TEXAS COMMISSION ON ENVIRONMENTAL QUALITY

WORK ASSIGNMENT 5

DRAFT FLARE WASTE GAS FLOW RATE AND COMPOSITION MEASUREMENT METHODOLOGIES EVALUATION DOCUMENT

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Executive Summary

The Texas Commission on Environmental Quality (TCEQ) has determined that Volatile Organic Compound (VOC) emissions may be underestimated in air shed emission inventories. It is expected that emissions from flares would be better estimated if they were based on waste gas flow rate and composition measurements. The TCEQ has established data quality objectives for conducting such measurements. This study evaluates currently available flow measurement and gas composition measurement techniques; their applicability to the measurement of waste gas flow and composition in flare systems and their ability to meet the data quality objectives established by TCEQ. Additionally, this study evaluates current practices for controlling assist gas to waste gas ratios in flares.

The overall objective of the Texas Commission on Environmental Quality (TCEQ) studies on flare emissions is to obtain performance specifications that ensure quality assured sampling, testing, monitoring, measurement, and monitoring systems for waste gas flow rate, waste gas composition, and assist gas flow rate. Specific objectives of this report are shown below.

To evaluate existing methods of monitoring or measuring waste gas flow rate and composition to determine the mass rate of volatile organic compounds (VOC) being routed to the flare within a known certainty. The overall desired accuracy, precision, and sensitivity is ± 20 percent. Specifically for flow rate, composition measurements and the resulting calculated mass rate to the flare the desired accuracy, precision and sensitivity is ±20% (never to exceed ± 5000 lb/hr) of total VOC emitted from the flare, whichever is greater. An additional consideration is the desire that the waste gas composition measurement methods must be able to provide 90% speciation by mass of the individual VOC in the waste gas with specific focus on propylene, ethylene, formaldehyde, acetaldehyde, isoprene, all the butenes/butylenes, 1,3-butadiene, toluene, all pentenes, all trimethylbenzenes, all xylenes, and all ethyltoluenes.

To evaluate methods of controlling the assist gas (steam or air) to waste gas ratio to assure the proper ratio is maintained within a known certainty. The overall desired accuracy, precision, and sensitivity is ± 20 percent.

Flare systems are typically designed to burn large quantities of gas resulting from de-inventorying process units during emergencies. However, frequently they are also used to dispose of smaller quantities of waste gas, which are uneconomical to recover for beneficial use or as fuel. This dual mode of operation results in typical flows that are quite low, but sporadic high flow events. By design the number of compounds of interest and the dynamic range of these compounds can be quite large and variable. As a result of a detailed review of operating data from over 40 flares systems, current flow measurement techniques, and gas composition measurement techniques the following conclusions and recommendations have been developed.

Waste Gas Flow Measurement Range

Due to the unique requirements of flare systems (low pressures, large pipe sizes, and 1000:1 turndown on flows) only multi-ranged pitot tubes, thermal mass meters, and ultrasonic time-of-flight meters are broadly applicable to the measurement of flows in flare systems.
Ultrasonic time-of-flight meters and Thermal mass meters can measure a greater range of gas velocities, and therefore are easier to apply to flare systems than pitot tubes. For the flares examined, all flows were below velocities of 300 fps, the high end measurable by ultrasonic and thermal mass meters. However, many flares are designed for worst-case events that will exceed this measurement capability.

Flow measurement systems that combine multiple measurement techniques can measure this design worst case. Using multiple measurement techniques increases the costs associated with purchase, installation, calibration, and maintenance of dual meters. Design worst-case events are infrequent and rarely occur. Typically, design worst-case events are associated with emergency, unplanned shutdowns of a complete process unit or the shutdown of several process units serving a flare due to a power failure. Other process data usually exist which can be used to estimate the mass flow during such events. Thus, the additional expense of installing multiple measurement systems may not be warranted due to the relative infrequency of such events and the availability of process data that can be used to estimate mass flow during worst-case design events.

Effects of Waste Gas Composition on Flow Measurements

Ultrasonic time-of-flight meters have greater accuracy and precision for measuring flows in flare gas systems, because they are less sensitive to changes in gas composition and can correct for variable gas composition using only flow meter inputs. Thermal mass meters and pitot tubes need significant correction for changing gas compositions. Currently, real time correction for gas composition changes has not been demonstrated in field applications with thermal mass meters or pitot tubes, although vendors claim such meters are available. Correcting with periodic composition data adds to the uncertainty of the flow measurement of thermal mass meters and pitot tubes used in flare applications. Measurement of flows in flare systems can be made with an uncertainty in the range of ± 5-10 percent. However, obtaining this accuracy in flare systems with highly variable compositions or where the meter cannot be located in a section of pipe with a representative flow profile will be a challenge.

Overall Flow Measurement Assessment

Currently, ultrasonic time of flight meters show the most promise of meeting the stated data quality objectives of this study in waste gas service. However, their cost probably limits their application to flow measurements at the terminal end of flare systems . Thermal mass meters offer a suitable alternative in services where the waste gas composition does not vary greatly, and as a sturdy portable instrument that can be used to troubleshoot flare systems (e.g. identify stray flows in complex flare headers).

Flare Waste Gas Composition Measurement

Measurement of the gas composition in flare systems on a continuous basis will be a challenge due to the number of compounds of interest and the dynamic range of concentrations, that may be present for the compounds of interest.

To design and implement a continuous monitoring system capable of detecting the full range of compounds of interest across all concentrations of interest using conventional GCs will require considerable up-front data collection, and fairly sophisticated combinations of columns and detectors.

If aldehydes happen to be present at quantities that would impact achieving the data quality objectives, the GC system required to analyze for them will become even more complex. Portable multi-channel, micro GCs have proven extremely capable of detecting most compounds of interest in flare systems across an extremely large dynamic range (10^5). Application of such instruments in online applications will significantly reduce the complexity of the GC instrumentation needed to achieve the data quality objectives of this study. However, online versions of these instruments have yet to be demonstrated in flare applications. While online GC systems can be designed to meet the data quality objectives of this study a high percentage of the time, the actual percent of time the data quality objectives can be met will be a strong function of the specific flare system, in particular the variability of the waste gas composition. There is insufficient data available to make a fact-based estimate on this percentage.

Application of US EPA Performance Specification 9 to online GCs in flare service is problematic given the potential number of compounds of interest and the dynamic range potentially encountered for these compounds. The linearity requirement will be extremely difficult to meet and the calibration procedures impractical.

Picking a few representative compounds with which to calibrate and using relative response factors for other compounds of interest seems a practical solution. Due to the large dynamic range, the linearity requirement of PS9 may need to be relaxed in favor of a multipoint calibration curve.

Assist Gas Rate

Automatic controlling of the assist gas to waste gas ratio based on waste gas flow to the flare appears to be more effective at controlling this parameter at a desired value than manual control, but there was very little data available from which to make this conclusion. Additional data collection on the effectiveness of manual control would be warranted.

Waste Gas Flow and Composition Measurement Data Quality

The author's assessment is that current flow and measurement technologies are capable of meeting the stated data quality objectives a high percentage of the time in most flares applications. However, the scarcity of data on real world applications and the high degree of variability in flare applications make it impossible to quantify what percentage of the time these data quality objectives can be met, and on what percent of flare systems they may be met. Both flow and gas composition measurement vendors have responded to the added interest in measurement of waste gas flow and composition. Significant recent developments have been made in both flow and composition measurement techniques. Demonstration of these advancements could significantly enhance the ability of sources to meet these data quality objectives over a wider range of operations in the near future.

Under ideal conditions the mass flow in flare systems can be measured with an uncertainty in the ± 5-10% range. However, problematic applications with widely varying gas compositions and poor meter installation geometries will have difficulty meeting the ± 20% data quality objectives of this study.

Obtaining measurement of flare emissions within an absolute uncertainty of ± 5,000 lb/hr appears doable for all but the very largest flare. However, this assessment is strongly influenced by the 98% destruction efficiency assumption used in this study.

