the canister. If the second canister fails again, troubleshoot the instrument, re-clean the entire batch.

20.0 Contingencies for Handling Unacceptable Data

This section is deliberately left blank for reasons of inapplicability.

21.0 Waste Management

Refer to LSD's Lab Waste Disposal SOP_1197.

22.0 Data and Records Management

22.1 The canister cleaning worksheet is clipped together with the FID quantification report and a full report from Results Entry, containing each sample in the batch and all methods used during the certification marked "Done". This record will be kept in Laboratory Services Division for 10 years. The information is also maintained by, and available through, Laboratory Services Division, or the LIMS.

22.2 For each cleaning system, a database file (Table 2) that summarizes the cleaning history is maintained. This file contains the information of date of cleaning, batch number, total number of samples, LIMS# of the control sample, initial concentration of the control and analysis results. This database serves as reference for gaining access to **Canister Cleaning Worksheets**. In column **TNMOC of Control Canister,** zero is assigned if all the canisters in the batch are process/voided samples.

22.3 Canister inventory forms (Table 3) are placed in the room for the cleaned canisters. The form must be filled whenever a canister is checked out. The first line shows an example how the form is filled out. The filled forms will be kept in the secretary's office (A-05) to keep track of the canister flow.

23.0 Tables, Diagrams, Flowcharts, and Validation Data

Tables and diagrams are inserted in this SOP. Data are validated by the supervisor or the manager.

TABLE 2 SUMMERY OF CLEANING HISTORY FOR SYSTEM 1

Cleaning Date	Batch Number	Total Number of Canisters	LIMS # of Control Canister	TNMOC of Control Canister	FID Results
3/1/07	151080	12	AK03684	161	4.61
3/6/07	151342	12	AK03689	1237	2.52

TABLE 3 CANISTER INVENTORY

Canister #	Site	Date Out	Print Name	Initials
10010	LSU	08/16/07	R. Bailey	*REB*

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 of Methods for the Determination of Toxic Organic Compounds in Ambient Air. Compendium Method TO-15. Determination of Volatile Organic Compounds (VOCs) In Air In Specially-Prepared Canisters and Analyzed By Gas Chromatography/Mass Spectroscopy (GC/MS). EPA-625/R-96/010b. Center for Environmental Research Information, U.S. Environmental Protection Agency. Cincinnati Ohio: June 1999.

24.4 Cleaning and Certification of Specially Prepared Canisters for Air Sampling. Standard Operating Procedure #312. USEPA REGION 9 LABORATORY. Richmond, CALIFORNIA. Rev. #0. Date: 07/08/99.

Exhibit 5

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
REGION 6
1201 ELM STREET, SUITE 500
DALLAS, TEXAS 75270

January 16, 2024

William L. Felicien
Environmental Scientist Senior
Air Planning and Assessment Division, Louisiana DEQ
602 North 5th Street, Galvez Building
Baton Rouge, LA 70802

Dear Mr. Felicien:

The Louisiana Division of Environmental Quality (LDEQ) Quality Assurance Project Plan (QAPP) Photochemical Assessment Monitoring Stations (PAMS) and Air Toxics Sampling Network, Q-Trak No. 24-061. I am pleased to inform you that the QAPP has been reviewed and approved by Brenton Gildner, R6 Air QA Coordinator, Region 6, EPA. The QAPP has an expiration date of February 10, 2026.

Please send all QAPP's **sixty days prior to** the expiration of the recipient's approved QAPP, if there are any significant changes to operating procedures or regulations, please submit earlier than sixty-days. The recipient shall submit to the Project Officer a revised QAPP or certification that the QAPP is current and include a signed copy of the new approval page(s) for the QAPP.

Please find attached your digitally signed QAPP signature page(s), should you have any questions, please call me at (214) 665-8453.

Sincerely,

TERRIE WRIGHT
Digitally signed by TERRIE WRIGHT
Date: 2024.01.16 07:28:57 -06'00'

Terrie Wright
Project Officer
Air Grants Section

cc: Grant File

QUALITY ASSURANCE PROJECT PLAN

FOR

PHOTOCHEMICAL ASSESSMENT MONITORING STATIONS (PAMS)

AND

AIR TOXICS SAMPLING NETWORK

Louisiana Department of Environmental Quality
Office of Environmental Assessment
Office of Environmental Compliance

Revision: 19
November 2023

Document Review and Revision Record

Note: Actions older than 5 yrs may be removed from this record

Date	Revision No.	Record of Activity
3/5/2001	1	Initial document approved. This QAPP for the VOC analysis of PAMS was separated from a previous larger combined QAPP. The LDEQ Air Toxics Program was added to this QAPP.
8/31/2012	9	Specified onsite performance auditing activities in Section A4.0, removed all references to EPA's activities in Section D3.2 and made some other minor changes asked by EPA region 6 after their initial review.
7/03/2013	10	Updated and clarified Tables A3 and C2. Made some other minor changes.
6/26/2014	11	Updated Table A1 and Section A9.1.2. Made some other minor changes.
6/23/2015	12	Updated names of some units at LDEQ and made some other minor changes.
8/2/2016	13	Discontinued PAMS monitoring at Bayou Plaquemine and Pride; replaced Hahnville with Kenner in Table A3; removed the NOx monitoring at the LSU and Carville in Section A6; made some other changes including personnel and Division name.
11/3/2017	14	Made changes to accommodate LDEQ's re-organization and also made some other minor changes.
10/31/2018	15	Only several minor changes made.
11/19/2019	16	Marrero and St. Rose sites added to Table 3 and the contract lab name changed.
11/23/2020	17	No changes
11/26/2021	18	No changes
11/27/2023	19	No changes

A PROJECT MANAGEMENT

A1 Title and Approval

**QUALITY ASSURANCE PROJECT PLAN
FOR
PHOTOCHEMICAL ASSESSMENT MONITORING STATIONS
AND
TOXICS SAMPLING NETWORK**

Approved by:

_____ Date: 12/05/2023
William L. Felicien, Environmental Scientist Senior
Air Planning and Assessment Division
Office of Environmental Assessment
Louisiana Department of Environmental Quality

_____ Date: 12/05/2023
Peter Cazeaux, Environmental Scientist Manager
Air Field Services Section
Air Planning and Assessment Division
Office of Environmental Assessment
Louisiana Department of Environmental Quality

_____ Date: 12/5/23
Jason Meyers, Administrator
Air Planning and Assessment Division
Office of Environmental Assessment
Louisiana Department of Environmental Quality

_____ Date: 12/6/23
Brian Tusa, Administrator
Surveillance Division
Office of Environmental Compliance
Louisiana Department of Environmental Quality

MICHAEL GILDNER Digitally signed by MICHAEL GILDNER
Date: 2023.12.12 07:40:03 -06'00' Date: _____
Brenton Gildner
Region 6, Ambient Air Program Quality Assurance Coordinator
U.S. Environmental Protection Agency

A2 Table of Contents

LIST OF FIGURES

LIST OF TABLES

A3 Distribution List

An electronic copy of this QAPP will be maintained on the LDEQ's QA Intranet Website. It will be available to all LDEQ personnel. The following individuals will be notified of the posting:

William Felicien, Environmental Scientist Senior
Air Planning and Assessment Division
Office of Environmental Assessment
Louisiana Department of Environmental Quality

Peter Cazeaux, Environmental Scientist Manager
Air Field Services Section
Air Planning and Assessment Division
Office of Environmental Assessment
Louisiana Department of Environmental Quality

Jason Meyers, Administrator
Air Planning and Assessment Division
Office of Environmental Assessment
Louisiana Department of Environmental Quality

Randy Creighton, Environmental Scientist Senior
Laboratory Information Management Services
Surveillance Division
Office of Environmental Compliance
Louisiana Department of Environmental Quality

Brian Tusa, Administrator
Surveillance Division
Office of Environmental Compliance
Louisiana Department of Environmental Quality

All PAMS and Air Toxics Monitoring Network site operators
Louisiana Department of Environmental Quality

A printed or PDF versions of the QAPP will be distributed to the following:

Terrie Wright, Project Officer
Air Quality Programs, U.S. Environmental Protection Agency, Region 6

LDEQ’s Contractor for Analysis of PAMS and Air Toxics Canister Samples,
SGS North America Inc., Houston.

A4 Project/Task Organization

The Louisiana Department of Environmental Quality (LDEQ) is responsible for establishing air monitoring stations statewide, which includes Photochemical Assessment Monitoring Stations (PAMS) and air toxics monitoring stations. The purpose is for gathering data to demonstrate compliance with Louisiana Ambient Air Standards (LAAS) and National Ambient Air Quality Standards (NAAQS) as required by the Clean Air Act Amendment (CAAA) of 1990.

LDEQ's Office of Environmental Assessment (OEA) and Office of Environmental Compliance (OEC) shall develop and manage the Quality Assurance Project Plan (QAPP), and perform operation of the air-monitoring network. The OEA's Air Planning and Assessment Division (APAD) is responsible for the network's field operation, data assessment, data management and reporting. The OEC's Surveillance Division (SD) is responsible for reviewing, validating and managing data generated by LDEQ's contract laboratory for analyses of the canister samples for speciated volatile organic compounds (VOCs), including ozone precursors and air toxic compounds.

This document focuses on the monitoring/sampling activities related to canister samples for speciated VOCs, continuous gas chromatography with flame ionization detector (GC/FID) for hourly total non-methane organic compounds (TNMOCs) at the PAMS sites and meteorological parameters that pertain to the LDEQ PAMS and Air Toxics sampling network. Figure A1 shows the organization chart responsible for this project. Activities related to ozone and oxides of nitrogen monitoring that are referred to in this QAPP can be found in LDEQ's *Quality Assurance Project Plan for the Ambient Air Monitoring Project.*

A4.1 Description of Organization

A4.1.1 Air Field Services Section

The APAD Air Field Services (AFS) Section is supervised by an Environmental Scientist Manager and is assisted by Engineer Supervisors and Environmental Scientist Supervisors.

This section provides engineering for proper sampling station siting, construction and installation. Each year, an evaluation of each monitoring site is conducted to ensure that site documentation is updated and that all siting criteria continue to be met.

The Air Toxics PAMS Monitoring Unit is responsible for the field operation of the continuous GC/FID for hourly TNMOCs and canister samplers at the PAMS sites. The canister samplers at these PAMS sites are those for regular 3-hour samples for ozone VOC precursors, 24-hour samples for ozone VOC precursors and VOC

air toxic compounds, and event-based samples for ozone VOC precursors and VOC air toxics. The event-based samplers are “triggered” whenever the 10-minute average TNMOC readings of a continuous methane/TNMOC analyzer (Thermo Environmental 55C) exceed the preset value.

The Site Operations Unit is responsible for the field operation of meteorological equipment and continuous methane/TNMOC analyzers for all the sites across the state. It is also responsible for the field operation of 24-hour regular and event-based canister samplers for the other sites across the state not covered by the Air Toxics PAMS Monitoring unit.

The Air Data Analysis Unit in this section consists of an Engineer Supervisor, Engineers, Environmental Chemical Specialists, Environmental Scientists and Instrument Support Staff. This unit is responsible for all operations concerned with collection, verification, validation and reporting of data from LDEQ ambient air monitoring sites. Reduced data from continuous GC/FID TNMOC analysis and from VOC analysis of canister samples are submitted to this unit for evaluation. The evaluated and validated data are submitted to the US EPA in Air Quality Systems (AQS) database format. The Instrument Support Staff are responsible for repairing malfunctioning equipment brought to the electronics repair lab.

The onsite performance audits for AFS are done by URS Corp under contract. The monitoring operations not covered by URS are audited by AFS staff. The auditing staff must be Environmental Scientists (3) or above and not be the staff who perform the audited operations.

A4.1.2 Surveillance Division

The LDEQ contractor, SGS North America Inc., Houston (its previous names were SGS Accutest Gulf Coast, Inc., Houston), will be responsible for analysis of all canister samples. The contractor is accredited by Texas’s Environmental Lab Accreditation Program under National Environmental Laboratory Accreditation Conference (NELAC). Specific air methods for LDEQ’s canister samples are accredited by Louisiana Environmental Laboratory Accreditation Program (LELAP).

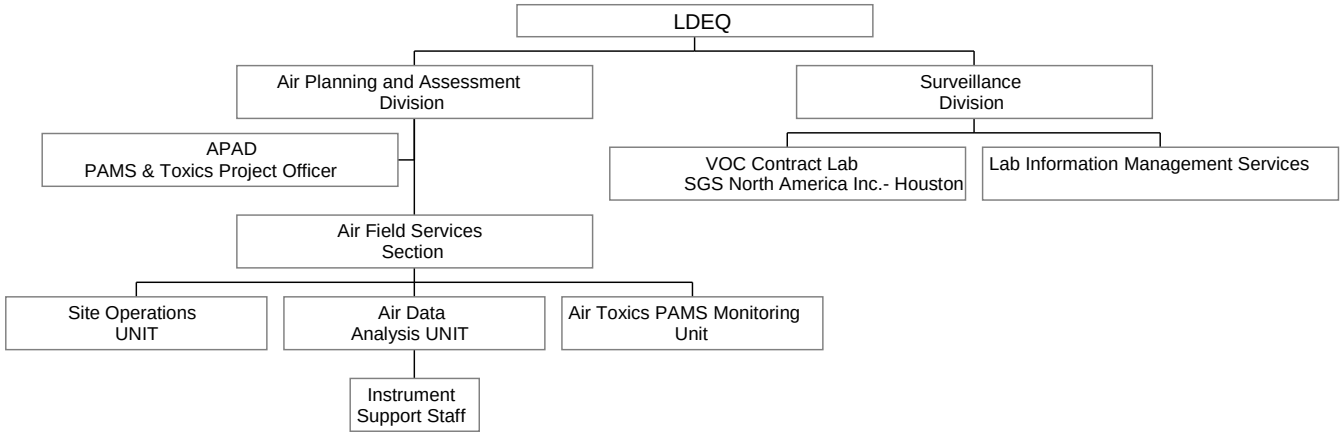
SD’s Laboratory Information Management Services receives speciated VOC data from the contract lab. The data are reviewed and validated by the SD staff. The validated data are stored in LDEQ’s EQuIS database. The data is then sent to APAD PAMS & Toxics project officer for further review and assessment. After final assessment, APAD staff will submit PAMS data to EPA.

Laboratory Information Management Services manages the EQuIS database and all the documents, electronic or printed, from the contract lab.

LDEQ is responsible for ensuring all activities included in this QAPP, including any corresponding contracted out work, meet the latest 40 CFR Part 58 and the QA Handbook Volume II requirements.

Figure A1

Project Organization



A5 Problem Definition/Background

A5.1 Louisiana PAMS Network

Between 1900 and 1970, the emissions of six principal pollutants increased significantly. These six principal pollutants are particulate matter, sulfur dioxide, carbon monoxide, nitrogen dioxide, ozone and lead. They are also called criteria pollutants. In 1970, the Clean Air Act (CAA) was signed into law. The CAA and its 1990 amendments provide the framework for all pertinent organizations to protect air quality. The framework provides for the monitoring of these criteria pollutants in Louisiana by state and local organizations through the LDEQ ambient air-monitoring program. The background and rationale for ambient air monitoring can be found in the Code of Federal Regulations Title 40, Part 58.

