MEASUREMENTS OF VOC SPECIES AT THE TCEQ CAMS 19 MONITORING SITE (LONGVIEW, TEXAS)

QUALITY ASSURANCE PROJECT PLAN

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Preface
This Quality Assurance Project Plan is submitted in fulfillment of the following quality assurance project plan requirements of the "Measurements of VOC species at the TCEQ CAMS 19 Monitoring site (Longview, Texas)"

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Quality Assurance Project Plan Approval Sheet

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1. PROJECT DESCRIPTION AND OBJECTIVES

1.1 STUDY PURPOSE, SITE, AND ENVIRONMENTAL SYSTEM TO BE TESTED

The Texas Commission on Environmental Quality (TCEQ) CAMS 19 air monitoring site is located in northeast Texas south and east of the city of Longview (latitude = 32.378611, longitude = -94.711667). The site location is important since measurements collected there can be indicative of both regional scale air quality issues (both regional and interstate sources of pollution) and local air quality impacts including both chemical manufacturing and natural gas production. Previous measurements collected at the site of both methane/non-methane hydrocarbons and speciated hydrocarbons have documented the impact of the local sources. The work to be performed in this project will extend the historical data base of methane (CH_4) and non-methane hydrocarbon (NMHC) measurements, augmented by nearly continuous compound class level speciation (i.e. – alkanes, alkenes, and aromatics). This data, taken in concert with the existing ozone, SO_2, NO, NOy, and meteorological measurements will allow a greater understanding of the impact of the various sources that contribute to the observed air composition at the CAMS 19 site.

1.2 PROJECT OBJECTIVES

The objectives of the project are:

- Evaluate the efficacy of using the Innova photoacoustic spectrometer to collect functional-class NMHC data in the ambient environment.
- Collect concentration data for Methane, ethylene, propylene, propane, and benzene at the CAMS 19 field site.
- Evaluate the impact of various VOC sources on the CAMS 19 site during the measurement period (8/1/07-9/30/07).

2. PROJECT ORGANIZATION

2.1 KEY POINTS OF CONTACT

- Dr. Gregory Yarwood, Environ International Corporation
- Dr. Martin Buhr, Air Quality Design, Inc.

2.2 QA MANAGER

- Dr. Martin Buhr, Air Quality Design, Inc.

2.3 PROJECT PARTICIPANTS AND RESPONSIBILITIES

2.3.1 Texas Commission on Environmental Quality (TCEQ)

Project Coordination [Doug Boyer]:

- Approves Quality Assurance Project Plan

2.3.2 Air Quality Design, Inc. (AQD)

Project Coordinator [Martin Buhr]:

- Coordinates the contract and budget issues for the AQD portion of the project;
- Coordinates the field deployment of the air monitoring equipment;
- Manages AQD data processing personnel;
- Coordinates the development and maintenance of the project related planning tools (e.g. QAPP, SOPs, etc.);
- Provides deliverables from AQD to Environ and TCEQ
- Provides project status reports from AQD to the Environ contract manager.

Measurement systems operations personnel [Martin Buhr and William Wallace]:

- Operates and maintains monitoring and sampling equipment according to the QAPP;
- Performs scheduled calibrations and quality control checks on sampling and measurement equipment in compliance with the QAPP;
- Maintains measurement support documentation;

Data processing personnel [Martin Buhr and William Wallace]:

- Coordinates the validation, analysis, management, and delivery of data according to the QAPP requirements;
- Coordinates development of graphical and non-graphical analysis products for the data collected;
- Responsible for the development of data and graphical products resulting from project activities;

2.3.3 Environ International Corporation

Project Coordinator [Greg Yarwood]:

- Coordinates the contract and budget issues for the project.
- Reviews and approves project related reports and data archive.