1.0 INTRODUCTION

The Texas Commission on Environmental Quality (TCEQ) has determined that flares may be a significant source of emissions of volatile organic compounds (VOC). Of particular interest are highly reactive volatile organic compounds (HRVOC), which may contribute to rapid ozone formation under certain atmospheric conditions. TCEQ is concerned that flare emissions may be one source of VOC and HRVOC emissions that are being underestimated in current air emission inventories and wants to investigate methods to improve emission estimates from this source. This study evaluates current flow measurement and gas composition measurement technologies, and their applicability to measuring waste gas flows and compositions to flares. In the past, other than requiring pilot lights to be monitored and lit at all times as well as limiting flare tip exit velocities and flare waste gas heating values, flares have not been subject to environmental regulations mandating accurate measurement of waste gas flows and compositions. Typically, flare waste gas flow rate and compositional measurements have been used to assist in designing flare gas recovery compressors, to identify sources upstream of the flare contributing to flare flows, to quantify the change in flare waste gas flow rates and compositions associated with process changes upstream of the flare header, and to assess normal flows versus design flows. The level of accuracy required for these purposes is not as stringent as that associated with regulatory requirements. Thus, existing instruments for measuring flare waste gas flows and compositions were not designed to meet stringent regulatory requirements.

TCEQ has established preliminary data quality objectives for measurements of waste gas flows to flares and wants to assess the ability of current technology to obtain these objectives. Further, as assist gas addition to flares is a primary means of improving combustion efficiency in flares at high load conditions, the TCEQ would like to evaluate methods used to control assist gas addition to flares, and assess the ability of these methods to control the assist gas ratio within known certainties. This study assesses the ability of three common methods to control the assist gas to waste gas ratio.

1.1 Objectives

The overall objective of the TCEQ studies on flare emissions is to obtain performance specifications that ensure quality assured sampling, testing, monitoring, measurement, and monitoring systems for waste gas flow rate, waste gas composition, and assist gas flow rate. The

purpose of this project is to provide data and methodologies to improve emission estimates from flares. Specific objectives of this report are:
To evaluate existing methods of monitoring or measuring waste gas flow rate and composition to determine the mass rate of volatile organic compounds (VOC) being routed to the flare within a known certainty. The overall desired accuracy, precision, and sensitivity is ± 20 percent. Specifically for flow rate, composition measurements and the resulting calculated mass rate to the flare the desired accuracy, precision and sensitivity is ± 20% (never to exceed ± 5000 lb/hr) of total VOC emitted from the flare, whichever is greater. An additional consideration is the desire that the waste gas composition measurement methods must be able to provide 90% speciation by mass of the individual VOC in the waste gas with specific focus on propylene, ethylene, formaldehyde, acetaldehyde, isoprene, all the butenes/butylenes, 1,3-butadiene, toluene, all pentenes, all trimethylbenzenes, all xylenes, and all ethyltoluenes.

To evaluate methods of controlling the assist gas (steam or air) to waste gas ratio to assure the proper ratio is maintained within a known certainty. The overall desired accuracy, precision, and sensitivity is ± 20 percent.

1.2 Flare System Design and Operations

1.2.1 Purpose

Process flares are used as safety devices to combust large quantities of waste gases during emergency conditions, such as power failures or process upsets. Additionally, many facilities routinely flare smaller quantities of hydrocarbon gases that are exhausted at pressures too low to allow them to be routed to the facility fuel gas system or hydrocarbon gases that are uneconomical to recover. Smaller ground flares are sometimes used to handle the smaller, more routine flows while higher capacity elevated flares are used for emergency condition flaring. Ground flares are designed for lower flow rates than elevated flares and typically the burners are enclosed in a stack. Also, their design (in the case of thermal oxidizers such as the one shown in Figure 2) results in a wider, less elevated, less visible, and less noisy flame. In simple terms, a thermal oxidizer ground flare flame is similar to a burner on a gas stove (several small flames from several points on a circle) while a traditional elevated flare flame is similar to a lit match (a larger, more defined flame emitted from a point). Figure(s) 1 and 2 provide schematics of typical ground and elevated flare systems.

1.2.2 Schematics

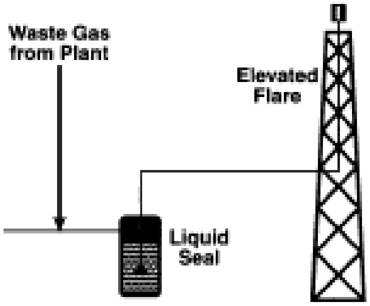

Figure 1. Elevated Flare[1]

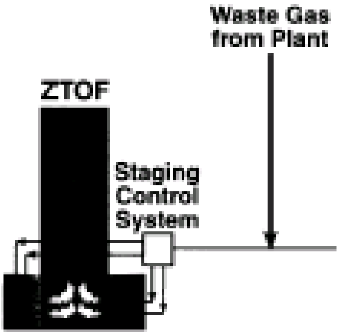

Figure 2. John Zink Thermal Oxidizer Flare "Ground Flare" [2]

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[1] Figure 1 is courtesy of John Zink Company.
[2] Figure 2 is courtesy of John Zink Company.

1.3 Typical Flare Header/Tip Sizes

The authors have worked with or knowledge of the design and operation of approximately 40 flare systems in numerous U.S. refineries and chemical plants. The range in size of the terminal flare header, just prior to the flare, in these flare systems is from 24 to 60 inches in diameter with about 75% having a terminal diameter in the 36 to 48 inch range. Flare tip diameters utilized in these 40 flares range from 24 to 36 inches with over 80% in the 30 to 36 inch range. Therefore, to be broadly applicable flare waste gas flow measurement devices should be capable of being applied in line sizes from 4" up to 72".

1.4 Typical Operating Conditions

The operating temperature in flare headers is typically at or very near ambient temperature due to the long lengths of pipe from the process unit boundary to the flare. Flare headers normally operate at very low pressures, typically at 1 to 2 psig. Some upstream relief valves relieve at pressures as low as 5 psig, necessitating the flare header operating pressure be designed as low as possible to insure flow from all required process relief systems to the flare system. The low operating pressures of most flare systems requires that a maximum pressure drop specification across any potential flare waste gas flow measurement device be set at less than 0.5 psig.

Assist gas (usually steam or air) may be routed to the flare flame at the flare tip to assist mixing of combustion air, minimize smoking, and to maximize combustion efficiency. Since assist gas is added at the flare tip or into the flare riser, this gas will have no impact on the measurement of waste gas flows and compositions to the flare.

1.5 Typical Flow Rates/Ranges

Flare waste gas flows can range from nominally small flow rates of a few standard cubic feet per hour (SCFH) to several million SCFH. The U.S. EPA New Source Performance Standard for Flares (40CFR60.18) limits the maximum tip velocity for all flares constructed since 1973 to 400 feet per second, if the flare gas has a BTU content of at least 1,000 BTU/SCF and 60 feet per second for flares combusting gas with a BTU content of 300-1000 BTU/SCF. For the tip and header sizes in the flare systems the authors have worked with this velocity limitation equates to a maximum allowable volumetric flow rate of 4.5 million to 10 million SCFH or 100 to over 240 million standard cubic feet per day (for 24-36” flare tips). The authors’ discussions with knowledgeable individuals from other companies would indicate that the above flow rate ranges are representative of flares at many of the petrochemical facilities in the Houston-Galveston airshed.

1.5.1 Typical Velocity Ranges in Flare Systems

Most flow measurement devices that will be applicable to flare systems work on the principle of sensing the velocity of the waste gas stream, which is then converted into a volumetric or mass flow measurement. The large difference in flows between design maximums and normal operating flows for most flare systems leads to a requirement that any flow measurement device applied in flare systems to be capable of sensing a wide range of velocities. While there is no such thing as a typical flare system, hourly average data from 5 flares were examined over an eight-month period to demonstrate the range of velocities encountered in flare systems. These data are presented in Figure 3. A cursory analysis of the data would indicate that anywhere from 90-98% of the hourly averages are in the 0.1-20 fps range, and the balances of the hourly averages (2-10%) are in the 20-100 fps range. While the design case for some of these flares is in the 275-400 fps range, velocities in this range are rare and seldom, if ever, seen. In the event that a design case scenario does occur, there frequently will be other process data available that can be used to estimate the quantity of material that is sent to the flare, such as which portions of the unit were isolated and de-inventoried.