Louisiana's parishes have historically been in compliance with the Ozone NAAQS except for one area. This nonattainment area is the Baton Rouge, Louisiana metropolitan statistical area (MSA) which includes the parishes of Ascension, East Baton Rouge, Iberville, Livingston and West Baton Rouge. In 1991, the Baton Rouge

was designated nonattainment and was classified as a serious ozone nonattainment area. The attainment date for the Baton Rouge was November 1, 1999. In 2001, this area was re-classified as severe for ozone non-attainment since it failed to achieve attainment by the 1999 target date as defined in the Clean Air Act Amendment (CAAA) of 1990 for the one-hour standard. In 2004, the EPA revised the standard to a more stringent 8-hour standard, at the same time revoking the 1-hour standard. The Baton Rouge MSA reached attainment of both the 1-hour standard and the 1997 8-hour standard in December 2008 and was re-designated to attainment with the 1997 8-hour standard by EPA in 2011. In 2008, EPA revised the standard and the area was once again designated as nonattainment. On December 31, 2011, the area reached attainment with the 2008 8-hour ozone standard and EPA issued a Clean Data Determination. In December, 2016, EPA re-designated the Baton Rouge MSA to attainment for the 2008 8-hour ozone standard and also approved the state's 10-year plan for maintaining attainment of the 2008 8-hour ozone standard in the area. In October 2015, EPA revised the ozone standard to the 8-hour average concentration of 70 ppb. In March, 2018, EPA designated the Baton Rouge MSA to attainment for the 2015 8-hour ozone standard.

The PAMS network was required in each ozone non-attainment area designated serious, severe, or extreme. The PAMS sites provides enhanced ambient air monitoring of ozone (O_3) and oxides of nitrogen (NO_x), monitoring of VOCs and TNMOCs, and measurement of meteorological parameters. The purpose is to determine the extent of the effect ozone precursor compounds have on the formation of ozone. Louisiana DEQ established a PAMS site at Capitol as early as June 1, 1993. Since 2001, Louisiana DEQ had been operating the PAMS network including three PAMS sites, Capitol, Bayou Plaquemine and Pride to meet PAMS requirements for the severe reclassification even though the above-mentioned progress in reducing ozone was made through these years but because of the provisions of anti-backsliding. In 2009, Louisiana added another PAMS site, Dutchtown and this addition exceeded the PAMS minimum requirements for the Baton Rouge MSA. The PAMS site Dutchtown has been also operating since 2009. According to the final rule for the National Ambient Air Quality Standards for Ozone dated October 26, 2015, and effective December 28, 2015 (Federal Register Vol. 80, No. 206, October 26, 2015, pgs 65292-65468), the Baton Rouge MSA is currently not subject to the PAMS monitoring provisions found in 40 Code of Federal Regulations Part 58, Appendix D, Section 5. In March, 2016, LDEQ sent a request to EPA Region 6 to discontinue PAMS monitoring effective May 1, 2016 at the Pride and Bayou Plaquemine sites, but continue PAMS monitoring at Dutchtown and Capitol sites, which will provide ozone and ozone precursor concentration data for the Baton Rouge MSA. This area exceeds the 2015 8-hour ozone standard with a preliminary 2013-2015 8-hour ozone design value of 71 ppb. The EPA Region 6 approved the request in April, 2016.

The objectives of the PAMS network are as follows:

- NAAQS Attainment and Control Strategy Development
  - ✓ Provide an air quality database to help assess ozone attainment status.
  - ✓ Extend the air quality database for future attainment demonstrations.
  - ✓ Characterize ozone and precursor transport.
  - ✓ Support photochemical model input requirements and model performance for future attainment demonstrations and control strategy development.

- State Implementation Plan (SIP) Control Strategy Evaluation
  - ✓ Evaluate effectiveness of various control strategies.
  - ✓ Assist in developing cost-effective VOC and NOx reductions.
  - ✓ Provide additional information to demonstrate “Reasonable Further Progress” (RFP) toward attainment of NAAQS for ozone.
  - ✓ Corroborate and assess accuracy of VOC and NOx emission inventories.

- Trends
  - ✓ Prepare long-term ozone, VOC, NOx and toxic air pollutant trends.
  - ✓ Improve effectiveness of the trends database.

- Exposure Assessment
  Characterize population exposure to ozone and toxic air pollutants.

With the end use of the air monitoring data as a prime consideration, the PAMS network is designed to meet one or more of the five basic monitoring objectives listed below:

- Determine the highest concentrations to occur in the area covered by the network.
- Determine representative concentrations in areas of high population density.
- Determine the impact on ambient pollution levels of significant source or source categories.
- Determine general background concentration levels.
- Determine the extent of regional pollutant transport among populated areas, and in support of secondary standards.

A5.2 Louisiana Air Toxics Program

There are currently 187 hazardous air pollutants (HAPs), or air toxics, regulated under the Clean Air Act (CAA) that have been associated with a wide variety of adverse health effects, including cancer, neurological effects, reproductive and developmental effects, as well as ecosystem effects. These air toxics are emitted from multiple sources, including major stationary, area, and mobile sources, resulting in population

exposure to these air toxics as they occur in the environment. While in some cases, the public may be exposed to an individual HAP, more typically people experience exposures to multiple HAPs. Exposures of concern result not only from the inhalation of these HAPs, but also, for some HAPs, from multi-pathway exposures to air emissions.

In 1989, LDEQ proposed 100 air toxics to be regulated under ACT 184 of Louisiana. These 100 air pollutants were chosen because they represented approximately 99% of industrial toxic air release in the state. For these 100 pollutants, LDEQ not only set the Minimum Emission Rates (MER), but ambient air standards, which surpassed the federal regulations for air toxics promulgated later. ACT 184 allows the list to be revised by either additions or deletions and the standards to be updated. The current standards are listed in Title 33 Part III Table 51.2 of the State Environmental Regulatory Code.

Emissions data, ambient concentration measurements, modeled estimates, and health impact information are all needed to fully assess air toxics impacts and to characterize risk. Specifically, emissions data are needed to quantify the sources of air toxics impacts and aid in the development of control strategies. Ambient monitoring data are then needed to understand the behavior of air toxics in the atmosphere after they are emitted. Since ambient measurements cannot practically be made everywhere, modeled estimates are needed to extrapolate our knowledge of air toxics impacts into locations without monitors. Exposure assessments, together with health effects information, are then needed to integrate all of these
data into an understanding of the implications of air toxics impacts and to characterize air toxics risks.

To address the concerns posed by air toxics emissions and to meet the state's strategic goals, LDEQ has developed an Air Toxics Monitoring Program designed to characterize, prioritize, and equitably address the impacts of HAPs on the public health and the environment.

The principal objective for the Air Toxics Monitoring Program is to determine and ensure that all major urban and industrial areas of the state are in compliance with the state Ambient Air Standards. The monitoring network will primarily emphasize long-term measures of air quality. The major part of the effort to develop air quality and emissions data, therefore, will focus on year-round information. To provide maximum flexibility in data use, however, the data collection will be based on regular (e.g., every sixth day) collection of 24-hour samples throughout the year. Individual 24-hour data will be stored in LDEQ's EQuIS database.

A6 Project/Task Description

The following are the sampling stations in the Baton Rouge area and the parishes they are located in:

- LSU site in East Baton Rouge Parish (AQS code: 220330003; monitoring for O_3, TNMOC, wind direction and wind speed)
- Port Allen site in West Baton Rouge Parish (AQS code: 221210001; monitoring for O_3, NOx, TNMOC, wind direction and wind speed)
- USPHS, Carville site in Iberville Parish (AQS code: 220470012; monitoring for O_3, TNMOC, wind direction and wind speed)
- Convent site in St. James Parish (AQS code: 220930002); monitoring for O_3.
- New Roads site in Pointe Coupee Parish (AQS code: 220770001); monitoring for O_3, wind direction and wind speed)
- French Settlement site in Livingston Parish (AQS code: 220630002; monitoring for O_3, NOx, TNMOC, wind direction and wind speed)
- Capitol site in East Baton Rouge Parish (NCore and PAMS Type 2 site)
- Pride site in East Baton Rouge Parish (AQS Site Code 220330013: monitoring for NOx, TNMOC, wind direction and wind speed)
- Bayou Plaquemine site in Iberville Parish (AQS Site Code 220470009: monitoring for NOx, TNMOC, wind direction and wind speed)
- Dutchtown site in Ascension Parish (PAMS Type 1/3 site)

The Capitol monitoring station is a National Core Network (NCore) and PAMS Type 2 site. It is to be established near the predominantly downwind edge of the central business district or area of maximum precursor emissions from a large industrial area. The Capitol site (AQS site code: 220330009; Latitude & Longitude: 30° 27' 43.13" N 91° 10' 45.19" W) best meets this description and was established as a PAMS Type 2 site on June 1, 1993. The parameters monitored at this site are:

- Ozone (O_3)
- Oxides of nitrogen ($NO/NO_x/NO_2$)
- Total reactive nitrogen compounds (NOy)
- Carbon monoxide (CO) – trace level
- Sulfur dioxide SO2 – trace level
- Continuous methane/TNMOC by Thermo Environmental 55C
- Continuous hourly TNMOC by automated GC/FID
- 24-hour canister samples every six day
- Multi 3-hour canister samples
- Event-based “strike” canister samples

- Meteorological Parameters (MET):
  - ✓ Wind speed (WS)
  - ✓ Wind direction (WD)
  - ✓ Ambient temperature (T)
  - ✓ Relative humidity (RH)
  - ✓ Barometric pressure (BP)
  - ✓ Solar radiation (SR)
  - ✓ Ultra violet radiation (UVR)
  - ✓ Rainfall gauge
- Upper Meteorological Parameters of Mixing Heights

Because of higher ozone readings at Dutchtown site (AQS code: 220050004; Latitude & Longitude: 30° 13' 45.91" N 90° 57' 55.86" W), canister sampling for speciated VOCs was added to this site beginning on May 1, 2009. This site has been designated as a PAMS Type 1/3 site. The parameters monitored at this site are:

- Ozone (O_3)
- Oxides of nitrogen ($NO/NO_x/NO_2$)
- Continuous methane/TNMOC by Thermo Environmental 55C
- 24-hour canister samples every six day
- Multi 3-hour canister samples
- Event-based “strike” canister samples
- Meteorological Parameters (MET):
  - ✓ Wind speed (WS)
  - ✓ Wind direction (WD)
  - ✓ Ambient temperature (T)

A 24-hour VOC canister sample will be collected every sixth day at all the PAMS sites year round. Intensive PAMS sampling will take place from May 1 through September 30 with more 3-hour samples collected. During this intensive sampling period, at the Capitol site, eight 3-hour samples will be collected daily between the hours from midnight to midnight, LST (local standard time); at Dutchtown site, four 3-hour samples will be collected every 3rd day. For four 3-hour samples collected at Dutchtown, two 3-hour samples are collected from 3:00 am until 9:00 am and the other two 3-hour samples are collected from 3:00 pm until 9:00pm, LST. In the rest of the year, eight 3-hour sample will be collected every sixth day. Canister samples will be analyzed by LDEQ’s contract lab, SGS Accutest Gulf Coast Inc., Houston. Three-hour samples will generally be analyzed for ozone precursors only as shown in Table A1 by GC/FID. Table A1 has been updated in 2014 in accordance with EPA’s Memo in November, 2013: Revisions to the Photochemical Assessment Monitoring Stations Compound Target List. The list in the table includes all priority compounds, three optional compounds (acetylene, isopropylbenzne and n-undecane) and TNMOC (total non-methane organic compounds) in the 57 target compounds prior to the revisions. Table A1 also includes 1,3-butadiene

that is not a compound in the 57 target compounds prior to the revision but a new priority compound proposed in the EPA's 2013 memo. The compound, 1, 3-butadiene, will not be reported to EPA till EPA finishes its evaluation of the sampling and analytical methods for new priority compounds. If some 3-hour samples have large amounts of untargeted compounds or some targeted compounds are suspected to be incorrectly identified, the samples will be analyzed by GC/MS for the purpose of identification and confirmation. Twenty four-hour canister samples will be analyzed for ozone precursors shown in Table A1 by GC/FID and air toxic compounds shown in Table A2 by GC/MS. The data for ozone precursors are reported in parts per billion carbon (ppbC) and for air toxics in parts per billion (ppb or ppbv to be distinguished from ppbC).

Hourly TNMOCs are continuously monitored year round at Capitol site by GC/FID. The hourly continuous TNMOC data at the sites are collected by a computer interfaced with the analyzer and stored in a custom designed program. The data will be pulled into the computer in the office. Data for hourly TNMOC are reported as ppbC.

Thermo Environmental 55C/55i provides continuous monitoring of methane/TNMOC. Time average TNMOC data in minutes can be produced. The data is collected by a data logger. Ten-minute average TNMOCs are used to "trigger" a canister sampler. Whenever 10-minute average TNMOCs exceed the preset value, the data logger will send a signal to the canister sampler to collect the air sample for 25 minutes. The event canister sample will be analyzed for both ozone VOC precursors and air toxics as shown in Table A1 and Table A2.

The data logger will collect data for meteorological parameters. Meteorological parameters are calculated in miles per hour (mph) for wind speed, degrees for wind direction, degrees Celsius (°C) for temperature, % for relative humidity, inches of mercury (in. Hg) for barometric pressure, and watts per square meter (w/m^2) for solar radiation and ultra violet radiation.

In addition to sampling at the PAMS sites above-mentioned, LDEQ collects 24-hour canister samples every sixth day in 16 monitoring stations and 25-minute canister strike samples in 12 monitoring stations across the state as shown as in Table A3. In some of these stations, event-triggered strike canister samples are also collected. In French Settlement site, only event-based strike canister samples are collected. These samples will be analyzed for ozone precursors and air toxics by LDEQ's contract lab, SGS North America, Inc. Houston.

Table A3 summarizes the sites for VOCs across the state.