3. EXPERIMENTAL APPROACH

3.1 GENERAL APPROACH AND CONDITIONS

The measurement approach that will be used to provide the CH_4-NMHC measurements is multi-wavelength Photo-Acoustic Spectroscopy (PAS). A commercial PAS, manufactured by Innova-AirTech Instruments will be used with an appropriate filter set to provide 5-10 minute resolution measurements of CH_4, total NMHC calibrated as propane, alkenes, calibrated as both propene (C_3H_6) and ethene (C_2H_4), and aromatics calibrated as benzene (C_6H_6). Use of the Innova-Air tech PAS for ambient measurements requires that the sample gas is dried using a Naphion® drier, and that the analyzer is calibrated with each target gas. We have used the Innova PAS for ambient monitoring previously as part of a system called the Ambient Air Analyzer (AAA).

3.2 SAMPLING STRATEGY

We plan on substituting our instrument system for the currently non-operational automated canister sampling system in place at the CAMS 19 site. We will sample the atmosphere at the site in a semi-continuous way (5-minute integrated samples) for the period August 1- September 30, 2007.

3.3 SAMPLING AND MONITORING POINTS

We will use the existing glass-lined stainless steel sampling line currently in place and attached to the special-project automated canister sampling system.

3.4 FREQUENCY OF SAMPLING

We will sample in a semi-continuous way during the project period and will report 5-minute integrated values for the target species.

3.5 MEASUREMENTS

The measurements to be collected using the Innova PAS include those listed in Table 3-1.

Table 3-1. Measurements to be collected using the Innova PAS

Innova filter number	Wavelength (cm-1)	Calibrated species	Estimated Detection limit (5 minute integration)
968	1291	Methane	0.1 ppmv
987	2950	Propane (NMHC)	0.01 ppmv
976	941	Propene	0.1 ppmv
974	1061	Ethene	0.15 ppmv
982	710	Benzene	0.7 ppmv

3.6 PLAN FOR EVALUATING PROJECT OBJECTIVES

The plan for evaluating the project objectives are presented in Sections 5 through 7.

4. SAMPLING PROCEDURES

4.1 METHOD TO ESTABLISH STEADY-STATE CONDITIONS

Sampling will be performed on a semi-continuous basis. The duty cycle of the PAS instrument includes 2 minutes of sample chamber flushing and 3 minutes of analysis. Thus the sample inlet will be under flow for 2 out of every 5 minutes. This equilibration period should be adequate to establish steady-state conditions.

4.2 SITE SPECIFIC FACTORS

There are no site-specific factors associated with the sampling procedures.

4.3 SITE PREPARATION

The PAS instrument system will be installed at the CAMS 19 site in place of an existing automated canister sampling system. The PAS instrument will be physically located on the top of the canister sampling system rack and will utilize the existing glass-lined stainless steel sample line currently installed at the CAMS 19 site.

4.4 SAMPLING PROCEDURES

The Innova PAS instrument operates in a semi-continuous mode. A sample is drawn by an internal sampling pump into an analysis chamber. The chamber is sealed and the sample is subjected to various wavelengths of infrared (IR) radiation by means of a broadband IR source and a carousel of narrow band-pass filters. Absorption of the IR radiation by the sample is proportional to the amount of analyte in the sample and is measured by a change of pressure within the sample chamber.

Water is a strong absorber in virtually all regions of the IR and therefore must be removed from the sample before the IR analysis. We will accomplish this by passing the sample gas through a Naphion® dryer manufactured by PermaPure™. In turn, the Naphion® dryer will be “pumped” by a pressure-swing-absorption (PSA), molecular sieve-based dryer (PermaPure model HD-1000).

Zero and calibration gases will be added to the sample stream upstream of the Naphion® dryer to allow assessment of sample transmission. A schematic diagram of the sampling and calibration system is shown in Figure 4-1.