1.5.2 NSPS J Flow Rate Limitations

Given the NSPS Subpart J regulatory limit of 400 feet per second (fps) tip velocity limit applicable to many flares, a working range of 0-400 fps was established as the desired range for flow measurement devices applicable to flare systems. The limited data presented suggest that for many applications a range of velocities from 0-100 fps will cover the bulk of the flaring events. In addition to the ability to detect velocities up to this maximum velocity, the flow measurement device must also have the ability to quantify velocities across a three decades range of velocities (e.g. 1000:1 turndown ratio) to give sufficient accuracy to cover the range of encountered flows.

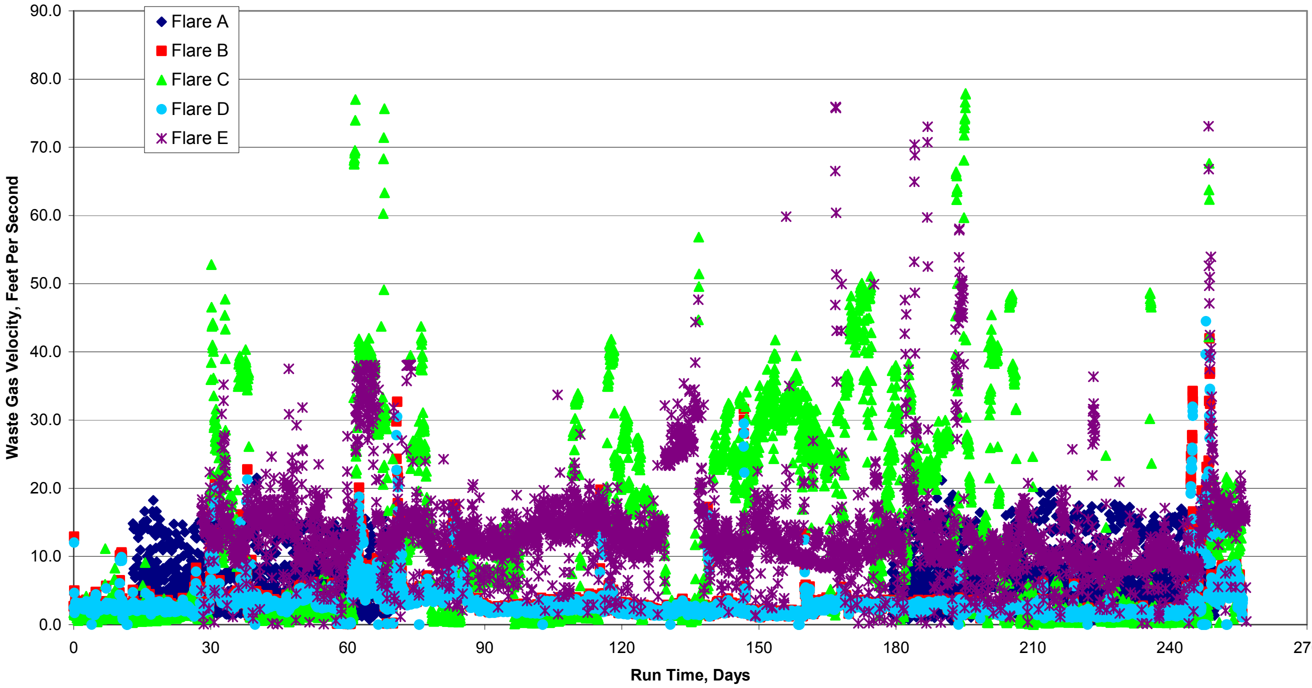
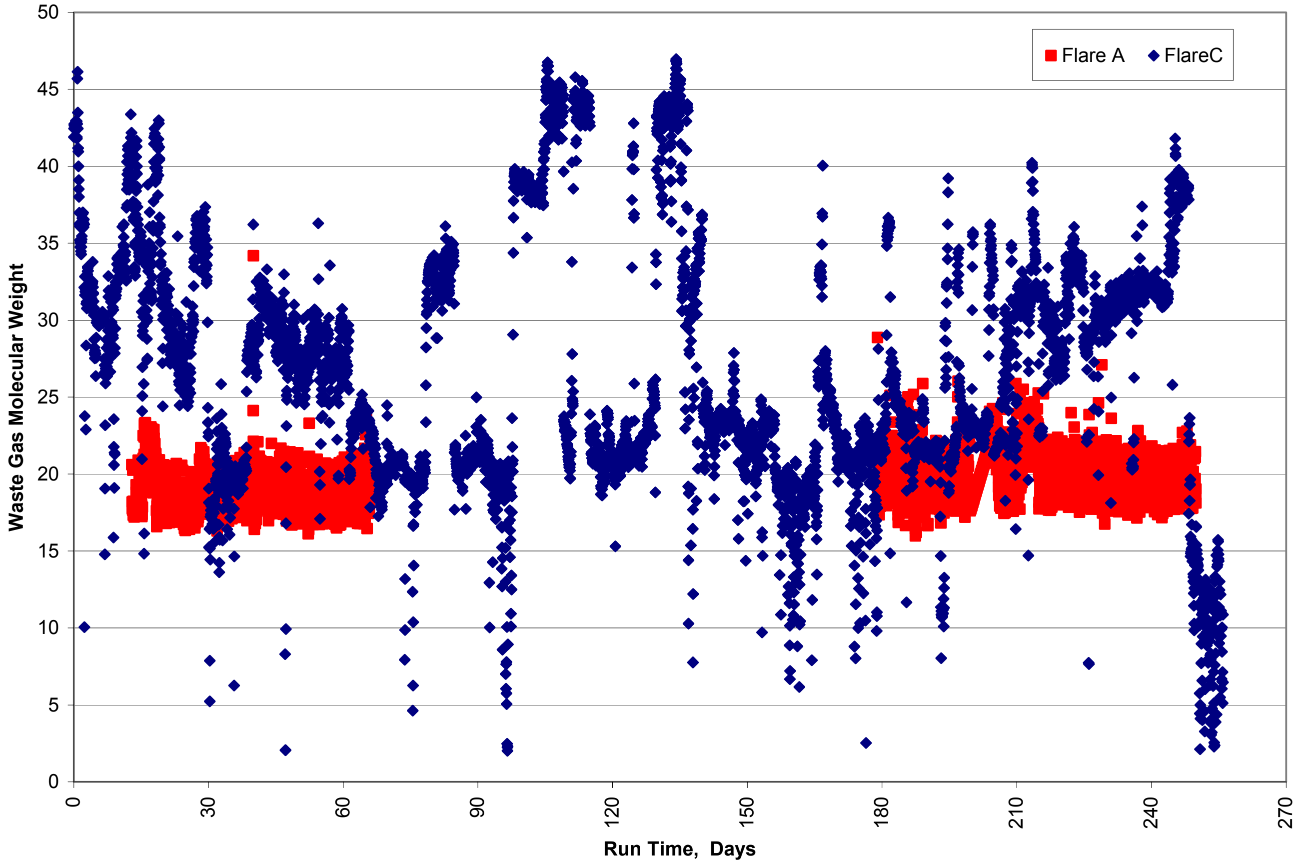


Figure 3. Range of Observed Waste Gas Velocities in Flare Systems

1.6 Typical Ranges/Variability of Waste Gas Composition

Compositions of waste gases routed to flares can vary significantly depending on the nature of the event(s) that are causing the need to flare waste gas. Sweep or "purge" gas is maintained in the flare header at all times to ensure clear lines and positive flow to the flare tip. Sweep gas normally is natural gas or fuel gas. At low flow rates the sweep gas flow may have a significant impact on the flow and composition measurements depending on the actual locations of the meters and the sweep gas injection point. Figure 4 illustrates the variability in the molecular weight of waste gas observed at two process unit flares, as measured by online flow measurement instrumentation.

Figure 4. Molecular Weight Variations of Waste Gas



These two examples clearly illustrate significantly different types of flare applications. A flare that is has a relatively consistent composition, and one that sees great changes in composition, in terms of molecular weight and perhaps even in components of interest. Table 1 gives additional examples of waste gas compositions in terms of both constituent of interest and the degree of variation of these components. Table 1 shows 2 cases as measured at different times for each of three flares. Note there is significant variation between the first and 2nd case for each flare. Also note that the recoveries ranged from 89.86 to 100.02 depending on the flare, the components analyzed for, and the components identified. The composition of the waste gas being measured can have a significant impact on the accuracy of many flow measurement technologies. Correcting measured flow rates for these compositional changes will be discussed later.