Table A1

PAMS VOCS Determined by GC/FID
Using SOP TAE006-03 Based on EPA /600-R-98/161

Ethylene	Benzene
Acetylene	2,2,4-Trimethylpentane
Ethane	Toluene
Propylene	Ethylbenzene
Propane	*m/p*-Xylene
Isobutane	Styrene
1-Butene	*o*-Xylene
1,3-Butadiene	Isopropylbenzene (Cumene)
n-Butane	*m*-Ethyltolene (1-Ethyl-3-Methylbenzene)
trans-2-Butene	*p*-Ethyltolene(1-Ethyl-4-Methylbenzene)
cis-2-Butene	*o*-Ethyltoluene(1-Ethyl-2-Methylbenzene)
Isopentane	1,2,4-Trimethylbenzene
n-Pentane	1,2,3-Trimethylbenzene
Isoprene(2-Methyll-1,3-Butadiene	*n*-Undecane
n-Hexane	TNMOC

Table A2

Air Toxics VOCs Determined by GC/MS Using SOP TAE007-04 Based on EPA Method TO-15

Freon-12	Carbon Tetrachloride
Chloromethane	2-Nitropropane
Freon-114	1,2-Dichloropropane
Vinyl Chloride	Trichloroethylene
1,3-Butadiene	Methyl Methacrylate
Bromomethane	*cis*-1,3-Dichloropropene
Chloroethane	4-Methyl-2-Pentanone
Acetonitrile	*trans*-1,3-Dichloropropene
Acetone	1,1,2-Trichloroethane
Freon-11	Toluene
Acrylonitrile	Ethyl Methacrylate
Diethyl ether	2-Hexanone
1,1-Dichloroethene	1,2-Dibromoethane
Methylene Chloride	Tetrachloroethylene
Allyl Chloride	Chlorobenzene
Carbon Dislufide	Ethylbenzen
Freon-13	*m/p*-Xylene
1,1-Dichloroethane	Styrene
MTBE	*o*-Xylene
Methacrylontrile	1,1,2,2-Tetrachloroethane
2-Butanone	1,3,5-Trimethylbenzene
cis-1,2-Dicloroethane	1,2,4-Trimethylbenzene
Methyl Acrylate	Benzyl Chloride
Chloroform	1,3-Dichlorobenzene
Tetrahydrofuran	1,4-Dichlorobenzene
1,2-Dichloroethane	1,2-Dichlorobenzene
Chloroacetonitrile	Nitrobenzene
1,1,1-Trichloroethane	1,2,4-Trichlorobenzene
Chlorobutane	1,3-Hexachlorobutadiene
Benzene	

Table A3

Monitoring Sites for Speciated VOCs

Site	Strike Sampling	24-hour Canisters for Air Toxics	24-hour Canisters for Ozone Precursors	AQS Site Code
Capitol	Yes	Yes	Yes	220330009
Bayou Plaquemine	Yes	Yes	Yes	220470009
Pride	Yes	Yes	Yes	220330013
Dutchtown	Yes	Yes	Yes	220050004
Carville	Yes	Yes	Yes	220470012
Port Allen	Yes	Yes	Yes	221210001
Southern	Yes	Yes	Yes	220332002
LSU	Yes	Yes	Yes	220330003
New Roads	No	Yes	Yes	220770001
Madisonville	No	Yes	Yes	221030001
Westlake	Yes	Yes	Yes	220190008
Lighthouse	Yes	Yes	Yes	Special 3
Monroe	No	Yes	Yes	220730002
Shreveport	No	Yes	Yes	220150008
Kenner	No	Yes	Yes	220511001
Chalmette Vista	Yes	Yes	Yes	220870009
Lower Ninth Ward (1)	Yes	Yes	Yes	220717013
Marrero (2)	Yes	Yes	Yes	220512001
French Settlement	Yes	No	No	220630002

(1), Started in April, 2023; (2), started in January, 2018

A7 Data Quality Objectives and Criteria

A7.1 Purpose for Quality

Quality control activities are conducted on the PAMS and air toxics sampling network to assure that data of acceptable precision and accuracy are collected from each parameter to meet the goals of the network. LDEQ has established goals to produce data that are adequately documented in terms of completeness, precision, accuracy, representativeness and comparability.

A7.2 Quality Objectives

The Data Quality Objective (DQO) process described in EPA's QA/G-4 document provides a general framework for ensuring that the data collected by LDEQ meets the needs of the intended decision makers and data users. The process establishes the link between the specific end use(s) of the data with the data collection process and the data quality (and quantity) needed to meet a program's goals.

The Air Quality System (AQS) database is used as the national repository for PAMS data and can be used to assist State and local agencies in determining if the program objectives and Data Quality Objectives described in the PAMS Implementation Manual are met. Data submitted to AQS by LDEQ will be consistent with the PAMS monitoring DQOs and of adequate quality to meet the Clean Air Act Title I objectives. The data will allow LDEQ to develop, evaluate, and refine new O_3 control strategies; determine NAAQS attainment or nonattainment for O_3; track VOCs and NO_x emissions

inventory reductions; provide photochemical prediction model input; evaluate photochemical prediction model performance; analyze ambient air quality trends; and characterize population exposure to VOCs and O_3.

PAMS and air toxics sampling sites are evaluated yearly (Section B1.4) to ensure that siting requirements are met. Hard copies of this evaluation are prepared and maintained in the site documentation files.

All data generated will be reviewed for internal consistency to identify values in the data set, which appear atypical when compared to values of the whole data set. Tests for internal consistency include the identification of outliers and extreme differences in adjacent values that require further investigation. A number of statistical tests will be used for internal consistency checks and determining outliers. Graphical and visual presentation of the data, such as review of summary report file information, scatter plots, time series, or fingerprints will also be used for consistency checks.

Once an outlier has been identified using any of the approaches identified above, treatment of the outlier must be decided. Outliers that are found to be errors will be corrected, if possible. If the correct value cannot be obtained, the value may be appropriately annotated and excluded from the data set. Alternatively, if the suspect data are retained in the data set, the necessary qualifying information in the form of a “flag” must be included with the value. There should be an explanation that warrants the exclusion or replacement of data along with documentation reflecting the action taken. If no explanation is available, the outlier should not be excluded. Data will only be excluded by LDEQ when the values are verified as not representative of ambient data, such as calibration runs, instrument malfunction, contamination, etc.

A7.3 Measurement Performance Criteria

The quality of analytical data must be evaluated and controlled to ensure that it is maintained within the established acceptance criteria. Measurement Quality Objectives (MQOs) are designed to evaluate and control various phases (sampling, preparation, analysis) of the measurement process to ensure that total measurement uncertainty is within the range prescribed by the DQOs. MQOs can be defined in terms of the following data quality indicators:

Precision -- a measure of mutual agreement among individual measurements of the same property usually under prescribed similar conditions. This is the random component of error. Precision is estimated by various statistical techniques using some derivation of the standard deviation.

Accuracy -- a measure of the closeness of an observed analytical value to the actual or referenced value.

Bias -- the systematic or persistent distortion of a measurement process that causes error in one direction. Bias will be determined by estimating the positive and negative deviation from the true value as a percentage of the true value.

Representativeness -- a measure of the degree which data accurately and precisely represent a characteristic of a population, parameter variations at a sampling point, a process condition, or an environmental condition.

Detectability -- the determination of the low range critical value of a characteristic that a method specific procedure can reliably discern (40 CFR Part 136, Appendix B).

Completeness -- a measure of the amount of valid data obtained from a measurement system compared to the amount that was expected to be obtained under correct, normal conditions. Data completeness requirements are included in the reference methods (40 CFR Part 50).

Comparability -- a measure of confidence with which one data set can be compared to another.

The performance criteria for data precision, accuracy, completeness, representativeness and comparability used by LDEQ's PAMS and air toxics sampling network are presented in Table A4. Accuracy has been a term frequently used to represent closeness to "truth" and includes a combination of precision and bias error components. If possible, LDEQ will attempt to distinguish measurement uncertainties into precision and bias components. Data from each monitoring site must characterize and represent actual ambient air levels in the area or neighborhood of the monitoring site.

Method Detection Limits (MDL) for the laboratory analysis have been determined on various occasions and run below 0.2 ppbv for the GC/MS analysis and below 2.0 ppbC for the PAMS GC/FID analysis.

Data are maintained and submitted in consistent units into the AQS database, a nationwide summary designed for ease of use and comparison by various agencies. Table A5 lists preferred and alternate units and the number of decimal places reported to ensure data comparability with historical and other state reporting agencies.

A8 Special Training/Certification

A8.1 Training

LDEQ is made up of career civil service employees. Job qualifications and job duties are set forth in job descriptions, which are prepared by LDEQ and approved by Louisiana State Civil Service Commission. Personnel working for LDEQ meet the educational, work experience, responsibilities, and training requirements for their positions. Records on personnel qualifications and training will be maintained in personnel files. These files will be reviewed yearly, at the time of the employee's performance appraisal, to ensure that the employee remains qualified to perform his/her assigned job duties. Adequate education and training are integral to the air-monitoring program in order to obtain data that are reliable and comparable. Training courses are available for all employees, depending on the job.

A8.1.1 Ambient Air Monitoring Training

Environmental Scientists hired as site operators receive on-the-job training from experienced site operators and supervisors. During this training period, their trainer and supervisor assess the progress. As training progresses the employee is allowed to work more independently until it is determined that this person can operate a monitoring station on his/her own. At this time, he/she is assigned one or more stations to operate.

Table A4

Summary of Precision, Accuracy, and Completeness Objectives

PARAMETER	***PRECISION***	***ACCURACY***	***COMPLETENESS***
Canister Sampler	±20%	±10%	85%
Continuous G.C.	± 20%	±10%	85%
Wind speed	±5%	±5%	85%
Wind Direction	±5°	±5°	85%
Temperature	±1.0°C	±1.0°C	85%
Relative Humidity	±3%	±3%	85%
Barometric Pressure	±1%	±1%	85%
Solar Radiation	±5%	±5%	85%
Ultra Violet Radiation	±5%	±5%	85%
Rainfall	±1%	±1%	85%
Laboratory GC/MS	±25%	±30%	85%
Laboratory GC/FID	±25%	±20%	85%

A8.1.2 Quality Assurance Training

Field or lab quality assurance officers must be familiar with air monitoring equipment and experienced in operation of air monitoring sites and equipment, and lab instrument and analytical procedures. An assurance auditor who will be conducting audits must undergo the same training as a site operator or lab analyst for their first six months. After completing this phase of training, he/she is removed from daily site operations and trained in QA procedures by an experienced QA Officer. As becoming familiar with QA procedures, he/she will be allowed to work independently.

A8.1.3 Contract Laboratory Training

The Contract lab's key staff attended special training on LDEQ's ozone precursor and air toxics analytical methods before the contract was awarded in 2010. Other general training of the contract laboratory follows the guidelines under NELAC.

Table A5

Data Comparability

PARAMETER	***PREFERRED UNITS***	***NUMBER OF DECIMAL PLACES***	***ALTERNATE UNITS***	***NUMBER OF DECIMAL PLACES***
VOC, NMOC	ppbC or ppbv	2*	--	--
Wind Speed	mph	0	--	--
Wind Direction	Degrees	0	--	--
Temperature	°C	1	--	--
Relative Humidity	%	0	--	--
Barometric Pressure	in Hg	2	--	--
Solar Radiation	Watts/m^2	0	--	--
Ultra Violet Radiation	Watts/m^2	0	--	--
Rainfall	in	2	--	--

**: The data have 3 significant figures, but by convention, data will be reported to two digits after the point.*

A8.1.4 Training Courses

Appropriate training is available to employees, commensurate with their duties. Such training may consist of classroom lectures, workshops, teleconferences, and self-instructional courses.

A9 Documentation and Records

The LDEQ PAMS and air toxics sampling network perform environmental sampling, analysis and project reporting. The procedures for the timely preparation, review, approval, issuance, use, revision, and maintenance of documents and records, whether they be electronic or hard copy, must comply with 40 CFR 58, Appendix A. Data verification, validation, management and reporting are the responsibility of the data management unit of the OEA/APAD Air Field Services Section.

The VOC data from the canister analyses are entered into LDEQ's EQuIS database. Reports from EQuIS are generated and submitted each quarter to the data management unit for submission into AQS.

A9.1 Data Reporting Information

A9.1.1 Routine Data Activities

The data management unit has a structured records management retrieval system referred to as the consolidated air database that is based on the EPA's AQS database. This system allows for the efficient archiving and retrieval of records. It follows the same coding scheme as AQS in order to facilitate retrieval of information during EPA technical systems audits and network reviews.

A9.1.2 Quarterly and Annual Summary Reports

Each quarter, the APAD Project Officer will write a brief summary of speciated VOCs (ozone precursors and air toxics). The summary will summarize the data for the quarter to see any violations of Louisiana's Ambient Air Standard and any abnormal high readings in comparison with the historical data. The summary also addresses the sampling completeness and other quality assurance issues in both sampling and sample analysis.

Annually, the APAD Project Officer will generate a summary on Louisiana

Ambient Air Toxics Monitoring. The summary will summarize most recently five-year air toxic data, including TNMOC. It contains the following information:

- An overview of Louisiana's ambient air toxics monitoring programs
- Current LDEQ's ambient air monitoring network
- Current Louisiana's ambient air standards
- Sampling and analytical methods
- Quality control procedures for sampling and analysis
- Data completeness and data deficiency report
- An air quality review, by parameter, detailing annual averages and daily maximum for each sites and if there were any violations of Louisiana's ambient air standards.
- Five-year trends of TNMOC and four air toxic compounds that are normally relatively high in Louisiana , 1,3-butadiene, benzene, 1,2-dichloroethane and vinyl chloride.

Both quarterly and annual summaries are used by LDEQ for the data quality control and addressing violations of its standards and any abnormal emissions of facilities around the monitoring sites in a timely manner.

A9.2 Data Reporting Package Format and Documentation Control

A9.2.1 Field Data Forms

Field data forms are used for canister samples. Field data forms are filled out in indelible ink. To make corrections on field data forms, operators must strike through the incorrect data with only one line and initial the correction. If that cannot be done legibly, then the correct entry may be placed on a new line.

A9.2.2 Logbooks

Site Logbooks: A logbook is assigned to each air monitoring station. These logbooks have numbered pages with detachable carbon copies. Each site visit must be recorded in the logbook along with details of all events occurring at the site that may affect the data quality. Each week site operators send in the carbon copy page of log entries to their supervisor for review and enter site operation information into an Access database. The original logbook page remains in the logbook at the site. Completed site logbooks are maintained for a minimum of 5 years, from the final dated entry in the logbook, at the site shelter.

The department maintains separate logbooks at the PAMS sites for recording operations at the site as they pertain to the continuous GC and canister samplers. A supervisor reviews the logbook entries.

Laboratory Logbooks: Sample log-ins and data recording are all done in accordance with the governing SOPs.

A9.2.3 Data Collection

A computer directly interfaced to the continuous GC/FIDs at the sites collects the raw data (chromatograms). These data are downloaded via modem every day from the site computer to a computer at the lab where the sample results are computed and formatted into a spreadsheet that is then imported into a database system. Meteorological data is downloaded from the site data logger into office computers. For canister samples, a computer that is interfaced with GC/FID or GC/MS collects the analysis data. These data are then stored in a result file. The data from the result files are converted into spreadsheets and imported into EQuIS. These spreadsheets are also submitted to the AD data management unit for conversion and submission into AQS.

A9.3 Data Reporting, Archiving and Retrieval

Electronic data from ambient air monitoring, TNMOC, VOC analysis is maintained and submitted into AQS databases by the Air Data Analysis Unit. Site operators fill out and turn in to the Air Data Analysis Unit all of the calibration, precision checks, and sample data sheets for monitoring equipment at their sites.

All data forms, logbook sheets, sample forms, and audit reports must be retained for at least five years (ten years for the records of lab VOC analyses). If any litigation, claim, negotiation, audit or other action involving the records has been started before the end of the five-year (10-year for the records of lab VOC analyses) period, the records must be retained until completion of the action and resolution of all issues, which arise from this action.

B DATA GENERATION AND ACQUISITION

B1 Sampling Process Design

B1.1 Purpose

This section will describe all of the relevant components of the monitoring network to be operated by LDEQ including the network design for evaluating the quality of the data. This entails describing the key parameters to be estimated, the rationale for the locations of the monitors, the frequency of sampling at the samplers, the types of samplers used at each site, frequency and performance evaluations. The network design components comply with the regulations stipulated in the EPA document *Network Design and Site Exposure for Selected Noncriteria Air Pollutants.*

LDEQ operates two (2) PAMS sites in the Baton Rouge metropolitan area and fifteen (15) additional air toxics sampling sites throughout the state. The PAMS sites have been established in locations that were determined in relation to ozone precursor source areas and predominant wind directions associated with high ozone events.

The purpose is to determine the extent of the effect ozone precursor compounds have on ozone formation.