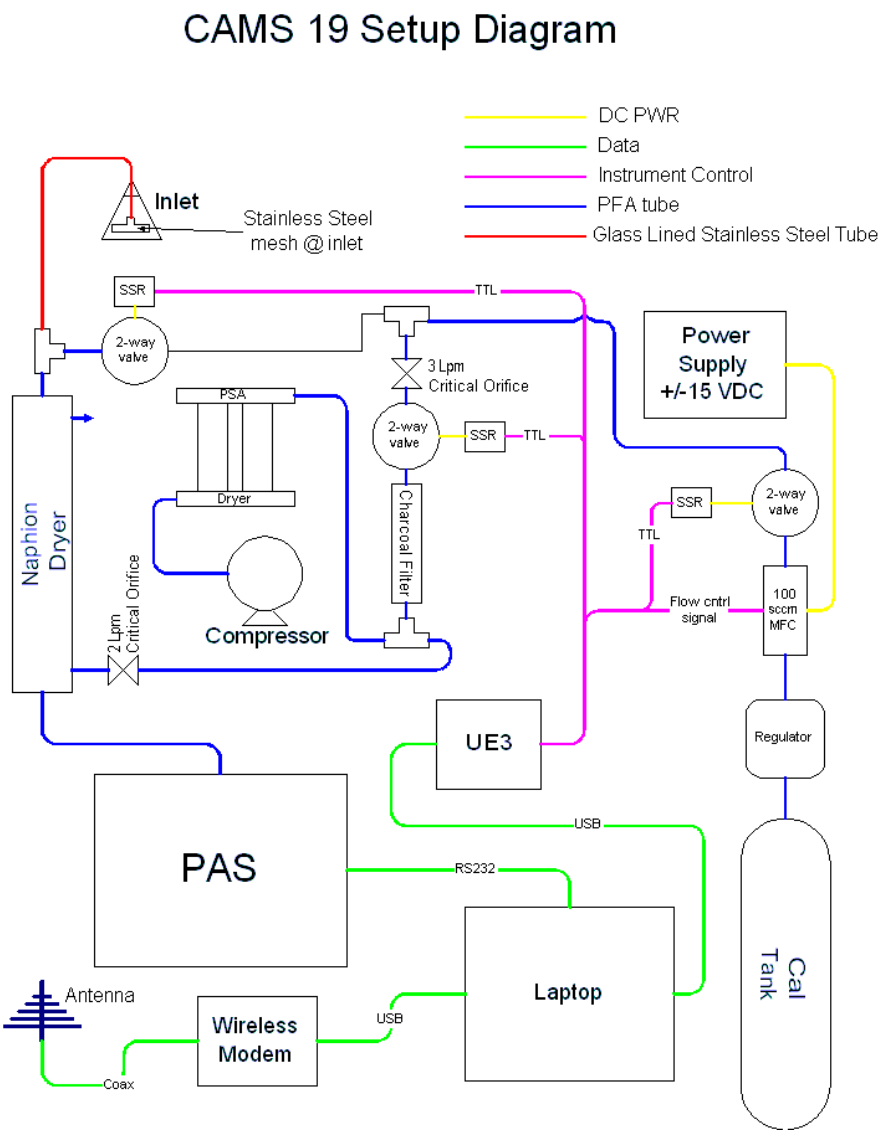

Figure 4-1. Diagram of the sampling and measurement system to be installed at the CAMS 19 site.

4.5 CALIBRATION OF THE SAMPLING EQUIPMENT

Calibration of the sampling equipment will include flow calibration of the various flows using a Sensidyne Gilibrator®. Calibration of the PAS itself is discussed in Section 5.

4.6 AVOIDING CROSS-CONTAMINATION

There are no discrete samples for this method. The identity and disposition of sample measurements are documented electronically by the log associated with the instrument support computer and processing software.

4.7 ASSURING REPRESENTATIVE SAMPLES

The sampling site and sampling line we will use have been in operation for several years and have been determined by TCEQ scientists to be representative of the region.

4.8 SAMPLE QUANTITIES

There are no discrete samples for this method. The identity and disposition of sample measurements are documented electronically by the log associated with the instrument support computer and processing software.