Table 1. Flare Waste Gas Compositions – Constituents and Variability

Table 1. Examples of Flare Waste Gas Compositons-Constituents of Interest and Variability

	Flare 1		Flare 2		Flare 3	
Component	mole %	mole %	mole %	mole %	mole %	mole %
hydrogen	86.18	48.77	0.02	0.04	37.11	0.00
methane	5.93	3.52	86.22	47.09	14.73	0.70
ethane	0.81	0.26	1.06	0.41	0.44	0.21
ethylene	0.02	0.01	0.13	0.22	0.18	16.37
propane	0.34	0.14	0.10	43.30	0.07	0.89
propylene	0.00	0.01	0.01	0.23	0.12	24.29
n-butane	0.11	0.05	0.02	0.21	0.35	0.03
i-butane	0.11	0.06	0.03	0.05	0.02	0.00
cis, 2-butylene	0.16	0.06	ND	ND	0.24	0.01
trans, 2-butylene	0.17	0.06	ND	ND	0.26	0.00
isobutylene	0.12	ND	ND	ND	0.21	
1,3-butadiene	ND	ND	ND	ND	0.74	0.01
n-pentane	0.03	0.08	0.02	ND		
i-pentane	0.05	0.05	0.03	ND		
pentenes	ND	ND	ND	ND		
C_6^+	0.01	0.01	ND	ND		
CO	0.02	0.04	ND	ND		
N2	4.99	45.80	0.38	1.69	$\left\{ 31.01 \right.$	$\left\{ 50.40 \right.$
O2						
CO_2	0.06	0.04	1.11	0.07	0.15	
hydrogen sulfide	0.24	0.35	0.00	0.00		0.03
water vapor	0.68	0.70	0.73	0.87		
Totals	100.02	100.00	89.86	94.18	85.63	92.94

1.7 Inherent Flow Meter Precision and Accuracy

Each flow measurement device will have an inherent precision and accuracy associated with that technology and model. These metrics will be a function of the fundamental property being measured (e.g. pressure, temperature, frequency, etc.) and the components used in the meter. These metrics are determined under ideal conditions in the laboratory. While the inherent precision and accuracy of the meter is but one of the components that goes into determining the precision and accuracy of the flow measurement in a field application, it is an important specification to qualify flow measurement technologies. Due to the extreme variations and conditions encountered in flare applications, it is important to have relatively high specifications for the inherent precision and accuracy of flow measurement devices. For this reason an inherent precision specification of ±1% and an inherent accuracy of ±5% was selected for this study. The reason for selecting such tight inherent flow meter precision and accuracy specifications will be addressed later in the discussion of the roll up of errors in the overall uncertainty of the mass flow of waste gas to flares.

1.8 Secondary selection criteria

There are a number of other selection criteria, which while important in the selection of a flow measurement device can to some degree be engineered around. These include such characteristics as applicability to corrosive environments and environments with aerosols and particulate matter. As well as what temperatures and pressures the flow measurement device can be applied. Other factors such as the length of straight pipe required for installation, and the ability to detect backflow in the line can also be of importance. While not primary selection criteria, these characteristics where also assessed for flow measurement technologies which satisfied all of the primary selection criteria.

1.9 Summary

Based upon the above description of flare design and operating parameters the following list of primary design specifications were selected to assess whether available flow measurement technology was applicable to measuring flows in flare systems.

- Applicable in lines from 4”-72” in diameter.
- Maximum pressure drop across measurement device of $\leq$0.5 psig.
- Applicable to measurement of velocities from 0-400 ft/sec.
- Quantification of flow (velocities) across 3 decades (1000:1 turndown).
- Inherent flow meter accuracy of ± 5 percent.
- Inherent flow meter precision of ± 1 percent.

There are a number of secondary criteria such as applicability to corrosive service, specific temperature and pressure constraints, length of straight pipe required, and the ability to sense backflow that are important, but can potentially be engineered around or into a particular application. These criteria were reviewed and used to evaluate the performance of flow measurement technologies for application in flare service.

2.0 FLARE WASTE GAS FLOW MEASUREMENT

2.1 Flow Measurement Fundamentals

Virtually all flow measurement devices calculate volumetric flow by sensing a velocity in the pipe and multiplying that velocity by the cross sectional area of the pipe in which the velocity is being sensed. This velocity is assumed to be uniform across the cross section. Applications where this may not be a good assumption may have reduced precision and accuracy. In fact, the consensus of the flow measurement vendor representatives at a recent API meeting to begin developing an API Standard for measuring flow rates in flares was that the flow profile is the most important consideration in the choice, location, and operation of any flare flow meter.[28] Inherent in all of these velocity measurements is an assumption that the gas is of a known composition. Deviation from this assumed composition must be corrected to maintain the overall precision and accuracy of the flow measurement.

2.2 Flow Meter Evaluations

A variety of flow meters were evaluated as a part of this report. The following types of flow meters were evaluated:

Differential Pressure

- Orifice Run with Differential Pressure Taps
- Venturi Run with Differential Pressure Taps
- Pitot Tubes
- Rotameters

Mechanical

- Turbines
- Pistons/Disks/Impellers
- Dry and Wet Test Meters

Mass

- Thermal
- Coriolis

Electronic

- Magnetic Meters
- Vortex Meters
- Ultrasonic Meters

A brief description of the principles of operation for each of these meters and their applicability to flare applications is given in Appendix A. The performance characteristics of each meter type versus the evaluation criteria developed previously for flare systems is summarized in Table 2.

If a flow measurement technique failed one or more of the primary evaluation criteria developed for flare systems, it was not considered further. Of the technologies evaluated only constant temperature anemometers (thermal mass meters), pitot tubes, ultrasonic time of flight meters, and possibly a recently developed Doppler shredding vortex meter did not fail one or more of the primary evaluation criteria. However, all of these meters had at least one or more concerns when evaluated against the complete list of flare flow measurement selection criteria. Application of these four techniques to flare applications will be discussed in more detail in the following sections.

Table 2. Flow Meter Selection Table

- See Note At Bottom of Table

Flare Waste Gas Flow Meter	Vapor Service	Pipe ID Range	Backpressure @ Max Design Flow	Obstructs Flare Header Flow	Corrosive Service	Backflow Measurement Capability	Aerosols and Particulates	Transmitter Signal Output	Straight Pipe Required	Principle of Operation	Process Velocity Range	Process Temperature Range	Process Pressure Range	Stated Model Accuracy	TD Ratio
Table I Flow Meter Evaluation Results															
Evaluation Criteria	Yes	4"-72"	<0.5 psig	No	Yes	Yes	Yes		< 100'		0-1000 FPS	-20F to 300F	0 to 60 psig minimum	+ **5%**	1000:1 minimum
FLOWMETER															
Constant Temperature Anemometer (Thermal Mass Meter)	Yes	all	< 0.1 psig	N	not recommended	No	Yes	analog	10 Feet	Thermal - Mass	0-300 FPS	-40C to 200C or 500C model variation	150 psig	1-3% varying with Temperature	High
Pitot Tubes and Annubars	Yes	0.5 to 72"	< 0.5 psig	No	not recommended	Yes	Yes	transducer (mA)	48 Feet	Pressure - Velocity	10 to 1000 FPS	up to 546C	2600 psig	1%, depending on application (sensor)	Medium 30:1
Ultrasonic Time Of Flight Flowmeters	Yes	3-120"	< 0.1 psig	No	not recommended	Yes	Yes		100 Feet	time transit	0.1-275 FPS	-166 to 300F or 500F optional	1500psig	1 path 3 - 7%, 2 path 2.4 - 5%	High 2750:1
Vortex Meters	Yes		1-5 or more psig	Yes	not recommended										
Magnetic Meters	No				not recommended										
Coriolis Meters	Yes	< 6"	10 or more psig		not recommended										
Dry Test Meters	Yes	< 6"	1-5 or more psig	Yes	not recommended										
Wet test Meters	Yes	< 6"	1-5 or more psig	Yes	not recommended										
Pistons/Discs/Impellers	Yes		1-5 or more psig	Yes	not recommended										
Turbines	Yes		1-5 or more psig	Possibly	not recommended										
Rotameters	Yes	< 4"	1-5 or more psig	Yes	not recommended										3-10:1
Venturis	Yes		1-5 or more psig	Yes	not recommended										3-10:1
Orifice Plates	Yes		1-5 or more psig	Yes	Not recommended										3-10:1

