

# Quality Assurance Project Plan

## Project 14-023

### Assessment of Two Remote Sensing Technologies to Control Flare Performance

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#### Summary of Project

**QAPP Category Number:** III  
**Type of Project:** Measurement

The University of Texas at Austin has prepared this QAPP following EPA guidelines for a Quality Assurance (QA) Category III Project: Measurement. It is submitted to the Texas Air Quality Research Program (AQRP) as required in the Work Plan requirements.

**QAPP Requirements:** Descriptions of project description and objectives; organization and responsibilities; scientific approach; sampling and measurements procedures; quality metrics; data analysis, interpretation, and management; reporting; and references.

**QAPP Requirements:**

Audits of Data Quality: 10% Required  
Report of QA Findings: Required in final report

May 29, 2014

## **Title and Approval Sheet**

This document is a Category III Quality Assurance Project Plan for the Assessment of Two Remote Sensing Technologies to Control Flare Performance project. The Principal Investigator for the project is Vincent Torres and the Co-Principal Investigator is Tom Edgar.

Approval Signatures:

**This QAPP was approved electronically on 4/29/2014 by David W. Sullivan, The University of Texas at Austin.**

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Dave Sullivan  
Project Manager, Texas Air Quality Research Program

**This QAPP was approved electronically on x/xx/2014 by Cyril Durrenberger, The University of Texas at Austin.**

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Cyril Durrenberger  
Quality Assurance Project Plan Manager, Texas Air Quality Research Program

**This QAPP was approved electronically on 4/23/2014 by Vincent Torres, The University of Texas at Austin.**

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Vincent Torres, PE  
Principal Investigator, The University of Texas at Austin

## **QAPP Distribution List**

Texas Air Quality Research Program

David Allen, Director

Dave Sullivan, Project Manager

Texas Commission on Environmental Quality

Russ Nettles, Project Liaison

The University of Texas at Austin

Vincent Torres, Principal Investigator

Tom Edgar, Co-Principal Investigator

And representatives from

Project Industry Advisory Committee

Aerodyne Research Institute, Inc.

Petrologistics, Limited Liability Company (LLC)

Leak Surveys, Inc.

Providence Photonics, LLC

## Quality Assurance Project Plan (QAPP)

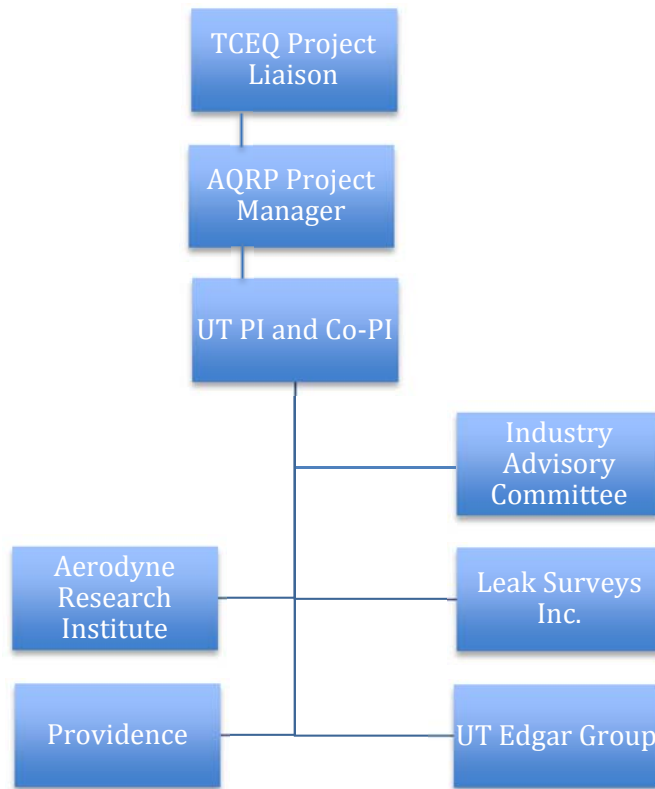
### 1.0 Project Description and Objectives

The purpose of the proposed project is to conduct a series of field tests to determine the technical, economic and operational feasibility of two approaches designed to maximize flare performance. The field tests would be conducted using an operational, full-scale industrial flare at the Petrologistics, LLC plant in Houston, Texas to obtain directly applicable data from the approaches evaluated. The flare that will be used is a Calludus 54-inch outside diameter (OD) flare with center, lower and upper steam, 199-ft tall. It has an overall capacity of 1,160,000 pounds per hour (lb/hr) with a smokeless capacity of 180,000 lb/hr. The average steady flow to the flare is 2,000 lb/hr. For these tests the fuel gas and natural gas flow rates going to the flare will be varied to vary the composition of the vent gas going to the flare. The latter cannot be determined until after the initial site visit to the plant. The proposed project addresses the AQRP 2014-2015 priority research area “Measurements, analyses and modeling that identify and describe industrial flare operating regimes that provide both high combustion efficiency and minimal smoke formation” by helping to identify potential technologies that can determine the combustion efficiency (CE) and use this information to control the performance of a flare to provide high CE.