4.9 SAMPLE CONTAINERS

There are no discrete samples for this method. The identity and disposition of sample measurements are documented electronically by the log associated with the instrument support computer and processing software.

4.10 SAMPLE IDENTIFICATION

The identity and disposition of sample measurements are documented electronically by the log associated with the instrument support computer and processing software.

4.11 SAMPLE PRESERVATION

There are no discrete samples for this method. The identity and disposition of sample measurements are documented electronically by the log associated with the instrument support computer and processing software. The electronic media is stored in the computer that collects the data and is backed-up on a CD after downloading to the AQD computer.

4.12 SAMPLE HOLDING TIME

There are no discrete samples for this method. The identity and disposition of sample measurements are documented electronically by the log associated with the instrument support computer and processing software.

4.13 SAMPLE SHIPPING

There are no discrete samples for this method or shipping required. The identity and disposition of sample measurements are documented electronically by the log associated with the instrument support computer and processing software.

4.14 SAMPLE CHAIN-OF-CUSTODY

There are no discrete samples for this method. The identity and disposition of sample measurements are documented electronically by the log associated with the instrument support computer and processing software.

4.15 SAMPLE ARCHIVE

Data obtained by AQD will be archived on our local computers and archived on CD-ROM.

5. TESTING AND MEASUREMENT PROTOCOLS

5.1 MEASUREMENT METHOD DETAIL

The instrument that will be used to collect the VOC measurements is a photoacoustic spectrometer. The instrument works by illuminating a sample volume with infrared radiation that has passed through one of six band-pass filters that are fixed to a revolving carousel. The change in pressure in the sample cell due to absorption of the filtered IR radiation by a VOC species constitutes the instrument signal. The pre-deployment instrument preparation task will be focused on calibration of the PAS instrument and testing to ensure that the integral cross-compensation of the six filters allows us to operate the instrument at maximum performance. The instrument will be controlled via a serial interface connected to a laptop computer running software designed explicitly for the Innova PAS. We will use certified calibration gases both as individual components and as a mixture to calibrate and test the instrument. Calibration of the instrument will be checked regularly during the course of the study via on-site, automated span checks using the same calibration gases used for the instrument calibration.

5.2 DATA VALIDATION FOR UNPROVEN METHODS

Application of the PAS method for measurement of the target VOC species in ambient air is an un-proven method. Our Level 1 data validation will include a comparison to the proven FID-based Methane/total Non-Methane hydrocarbon instrument in operation at the CAMS 19 site. In particular we expect that the PAS methane and Propane channels should compare well. An evaluation of the data from both instruments will be included in the final report. In addition, we will cross calibrate the instruments using the PAS calibration standard with the FID-based instrument and the FID calibration standard with the PAS instrument. The cross calibration will be performed at least twice during the field study.

5.3 MEASUREMENT SPECIFIC CALIBRATION PROCEDURES

Calibration of the PAS will be performed in two separate modes. First, prior to deployment, the instrument will be calibrated using individual component gas standards. The individual components will be blended as necessary using mass-flow controlled dynamic dilution to allow for cross compensation of the response from the separate filters to each calibrated gas. Once complete this calibration will allow measurement of the individual species in a mixed, ambient atmosphere.

The second calibration will be performed both in pre-deployment and on a daily basis during the deployment. The daily calibration will be performed using mass-flow-controlled dynamic dilution of a mixture of the target gases. The results of this calibration will be used to evaluate instrument performance in terms of the acceptance criteria discussed in Section 6. The daily calibrations will be performed as a multi-point calibration including the levels presented in Table 5-1. We expect that performance of the multipoint calibration check will take about 1 hour each day. We will perform the calibration on an every 23 hour schedule so that a given period of the day is not lost entirely to calibration.

Table 5-1. Calibration levels for the daily performance check.