* Traditional Vortex Meters were ruled out here due to their bluff body design creating excessive pressure drop. A new, novel design, Doppler Shredding Vortex meter that may be able to overcome this limitation was recently developed. According to the Manufacturer and their representative, several of these meters were recently installed in flare headers. The authors have no data or experience with these meters. However, they seem to have potential. Additional information on these meters is available from the manufacturer's representative.[30]

2.2.1 Pitot Tubes

Principle of Operation

A pitot tube calculates a point velocity by measuring the static pressure and the impact or velocity pressure. The static pressure is the operating pressure of the pipe, duct, or stack at a specific point. The impact pressure is a combination of the static pressure and the pressure created by the flowing fluid. Pitot tubes generally measure the impact velocity by situating the opening directly into the oncoming fluid stream. Static ports are often located perpendicular to the fluid flow either on the tube itself or on the pipe or duct. The two pressures create a differential pressure that is directly related to the velocity through the following equation:

Equation 1

$$\mathrm{V}_p = \mathrm{C} \times \left(\left(\mathrm{P}_\mathrm{T} - \mathrm{P}_\mathrm{S}\right) / \wp_f\right)\frac{1}{2}$$

Where:
V_p = Point Velocity
C = Dimensional constant
ρ_f = Density of the fluid
P_T = Impact Pressure (a)
P_S = Static Pressure (b)

This equation gives a linear velocity, not the mass flow rate. The mass flow rate is calculated from the flare header's cross-sectional area and the molecular weight of the fluid being measured assuming ideal gas behavior of the flared waste gas. In the petrochemical industry, pitot tubes are primarily used to conduct isokinetic sampling traverses in boiler and process heater stacks. The measured flow rate is corrected for the actual fluid using empirically derived K-factors. These measurements are traditionally post-combustion measurements in internal or external combustion device stacks where the gas is primarily air, nitrogen, and water vapor with trace concentrations (<0.1% by volume) of other constituents. Some vendors of averaging pitot tubes are currently advertising them as capable of accurately (within ± 2-3%) measuring flows from 10-1000 feet per second in flare headers when used in conjunction with an online gas chromatograph to determine the actual composition of the gas being measured.

Design Variations

There are several variations of pitot tubes: single-port, averaging, area averaging, and s-type. Single-port pitot tubes similar to the one shown in Figure 5, below measure velocity at one point in the flow stream with one static port and one impact port. They are typically used for turbulent streams with well-defined velocity profiles.

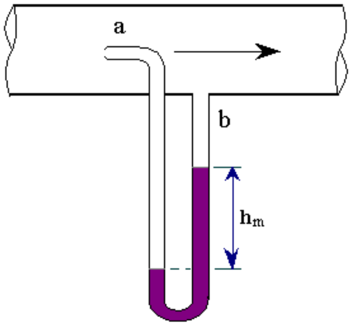


Figure 5. Generic Model of Pitot Tube[3]

To overcome the limitations of a single-port pitot tube, averaging pitot tubes were developed. Averaging pitot tubes have multiple impact pressure and static pressure ports that measure pressure across the pipe diameter. The pressures are tabulated and averaged, thereby negating the issue of placement of a single tube.

Area averaging pitot tubes measure multiple impact and static pressures over the pipe diameter and also over a length of pipe. Area averaging pitot tubes usually are comprised of several sets of pitot tubes connected to a manifold. These are typically used for large stacks or ducts.

S-type pitot tubes are specially designed to withstand dirty flows with a high level of particulate matter. Any of the above instruments could employ the s-type design for use in flows with high levels of particulate matter. For flare applications averaging pitot tubes are typically used. For the remainder of this section the applicability of pitot tubes to measuring flare flows will be discussed.

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[3] http://www.svce.ac.in/~msubbu/FM-WebBook/Unit-III/PitotTube.htm

Applicability to Flares

Pitot tubes have been used for years to measure flare flows. This is primarily because until fairly recently pitot tubes were the only viable flow measurement option. Although pitot tubes are fully capable of measuring flare flows, they may not be the best solution for all applications. Using an averaging pitot tube to measure flare flow has several positives; but there are several limitations to the design and operation of the device as compared to some newer waste gas flow measurement technologies.

Pitot tubes are capable of meeting the data quality objectives of this study across a limited range of flows (10-1000 feet/second). However, the stipulation that the flow meters measure through the entire range of the potential flow may cause problems for pitot tubes. As stated previously, flares are capable of having wide ranging flare flows, upwards of 100-1000:1. A typical averaging pitot tube turndown ratio is 30:1[2]. A particular problem with pitot tubes is their ability to measure low flows in large diameter pipes, as the pressure differentials that must be sensed are quite low. To accurately measure over the entire possible design window for flares would require multiple pitot tubes calibrated over several ranges of flow. While this could be considered an acceptable approach to measuring flare waste gas flow rates, this has to the authors' knowledge not been done. Several flow meter suppliers are now offering multiple ranges averaging pitots, but there is limited data available on their use in flare applications.

Under ideal conditions the precision and accuracy of pitot tubes is quite good. For example, the quoted accuracy of the Dieterich Standard Diamond II Annubar is $\underline{+}$1% with a precision of 0.1% for the sensor[3]. Ideal conditions for pitot tubes are stable flows, operating temperatures and pressures, and constant density of the stream being measured. These unfortunately are not common conditions in most flare applications. Correcting for the actual gas composition in most cases will induce as much or more uncertainty into the flow measurement than the inherent error of the flow meter being used. A more detailed discussion of the roll-up of error in flow measurements is presented in Section 4.0, but in most field applications of pitot tubes in waste gas service the total uncertainty of the flow measurement will be in the range of 5-20 percent. The exact value being a function not only of the inherent uncertainty of the flow meter, but also of the variability of the gas composition and one's ability to measure and compensate for the actual gas composition.

Pitot tubes require a rather large amount of straight run piping prior to the device. If straightening vanes are not used, a straight run of between 10-25 pipe diameters is often quoted. Typical downstream straight pipe run requirements are 5-10 diameters. In many flare applications this may not be an issue due to the length and amount of piping needed to transport the flare gas to the remote areas usually used for flare locations. Where space is limited and the flare stacks are very near the flare knockout drum, this 10-25-pipe diameter requirement will definitely be problematic. Straightening vanes or other flow correcting devices can be used to minimize the impact on observed meter accuracy of not having the desired runs of straight pipe for installing pitot tubes. However, the installation of straightening vanes and/or other flow correcting devices in flare headers can pose a serious safety hazard, due to the potential to collect debris and inhibit flow, and may not be allowed in many flare installations.

Other than applications requiring straightening vanes, the application of pitot tubes to flare systems should not pose any significant safety risk. The actual instrument is a slim, aerodynamic tube that does not obstruct the flow enough to be of significant concern for collecting hydrocarbons. Additionally there are no mechanical or moving parts that could be affected by electrical problems. Pitot tubes also induce very low-pressure loss across the device due to the unobtrusive design, typically less than 0.5 psig. One potential problem area for pitot tubes is measuring flows in corrosive service or applications with high levels of particulate matter. The pressure ports are prone to plug when used in dirty flows. Some designs attempt to alleviate this problem by using larger size portholes or flushing the holes with an inert gas. Periodically cleaning the ports and checking the differential pressure cell ensures device accuracy and usually is a routine task. Annual calibrations may also be required to ensure accurate performance.

Pitot tubes can be used to measure flows in virtually any size pipe. Pitot tubes can be installed in piping in excess of 48" without incurring additional costs for installation. For example, the Diamond II+ Annubar is capable of being installed in piping from 0.5” to 72".[3] Additionally, most pitot tubes can function across a wide range of temperatures and pressures, up to 546^{o}C and 2600 psi. This is well within the operating range for almost all flares in terms of temperature and pressure.