The locations of the ambient air monitoring stations take into account the basic monitoring objectives for the site location. The general criteria for identifying stations that most closely match one or more of the monitoring objectives are based on a spatial scale. These spatial scales are defined from 40CFR58 as:

- Micro scale – defines the concentrations in air volumes associated with area dimensions ranging from several meters up to about 100 meters.
- Middle scale – defines the concentration typical of areas up to several city blocks with dimensions ranging from about 100 meters to 0.5 kilometers.
- Neighborhood scale – defines concentrations within some extended area of the city that has relatively uniform land use with dimensions in the 0.5 to 4.0 kilometers range.
- Urban scale – defines the overall, citywide conditions with dimensions on the order of 4 to 50 kilometers. This scale would usually require more than one site for definition.
- Regional scale – defines usually a rural area of reasonably homogeneous geography and extends from tens to hundreds of kilometers.
- National and Global scales – these measurement scales represent concentrations characterizing the nation and the globe as a whole.

The relationships between monitoring objectives and scale of representativeness are found in Table B1. For the purpose of PAMS monitoring, the sites are classified as either Neighborhood or Urban scales.

Table B1

Monitoring Station Scale of Representativeness

Site	Parish	AQS Code	Scale of Representativeness
Capitol	EBR	220330009	Neighborhood Scale for O_3, CO, SO_2 , NO_2, VOCs, PM 2.5
Dutchtown	Ascension	220050004	Urban Scale for O_3, NO_2, VOCs

B1.2 Sampling Activities

The monitoring equipment used to sample for compliance is designated as continuous or non-continuous. Continuous monitors operate 24 hours a day on a year round basis collecting consecutive hourly averages with the exception of periods of routine

maintenance or periods of instrument calibration. Meteorological parameters and TNMOCs with auto continuous GC/FIDs operate on a continuous basis. Non-continuous samplers are operated year round on a national six (6) day schedule for 24 hours and 3 hours from midnight to midnight local time. Sampled on a non-continuous basis are VOCs using evacuated Summa canisters for PAMS and air toxics. Intensive PAMS sampling will take place during the ozone season (May through September. See Section A6). The event based canister samplers are operated throughout the year at the PAMS sites. The purpose of these samplers is to capture canister samples during peak concentrations of VOCs.

To determine compliance with the NAAQS, criteria have been established to represent data completeness. For the parameters sampled, data completeness criteria are shown in Table A4.

The purpose of the air toxics sampling network is to ascertain the spatial/temporal variability of hazardous air pollutants within the state. By complying with the sampling frequency requirements of the EPA document *Network Design and Site Exposure Criteria for Selected Noncriteria Air Pollutant,* the LDEQ assumes that the sampling frequency is sufficient to attain the desired confidence in the annual 95th percentile and annual mean of concentrations in the vicinity of each monitor. By selecting sampler locations using the rules outlined in *Network Design and Site Exposure Criteria for Selected Noncriteria Air Pollutants*, the LDEQ can be confident that the concentrations within its jurisdiction are adequately characterized.

B1.3 Network Design Assumptions

The Louisiana ambient air monitoring network, which includes the PAMS and air toxics sampling network, is designed so that the selection of specific monitoring sites includes these four major activities:

- Developing and understanding the monitoring objectives and appropriate data quality objectives.
- Identifying the spatial scale most appropriate for the monitoring objectives of the site.
- Identifying the general locations where the monitoring site should be placed.
- Identifying specific monitoring sites.

The ambient air quality data collected at the monitoring stations are used for one or more of the following purposes:

- To judge compliance with and/or progress made towards meeting ambient air quality standards.
- To activate emergency control procedures that prevent or alleviate air pollution episodes.

- To observe pollution trends throughout the region, including non-urban areas.
- To provide a database for research evaluation of effects; urban, land-use, and transportation planning; development and evaluation of abatement strategies; and development and validation of diffusion models.

Sampling site locations and parameters sampled are based on the information obtained from isopleth maps, population density maps and source locations following these guidelines:

- Locate one or more stations in the priority area, the zone of highest pollution concentration within the region.
- Give close attention to densely populated areas within the region, especially when they are near heavy pollution.
- Assess the quality of air entering the region using stations on the periphery of the region; meteorological factors (e.g., frequencies of wind directions) are most important in locating these stations.
- Sample in areas of projected growth to determine the effects of future development on the environment.
- It is important to locate stations so as to facilitate evaluation of progress made toward air quality goals.
- Some information on air quality should be available to represent all portions of the regions.

Some monitoring stations are capable of fulfilling more than one of these guideline objectives. Ambient air monitoring sites in those areas that are in non-compliance for the NAAQS are set up for rapid data collection, retrieval and analysis with automated equipment whenever an excursion occurs. These monitoring sites are located to maximize the measurements of pollutant concentration over the range of the affected area and, as near as possible, are located in areas when human health and welfare are most threatened. A minimal number of monitoring sites are set up over as large an area as possible, while still meeting the monitoring objectives to track air pollution trends. The objective is to determine the extent and nature of the air pollution and to determine the variations in the measured levels of atmospheric contaminants in respect to the geographical, socio-economic, climatological, and other factors. The data collected is useful in planning epidemiological investigations and in providing the background air quality data.

In interpreting trend data, limitations imposed by the network design are considered. Precautions are taken to ensure that each sampling site is as representative as possible of the designated area, and that measurements obtained are not unduly influenced by local factors. Such factors can include topography, structures, sources of pollution in the immediate vicinity of the site, and other variables.

Air monitoring sites set up to determine health effects are composed of integrating samplers both for determining pollutant concentrations for ≤24 hours and for developing long term (≥24 hour) ambient air quality standards. The monitoring sites are located so that the resulting data will represent the population group under evaluation, so that data correlations are made between observed health effects and observed air quality exposures.

Requirements for monitoring in support of health studies are as follows:

- The stations are located in or near the population under study.
- Pollutants sampling averaging times are sufficiently short to allow use in acute health effect studies that form the scientific basis for short-term standards.
- Sampling frequency, usually daily, is enough to characterize air quality as a function of time.
- The monitoring system is flexible and responsive to emergency conditions with data available on short notice.

B1.4 Siting Criteria

B1.4.1 Network Siting Requirements

The Louisiana air-monitoring network is designed so that the siting criteria for the monitoring stations meet one or more of the following monitoring objectives:

- Locate the network in areas of expected highest concentrations.
- Measure representative concentrations in areas of high population density.
- Determine impact of significant sources or source categories on ambient pollution levels.
- Obtain general background concentration levels.
- Determine extent of regional pollutant transport in populated areas, and in support of secondary standards.
- Determine welfare-related impacts in more rural and remote areas.

These six objectives are used to ensure that the monitoring station locations in the network are representative of the spatial scale defined for the station parameters.

The sampling equipment falls into one of the two following categories:

- Continuous -- where pollutant concentrations are measured using automated methods and the data are collected and recorded continuously.
- Integrated or non-continuous -- where pollutant concentrations are collected by a manual method for 24 hours on a fixed schedule.

The continuous automated methods are an integral part of the air pollution episode warning system.

Monitoring stations are sited to match the appropriate spatial scale, as defined in Section B1.1, for the monitoring objective of the station. The relationship of the monitoring objectives to the spatial scales is shown in Table B2.

Table B2

Relationship among Monitoring Objectives and Scales of Representativeness

Monitoring Objective	Appropriate Siting Scale
Highest Concentration	Micro, middle, neighborhood, sometimes urban
Population	Neighborhood, urban
Source impact	Micro, middle, neighborhood
General/background	Neighborhood, regional
Regional Transport	Urban/regional
Welfare-related	Urban/regional

B1.4.2 Site Location

Monitoring sites are located in order to best fit the sampling objectives defined in Section B1.1. Other factors that affect site location are:

- Economics
- Security
- Logistics
- Traffic Patterns

- Atmospheric Considerations
- Topography
- Pollutant Considerations

These factors along with the sampling objectives and the information provided in 40 CFR Part 58, Appendix D are used in determining site locations for State and Local Ambient Monitoring Stations (SLAMS), National Air Monitoring Stations (NAMS), Special Purpose Monitoring Stations (SPMS), PAMS and Air Toxics monitoring. Monitoring station information is found in Section A6 of this document.

B1.5 Monitor/Sampler Placement

Placement of the monitor or sampler site depends on physical obstructions and activities in the immediate area; accessibility, availability of utilities and other support facilities; and correlation with the defined purpose of the specific monitor and monitor design. Obstructions such as trees and fences can significantly alter the airflow; monitors are placed away from obstructions. Airflow around the monitor is representative of the general airflow in the area to prevent sampling bias.

Detailed information on urban physiography (e.g. buildings, street dimensions) is determined through visual observations, aerial photography and surveys. This information is important in determining the exact locations of pollutant sources in and around the prospective monitoring areas. This information is maintained in the site documentation file. Sampling locations are chosen to avoid undue influence by ground level dust and are located away from the source, such as an unpaved road.

Depending on the defined monitoring objective, the monitors are placed according to exposure to pollution, but due to physical or meteorological constraints, monitoring sites are located to optimize representativeness of sample collection. Table B3 is the summary of probe and monitoring path siting criteria.

Any changes to the PAMS monitoring network regarding site locations, sampling frequency and sampling methods will not occur until approved by EPA Region 6.

Table B3

Summary of Probe and Monitoring Path Siting Criteria

POLLUTANT	SCALE (maximum monitoring path length, meters)	Height from ground to probe or 80% of monitoring path (meters)	Horizontal and vertical distance from supporting structures to probe or 90% monitoring path (meters)	Distance from trees to probe of monitoring path (meters)
Ozone precursors for (PAMS)	Neighborhood and urban (1km)	3-15	>1	>10

B1.6 Classification of Measurements as Critical or Non-critical

All of the measurements of the pollutants sampled by the PAMS and air toxics sampling network are considered to be critical. The measurements meet federal monitoring requirements to show compliance with the NAAQS. To meet these requirements, continuous sampling is specified for O_3 and NO_2 and field GC. Three-hour and 24-hour measurements are required for VOC canisters. The 3-hour and 24-hour samples are collected midnight-to-midnight local time on a national schedule to permit the use of the data in standard summaries. Meteorological data are used to supplement the sampling of the criteria pollutant parameters. The data collected from PAMS sites are submitted to AQS. The minimum amounts of data for appropriate summary statistics are taken with at least 75% of total possible observations present for summary statistical calculation. The minimal collection requirements are given in Table A1.

B1.7 Validation of any Non-Standard Methods

The PAMS Network is operated according to the CFR, the EPA, *Quality Assurance Handbook for Air Pollution Measurement Systems, Volume II,* and the EPA, *Technical Assistance Document for Sampling and Analysis of Ozone Precursors*. Since the operation of the PAMS network is under these requirements, there will not be any non-standard methods used. Modifications to standard methods, if any, must be scientifically defensible and be highlighted in the SOPs and explained.

B2 Sampling Methods

B2.1 VOC Canister Sampling

B2.1.1 Site Selection

Site selection for VOC canister samplers will be done in accordance with the EPA QA Handbook, Volume II, Part I, Section 6.0.

B2.1.2 Sampling Method

- A XonTech 911A Sampler with an evacuated Summa® Canister is used to sample 24-hour 6-day samples.
- A XonTech 911A Sampler attached to one to three XonTech 912 multi-canister sampling adapters for 8 3-hour samples.
- A XonTech 911A Sampler combined with a continuous Thermo Environmental 55C methane/TNMOC analyzer is used to collect event-based canister samples. The sampling period is 25 minutes.

B2.1.3 Sampling Volume

The volume of air to be sampled is specified in the manufacturer's specifications. The total volume of air collected is based upon a canister size and the canister final pressure. The volume sampled in a 6-liter canister with zero final pressure is sufficient for two analyses: ozone precursors and air toxics. In case of a power outage, a valid sample run will be no less than 75% of the scheduled sample time. If the sample time is less than this, the sample will be invalidated & flagged.

B2.2 Continuous GC/FID for Hourly TNMOCs

The GC/FID is located at the Capitol site. Air are continuously drawn into a trap using a XonTech Model 930 organic vapor concentrator and followed by thermally desorption into a Shimadzu gas chromatograph Model GC-14A with an FID detector. The system analyzes air in batches. Sampling time for each batch is 24 minutes and the sampling volume is 240 cc. The data from each batch is treated as half hour data. Hourly data are obtained by averaging two half hour data and submitted to EPA. The procedure is detailed in LDEQ's SOP # 1065 that has been developed based on EPA Compendium Method TO-12.

B2.3 Meteorological Parameters Sampling

Site selection for continuous meteorological parameter sampling will be done in accordance with EPA QA Handbook, Volume II, Part I, Section 6.0. Parameter probe siting will be done in accordance with EPA QA Handbook, Volume IV. Meteorological sampling probes are attached to a 10-meter high sampling tower with electrical wiring connecting the probe to translator cards specific for each parameter and located inside the site shelter. The translator card is attached to the data logger where the electrical impulses are converted and stored as data.

B2.4 Support Facilities

The main support facility for the VOC sampling and field continuous GC is the laboratory, located at 5825 Florida Blvd., Baton Rouge, Louisiana. Equipment, supplies and other necessary materials for field operation are distributed to the field laboratory site operators from this location. Instrumentation requiring repair is returned to the laboratory for reconditioning to optimal working condition before being placed back into service at the PAMS stations.

B3 Sample Handling and Custody

B3.1 Sample Custody of Continuous TNMOC Samples

Continuous hourly TNMOC samples are taken and analyzed directly in the field using continuous auto GCs. The information about the sampling time, analysis time and sampling flow rate is recorded in electronic data files. There is no individual paper chain-of custody. A field logbook records all of the activities related to the site auto GCs' quality controls, maintenance, operators' site visits, etc.

B3.2 Sample Custody for Canister Samples

All air samples are collected under the guidelines established by LDEQ. Samples are picked up by the contract lab at the LDEQ Lab located at 5825 Florida Blvd., Baton Rouge, Louisiana and all of the LDEQ regional Offices as directed.

VOC samples are collected in stainless steel Summa canisters. Site operators complete the necessary information on the field data sheets and the sample identification tags that are attached to canisters. Canisters are delivered to the LDEQ Lab located at 5825 Florida Blvd., Baton Rouge, Louisiana and all of the LDEQ regional Offices for the contract lab to pick up. The maximum holding time between sample collection and analysis is 30 days.

When the sample arrives at the laboratory, the individual accepting the delivery signs and dates the chain of custody on the accompanying field data sheet.

The individual receiving the canister sample notes the overall conditions of the canister and compares the information on the chain of custody with the data recorded on the sample identification tag attached to the canister. Any discrepancies must be noted on the field data sheet and in the sample log entry book.

A pressure gauge is attached to the canister inlet to check the pressure of the canister. The canister valve is opened briefly and the pressure (psig) is recorded in the

appropriate location on the chain of custody. If the pressure on the canister is 2 psi less or larger than the projected pressure (normally 23 psig), the flow rate of the sampler may need to be adjusted. If the pressure is greater than the pressure threshold of the sampler, the canister will be recorded with an appropriate cautionary flag as governed by the laboratory SOP. This will be noted in the LIMS database.

All canister samples received by the laboratory must be assigned a unique laboratory number generated by the Laboratory Information Management System (LIMS). Any irregularities associated with the samples must be noted in the LIMS database.