Calibration level	Species Concentration	Time in calibration
0	0 (zero-gas)	15 minutes
1	5 ppm	15 minutes
2	25 ppm	15 minutes
3	50 ppm	15 minutes

6. QA/QC CHECKS

6.1 ACCEPTANCE CRITERIA

The data collected will be evaluated based on daily calibration and zero-gas challenges. Acceptance of the data will be made if the results fall within the criteria outlined in Table 6-1.

Table 6-1. Acceptance Criteria for the data to be collected.

Parameter/ Target Compound	Analytical Method	Detection Limit	Precision (95% probability limits)	Accuracy	Completeness
Methane	PAS, 1291 cm^{-1}	0.1 ppmv	+/- 15%	+/- 20 %	85 %
Ethylene	PAS, 1061 cm^{-1}	0.15 ppmv	+/- 15%	+/- 20 %	85 %
Propylene	PAS, 941 cm^{-1}	0.1 ppmv	+/- 15%	+/- 20 %	85 %
NMHC as Propane	PAS, 2950 cm^{-1}	0.01 ppmv	+/- 15%	+/- 20 %	85 %
Benzene	PAS, 710 cm^{-1}	0.7 ppmv	+/- 15%	+/- 20 %	85 %

6.2 PROJECT-SPECIFIC QA OBJECTIVES

A project-specific QA objective is that the measured Methane and NMHC (as propane) are in agreement the comparable parameters measured using the TEI model 55C instrument within the stated uncertainties of both instruments.

6.3 ASSESSMENT OF QA OBJECTIVES

Assessment of the QA objective will be performed by review of the daily calibration and zero-gas checks that will be performed as outlined in Section 5.

6.4 OTHER QC CHECKS

In addition to the daily calibration checks we will challenge the PAS instrument with zero-gas to ensure that the data is not impacted by any artifact signals.

6.5 REQUIRED FREQUENCY FOR QC CHECKS

The PAS instrument will undergo automated zero and calibration checks on a daily basis. We plan on calibrating every 23 hours to minimize the possibility that QC checks mask the occurrence of any recurrent events impacting the site.

7. DATA REPORTING, REDUCTION, AND VALIDATION

7.1 REPORTING REQUIREMENTS

Measurements of the species listed in Table 7-1 will be submitted as 5-minute integrated values along with the sampling time in a format to be specified by TCEQ for integration into the TCEQ LEADS data management system.

Table 7-1. Reported species and Units

Reported species	Units
Methane	ppmC
Ethylene	ppmC
Propylene	ppmC
NMHC as propane	ppmC
Benzene	ppmC

7.2 DELIVERABLES

- TCEQ-approved Quality Assurance Project Plan (QAPP)
- Raw sampling data files, events sampling logs, individual species time series graphs
- NARSTO Level 1(5-minute integrated data) will be submitted to the TCEQ LEADS system on a weekly basis.
- Monthly progress report
- Final report. Draft Final report will be submitted and will be modified to include comments or suggestions for changes from Environ staff or other readers.
- AQD will deliver time-series plots for the species measured, comparison of the PAS-measured species to the TEI model 55C methane and NMHC data. Additionally, averaged 5-minute data files will be delivered.

A final report that summarizes the project and results will be delivered to Environ.

7.3 DATA REDUCTION PROCEDURES

The data collected at the CAMS 19 site will be downloaded on a daily basis and processed from the native Innova PAS data format to a format compatible with the TCEQ LEADS data management system. The overall process is shown graphically in Figure 7-1. AQD will coordinate with TCEQ personnel in connection with the appropriate data format and the appropriate TCEQ ftp folder where the processed data will be placed. Review of the daily calibration and zero tests will be included as part of the data processing. All reported data will

include a data quality flag following the NARSTO data quality guidelines. Any data edited from the record will include the reason for invalidation.