### 2.0 Organization and Responsibilities

This project is administered by the AQRP, which has assigned a Texas Commission on Environmental Quality (TCEQ) Liaison, Russ Nettles, and an AQRP Project Manager, Dave Sullivan, to oversee the project. The UT Austin Principal Investigator (PI), Vincent Torres, and Co-Principal Investigator, Tom Edgar, will report to the AQRP Project Manager and will have responsibility for maintaining the project schedule and providing project deliverables. There will be three subcontractors involved in the project as described in Section 3.0 Research Approach and they will report to the Project PI. These three subcontractors and their responsibilities are: Aerodyne Research Institute – CE Reference Measurements; Leak Surveys, Inc. (LSI) – forward looking infrared (FLIR), Infrared (IR) and visible light video recordings of the flare plume during all tests; and Providence Photonics, LLC (Providence) – CE measurements using their staring multispectral mid-wave infrared (IR) imaging camera. The Edgar Group at UT Austin will use the video images obtained by LSI to apply their principal component analysis (PCA) based multivariate image analysis technique to determine the CE of each test. UT Austin (Vincent Torres) will be responsible for performing the evaluation of the CE measurements made by Providence and determined by the Edgar Group. An Industry Advisory Committee (IAC) will provide input and review at four points in the project: 1) Initially in development of the field test plan, review of the methodology for making the combustion efficiency (CE) reference measurements, and review of the criteria that will be used for evaluating the technologies being tested; 2) Review of the Quality Assurance Project Plan (QAPP); 3) Observation of the Field Tests; and 4) Review of the draft final report. The TCEQ Project Liaison will be an ex-officio member of the IAC. The IAC will report to the Project PI and Co-PI.

## Project Organizational Chart



### 3.0 Research Approach

To evaluate the two technologies, a series of tests will be planned to obtain CE data points over as wide a range of CEs as possible for the flare that will be used while still complying with the Environmental Protection Agency's 40CFR § 60.18 (US CRF, 60.18) and 40CFR § 63.11 (US CFR, 63.11) as appropriate. The maximum range of CE that will be permissible at the plant will be determined during the initial site visit to the plant.

The test series will be conducted in a single blind manner, i.e., for each test series, only limited flare test operational data will be provided to each of the technology participants so as to not influence their measurements or determination of CE. Each of the technology participants will make their measurements or conduct their analysis continuously during each test series or after the field tests are completed. A detailed test plan will be developed subsequent to the initial site visit to the plant and will be provided in an update to this QAPP. However, it is anticipated that to the extent possible, the test series would include operating the flare at a constant steam assist rate while the vent gas composition is varied over a sufficiently large enough range to see the CE reduced to 90% or less. The vent gas flow rate would then be changed. Once the series of vent gas flow rates selected are run, the composition of the vent gas stream would then be varied and the previously used combinations of vent gas flow rates and steam assist levels would be repeated. To the extent that other vent gas compositions can be used, the test series would be repeated with other vent gas compositions. The intent of the test plan would be to see how well

the two approaches estimate CE over a wide range of process conditions. While it is anticipated that most of these tests would be conducted during a five-day period, up to two evenings will be planned to repeat some of the test conditions at night.