In the authors’ experience, pitot tubes were originally installed in many flare headers to measure waste gas flow rates for informational purposes rather than for critical process controls or meeting regulatory requirements. Typically, the pitot tubes ports were found to have “plugged up" from salts, polysulfides, ammonium sulfide, and other particulates that may form in flare headers from time to time. Also, many of the originally installed pitot tubes were found to be bent or broken as a result of maintenance activities on the flare headers. Typically, since the flow signal was not a critical control variable or a compliance parameter, the level of maintenance was not adequate to keep the pitot tube functioning. Also, the readings from these meters became more and more suspect as additional sources were tied into the flare line thereby increasing the potential for the waste gas composition to vary considerably.

2.2.2 Thermal Mass Meters

Principle of Operation

Thermal mass flow meters operate on the principle of measuring temperature differences between two sensors. Generally, a unit contains two temperature sensors, such as thermocouples, and a heating element. The temperature difference between the two sensors is a function of the flow past the sensor. There are two methods to achieve the temperature differential, constant temperature and constant power.

In the constant power approach, one of the sensors receives a constant supply of energy, or heat, from an electric heater. The temperature rise of the sensor is measured as well as the heat supplied. The other sensor measures the operating temperature of the fluid.

The constant temperature approach maintains one of the sensors at a specific temperature above operating conditions. The amount of energy needed to maintain the temperature is measured and used to compute a mass flow rate. As in the previous method the second sensor measures operating temperature conditions.

One recently developed constant temperature thermal mass meter has two sets of sensors with one set in the traditional waste gas flow area and the other set very near the flare header wall. According to the vendor, this allows the meter to continually measure both a waste gas flow and a near-zero flow in real time. [29] Having two pairs of sensors, one in the main waste gas flow stream and one near the walls, allows the meter to obtain a flowing stream waste gas velocity and a near zero waste gas velocity. One pair of sensors could conceivably give the same velocity reading for two or more widely varying gas mixtures. According to the vendor[29], no two gas compositions will have identical velocity readings at both the in stream velocity and at a near zero velocity. Thus, the meter is able to identify the actual composition of the waste gas by comparing the two readings and correct the velocity measurement for the actual composition in real time.

The underlying equation governing both methods of thermal mass flow meters is essentially the same:

Equation 2:

$$M = KQ/\left[C_p\left(T_2 - T_1\right)\right]$$

Where:
M = Mass flow rate
K = Meter coefficient
Q = amount of energy supplied
C_p = specific heat of the flow
T_2 = Temperature of the constant power sensor
T_1 = Temperature at operating conditions.

Per Equation 2, one can see that the observed flow from a thermal mass meter requires knowledge of the gas composition. Any significant deviation in composition of the waste gas being measured from the composition of the gas on which the meter was calibrated will impact the accuracy of the observed flow measurement. While real time correction of thermal mass meters for changes in gas composition are possible (correction for variable gas composition will be discussed further in Compositional impacts on calibration), there are a limited number of applications where this has been done in the petrochemical industry.

Design Variations

There are several variations of thermal mass flow meters that use one of the methods mentioned above to measure mass flow rate including heated tube designs, bypass, insertion probes, and hot wire anemometers. Heated tube mass meters are designed to protect the heater and temperature sensor elements from corrosive or dirty flows. The heater is mounted on the outside of the pipe and directly heats a section of the pipe wall. One temperature sensor is situated far enough downstream of the heater to measure operating temperature conditions. A second sensor is upstream in close proximity with the electric-driven heater. The mass flow rate is a nonlinear function of the heat transfer of the pipe walls and the sensor. Bypass thermal mass meters are generally used in high flow, high-pressure applications. Essentially a portion of the flow is bypassed into a tube that is heated. A portion of the energy is transferred to the gas, which is measured by temperature sensors. Due to the bypassing of flow, a large pressure drop is incurred across this type of meter, and generally is not suitable for flare applications.

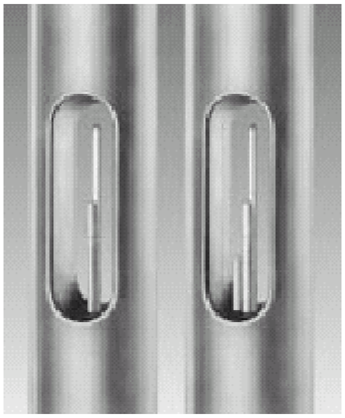

Figure 6. Generic Example of Thermal Mass Flow Meter [4]

Insertion probes use the constant temperature method stated above except the sensors or probes are inserted into the flow stream. One sensor is maintained at a constant temperature above ambient conditions. The energy necessary to maintain the temperature is recorded and used to calculate mass flow. Hot wire anemometers use the same principles as constant-temperature or constant-power mass flow meters. Anemometers use thin filaments to measure the heat transfer between a reference and a heated sensor.

Thermal mass meters are capable of obtaining and relaying continuous measurements. There are several current petrochemical industry examples of this process. Turndown ratios are a minor issue for thermal meters as most can quantify flow velocities across a two-decade range (100:1) or more. Flares can have turndown ratios of 1000:1; therefore the use of two or more thermal meters may be necessary to cover the whole range of flow seen in these applications.

The quoted accuracy from the K-bar 2000 from Kurz Instruments is listed as ±1-3%, depending on operating temperature.[69] Because thermal mass meters require the composition of the gas to be known to compute the flow, the uncertainty of the flow will also be a function of the uncertainty of the gas composition. In the authors' experience, total flow measurement error can be in the 5-10% range and could be as high as 20% in applications with widely varying compositions. Correcting measured linear velocities to actual mass flow rates can be problematic if the molecular weight of the waste gas varies by more than 20% from the molecular weight of the meter's calibration gas. [More detail on this problem is presented Section 2.3 "Factors Influencing Measurement Performance".] The repeatability of the instrument is given as 0.25%[4].

Many source-testing protocols dictate that flow meters have a minimum of 8 pipe diameters of straight pipe upstream and 2 pipe diameters of straight pipe downstream of the meter to ensure consistent velocity and velocity profiles. For most circumstances, thermal meters do not require additional space beyond these requirements. It is possible to install thermal meters by inserting them through existing gate valves on flare lines or permanently installing by hot-tapping into the flare system. Thermal meters do not present safety concerns as they induce very little pressure drop and do no not act as an obstruction in most circumstances. The instrument has low-pressure drops (< 0.1 psig) due to the unobtrusive design. Typical thermal meters consist of a metal probe that houses two thermal transducers. Corrosive or hazardous flows may be a problem for carbon steel instruments, but most instruments are typically constructed of stainless steel or other materials that resist corrosion or rusting.

Thermal meters can be used across a wide range of temperatures and pressures, and for the most part are unaffected by density, viscosity, pressure, or temperature fluctuations. Therefore, process conditions tend to not be an issue when evaluating the applicability of a thermal mass meter. For example, the operating limits for the K-bar 2000 can range from -40 to 500°C over a pressure range of 150 psig. The flow meter is designed to measure flows from 0-18000 standard cubic feet per minute (SCFM).

Thermal meters can be installed in pipe sizes well in excess of 48 inches. Typical costs of thermal meters are between $3,000-$5,000. Permanent installment increases the cost as does harsh operating conditions and maintenance due to operator error. Flows with high levels of particulate matter may induce error by coating the transducers and limiting transducer life. Typical maintenance for thermal flow meters consists of periodic cleaning of the transducers. In severe applications additional particulate removal equipment or frequent meter change outs may

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[4] http://kurzinstruments.com/K-BAR1.pdf

be required to keep the meter functional. When thermal mass meters are removed from the flare header for cleaning or being moved to new locations (temporary installations) care must be taken when removing and reinserting to avoid damaging the transducers. Additionally, annual calibrations of the probe may be required in order to ensure accurate measurement.

One drawback of thermal meters is the inability to measure bi-directional flow and compensate for backflow. Unlike most other flow meters, thermal mass meters are not unidirectional, meaning that they sense flow in either direction as a positive signal. While this would be of little concern when detecting flows at the terminal end of a flare system, it may be a confounding factor when using a thermal mass meter to detect the source of waste gas flows in a complex flare piping system.