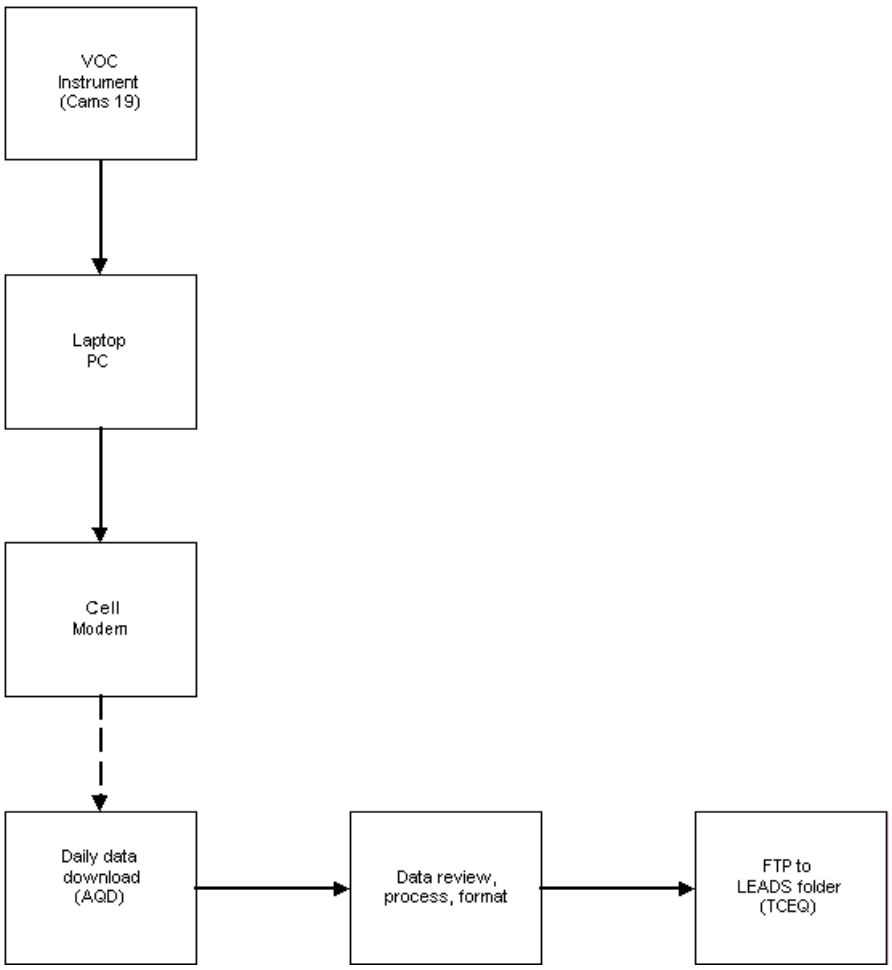

Figure 7-1. Diagram of the data processing steps to be followed during the project.

7.4 DATA VALIDATION PROCEDURES

Comparison of the data collected using the PAS will be made with the TEI model 55C Methane/NMHC instrument in operation at the CAMS 19 site. This activity will be considered a Level 2 data quality process.

7.5 DATA STORAGE REQUIREMENTS

Stored on computers for 3 years and backed up to optical media.

7.6 FINAL DOCUMENTS

The results of this project will be summarized in a Final Report and Data Atlas.

8. ASSESSMENTS

8.1 AUDITS

We do not plan on a formal audit of the measurement equipment.

8.2 CORRECTIVE ACTIONS

Daily assessment of the instrument performance will be conducted at AQD. If the performance of the instrument is outside the acceptance criteria AQD will first try to correct the problem remotely via our computer interface and if necessary AQD personnel will travel to the CAMS 19 site to perform corrective action.

8.3 PARTIES RESPONSIBLE FOR CORRECTIVE ACTIONS

AQD will be responsible for corrective action necessary to accomplish the goals of the project.

APPENDIX A. CALIBRATION GAS CERTIFICATIONS

(attached)