#### CE Reference Measurement

Aerodyne Research, Inc. (ARI) will make the reference measurement of the flare’s CE using their mobile laboratory van, as was used in the TCEQ 2010 Flare Study (TCEQ, 2011), and a tethered balloon or crane system with a sampling line located downwind in the flare plume to extract a sample of the plume. CE will be calculated from direct measurement of the diluted carbon dioxide (CO<sub>2</sub>), carbon monoxide (CO), and total hydrocarbon concentrations in the plume sample. Two approaches will be used to corroborate the measured CE calculations. In the first, a tracer gas of known flow rate will be injected into the header of the flare and used to locate the plume of the flare and to determine the dilution of flare combustion constituents at the point of sample collection. Knowing the dilution rate, the concentration of emissions at the flare can be determined and, from that, the CE using Equation 1. In the second method, an alternate form of Equation 1 applicable only to plume event analysis will use compound ratios to determine the CE.

$$CE (\%) = \left( \frac{CO_2 (plume)}{CO_2 (plume) + CO (plume) + \sum hydrocarbons (plume)} \right) \times 100 \quad \text{Eq. 1}$$

where,

- CE (%) = combustion efficiency (%)
- CO<sub>2</sub> (plume) = volume concentration of carbon dioxide in the plume (ppmv) after combustion has ceased
- CO (plume) = volume concentration of carbon monoxide in the plume (ppmv) after combustion has ceased
- Σ hydrocarbons (plume) = volume concentration of all the unburned hydrocarbons in the plume after combustion has ceased multiplied by the number of carbons in the hydrocarbon (ppmCv)

Note: The soot term would also appear in the denominator of Equation 1 but has been neglected because it is zero for smokeless flare operation, which is required by federal regulations, and was shown to be effectively zero in the TCEQ 2010 Flare Study for smokeless flare operation.

The sampling line will be positioned each day and, potentially, repositioned during the day to be downwind and in line with the plume. Due to changes in wind direction, samples of the plume may only be obtained on a 50% to 75% duty cycle. Part of the pre-deployment task will be to meet and develop plans to exceed this duty cycle. Determination of CE by the two approaches will be compared to CE calculations made by ARI for the time periods plume samples were collected. Measurements of the background concentrations of CO<sub>2</sub>, CO, and total hydrocarbon concentrations will be made periodically by ARI during the tests and plume measurements of these concentrations will be corrected for these background levels.

#### 4.0 Sampling Procedures

No samples will be collected for this project.

## 5.0 Measurement Procedures

The primary flare process measurements that will be made are the mass flow rates of the flare vent gas flow and steam assist to the flare using flow meters, the composition of the vent gas going to the flare using a gas chromatograph and the net heating value of the vent gas by calorimetry. These measurements will be made using in-line existing Petrologistics, LLC plant instrumentation. The next update to this QAPP will provide names, models, accuracies and precisions of the instruments that will be used for all of these process measurements, including calibration and span and zero procedures that will be performed before and during the tests. All equipment will be calibrated per manufacturer's specifications before the test series begins. The report of QA findings will be included in the final report.

Measurements of the flare plume (continuously during tests) and background (at least hourly) concentrations of CO<sub>2</sub>, CO, and total hydrocarbon concentrations will be made by ARI during the tests. Plume measurements of these concentrations will be corrected for background levels. At this point and until confirmed at the plant site visit, a listing of the specific compounds to be measured and the analytical method that will be used for each is shown in Table 1.

Table 1. Flare Plume Compounds to be Measured, Analytical Method and Instrument Proposed

Compound	Measurement Technique	Instrument
CO <sub>2</sub>	non-dispersive IR absorbance	LiCor 6262
CO	tunable IR laser differential absorbance	Aerodyne QCL Trace Gas Monitor
propene	chemical ionization mass spectrometry	Ionicon Analytik PTR-MS
methane	tunable IR laser differential absorbance	Aerodyne QCL Trace Gas Monitor
total hydrocarbons (HC)	continuous flame ionization detector	California Analytical Model 300 HFID Analyzer
Speciated Organic Gases		
ethyne, ethene, formaldehyde	tunable IR laser differential absorbance	Aerodyne QCL Trace Gas Monitor
methanol, acetaldehyde, benzene	chemical ionization mass spectrometry	Ionicon Analytik PTR-MS
butenes, acrolein, propene oxide, propanal, acetone	gas chromatography/mass spectrometry (GC/MS)	Hewlett Packard (HP) 5890 Series II GC Ionicon Analytik PTR-MS Homebuilt interface

QCL – quantum cascade laser

HFID – hydrogen flame ionization detection

PTR-MS – proton transfer reaction mass spectrometer

## CO<sub>2</sub>

A LiCor 6262 non-dispersive infrared absorption instrument will be used to measure the carbon dioxide concentration. Zero and spans will be evaluated by overblowing the inlet with either nitrogen (N<sub>2</sub>) or Span gas. Spans in the past have been determined using a gas standard specified to be 1000 +/- 20 ppm by the manufacturer (Scott Specialty Gases) and certified to be 994 ppm by an Aerodyne Research Inc. absolute CO<sub>2</sub> measurement (accurate to 1%).