Applicability to Flares

Both constant-power and constant-temperature thermal meters have been used to measure petrochemical industry waste gas flows to flares. John Zink engineers use thermal mass meters exclusively in measuring flare header waste gas flows for designing flare gas recovery compressors. Several petrochemical facilities use thermal mass meters to isolate potential sources of flows to flare headers. One petrochemical facility has over 50 thermal mass meters installed for this purpose. The authors' experience is that thermal mass meters are more reliable than pitots since they aren't as prone to the mechanical integrity problems mentioned previously concerning pitot tubes. Figure 7 shows a comparison of flare waste gas measurements between single point pitot tubes and thermal mass meters. Note that both the high-range and low-range pitot tubes only provide measurements over a narrow range at each end of the measured flows while the thermal mass meter covers the entire range. Also, note that the flows in Figure 7 are in typical flare waste gas ranges all of which both the thermal mass meter and the pitot tube vendors claim they can handle accurately. Using the pitot tubes only, one could conclude that either the low or high flow pitot is not giving accurate readings and base the measurements on either a very high or a very low flow compared to the oscillating flow rates as measured by the thermal mass meter and the tracer injections. This can be particularly misleading for flare systems that are subject to surge or oscillating flows, as was the case for this example.

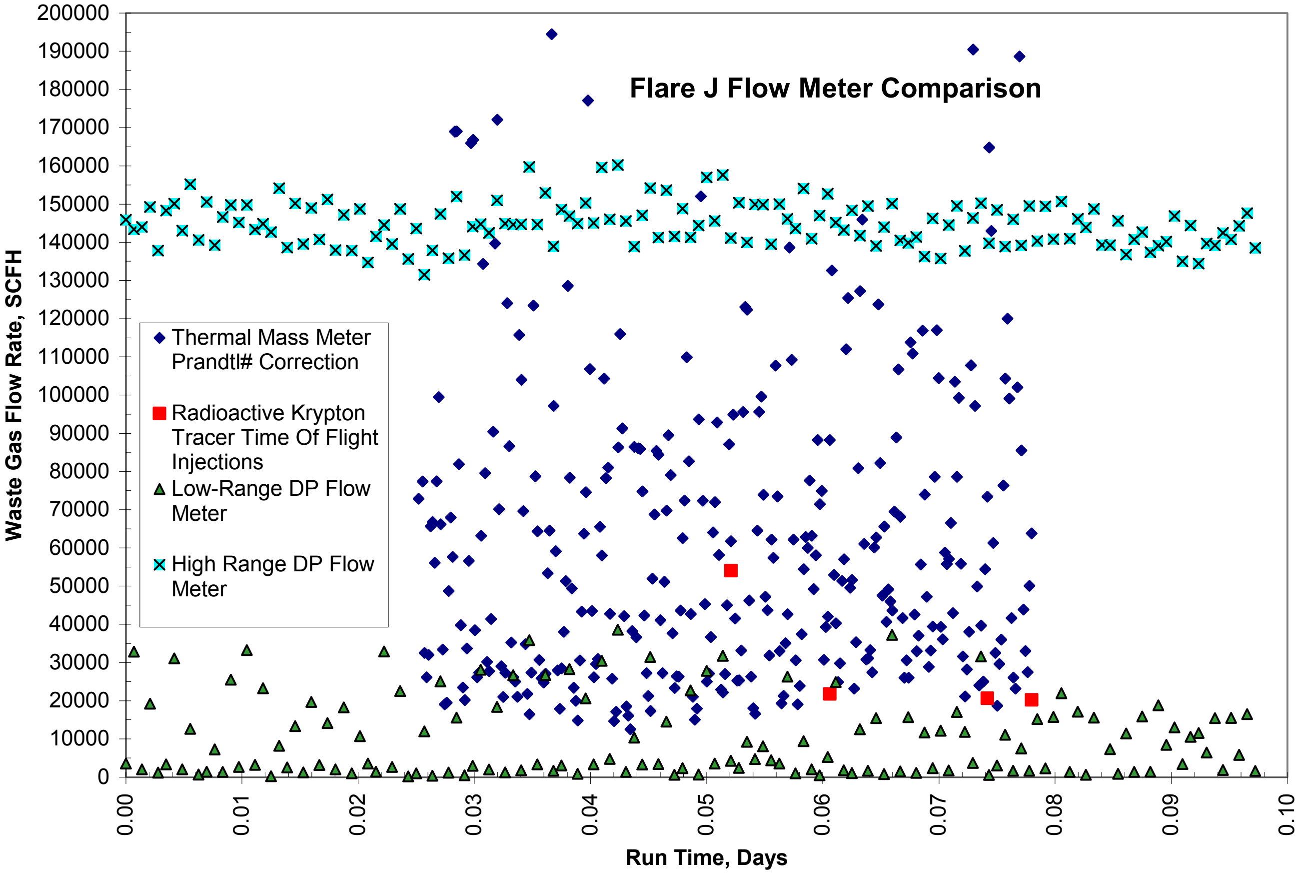

Figure 7. Comparison of Various Flow Measurement Techniques

2.2.3 Ultrasonic Time-of-Flight Meters

Principle of Operation

There are two types of ultrasonic flow meters, Doppler shift and transit time. Flow meters that use Doppler shift technology rely on the principle that wavelengths are perceived as shorter as the source approaches and longer as the source retreats. In fluid applications, Doppler shift flow meters are anchored or clamped onto the pipe and house a transmitter and a receiver. The transmitter emits signals that are reflected back to the receiver by discontinuities in the flowing fluid such as air bubbles, particles, or other turbulent phenomena. The receiver detects the change in wavelength of the signal reflected from these discontinuities in the flowing fluid, rather than the fluid itself. For this reason Doppler shift only works on fluids with appreciable levels of discontinuities. The underlying equation governing flow meters using Doppler shift is:

Equation 3:

$$V = (f_o - f_1)K$$

Where:

V = Velocity of the fluid

f_o = transmitter frequency

f_1 = receiver frequency

K = constant of the transmitter and system

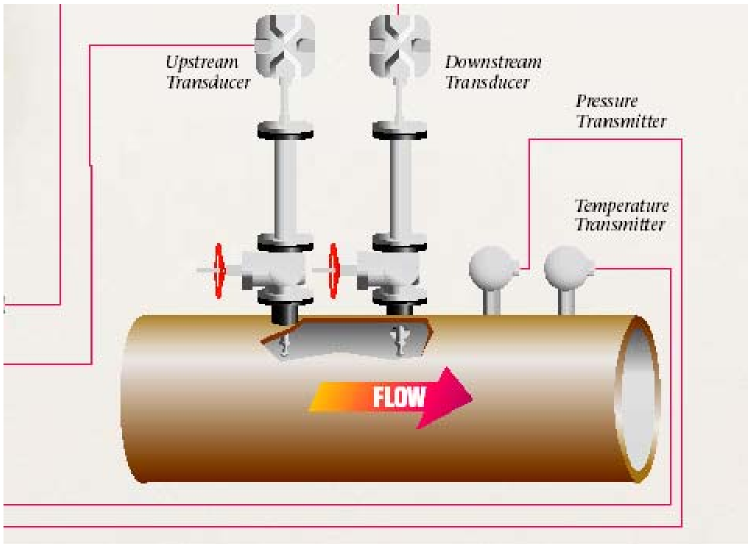

Figure 8. Generic Example of Ultrasonic Flow Meter[5]

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[5] http://www.gepower.com/dhtml/panametrics/en_us/products/ultrasonic_gas_flow meters/gf868_flare_gas_flow meter.jsp

Flow meters that operate on transit time measurement operate on the principle that ultrasonic signals travel faster with the flowing fluid and slower when traveling against the flowing fluid. Typically, one transducer is mounted upstream while another is mounted downstream at a fixed separation. The transducers act as transmitters and receivers alternatively, and emit and receive sound waves simultaneously. Waves that travel with the fluid flow exhibit a faster velocity than waves that travel against the flow, giving a differential time. In the absence of flow, sound waves travel from both transducers to each other in the same amount of time, therefore the differential is zero. The basic equation used to calculate the velocity of the fluid is[37]:

Equation 4:

$$V = \frac{L^2}{2X}\left[\frac{T_{21} - T_{12}}{T_{21} \cdot T_{12}}\right] 1$$

Where:
V = Velocity of the flow
L = direct distance between transducers
X = lateral distance between transducers
T_{21} = travel time from downstream transducer to upstream transducer
T_{12} = travel time from upstream transducer to downstream transducer

An additional advantage of ultrasonic time of flight meters is that the differential times may also be use to solve for the speed of sound in the flowing gas. For an ideal gas the speed of sound, c, can be related to the molecular weight of the gas by the following,[39]

Equation 5:

$$c = \sqrt{\gamma RT \ / \ MW}$$

Where:
c = speed of sound in gas
R =universal gas constant
T = absolute temperature
γ = specific heat ratio
MW= molecular weight of gas

Thus, in addition to the velocity of the gas, ultrasonic time of flight meters can be used to estimate the molecular weight of the gas. This allows one to estimate the mass flow rate without doing any other composition measurements.