Canister samples are required to have the following information:

- The LIMS Laboratory Number
- The site or location where the sample was collected
- The date the sample was collected
- The date the sample was received in the laboratory
- The analyst who received the sample
- The canister identification number (serial number)
- The initial pressure of the canister upon receipt in the laboratory
- The start hour the canister was sampled
- The duration canister was sampled
- The dilution factor (if any)
- A notation of any discrepancies and/or comments observed during the sample entry

Figure B1 is the chain of custody (COC) record for canister samples.

When all information has been completed on the COCs and LIMS database, the samples and the accompanying the COCs shall be directed to the analyst. The laboratory manager will regularly review the field data sheets and LIMS database to ensure consistency and eliminate data entry errors.

A canister sample may be declared invalid, flagged and/or annotated if any of the following conditions exists,

- The chain of custody 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 or close to the pressure threshold of the sampler. Generally, the pressure threshold of a sampler is 25 psig. The canister pressure should be ~ 2 psi less than the pressure threshold.
- The sample was collected in an expired canister.
- The sample is beyond the prescribed holding time after sample collection.

If the sample is declared invalid, the site operator or sample collector must be contacted via telephone for the problem. Depending on the severity or complexity of the problem, adjustments must be made to the sampling equipment under the advice of the field supervisor. All invalid samples must be logged into the LIMS and reasons for invalidation noted. At the discretion of the sample collector, his/her supervisor or the AD project officer, these samples may not be analyzed. The laboratory shall be notified within 72 hours of sample submittal if the analysis is to be cancelled. Otherwise the samples will be analyzed. Any analyses performed on these samples shall be documented in the LIMS database with appropriate flagging and/or annotation to indicate the nature of any problems with the data. Data users may choose to exclude data sets that are flagged from being reported to the agency's EQuIS database or to AQS.

Figure B1

Louisiana Department of Environmental Quality
Air Chain of Custody Record

Page ____ of ____

AI No: _____ AQS No. _____ Collection Date: _____

Location Name: _____
Address: _____

Sample Collector(s): _____

Sample ID	Sampler ID	Canister Serial #	Collection Start Time	Duration	Final Pressure	Parameters Requested with Method Reference: PAMS Method -GC/FID	TO-15 Method - GC/MS	Canister Clean & Certify	Rapid Turn-Around (day/s) (Same day,1,3,5,7,14,21)		Remarks

Additional Comments: _____

Relinquished by:	Date & Time:	Received by:

B3.3 Sampling Custody for Meteorological Parameters

There are no discrete samples handled by individuals for meteorological parameters. The data produced from the monitors are identified electronically within the instrument data logger, support computer and processing software. The site logbook will record the instrument maintenance and operators' site visits and activities.

B4 Analytical Methods

B4.1 Canister Analytical Method for VOC Ozone Precursors

LDEQ's contract lab, SGS North America Inc., Houston, analyzes canister samples for ozone precursors shown in Table A1 in accordance with its SOP TAE006-03 that has been developed based upon *Technical Assistance Document for sampling and analysis of ozone precursors (EPA/600-R-98/161).* The procedure uses an Entech cryogenic concentrator to concentrate the condensable portion of the air sample where the sample is cryogenically concentrated on the multi-bed cryo-trap, desorbed at a higher temperature, and cryofocused (-195^{0}C) on the head of the column of the

Agilent 6890 GC equipped a flame ionization detector (FID) with pressure control. The hydrocarbons are separated and detected via a Restek Corporation, ™ Rtx® -1, capillary column with a 1-micron dimethylpolysiloxane phase thickness, an internal diameter of 0.32 mm, and a length of 100 meters.

B4.2 Canister Analytical Method for VOC Air Toxics

Numerous compounds, many of which are chlorinated VOCs, have been successfully tested for storage stability in pressurized canisters. The contract lab analyzes canister samples for VOC air toxic compounds shown in Table A2 in accordance with the contract's SOP TAE007-04 that has been developed based upon EPA Compendium Method TO-15, *Determination of Volatile Organic Compounds (VOCs) In Air Collected In Specially-Prepared Canisters and Analyzed by Gas Chromatography/Mass Spectrometry (GC/MS)*. The laboratory uses an Entech concentrator, Agilent 6890 Series gas chromatograph with a Restek Corporation, ™ Rtx® -1, capillary column with a 0.5-micron dimethylpolysiloxane phase thickness, an internal diameter of 0.32 mm, and a length of 100 meters in conjunction with Agilent 5973 or 5975 quadruple mass selective detector.

B4.3 Analytical Method for Continuous Hourly TNMOCs

See B2.2.

B4.4 Analytical Method for Meteorological parameters

Meteorological measurement methods are in accordance with LDEQ's SOP# 1350 that has been developed based upon EPA's *Quality Assurance Handbook Volume IV*, March 2008.

B5 Quality Control

B5.1 Quality Control Policy and Objectives

Data quality objectives and criteria are discussed in Section A7.

PAMS and Air Toxics Sampling sites are evaluated yearly by OEA/APAD to ensure that siting requirements are met. Hard copies of this evaluation are prepared and maintained in the LDEQ site documentation files. Continuous GCs for TNMOC are operated year round.

B5.2 Internal Quality Control Procedures

B5.2.1 Canisters

Canisters are cleaned in accordance with the contract lab's SOP TAE003-03. Canisters are cleaned in batches (8 or 12 canisters per batch) using Xontech 960. The dirtiest canister (with the highest TNMOC) in each batch is selected for certification using GC/FID analytical results. The certification criteria are: individual ozone precursors must be less than 2 ppbC and TNMOC must be less than 20 ppbC. When the canister is used for sampling, its pressure must be less than -28 in. Hg and it must be cleaned within last 90 days.

B5.2.2 Samplers

All flow measuring devices used in calibrations, audits, and precision checks are calibrated every three months against an NIST traceable bubble flow apparatus.

VOC canister samplers are certified for volumetric flow on initial installation and set-up, and every 3 months thereafter.

Canister samplers are flow checked when a sample run is set up. Sample flows are adjusted so that the final canister pressure is ~2 psi lower than the sampler's manifold pressure threshold. The final canister pressure is generally of 20 psig $\pm$ 3 psig.

Samplers may be contaminated. The contaminated sampler is brought into the lab for cleaning. The cleaned sampler will be certified by sampling zero air through it and sending the sample for GC/FID analysis. The criteria specified in B5.2.1 must be met.

B5.2.3 Continuous GC/FIDs for TNMOCs

A zero air blank is run weekly. TNMOC must be less than 20 ppbC. A 300 ppbC of humidified working calibration standard is prepared in a 15-liter summa canister from a stock of propane standard every 30th day. This working standard is used for continuous calibration verification (CCV). The CCV standard is run once per week. The deviation must be within 10% of the initial calibration.

B5.2.4 Canister Analysis for Ozone VOC Precursors

The canister samples are analyzed in batches. Number of canister samples in each batch is up to 19. For each batch, the following quality control samples are run:

- One dry zero-air blank directly from a zero air cylinder and one humidified zero air blank are analyzed. For both zero air blanks, TNMOC must be less than 20 ppbC and all the target compounds must be less than 2 ppbC.
- One CCV standard is analyzed twice. Two runs bracket the samples in the batch. The standard is 100 ppbC of humidified propane and prepared in a 6-liter or 15-liter canisters every 30th day. The response factors (RF) of both CCVs must be within 90-110% of the RF obtained in the initial calibration.
- One humidified retention time standard containing all the targeted compounds is analyzed once. The retention times must be within ±0.1 min of the retention times in the initial calibration.
- At least one sample is randomly selected as a replicate sample. The relative percent difference (RPD) for the targeted compounds must be within 25% in the calibration range.
- One second-source LCS containing all the targeted compounds is run once. At least one compound from each carbon group must have the recovery of 80-120%. All compounds must have a recovery of 70-130%.

For any suspected identification, a GC/MS analysis will be conducted for confirmation. MDLs are run 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. MDLs must be less than 2 ppbC. Performance evaluation samples are analyzed at least twice per year. The results are sent to Louisiana Environmental Laboratory Accreditation Program for evaluation. The criteria from performance evaluation sample providers or in the lab control standard above-mentioned must be met.

B5.2.5 Canister Analysis for Air Toxics

The canister samples are analyzed in batches. The number of canister samples in each batch is up to 19. For each batch, the following quality control measures are conducted.

- Before the analysis of samples, the GC/MS must meet the mass spectral ion abundance criteria for the instrument performance check. The instrument performance check compound, p-Bromofluorobenzene (BFB) is added to each analysis as the internal standard. It is also used as a instrument performance compound. Before the batch continues, the GC/MS must meet the mass spectral ion abundance criteria specified in TO-15.
- One dry zero-air blank directly from a zero air cylinder and one humidified zero air blank are analyzed. For both zero air blanks, all the target compounds must be less than 0.2 ppbv.
- One CCV standard containing all the targeted compounds is analyzed twice. Two runs bracket the samples in the batch. The standard is humidified and prepared in 6-liter or 15-liter canisters every 30th day. 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%.

- At least one sample is randomly selected as a replicate sample. RPD for the targeted compounds must be within 25% in the calibration range.
- One second-source LCS containing all the targeted compounds is run once. The accuracy should be 100 ± 30%. Random two compounds are allowed to vary greater than 100 ± 30%, but must be less than 100 ± 40%.
- The internal standard retention time must be within ± 0.33 minutes of the mean RT and the internal standard area must be ± 40% of the mean area of the 5 calibration points in the last multi-point calibration.
- BFB is used as a surrogate in this lab. Its recovery should be between 80 to 120% and must be between 70 to 130%.

MDLs are run 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. MDLs must be less than 0.2 ppbv. Performance evaluation samples are analyzed at least twice per year. The results are sent to Louisiana Environmental Laboratory Accreditation Program for evaluation. The criteria from performance evaluation sample providers or in the lab control standard above-mentioned must be met.

B5.2.6 Meteorological Instruments

On a weekly basis, site operators must make a visual and (where practical) a physical check of the sampling probes, record any noted problems in the logbook and report the problem to their supervisors. Once every three months, check the translator sensor cards (zero/span). Once every six months, check calibration of the meteorological instruments. Criteria and detailed procedure are described in Table A4 and LDEQ's SOP#1350.

B5.3 Precision Accuracy and Bias

Precision and accuracy data are submitted each quarter to EPA for inclusion in the AQS database. From the quarterly precision and accuracy reports each year EPA calculates and reports the properly weighted probability limits for precision for the calendar year from the equations found in 40 CFR 58, Appendix A. For each parameter, the upper 95 percent probability limit and lower 95 percent probability limit are calculated. Corrective action must be taken if a sampler exceeds the bias limits for precision and accuracy to ensure that future data collected meets this limit.

B6 Instrument/Equipment Testing, Inspection and Maintenance

B6.1 Purpose

To ensure that all equipment is in sound operating condition, procedures have been developed for testing new and repaired monitoring equipment.

B6.2 Testing, Inspection and Maintenance

Good practices are used to keep all equipment clean and free from dust and any adverse environmental conditions. Whenever laboratory equipment needs repairs, a service company, vendor, or the manufacturer is contacted; or, if the item cannot be repaired, a replacement is secured.

Repairs and service to the field equipment are provided as needed and usually done in house. However, if the analyst cannot take care of it, then a reputable technician must service it.

B6.2.1 Preventive Maintenance

LDEQ performs preventive maintenance on all samplers and monitors on a scheduled and/or as needed basis.

Preventive maintenance for sampling systems routinely performed on a regular basis includes the following:

- Check sample manifold exhaust motor to insure proper flow through sample system.
- Check sample line fittings for leaks.
- Change the in-line filter on the sampler line.
- Run a diagnostic check on the sampler or continuous GC.
- Check sample flow on the monitor.
- Check sample line and manifold for cleanliness, blockage, or moisture.

All sampling and analytical instruments must be checked by analysts /site operators daily for any malfunctioning parts, blown filaments, broken columns, or blown fuses. A small inventory of parts is maintained. If analysts/site operators can install a part, filament, or fuse, the maintenance is completed by them. If the part is not in inventory, or cannot be replaced, a service company is contacted for the needed repairs/service.

Preventive maintenance information is recorded in the field logbook for the VOC canister sampler or continuous GC. The site operator takes corrective action, whenever problems are encountered.

B6.2.2 Corrective Action

Corrective action measures will be taken to ensure good quality data. There is the potential for many types of sampling and measurement system corrective actions. Each of the SOPs will outline exact actions that will be taken if the analytical and sampling systems are out of control (see B5). Every unusual event that affects laboratory data quality will be reported through the laboratory corrective action system.

The performance of the instruments in the laboratory is defined by limits that fall into two categories: quality assurance limits and manufacturer's performance limits. Quality assurance limits are addressed in section A7 of this document. Manufacturer's performance limits are stated in the operations manual for each type of instrument.

Manufacturer's Performance Limits: The laboratory analyst/site operator makes the initial determination as to when the instrument is malfunctioning. Symptoms such as inadequate instrument response, broken columns, blown fuses, inadequate sample flow, etc., may be found. The analyst should make every effort to repair, if possible. If the repairs are beyond the scope of the in-house personnel, then the instrument service technician is called in to make repairs.

The instrument is returned back into service after the instrument passes the calibration standard checks. MDLs are run on the instrument after a major part, instrument temperature parameter or other parameter crucial to the overall functioning of the instrument process has been replaced or altered. The manager of the laboratory will make the determination to run MDL checks.

Quality Assurance Limits: If any laboratory instrument fails quality assurance requirements, the following items must be checked before any adjustment or recalibration.

- Try to pinpoint the problem by using a systematic approach. Check the minor sources of potential problems first by examining the sample line for leaks, moisture or dust.
- Check for leaks in the calibration system sample lines, broken columns, broken filaments, clogged detectors, etc.

Verify that the problem is fixed by running quality control calibration standards with standards that are within method specifications.

If the instrument fails to meet quality assurance limits, the following items must be checked before any adjustment or recalibration on the analyzer: The quality control limits are defined in the relevant SOPs.

- Check sample line for leaks, moisture or dust.
- Check the calibration system, sample lines, sampler flow, vent and dry air source.

If the above items are normal, the instrument may then be adjusted or re-calibrated. If one or more of the above items is found to be defective, each item is replaced, or repaired, and the control checks are repeated.

Equipment brought in for repairs is given a thorough test to determine the exact cause of the failure. Information derived from testing is recorded in the instrument's maintenance record and is checked against past failures to determine if this is a recurring problem or a routine failure. Recurring problems are checked to determine if the last repair was adequate and to establish further steps in the repair process to ensure better reliability. All failures are checked against other instruments, of the same make, to isolate any type of engineering defect or other problem that the manufacturer should address. All repairs are made using spare parts maintenance stock, local vendor sources or manufacturer-supplied parts. On occasion, a unit will be returned to the manufacturer due to an overload in the repair shop workload, for upgrading or for authorized manufacturer repairs that are beyond the capability of the repair shop. After repair, a unit must be calibrated and bench tested for an extended time (3 to 10 days) to ensure proper operation. If the unit has performed as specified in its operations manual, the unit is kept as a spare or placed back into use in the field. If the unit does not pass the test run, it is cycled back through the repair procedure. All information concerning the repair, outcome of the test run, and final diagnostic readings are recorded in the maintenance record.

B7 Instrument/ Equipment Calibration and Frequency

B7.1 Purpose

A calibration establishes the relationship between the actual pollutant concentration and the analyzer's response. This relationship is used to convert subsequent analyzer response values to corresponding pollutant concentrations until superseded by a new calibration.