## CO, Ethene and Formaldehyde

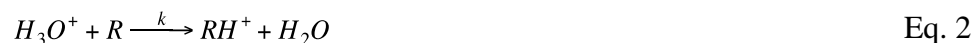
These compounds will be measured using two separate Aerodyne Quantum Cascade Laser Trace Gas Monitors. Each instrument uses a single multiple reflection gas cell and up to two laser devices. CO and formaldehyde will be measured on one instrument, while ethene will be measured individually on the second one. These instruments use pulsed quantum cascade lasers and employ Tunable Infrared Laser Differential Absorption Spectroscopy (TILDAS) as the fundamental analytical method for quantifying trace compounds. TILDAS is an absolute measurement method where the concentrations of the species of interest are computed by fitting the measured absorption spectrum to the spectral features tabulated in the high-resolution transmission (HITRAN) molecular absorption database. (HITRAN is a compilation of spectroscopic parameters that a variety of computer codes use to predict and simulate the transmission and emission of light in the atmosphere.) These computed concentrations will be validated via calibration experiments performed by dilution of certified gas standards for CO and ethene. Formaldehyde will be calibrated separately using a permeation device.

## Methane and Ethyne

Methane and ethyne will be measured using an Aerodyne Quantum Cascade Laser Trace Gas Monitor using a continuous wave room temperature laser system. This instrument employs a 210 m path-length absorption cell. Methane will be measured using the <sup>12</sup>CH<sub>4</sub> spectral line at 1294 cm<sup>-1</sup>, but it is anticipated that the spectral window will also quantify <sup>13</sup>CH<sub>4</sub>. Similarly, ethyne will be measured using the absorption feature centered at 1342.35 cm<sup>-1</sup>. The computed concentrations will be validated via calibration experiments.

## Propene and Other Selected Volatile Organic Compounds

Propene will be measured using proton transfer reaction mass spectrometry (PTR-MS). PTR-MS is a chemical ionization mass spectrometry technique that utilizes H<sub>3</sub>O<sup>+</sup> as the principal reagent ion.<sup>7</sup> H<sub>3</sub>O<sup>+</sup> will react with any molecule having a proton affinity greater than that of water. It is important to note that the primary components of air: N<sub>2</sub>, oxygen (O<sub>2</sub>), argon (Ar), CO<sub>2</sub>, and the alkanes all have proton affinities less than water and thus do not react with H<sub>3</sub>O<sup>+</sup>. Most other organic substances except for acetylene and ethene react with H<sub>3</sub>O<sup>+</sup> via a proton transfer reaction as shown in Equation 2.



In Equation 2, R represents the target compound. The proton transfer reaction forms the protonated molecule RH<sup>+</sup>, which is a stable reaction product in many cases. Quantification of propene will be based on the measured ion intensity of the RH<sup>+</sup> product ion detected at mass-to-charge ratio (m/z) 43.



Quantification of the PTR-MS ion signals is possible directly from first principles, but is most reliably done via calibration with certified gas standards. The concentrations deduced for propene, acetaldehyde, benzene and methanol will be evaluated from calibrated response factors. Minor combustion by-products for which gas standards are not available will be quantified using estimated sensitivity factors. These calibrated response factors are listed in Table 2.

The standard equation for quantifying a target compound, designated generically as (R) is shown in Equation 3.

$$[R] = \left( \frac{1}{S_R} \right) \left( \frac{I_{RH^+} \cdot 10^6}{I_{H_3O^+} + X_R I_{H_3O^+(H_2O)}} \right) \quad \text{Eq. 3}$$

The term [R] represents the concentration of R in ppbv. The term I represents the ion intensity (instrument signal).  $S_R$  is the sensitivity factor expressed as normalized counts per second (ncps) per ppbv. The term  $\left( \frac{I_{RH^+} \cdot 10^6}{I_{H_3O^+} + X_R I_{H_3O^+(H_2O)}} \right)$  represents the product ion response expressed in ncps, which is the mass spectral intensity of  $RH^+$  measured in cycles per second (cps) per 1-million reagent ions. This normalization step accounts for any variation in the product ion intensity resulting from changes in the reagent ion intensity. The intensity of  $H_3O^+$  is too large to measure directly and its intensity is determined by measurement of the O-18 isotope of this ion detected at mass to-charge-ratio (m/z) 21, which is then multiplied by 500 to correct for the isotopic dilution. Measurement of the intensity of  $H_3O^+(H_2O)$  is measured directly at m/z 37. Some components react with both  $H_3O^+$  and  $H_3O^+(H_2O)$  while others do not. The  $X_R$  term is a factor between 0-1 that accounts for the reactivity difference between  $H_3O^+(H_2O)$  and  $H_3O^+$  towards R.

Table 2. PTR-MS Calibration Factors Used in the TCEQ 2010 Flare Study

Compound	ion quantified	standard used	$S_R$ (ncps/ppbv)	$X_R$
propene	m/z 43	propene	9.66	0
methanol	m/z 33	methanol	19.6	1
acetaldehyde	m/z 45	acetaldehyde	25.0	1
butenes + acrolein	m/z 57	none - estimated	25.0	1
C <sub>3</sub> H <sub>6</sub> O isomers	m/z 59	acetone	37.8	1
benzene	m/z 79	benzene	20.1	0.1

Most applications of the PTR-MS are for trace level detection where the substrate concentrations are low, < 1 ppmv. Under these conditions the reagent ion population (intensity) is not

significantly altered by Equation 2 and can be considered to remain at a constant level. However, when the propene concentration is very high > 10 ppmv, the reagent ion intensity will be notably depleted. Under these measurement conditions, Equation 3 is not valid and a modified formula must be used for accurate quantification. This modified equation is shown in Equation 4.

$$[R] = \left( \frac{1}{S_R} \right) \left( \frac{I_{RH^+} \cdot 10^6}{\sum I_{R_i H^+}} \right) \cdot \ln \left( \frac{\sum I_{R_i H^+} + I_{H_3O^+} + X_R I_{H_3O^+ H_2O}}{I_{H_3O^+} + X_R I_{H_3O^+ H_2O}} \right) \quad \text{Eq. 4}$$

The only new term in this equation is the  $\sum I_{R_i H^+}$  term, which reflects the sum of all product ions. This equation reduces to Equation 3 when the sum of the product ion intensity becomes small relative to the total reagent ion intensity. All of the concentrations reported using the PTR-MS in this project will be computed using Equation 4.

The PTR-MS technique detects and records the response associated with an ion at a specified mass-to-charge ratio (m/z). The compound identities will be established using a second PTR-MS instrument that will be deployed with an associated GC. The GC/PTR-MS system will be used to determine whether an ion was produced from one or more components.

The GC/PTR-MS system will be operated in parallel to the primary PTR-MS. Both instruments will sample off the same sample line. The GC/PTR-MS could be operated as either a normal PTR-MS or as the detector for the GC, but the GC-PTR mode is described here. When instructed based on the measurement duty cycle (to be determined after the initial site visit), a portion of the sample will be pulled through a Teflon loop that is immersed in liquid N<sub>2</sub>, which traps the condensable components in the sample. The trapping time will be variable but usually lasts for about 2 minutes. At the conclusion of the trapping cycle, a 6-way valve will be used to transfer the contents trapped within the sample loop onto the chromatographic column, a 30m Restek Rtx-624 capillary column. Immediately after the 6-way valve is switched, the sample loop will be withdrawn from the liquid N<sub>2</sub> and immersed in hot water (temperature to be determined based on species anticipated in the vent gas being burned, which will be known more precisely after the initial site visit and anticipated vent gas components and their concentrations can be more accurately predicted) to desorb the condensable components. A 3-way valve on the PTR-MS will be switched so that the instrument samples the outflow from the GC instead of the normal sample line. The GC oven temperature will be ramped from 40 – 100 °C at 10°C/min. A typical GC run will last about 7 minutes.

#### Total Hydrocarbons

A California Analytical Model 300 Heated Total Hydrocarbon Analyzer will be integrated with the Aerodyne Mobile Laboratory sample line. This device uses a continuous flame ionization detection (FID) technique to provide a total gas phase organic carbon measurement. The FID will be used to provide a measure of propane, since propane is not detectable using either the QCL or PTR-MS instrument. (While the PTR-MS is the focus for the partially and unburned vent gas composition, it cannot measure propane.) This instrument provides a nearly uniform

response to all hydrocarbon species, but not to carbons bearing heteroatoms. This instrument will be calibrated with propene using certified gas standards. For propane measurements, the catalytic conversion of propane to CO<sub>2</sub> must be used to determine the amount of propane present in the plume.