B7.2 VOC Samplers

VOC canister samplers are certified for volumetric flow on initial installation. The flow rate is checked again if the final pressure of the canister is out of the acceptable range of 10-25 psig.

B7.3 Canister Analytical GC/FIDs for Ozone VOC Precursors

The Agilent GC/FID is calibrated according to the guidelines stated in the contract lab's SOP TAE006-003 referenced in the Appendix. A 5-point calibration of propane is run annually or after any major instrument maintenance. The correlation coefficient of the linear regression must be equal to or larger than 0.995. The calibration range is 5 to 500 ppbC. The response factor (ppbC/area counts) from this single compound calibration is entered into the calibration table and applied to all the target compounds and untargeted compounds. The concentrations calculated from this calibration for all the targeted and untargeted compounds are ppbC. A second-source standard that contains all the target compounds will verify the initial calibration. The criteria for the second source LCS in B5.2.4 is used for verification.

B7.4 Canister Analytical GC/MS for Air Toxic Compounds

The Agilent GC/MS is calibrated according to the guidelines stated in the contract Lab's SOP TAE007-04 referenced in the Appendix. A 5-point calibration is performed. The average response factor is used for curve fitting. 30% relative standard deviation for the relative response factors must be met with at most 2 exceptions of at most 40%. The calibration range is 0.5 to 10 ppbv. A second source standard that contains all the target compounds will be used to verify the initial calibrations. The criteria for the second source LCS in B5.2.5 is used for verification. The initial calibration will be conducted whenever the quality control criteria for LCS and CCV mentioned in B5.2.5 are not met or any major maintenance is performed.

B7.5 Field Continuous GC/FIDs for TNMOCs

The field continuous GC/FIDs for TNMOCs are calibrated in accordance with the guidelines stated in LDEQ's SOP #1065 listed in the Appendix. A propane standard is the calibration gas. The concentration of propane is recorded for the column and a multiplication factor is calculated. The data are entered into the detector calibration table and applied to the total area response to calculate TNMOC concentrations in ppbC. Whenever a daily check of the propane standard reveals a variance of ±10% from the actual concentration recorded in the field propane standard calibration mix, a new multiplication factor is calculated and substituted for the multiplication factor in the calibration table.

B7.6 Meteorological Sensors Calibration Method and Frequency

Meteorological parameters are calibrated in accordance with guidelines stated in LDEQ's SOP# 1350. The calibrations must be performed with the appropriate calibration device for each parameter whenever:

- A new sensor is set up for operation
- Twice yearly on a six month schedule

B7.7 Laboratory Standard Materials Requiring Calibration and/or Certification

Standards and their use are described in the SOPs. They may not be used beyond their expiration date without recertification.

B8 Inspection/Acceptance of Supplies and Consumables

B8.1 Supplies Management

Spare parts that meet the manufacturer's specifications for the maintenance and repairs of the monitoring and sampling equipment are kept on hand at the electronic repair facilities at the laboratory. Adequate consumable supplies are kept on hand at the monitoring stations. That point is covered in section B2.4 of this document.

LDEQ is subject to state purchasing policies and is limited in the ability to choose suppliers. Often the items come from the vendor with the lowest bid, unless a reason can be established that the lowest bidder does not meet required specifications. The state purchasing policies do allow purchase orders directed to reputable vendors for amounts less than $1,000 to be filled without competitive bidding. A list of consumable supply vendors is given below:

- Agilent
  Analytical Business Center MS37
  2850 Centerville Road
  Wilmington, DE 19808-1610

- SUPELCO, INC.
  Supelco Park
  P.O. Box B
  Bellefonte, PA 16823-9900

- Shimadzu
  7102 Riverwood Drive
  Columbia, Maryland 21046

- Scott Specialty Gases
  6141 Easton Road
  Plumsteadville, PA 18949-0310

- Anderson Instruments, Inc.
  500 Technology Court
  Smyrna, GA 30082-5211

- SGE, Inc.
  2007 Kramer Lane
  Austin, TX 78758

- Capitol Valve and Fitting Company
  9243 Interline Avenue
  Baton Rouge, LA 70809

- Tri-Gas, Inc.
  420 Allendale Drive
  Port Allen, LA 70767

- Fisher Scientific
  6614 Langley Drive
  Baton Rouge, LA 70809

- XonTech, Inc.
  6862 Hayenhurst Avenue
  Van Nuys, CA 91406

- Entech, Inc.
  950 Enchanted Way, #131
  Simi Valley, CA 93065

- Restek Corporation
  110 Benner Circle
  Bellefonte, PA 16823-8812

New supplies must be checked to see if they are damaged, clean, and if the quality and workmanship of the items meet specifications. If the specifications are not met, the items are sent back with the replacements required. The supplies are stored in a clean, adequately ventilated place.

B9 Non-Direct Measurements

The PAMS and air toxics sampling networks rely on data that are generated through field and laboratory operations; however, other significant data are obtained from sources outside the LDEQ or from historical records. This section addresses data not obtained by direct measurement from the PAMS and air toxics sampling networks and addresses quality issues related to the PAMS and air toxics sampling networks. These non-direct measurement data includes both outside data and historical monitoring data. Non-monitoring data and historical monitoring data are used in a variety of ways. Use of information that fails to meet the necessary data quality objectives (DQOs) for the PAMS and air toxics sampling networks can lead to erroneous trend reports and regulatory

decisions. The policies and procedures described in this section apply both to data acquired through the LDEQ monitoring program and to information previously acquired and/or acquired from outside sources.

B9.1 Chemical and Physical Properties Data

Physical and chemical property data and conversion constants are often required in the processing of raw data into reporting units. This type of information that has not already been specified in the monitoring regulations will be obtained from nationally and internationally recognized sources. The following sources may be used without prior approval:

- National Institute of Standards and Technology (NIST)
- International Organization for Standardization (ISO), The International Union of Pure and Applied Chemistry (IUPAC), American National Standards Institute (ANSI) and other widely-recognized national and international standards organizations

- U.S. EPA

- The current edition of certain standard handbooks may be used. Two that are relevant to the fine PAMS monitoring program are CRC Press' *Handbook of Chemistry and Physics*, and *Lange's Handbook.*

B9.2 Monitor/Sampler Operation and Manufacturers' Literature

Another important source of information needed for sampler operation is manufacturers' literature. Operations manuals and users' manuals frequently provide numerical information and equations pertaining to specific equipment. Department personnel are cautioned that such information is sometimes in error, and appropriate cross checks will be made to verify the reasonableness of information contained in manuals. Whenever possible, the field operators will compare physical and chemical constants in the operators manuals to those given in the sources listed above. If discrepancies are found, the correct value will be determined by contacting the manufacturer. The field operators will correct all the operator manuals and the vendor will be contacted to issue an errata sheet discussing the changes. The Department will also contact the EPA Region 6 Office to inform them of these errors. The following types of errors are commonly found in such manuals:

- Insufficient precision
- Outdated values for physical constants
- Typographical errors
- Incorrectly specified units
- Inconsistent values within a manual

- Use of different reference conditions than those called for in EPA regulations

B9.3 Information for Location

Another type of data that will commonly be used is geographic information. For the current sites, LDEQ will locate these sites using global positioning systems (GPS) that meet EPA Locational Data Policy of 25 meters accuracy. U.S Geological Survey (USGS) maps are used as the primary means for locating and siting stations in the existing network. Geographic locations of LDEQ monitoring sites that are no longer in operation will not be re-determined.

B9.4 Historical Monitoring Information of the LDEQ

The Louisiana Department of Environmental Quality has operated a network of ambient air monitoring stations since the 1970's. Historical monitoring data and summary information derived from that data may be used in conjunction with current monitoring results to calculate and report trends in pollutant concentrations. In calculating historical trends, it is important to verify that historical data are fully comparable to current monitoring data. If different methodologies were used to gather the historical data, the biases and other inaccuracies must be described in trends reports based on that data. Evidence must be presented to demonstrate that results of the two different methods are comparable before this data is reported. Trend reports, comparing current data with historical data, must be approved by the LDEQ before release. Direct comparisons of current data with historical data will not be reported or used to estimate trends.

B9.5 External Monitoring Data Bases

Data from the EPA AQS database may be used in published reports with appropriate caution. Care must be taken in reviewing/using any data that contain flags or data qualifiers. If data is flagged, such data shall not be used unless it is clear that the data still meets critical QA/QC requirements. It is impossible to assure that a data base such as AQS is completely free from errors including outliers and biases, so caution and skepticism is called for in comparing LDEQ data with data from other reporting agencies as reported in AQS. Users should review available QA/QC information to assure that the external data are comparable with LDEQ measurements and that the original data generator had an acceptable QA program in place.

B9.6 U.S. Weather Service Data

Meteorological information is gathered from the U.S. Weather Service station in Slidell, LA. Parameters include temperature, relative humidity, barometric pressure, rainfall, wind speed, wind direction, cloud type/layers, percentage cloud cover and visibility range. Historically, these data have not been used to calculate pollutant

concentration values for any of the monitoring sites, some of which each have the required meteorological sensors. However, National Weather Service (NWS) data are often included in summary reports. No changes to the way in which these data are collected are anticipated for the LDEQ PAMS and Air Toxics Sampling networks.

B10 Data Management

B10.1 Background and Overview

This section describes the data management operations pertaining to measurements for the PAMS and air toxics stations operated by LDEQ. This includes an overview of the mathematical operations and analysis performed on raw ("as collected") data. These operations include data recording, validation, transformation, transmittal, reduction, analysis, management, storage and retrieval.

The data manager, usually the Engineer Supervisor or his designee, OEA/APAD, is responsible for performing the following tasks on a regular basis:

- Merging/correcting the duplicate data entry files
- Running verification and validation routines and correcting data as necessary
- Generating summary data reports for management
- Uploading verified/validated data to EPA AQS

The sample tracking and chain of custody information are entered into the contract lab's LIMS. This information along with analytical data is delivered to SD's Laboratory Information management Services. VOC data from analyses of canister samples and TNMOC data from continuous field GC/FID are reported in parts per billion volume (ppbv) or parts per billion carbon (ppbC), depending upon which EPA method is used. The VOC data from canister samples are managed and stored in EQuIS. All final reports for canister samples are received from the contract lab in PDF format or are generated through LDEQ's EQuIS database. The TNMOC data from the continuous field GC/FID are stored in the computers in GC Filed Unit. Data are considered valid if they meet the Quality Control criteria specified in the corresponding. Any results not meeting the criteria are "flagged" with the explanations in the database.
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B10.2 Data Recording

Verified VOC data from the contract lab must be loaded into the LDEQ's EQuIS database. Environmental Scientist Senior in SD's Laboratory Information Management Services receive, review and verify VOC data from the contract lab. All analytical results including concentrations below the calculated detection limit will be reported. More information is gained when a result is reported even if the data are

somewhat inaccurate. All data reported not meeting all QC requirements will be marked with the appropriate data qualifier flags.

B10.3 Data Validation

Data validation is a systematic process consisting of data editing, screening, checking, auditing, verification, certification, and review for comparing a body of data to an established set of criteria to provide assurance that the data are adequate for their intended use. For air quality samples, the purpose of data validation is to detect and then verify any data values that may not represent actual air quality conditions at the sampling station. Effective data validation procedures usually are handled completely independently from the procedures of initial data collection. All data shall be validated and reviewed to insure the overall quality of the measurement before inclusion in the AQS database.

Data validation is necessary to identify data with errors, biases, and physically unrealistic values before they are used for identification of exceedances, for analysis, or for modeling. If problematic data are identified, the data can be corrected or invalidated, and corrective actions can be taken for field or laboratory operations.

When the data are processed, certain completeness criteria must be met. For example, each canister sample must have a start time, end time, average flow rate, starting and ending canister pressure, dates analyzed, and operator and technician names. The data entry operator will be notified if an incomplete record has been entered, before the record can be closed.

Errors found during statistical screening will be traced back to original data entry files and to the raw data sheets, if necessary. These checks shall be run on every month before any data submission to AQS. Data validation is the process by which raw data are screened and assessed before they can be included in the main database.

The related records will be kept to help data validation. The records consist of notebooks, workbooks, copies of chains of custody, field data sheets, instrument reports, final reports, and the like. All of these records shall be retained for at least five years (the records for lab VOC analyses for 10 years). Copies of the data retained by electronic storage must be kept both at the laboratory site and at the DEQ headquarters building.

B10.4 Data Review

The data review is performed by the field/site operators and the data analysis personnel. It would be extremely difficult for the data analysis personnel to review the raw data without the notations, notes and calibration information provided by the site operators. The review process for the site operator includes:

- Reviewing calibration information and any flags that could affect data and recording any information in the logbooks that might be vital to proper review of the data.
- Reviewing special relationship between data generated and historical data to determine potential irregularities such as reviewing the average concentration for a station or set of stations over a period of time.
- Performing regular secondary reviews on monthly maintenance sheets and site log notes.

B10.5 Data Input

In 2001, EPA changed the Aerometric Information Retrieval System (AIRS) to a database that is solely related to tracking the compliance of stationary sources of air pollution with EPA regulations: the Air Facility Subsystem (AFS). Information about air monitoring - the ambient concentrations of air pollutants - was moved out of AIRS to a separate database: the Air Quality System (AQS). AQS also contains meteorological data, descriptive information about each monitoring station (including its geographic location and its operator), and data quality assurance/quality control information.

All required data are submitted into the AQS database by the Data Management Unit.

Recommended procedures for coding, key punching, and data editing are described in various AQS user manuals.

One of the functions of the AQS is to read transactions coded by state, local, and regional users of AQS, validate these transactions, and use them to update the AQS database. To accomplish this, there are two primary players, AQS users and the AQS database administrator (ADBA).

The AQS users are responsible for the following steps in the update process:

- Load – transfer transactions (either from tape or a database) into a screening file.
- Edit – check the validity of the transactions in the screening file and produce a report to identify errors.
- Correct – alter, remove, or create transactions in the screening file to fix errors identified in the EDIT.
- Notify – inform the ADBA that transactions in the screening file are ready to be updated. This function can also be used to cancel a request to update a particular screening file for updating.

- Message – allow the user and the ADBA to track the above-mentioned functions performed to a screening file when they were performed, and who performed them.
- Delete – remove any transactions that exist in a screening file.

To update the ADBA the following functions are done:

- Scan – to produce a report used by the ADBA to coordinate the update processing across several screening files. This function also “locks” the screening file to prevent the user access to the screening file during the updating.
- Update – to change values and files on the AQS database identified during the SCAN process. This process also removes any transactions from the screening file that have been updated and releases the screening file back to the user.

C ASSESSMENT AND OVERSIGHT

C1 Assessments and Response Actions

An assessment is an evaluation process used to measure the performance or effectiveness of the quality system, the establishment of the monitoring network and sites, and various measurement phases of the data operation.

Quality assurance assessments indicate whether the control efforts are adequate, or need to be improved. Data users use quality control documentation to assess the impact of control efforts on the data quality. Both qualitative and quantitative assessments of the effectiveness of these control efforts will identify those areas most likely to impact the data quality and to what extent. Periodic assessments of data quality must be reported to EPA. On the other hand, the selection and extent of the QA and QC activities, used by a

monitoring agency, depend on a number of local factors. These include the field and laboratory conditions, the objectives for monitoring, the level of the data quality needed, the expertise of assigned personnel, the cost of control procedures, pollutant concentration levels, etc.