#### Other Instruments

The flare plume composition of small hydrocarbons C1-C3 will be periodically sampled using a SRI-8610 gas chromatograph equipped with a flame ionization detector (GC/FID). The GC will sample from the trunk line, ~ 1 liter per minute from the main sample line. The GC uses a heated adsorbent trap packed with Carbotrap B to preconcentrate the sample prior to injection onto the GC column. When triggered into the sample mode, a small flow (~ 40 ml/min) will be pulled off the trunk sample line for 30 seconds. At the conclusion of the trapping period, the adsorbent trap is heated and a 10-port valve is used to direct the sample onto a 6-ft Porapak-Q 0.125" OD packed column. The column oven will be temperature programmed to hold at 30 °C for 1.7 minutes, ramp at 50 °C per minute to 160 °C and hold at 160 °C for 3.7 minutes. This configuration will allow for quantification of ethane, propane, propene and the sum of ethyne + ethene. Methane may be observed in the chromatograms, but this compound is quantitatively retained on the Carbotrap B adsorbent. Ethyne and ethene are not resolved on the Porapak Q column and co-elute as a single peak. Sample concentrations will be determined as ppmC by integrating the peak areas and converting them to an equivalent concentration using a response factor evaluated for FID using a series of calibrated gas standards.

#### 6.0 Quality Metrics

A small quantity of a tracer gas, to be measured by ARI, will be continuously injected into the header of the flare and mixed with the vent gas being combusted in the flare. This tracer gas will serve two purposes. First it will help ARI confirm the presence of the plume coming from the Petrologistics, LLC flare. Knowing the quantity of the tracer gas injected into the flare header and the concentration measured downwind of the flare, the dilution of the tracer gas can be determined. The concentrations of CO<sub>2</sub> (plume only excluding background), CO (plume only excluding background), hydrocarbons and other gases measured in the flare plume can be used to determine quantities (mass flow rates using carbon counts for each species) of these hydrocarbons being combusted by the flare. These mass flow quantities will be compared to process measurement mass flows measured by the plant. An analysis of an acceptable level of agreement between these two quantities for each test point will be determined after the initial site visit when the accuracies of the process measurements will be obtained. The tracer gas that will be acceptable to the plant and the objectives of the project will be determined by mutual agreement of the plant representative and the project team at the initial plant visit. Once the trace gas is determined the instrument that will be used and the quantity required will be defined.

#### 7.0 Data Analysis, Interpretation & Management

There are no data reporting requirements. Data will be validated on site by plant personnel for the flare process measurements and by ARI after the test series for all flare plume measurements. All data will be collected independently and stored on computers by each entity and time-synced (checked twice per day) with the reference measurements of ARI. The period for time averaging

for CE measurements will be determined once data about plant process instrumentation can be obtained during the initial plant visit.

The audit of data quality (ADQ) is an examination of data after they have been collected and verified by project personnel. The ADQ documents and evaluates the methods by which decisions were made during the treatment of the data. The Principal Investigator will perform post field campaign data quality assessments of data (10%) provided by each of the parties on the project submitting data.

## 8.0 Reporting

All measurements made during the field tests and the analyses conducted after the field tests will be reported in the project final report. The report of QA findings will be included in the final report. Data from this project will be submitted to the AQRP with the final report and will be maintained by the researcher for a period of three years, minimum.

## 9.0 References

Texas Commission on Environmental Quality. 2011. 2010 Flare study final report, available at: <http://www.tceq.texas.gov/assets/public/implementation/air/rules/Flare/2010flarestudy/2010-flare-study-final-report.pdf>, accessed August, 2013.

U.S. Environmental Protection Agency. 2012. Parameters for properly designed and operated flares, available at <http://www.epa.gov/airtoxics/flare/2012flaretechreport.pdf> , accessed October, 2013.

United States 40 Code of Federal Regulations - Standards of Performance for New Stationary Sources, General Control Device and Work Practice Requirements, *40CFR § 60.18*. available at <http://www.ecfr.gov/cgi-bin/text-idx?SID=9593aed60ab1c6e47b7cebc901f5e9cc&node=40:7.0.1.1.1.1.151.18&rgn=div8> , accessed October 2013.

United States 40 Code of Federal Regulations - National Emission Standards For Hazardous Air Pollutants For Source Categories, General Control Device and Work Practice Requirements, *40CFR § 63.11*. available at: <http://www.ecfr.gov/cgi-bin/text-idx?SID=831a165b7f4d500bfae6d3403dd15d2f&node=40:10.0.1.1.1.1.5.11&rgn=div8> , accessed October 2013.