To ensure the adequate performance of the quality system, LDEQ will perform the following assessments as they pertain to the air monitoring network and they are summarized in Table C1:

C1.1 Network Reviews

Conformance with network requirements of the ambient air-monitoring network, including PAMS, set forth in 40 CFR Part 58 Appendices D and E are determined through annual network reviews of the ambient air monitoring system. An annual network review is used to determine how well the air monitoring network is achieving its objectives, and how it should be modified to continue to meet those objectives. The Engineering Manager and Environmental Chemical Specialists in Air Analysis Section will be responsible for conducting the network review.

The following criteria will be considered during the review:

- Date of last review
- Areas where attainment/nonattainment re-designations are taking place or are likely to take place
- Results of special studies, saturation sampling, point source oriented ambient monitoring, etc.
- Proposed network modifications since the last network review

In addition, pollutant-specific priorities may be considered (e.g., newly designated nonattainment areas, "problem areas", etc.).

Before the implementation of the network review, significant data and information pertaining to the review will be compiled and evaluated. Such information must include the following, where applicable:

- Network files (including updated site information and site photographs)
- AQS reports (AMP220, 225, 380, 390, 450)
- Air quality summaries for the past five years for the monitors in the network
- Emissions trends reports for major metropolitan areas
- Emission information, such as emission density maps for the region in which the monitor is located and emission maps showing the major sources of emissions
- National Weather Service summaries for the monitoring network area

The information will be checked to ensure it is the most current. Discrepancies will be noted on the checklist and resolved during the review. Files and/or photographs that need to be updated will also be identified. The following categories will be emphasized during network reviews:

- Number of Monitors -- For PAMS, the number of monitors required depend upon the measurement objectives discussed in 40 CFR Part 58, Appendix D. Section B1 of this QAPP discusses the PAMS monitoring network. Adequacy of the network will be determined from the following information:

  - ✓ Maps of historical monitoring data
  - ✓ Maps of emission densities
  - ✓ Dispersion modeling
  - ✓ Special studies/saturation sampling
  - ✓ Best professional judgment
  - ✓ SIP requirements
  - ✓ Revised monitoring strategies

  For PAMS, areas to be monitored must be selected based on urbanized population and pollutant concentration levels. To determine whether the number of PAMS sites is adequate, the number of NAMS sites operating will be compared to the number of PAMS sites specified in 40 CFR 58 Appendix D. The number of the PAMS sites operating can be determined from the AMP220 report in AQS. The number of monitors required, based on concentration levels and population can be determined from the AMP450 report and the latest census data.

- Location of Monitors -- For PAMS, the monitor locations are specified in the regulations, in order to meet the monitoring objectives specified in 40 CFR Part 58 Appendix D. Adequacy of the locations can only be determined from stated objectives. Maps, graphical overlays, and GIS-based information will be helpful in visualizing or assessing the adequacy of monitor locations. Plots of potential emissions and/or historical monitoring data versus monitor locations will also be used.

  During the network review, the objective for each monitoring location or site (see section B1) will be “reconfirmed” and the spatial scale “re-verified” and then compared to each location to determine whether those objectives can still be attained at the present location.

- Probe Siting Requirements -- Applicable siting criteria for SLAMS, NAMS, and PAMS are specified in 40 CFR 58, Appendix E. The on-site visit will consist of the physical measurements and observations to determine compliance with the Appendix E requirements, such as height above ground level, distance from trees, paved or vegetative ground cover, etc. Since many of the

Appendix E requirements will not change within one year, this check at each site will be performed every 3 years.

Before the site visit, the reviewer must obtain and review the following:

- ✓ Most recent hard copy of site description (including any photographs)
- ✓ Data on the seasons with the greatest potential for high concentrations for specified pollutants
- ✓ Predominant wind direction by season

A checklist similar to that used by the EPA regional offices during their scheduled network reviews will be used. This checklist from the *SLAMS/NAMS/PAMS Network Review Guidance* is intended to assist the reviewers in determining conformance with Appendix E. In addition to the checklist items, the reviewer must perform the following tasks:

- ✓ Ensure that the inlet is clean
- ✓ Check equipment for missing parts, frayed cords, damage, etc.
- ✓ Record findings in field notebook and/or checklist
- ✓ Take photographs/videotape in the 8 directions (every 45°)
- ✓ Document site conditions, with additional photographs/videotape

- Other Discussion Topics -- Other subjects for discussion regarding the network review and overall adequacy of the monitoring program include:

  - ✓ Installation of new monitors
  - ✓ Relocation of existing monitors
  - ✓ Siting criteria problems and suggested solutions
  - ✓ Problems with data submittals and data completeness
  - ✓ Maintenance and replacement of existing monitors and related equipment
  - ✓ Quality assurance problems
  - ✓ Air quality studies and special monitoring programs
  - ✓ Proposed regulations
  - ✓ Funding

A report of the network review will be written within two months of the review and appropriately filed.

C1.2 Audit of Data Quality

An audit of data quality (ADQ) reveals how the data are handled, what judgments were made, and whether uncorrected mistakes were made. ADQs can often identify the means to correct systematic data reduction errors. An ADQ must be performed every year. Enough time and effort must be devoted to this activity, so that the auditor or

team has a clear understanding and complete documentation of data flow. The ADQ will serve as an effective framework for organizing the extensive information gathered during the audit of laboratory, field monitoring, and support functions within the agency.

C1.3 Data Quality Assessments

A data quality assessment (DQA) is the statistical analysis of environmental data to determine whether the data quality is adequate to support decisions, which are based on the data quality objectives (DQOs). Data are appropriate if the level of uncertainty in a decision based on the data is acceptable. The DQA process is described in detail in *Guidance for the Data Quality Assessment*, EPA QA/G-9 and is summarized below.

- *Review DQOs and sampling design of the program*. Review the DQO or develop one, if it has not already been done. Define statistical hypothesis, tolerance limits, and/or confidence intervals.
- *Conduct preliminary data review*. Review precision & accuracy and other available QA reports, calculate summary statistics, plots and graphs. Look for patterns, relationships, or anomalies.
- S*elect the statistical test*. Select the best test for analysis based on the preliminary review, and identify underlying assumptions about the data for that test.
- V*erify test assumptions*. Decide whether the underlying assumptions made by the selected test hold true for the data and the consequences
- Perform *the statistical test.* Perform test and document inferences. Evaluate the performance for future use

Data quality assessments must be included in the *QA Annual Report.* Details of these reports are discussed in Section D1.

Measurement uncertainty will be estimated for both automated and manual methods. Terminology associated with measurement uncertainty is found within 40 CFR Part 58, Appendix A. and includes precision, accuracy and bias for the field measurements.

The individual results of these tests for each method or analyzer shall be reported to EPA. Estimates of the data quality will be calculated on the basis of single monitors and aggregated to all monitors.

Table C1

Assessment Summary

Assessment Activity	*Frequency*	*Personnel Responsible*	*Report Completion*	*Reporting/ Resolution*
Network Reviews 40 CFR Part 58, App. D and App. E	1/ year 1/3 years	EPA Region 6/Air Division LDEQ/OEA/APAD	30 days after activity	LDEQ Office of Environmental Compliance Asst. Secretary and APAD Administrator
Audits of Data Quality	1/ year	OEA/APAD	30 days after activity	LDEQ, OEA, Asst. Secretary, APAD Administrator
Data Quality Assessment	1/year	OEA/APAD	120 days after end of calendar year	LDEQ, OEA, Asst. Secretary, APAD Administrator

C2 Reports to Management

Important benefits of regular QA reports to management include the opportunity to alert the management to data quality problems, to propose viable solutions to problems, and to get necessary resources. Quality assessment, including the evaluation of the technical systems, the measurement of performance, and the assessment of data, must be conducted to help ensure that measurement results meet program objectives and that necessary corrective actions are taken early, when they will be most effective.

Effective communication among all personnel is an integral part of a quality system. Regular, planned quality reporting provides a means for tracking: adherence to scheduled delivery of data and reports; documentation of deviations from approved QA and test plans and the impact of these deviations on data quality; analysis of the potential uncertainties in decisions based on the data.

C2.1 Frequency, Content, and Distribution of Reports

Required reports to management for ambient air monitoring in general are discussed in various sections of 40 CFR, Parts 50, 53, and 58. Guidance for management report format and content are provided in guidance developed by EPA's Quality Assurance Division (QAD) and the Office of Air Quality Planning and Standards (OAQPS). These reports are described in the following subsections.

C2.1.1 QA Annual Reports

Periodic assessments of SLAMS data quality must be reported to EPA, according to 40 CFR 58 Appendix A, Section 1.4, revised July 18, 1997. The LDEQ air monitoring *QA Annual Report* is issued to meet this requirement. This document describes the quality objectives for measurement data and how those objectives have been met. Any changes to the PAMS monitoring network regarding site locations, sampling frequency and sampling methods will not occur until approved by EPA Region 6.

The *QA Annual Report* must contain an annual review of the ambient air monitoring network to show that the system meets the monitoring objectives defined in 40 CFR Part 58, Appendix D. This review will identify needed modifications to the network such as termination or relocation of unnecessary stations or establishment of new stations that are necessary.

The *QA Annual Report* will include quality information for each ambient air pollutant in the LDEQ monitoring network. These sections are organized by ambient air pollutant category (e.g., gaseous criteria pollutants, PAMS VOCs). Each section includes the following topics:

- Program overview and update
- Quality objectives for measurement data
- Data quality assessment

For reporting measurement uncertainties, the *QA Annual Report* contains the following summary information required by 40 CFR 58 Appendix A:

- Accuracy of automated methods (O_3, NO/NO_x/NO_2)
- Precision of automated methods (O_3, NO/NO_x/NO_2)
- Flow Rate Audits
- Assessment of Bias

C2.1.2 Network Review Reports

The EPA Regional office reviews the annual network plans submitted by the LDEQ in accordance with 40 CFR Part 58.10. The purpose of the annual network reviews is to determine if the system meets the monitoring objectives defined in 40 CFR Part 58 Appendix D. The review identifies needed modifications to the network including termination or relocation of unnecessary stations or establishment of new stations, which are necessary. Information gathering for these reviews will be coordinated through the Environmental Scientist Manager in AFS in OEA. Supervisors and other personnel in AFS will assist as necessary to provide information and support. The Environmental Scientist Manager is responsible for assuring that such changes are included in planning. The Environmental Scientist

Manager works with the data review and assessment staff to implement all findings affecting data quality.

As required by 40 CFR Part 58 Appendix A, Section 4(a), revised July 18, 1997, the LDEQ has provided a list of all monitoring sites and their AQS site identification codes and submits the list to the EPA Regional Office, with a copy to AQS. The Air Quality System (AQS) is EPA's computerized system for storing and reporting of information relating to ambient air quality data. Whenever there is a change in this list of monitoring sites in a reporting organization, LDEQ will report this change to the EPA Region 6 Office and to AQS.

C2.1.3 Quarterly Reports

Each quarter, LDEQ will report to AQS the results of all precision, bias and accuracy tests it has carried out during the quarter. The quarterly reports will be submitted, consistent with the data reporting requirements specified for air quality data as set forth in 40 CFR Parts 58.26, 58.35 and 40 CFR Part 58 Appendix A, Section 4.

The data reporting requirements of 40 CFR Part 58.35 apply to those stations designated SLAMS or NAMS and include the PAMS stations. Required accuracy and precision data are to be reported on the same schedule as quarterly monitoring data submittals. The required reporting period and due dates are listed in Table C2.

Air quality data submitted for each reporting period will be edited, validated, and entered into the AQS using the procedures described in the *AQS Users Guide.* The Engineering Supervisor of the data management unit will be responsible for preparing the data reports and transmitting them to EPA.

Table C2

Quarterly Reporting Schedule

The Period of Sample Collection	Report to AQS by
January 1-March 31	June 30
April 1-June 30	September 30
July 1-September 30	December 31
October 1-December 31	March 31 (following year)

C2.1.4 Response/Corrective Action Reports

The response/corrective action report procedure will be followed whenever a problem is found such as a safety issue, an operational problem, or a failure to comply with procedures. This report is in the form of a memo and will be used when problems are identified. The response/corrective action report is one of the most important reports to management, because it documents primary QA activities and provides valuable records that can be used in preparing other summary reports.

The response/corrective action report procedure is designed as a closed-loop system. The response/corrective action report identifies the originator, who reported and identified the problem. It states the problem, may identify a root cause, and may propose a solution. The form also must indicate the name of the person or persons assigned to the station where the problem occurred and the supervisor. The assignment of personnel to address the problem, and the schedule for completion will be assigned by the appropriate supervisor. The response/corrective action report procedure closes the loop by requiring that the recipient state in a memo how the problem was resolved and the effectiveness of the solution. Copies of the response/corrective action report will be distributed twice: first when the problem has been identified and the corrective action has been scheduled; and second when the correction has been completed. The action must not be viewed as complete until a root cause has been identified and a successful solution has been applied.

C2.2 Responsible Personnel

This section identifies the individuals responsible within the air monitoring organization for preparing quality reports, evaluating their impact, and implementing follow-up actions. Changes made in one area or procedure may affect another part of the project. Only by defining clear-cut lines of communication and responsibility can all the affected elements of the monitoring network remain current with such changes. The documentation for all changes must be maintained and included in the reports to management. The following are the key personnel involved with QA reporting:

- **Administrators**
  - ✓ *Office of Environmental Assessment (OEA)/Air Planning and Assessment Division (APAD)*
  - ✓ *Office of Environmental Compliance (OEC)/Surveillance Division (SD)*

  Each Administrator has subordinate units assigned to collect, analyze, review or report the data collected by the PAMS network.

- **Environmental Scientist Seniors, Surveillance Division**
  Environmental Scientist Seniors in SD's Laboratory Information Management Services is responsible for receiving, reviewing and verifying VOC data from the contract lab. They are also responsible for managing QA/QC documents from the contract lab.

- **Environmental Scientist Manager, Air Planning and Assessment Division**
  The Environmental Scientist Manager in Air Field Services Section, APAD is responsible for providing oversight and guidance to the ambient air network and for ensuring the operation and collection of the PAMS sites. The Environmental Scientist Manager is responsible for assuring the timely submittal of quarterly and annual data summary reports. The Environmental Scientist Manager works closely with SD's Laboratory Information Management Services to ensure accurate and timely reporting of all data for the PAMS and Air Toxics network.

- **Data Management Engineering Supervisor, Air Planning and Assessment Division**
  The Data Management Engineering Supervisor in Air Field Services Section, APAD is responsible for coordinating the information management activities for SLAMS/NAMS/PAMS data. Specific responsibilities related to management reports include:

  - ✓ Ensuring access to data for timely reporting and interpretation
  - ✓ Ensuring timely delivery of all required data to the AQS system

- **Environmental Scientist Supervisors, Air Planning and Assessment Division**
  APAD GC Field and Network Operation Supervisors are responsible for reporting problems and issuing appropriate response/corrective action reports. They are responsible for assigning specific personnel to address response/corrective action reports and assuring that the work is completed and that the corrections are effective. They are also responsible for assuring that the staff under their supervision maintains their documentation files as defined in the network design. Supervisors are responsible for disseminating information appearing in audit reports and other quality-related documents to operations personnel.

- **Environmental Scientists, Air Planning and Assessment Division**
  They do not normally write reports to management. However, they participate in the process by generating control charts, identifying the need for response/corrective action reports, and maintaining other quality-related information used to prepare QA reports.

- **Project Officer, Air Planning and Assessment Division**
  The project officer is responsible for the final data review and validation and ensuring the data is suitable for the intended use. The project officer is also responsible for data assessment and the generation of quarterly and annual reports.

D DATA VALIDATION AND USABILITY

D1 Data Review, Verification and Validation

This section will describe how LDEQ will verify and validate the data collection associated with the PAMS and Air Toxics monitoring network. Validation can be defined as confirmation by examination and provision of objective evidence that the particular requirements for a specific *intended use* are fulfilled. In addition, the major objective of the PAMS network is to determine the extent of the effect ozone precursor compounds have on the formation of ozone, with this being identified as the intended use. This section will describe the verification and validation activities that occur at a number of the important data collection phases.

D1.1 Sampling Design Verification

Section B1 describes the sampling design for the PAMS and air toxics sampling networks established by LDEQ. It covers the number of sites required, their locations, and the frequency of data collection. The objective of the sampling design is to represent the population of interest at adequate levels of spatial and temporal resolution. Most of these requirements have been described in the Code of Federal Regulations. However, it is the responsibility of LDEQ to ensure that the intent of the regulations is properly administered and carried out.

Verification of the sampling design will occur through three processes:

Network Design Plan Confirmation -- The Network Design Plan that discusses the initial deployment of the network has been submitted, reviewed and approved by EPA before implementation. This process verifies the initial sampling design.

Internal Network Reviews -- Once a year, LDEQ will perform a network review to determine whether the network objectives, as described in the Network Design Plan, are still being met, and that the sites are meeting the siting criteria.

External Network Reviews -- Every three years the EPA Regional Office must conduct a network review to determine whether the network objectives, as described in the Network Design Plan, are still being met, and that the sites are meeting the CFR siting criteria.

D1.2 Sampling Design Validation

The data derived from the sites will be used to validate the sampling design. LDEQ will use each year's collected data to validate that the monitors are properly sited and that the sampling design will meet the objectives of the network. This information will be included in network review documentation and appropriately communicated to the EPA Regional Office. In addition, the processes described in Section B1 will be used to confirm the network design.

D1.3 Sample Collection Verification

Sample collection procedures are described in detail in Section B2 and are developed to ensure proper sampling and to maintain sample integrity.

D1.4 Sample Collection Validation

Monitoring is just one phase of the measurement process. The use of QC procedures has been placed throughout the measurement process to help validate the activities occurring at each phase of monitoring. The review of QC data such as the replicate sampling data, zero/span checks, and precision checks are being used to validate the data collection activities. Any data that indicates unacceptable levels of bias or precision or a tendency (trend on a control chart) must be flagged and investigated. This investigation could lead to a discovery of inappropriate sampling activities.

D1.5 Sample Handling Verification and Validation

Sections B2, B3 and B4 give the sample-handling requirements for both continuous and non-continuous parameters. The preservation methods used are included to ensure that they are appropriate to the nature of the sample and the type of data generated from the sample. Sample handling is one of the phases where inappropriate techniques can have a significant effect on sample integrity and data quality.

Similar to the validation of sampling activities, the review of data from replicate sampling, precision checks, zero/span checks and performance audits are used to validate the sample handling activities. Acceptable precision and bias in these samples would verify that the sample handling activities are adequate. Any data that indicates unacceptable levels of bias or precision or a tendency (trend on a control chart) will be flagged and investigated. This investigation could lead to a discovery of inappropriate activities that require corrective action.

D1.6 Sample Analysis Verification and Validation

Section B4 details the monitoring and analytical methods used by LDEQ and the appropriate analytical requirements and specifications. This section includes the acceptance criteria for important components of the procedures.

Similar to the validation of sampling activities, the review of data from lab blanks, calibration checks, laboratory duplicates and other laboratory QC used for VOC analysis by the laboratory can be used to validate the analytical procedures. Acceptable precision and bias in these samples would lead one to believe that the analytical procedures are adequate. Any data that indicates unacceptable levels of accuracy, bias or precision or a tendency (trend on a control chart) will be flagged and investigated. All flagged data will be “re-verified” that the values are entered correctly. This investigation could lead to a discovery of errors, requiring corrective action. The data qualifiers or flags can be found in the laboratory quality manual.

D1.7 Verification and Validation of Quality Control Procedures

Section B4 and B7 of this QAPP specify the QC checks that are to be performed during sample collecting and handling. Laboratory SOPs will specify the quality control checks for each analytical batch to be used in laboratory analysis. These checks provide indications of the quality of data being produced by specified components of the measurement process. For each specified QC check, the procedure, acceptance criteria, and corrective action are specified in the SOP.

Validation activities of many of the other data collection phases mentioned in this subsection use the quality control data to validate the proper and adequate implementation of that phase. Therefore, validation of QC procedures will require a review of the documentation of the corrective actions that were taken when QC checks failed to meet the acceptance criteria, and the potential effect of the corrective actions on the validity of the routine data. Section B5 describes the techniques used to document QC review/corrective action activities.

D1.8 Verification and Validation of Calibration Procedures

Section B7, as well as the field (Section B2) and the analytical sections (Section B4) detail the calibration activities and requirements for the critical pieces of equipment for the PAMS and air toxics sampling networks.

Similar to the validation of sampling activities, the review of calibration data that is described in Sections B5 and B7 can be used to validate calibration procedures. Calibration data within the acceptance requirements would lead one to believe that the monitoring equipment, samplers, and analyzers are operating properly. Any data that indicates unacceptable levels of bias or precision or a tendency (trend on a control chart) must be flagged and investigated as described in Section B5 or B7. Validation would include the review of the documentation to ensure corrective action was taken as prescribed.

D1.9 Verification and Validation of Data Reduction and Processing

As part of the audits of data quality, discussed in Section C1, a number of sample IDs, chosen at random will be identified. All raw data files, including the following will be selected:

- Pre-sampling activity (VOC canister)
- Sampling (both continuous and non-continuous parameters)
- Data reduction
- Sample handling/custody (canisters)
- Post-sampling activity (canisters)
- Corrective action
- Calibration – the calibration information represented from that sampling period.

These raw data must be reviewed and final concentrations calculated by hand to determine if the raw data values are comparable to the final values submitted to AQS. The data must also be reviewed to ensure that appropriate corrective actions were taken for the appropriate data associated with flags or any other qualifiers.

D2 Verification and Validation Methods

The purpose of data validation is to detect and then verify any data values that may not represent actual air quality conditions at the sampling station. All data shall be validated and reviewed to insure the overall quality of the measurement before inclusion in the AQS database. Many of the processes for verifying and validating the measurement phases of the PAMS data collection operation have been discussed in Section D1. If these processes, as written in the QAPP, are followed, and the sites are representative of the boundary conditions for which they were selected, one would expect to achieve the PAMS and air toxics sampling DQOs. However, exceptional events may occur, and monitoring/sampling activities may negatively affect the integrity of data. In addition, it is expected that some of the QC checks will fail to meet the acceptance criteria. Information on problems that affect the integrity of data is identified in the form of flags. It is important to determine how these failures affect the routine data. The review of this routine data and their associated QC data will be verified and validated for each continuous monitor and on a sample basis for VOC analysis. If measurement uncertainty can be controlled within acceptance criteria, then the overall measurement uncertainty will be maintained within the precision and bias DQOs.

A thorough review of the ambient air monitoring and the PAMS data will be conducted for completeness and data entry accuracy. All raw data that are hand entered from data sheets will be double-checked before entry in the database. The entries are compared to reduce the possibility of entry and transcription errors. Once the data are entered into the database, the system will review the data for routine data outliers and data outside of acceptance criteria. These data will be flagged/annotated appropriately. All flagged data will be “re-verified” that the values were entered correctly.

Validation of measurement data will require four stages:

- During the level “0” data validation, routine checks are made during the initial data processing and generation of data, including proper data file identification, review of unusual events, review of field data sheets and result reports, instrument performance checks and QC performance. Computer file entries are checked against data sheets. Samples are flagged/annotated when significant deviations from measurement assumptions have occurred, or instrument malfunctions have occurred. Measurements biased by quantifiable calibration errors or interferences are adjusted appropriately & all changes are documented in the database. The Laboratory Manager usually conducts this validation & verification level.
- During the level “1” data validation, tests for internal consistency are conducted to identify values in the data which appear atypical when compared to values of the entire data set. This may include comparison of time series plots to expected diurnal patterns. The relationship between various VOC species may be investigated using scatter plots. This validation level may be conducted by the

Laboratory Manager or by the APAD Project officer.

- During the level “2” data validation a comparison of the current data set with historical data is conducted to verify consistency over time. This level can be considered a part of the data interpretation or analysis process. This investigation will include examining abundant species (fingerprints) & noting what changes have occurred over time. The spatial and temporal characteristics of the data are investigated. This validation level is conducted by the APAD Project officer or other person designated by the APAD administrator.
- During the level “3” Data Validation tests for parallel consistency with data sets from the same population (i.e., region, period of time, air mass, etc.) are conducted to identify systematic bias. This level can also be considered a part of the data interpretation or analysis process. VOC speciation and concentration among sites is compared using special studies data, etc. Determinations are made to explain differences by meteorology, photochemistry, contamination, analytical differences, etc. This validation level is conducted by the APAD Project officer or other person designated by the APAD administrator.

Data validations levels 1, 2 & 3 shall be used to determine if the data is suitable for the intended use. Any data found to be flawed or unsuitable shall be appropriately flagged/annotated and may be removed from the reporting dataset.

Records of all invalid samples will be filed for 5 years. Information will include a brief summary of why the sample was invalidated along with the associated flags. This record will be available on the LIMS since all samples that were analyzed will be recorded. At least one flag will be associated with an invalid sample or when no analysis result is reported. Additional flags will usually be used to describe the reason for these flags, as well as free form notes or comments from the field operator or laboratory.

If the amount of data being invalidated is relatively small, the department will report them every month to EPA Region 6. If however, more than 5 values from one site appear to require invalidation, EPA Region 6 will be notified immediately and the issue described.

D3 Reconciliation with User Requirements

D3.1 Purpose

The DQOs for the PAMS and air toxics sampling networks were developed in Section A7. This section of the QAPP will explain the procedures that LDEQ will follow to determine whether the data being produced complies with the DQOs and the actions taken as a result of the assessment process. Such an assessment is termed a Data Quality Assessment (DQA) and is described in *EPA QA/G-9: Guidance for Data*

Quality Assessment. Assessments must be made at the individual sampler as well as at the network level.

D3.2 Reconciling Results with DQOs

Section A7 of this QAPP contains the details for development of the DQOs including defining the primary objective of the PAMS Network, translating the objective into a statistical hypothesis, and developing limits on decision errors.

Section B1 of this QAPP contains the details for the network design, including the rationale for design assumptions and the monitoring locations and frequency. If any deviations from the network design have occurred, these will be indicated and their potential effect carefully considered throughout the DQA process.

A preliminary data review will be performed to uncover potential limitations to using the data, reveal outliers, and generally explore the basic structure of the data. Particular attention will be directed to looking for anomalies in the recorded data, missing values, and any deviations from standard operating procedures. This is a qualitative review. However, any concerns will be further investigated in the next two steps.

LDEQ will submit to EPA in AQS format valid precision and accuracy data for each continuous monitor each calendar quarter. LDEQ will calculate quarterly integrated estimates of precision and accuracy applicable to the data submitted as prescribed in 40 CFR Part 58.

LDEQ will calculate the properly weighted probability limits for precision and accuracy for the calendar year from the data submitted each calendar quarter. These calculations result from the formulas specified in 40 CFR Part 58, Section 5. The limits calculated will be associated with the data submitted by LDEQ in the annual report on monitoring activities. For precision data, for each monitor, standard deviation and 95 percent probability limits are calculated. For accuracy data of continuous monitors an integrated probability interval for all analyzers audited is calculated for each pollutant and separate probability limits are calculated for each audit concentration level. Also calculated are the percentage difference for each audit concentration, the individual percentage difference for all analyzers, the standard deviation of the percentage difference for all analyzers audited and 95 percent probability limits for each audit concentration level.

If any of the data from the precision and accuracy data submitted violates the statistical limits, LDEQ will investigate for the cause of the violation and take corrective action to alleviate the problem. In order to determine the level of corrective action to be taken, LDEQ will need to determine if the problem is unique to one or two sites, unique to LDEQ or caused by a broader problem, like a particular type of monitor/sampler

demonstrating poor QA on a national level. LDEQ understands that AQS will generate QA reports summarizing accuracy and precision statistics at the national and reporting organization levels, and by method designation. These reports will assist LDEQ in determining the appropriate level at which the DQO's are being violated. The procedure for determining the level of violation is,

- Review national reports for which LDEQ's DQA process indicated a violation. If large bias or imprecision is seen at the national level, LDEQ will request assistance from the EPA Region 6 Office and OAQPS. If no problem is seen at national level, LDEQ will proceed looking at the QA reports specific to its neighboring reporting organizations.
- Review neighboring reporting organizations' precision and bias reports for the method designations for which LDEQ's DQA process indicated a violation. If large bias or imprecision is seen in the neighboring organizations, LDEQ will request assistance from the EPA Region 6 Office. If no problem is seen in the neighboring reporting organizations, LDEQ will proceed looking at the QA reports specific to LDEQ.
- Within LDEQ, if the violations occur for only one method designation, performance evaluation data for that method from NPAP will be reviewed for confirmation. The performance evaluation data may show that one of the monitors has a problem and must be repaired or replaced. LDEQ will also use the national performance evaluation summaries to see if LDEQ is unique or like the national network. If LDEQ is similar to the national picture, then assistance will be requested from the EPA Region 6 Office and OAQPS. The results from the neighboring reporting organizations will also be reviewed. If the violations seem unique to LDEQ, then an investigation will continue on all the pieces that comprise the data.
- Communication with Regional Office. If a violation of the accuracy and precision DQOs is found, LDEQ will remain in close contact with the EPA Region 6 Office both for assistance and for communication.

Appendix Reference Documents

All Field Sampling Standard operating procedures are maintained on the LDEQ intranet site at the following location. http://intranet/sop/soplist.asp . The lab analytical SOPs are maintained with the contract lab that are subject to LELAP's audits. The document ID is 45970081. The SOPs that are used in the PAM/Air Toxics Program are as follows.

Automated Gas Chromatograph Determination of Total Non-Methane Organic Carbons LDEQ APAD SOP#: 1065

Sampling of Volatile Organic Compounds in Ambient Air Collected in Specially-prepared Canisters (Xontech Samplers), LDEQ APAD SOP#: 1099

Meteorological Parameters, LDEQ APAD SOP#: 1350

Methane--Non-Methane Analyzer Coupled with NMHC Ttriggered Sampling of Volatile Organic Compounds in Ambient Air, LDEQ APAD SOP#: 1746

Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air: Method TO14-A and TO-15, Second Edition, U.S. EPA 600/625/R-96/010B, January 1997 for Canister Cleaning, SOP TAE003-03, SGS North America Inc., Houston

Determination of Target Toxic Compounds in Ambient Air by Gas Chromatography/Mass Spectrometry (GC/MS) based on EPA Compendium Method TO-15 for Louisiana Department of Environmental Quality, SOP TAE007-04, SGS North America Inc., Houston

Determination of Determination of Ozone Precursors in Ambient Air by Gas Chromatography/Flame Ionization Detector by TO-12 Modified, SOP TAE006-03, SGS North America Inc., Houston