Design Variations

Aside from the design variations involved with Doppler shift and transit time, ultrasonic flow meters come in portable clamp-on models and installed tap-in models. While clamp-on Doppler shift meters have been used successfully to measure liquid flows, where substantial flow disturbances or particulate matter may be present, the authors are aware of no clamp-on Doppler shift meters used in gas service. The current generation of portable, clamp-on, transit time flow meter requires pressures approaching 80 psig or more when measuring gaseous flow. Thus, portable clamp-on transit time meters are not applicable to measuring waste gas flows in near atmospheric pressure flare headers. For petrochemical industry flare applications, permanently installed transit time devices are used. Available literature indicates that well over 2000 time of flight ultrasonic flow meters have been install in flare applications worldwide.[76] The remainder of this section will focus primarily on permanently installed transit time models.

Transit time flow meters are capable of providing continuous flow measurements and there are many industry applications. Ultrasonic flow meters are capable of handling very large ranges of flows, as is prevalent in flare systems. One supplier gives a typical turndown ratio of 2750:1, over a flow range of 0.1 to 275 ft/s.[5] As with most flow meters, the accuracy declines at very low and very high flow rates. For ultrasonic time-of-flight meters, the high level of sound at high flow rates (above 275 feet per second) makes it impossible to obtain a reading forcing their inaccuracy to approach infinity. At very low flow rates (<0.1 feet per second); the very low level of sound makes the sound very difficult to detect.

Panametrics quotes the accuracy of the Digital Flow GF868 Mass Flow meter at ± 2-5% at a velocity range of 0.1-275 ft/s and measuring gas of the same composition as that used to calibrate the meter.[5] However, actual accuracies depend on transducer design, electronics installed, flow rate, the actual composition of the waste gas, and the profile of the actual flow. Accuracies may range from 5-10% or higher with additional error incorporated for additional pieces of equipment and operating conditions (see Section C Factors influencing measurement performance). The quoted precision for the instrument is given as 1 percent.[5] Transit time models are claimed by the vendors to be the most accurate of all the flow meters currently used to measure flare or waste gas flows.

Manufacturers of transit time meters suggest installing the meter in a straight run of pipe with upstream to down stream ratios of straight pipe of 20 pipe diameters upstream and 10 pipe diameters downstream to ensure a smooth velocity profile and accurate performance. This may be an issue in flares that do not contain the necessary piping. As mentioned for pitot tubes, straighten vanes or other flow correction devices may be used in some applications to correct for not having enough straight pipe run, but due to safety concerns they may not be utilized in many applications.

Ultrasonic flow meters do not obstruct the flare lines and are not indirect safety hazards. Most meters consist of transducers that are slim in design and do not inhibit the flow of material. Due to the unobtrusive design, ultrasonic flow meters also offer negligible pressure drop (<0.1 psig) across the device. This, as stated in previous sections, is an important consideration due to the low operating pressures of most flares. Ultrasonic time-of-flight meters can also handle corrosive or hazardous flows with additional material expense incurred. Typically, all the parts of the meter exposed to the waste gas are made of stainless steel or other specialty materials making them appropriate for most petrochemical industry applications. For very harsh applications, it is possible to design the parts of the meter that come in contact with the waste gas using more expensive specialty materials.

Ultrasonic transit time meters are available for application in piping from approximately 3” up to 120",[5] which make them applicable to the large pipe sizes frequently found in flare systems. These meters may be used across temperature ranges of -110 to 150° C and pressures up to 1500 psig. Ultrasonic meters can accurately measure bi-directional flow due to the design of the meter. One transducer acts as an accelerated sound wave, while the second acts as a retarded wave. In the event of bi-directional flow the transducers simply measure this as a negative flow. The instrument can calculate the actual positive flow by adding the negative number from one transducer to the positive number from the other transducer. Additionally, ultrasonic meters can operate in flows that have a fairly high level of particulate matter. Past designs often had induced error associated with flows with high levels of particulate matter, however current models have been specifically designed to overcome these limitations. Changes to the design to reduce waste gas particulate limitations include orienting the two transducers at a 45 degree angle, decreasing the diameter of the transducer probes, and reducing the distance the transducer probes intrude into the flare header line. Additionally, process changes driven by regulatory requirements and economics reduced the particulate levels in flare waste gas considerably from those originally encountered.

Ultrasonic meters are typically permanently installed into the flare line and require a unit shutdown for installation. Some models can be hot-tapped into the process and are portable. However, some petrochemical facilities do not allow hot tapping of flare lines under any circumstances while many others only allow hot tapping under very specific process conditions due to safety concerns around the flare. In these cases, it may be necessary to take the flare out of service to install the meters.

For the most part ultrasonic transit time meters require little maintenance in order to ensure accurate performance well within the stated TCEQ data quality objectives. Panametrics states in the brochure for the GF868 mass flow meter that the unit "does not require regular maintenance", "has no moving parts to clog or wear", and " is constructed of titanium or other metals that withstand the corrosive environment usually found in flare gas applications".[5] Annual calibrations of the meter may be necessary to ensure accurate performance.

Applicability to Flares

Ultrasonic transit time meters have successfully measured flare flows in refineries and in flare gas applications. Since ultrasonic time of flight meters do not have to be corrected for varying gas composition, and in fact can be used to estimate the molecular weight from the observed speed of sound, they are in many instances the preferred flow meter for flare applications. One drawback to the time transit flow meter is the high purchase and installation cost. Typical costs for an ultrasonic time-of-flight meter are in the $20,000-30,000 range. The author’s experience is that design, site preparation, installation, field calibration, and connecting the meter to the distributed control system typically make the overall up-front cost for an ultrasonic time-of-flight meter approach $100,000.

2.2.4 Combination Systems

Because of the potential large dynamic range of velocities that can be encountered in flare systems, there has been some interest in flow measurement systems that use a combination of flow measurement technologies to cover different ranges of the flow spectrum (multiple range averaging pitots, time of flight meters used in conjunction with high flow pitots, etc.). While there are several vendors whose product literature mentions such combination systems, the authors were not able to identify any such systems that had been installed in flare systems to date. In theory extending the range of velocities that can be measured should be possible by combining flow measurement technologies to cover different ranges. The relative strength and weaknesses of the individual technologies is largely unchanged by combining them into an integrated flow measurement system. However, there are some inherent problems with matching the flows measured in the region where their measurement capability overlap and it remains to be demonstrated in a full scale application. In most cases the advantage of such a combined system may be to extend the range to cover large design case release scenarios that may seldom or never be seen. It is unclear to the authors whether this seldom-used extended range will warrant the additional complication of a combined flow measurement system.

2.3 Factors Influencing Measurement Performance

2.3.1 Measurement Uncertainties

The types of flow meters acceptable for flare measurement service have some differences in the standard accuracy and precision responses. The data for these metrics are shown in Table 2, along with other comparative data that will be discussed later.

One vendor of ultrasonic flare gas meters quotes velocity measurement accuracy within ± 1.4 to ± 3.5% [5]. However, using the vendor-supplied parameters in the International Organization for Standardization (ISO) TR 5168 root sum square model [6] results in a higher measurement error. This model, given in Equation 6, can be used to estimate flow measurement inaccuracy with a 95% confidence interval based on the principal sources of uncertainty in the measurement, Equation 6

$$\text{Overall Error} = \sqrt{(Vo)2 + (So)2 + (To)2 + (Po)2 + (Do)2}$$

Where:

V_o = Gas velocity uncertainty (Per vendor ± 1.4 to 3.5 % for a 2 path flow meter and velocities between 1 and 275 feet/second)
S_o = Uncertainty in speed of sound for gas being measured (± 1.0% per vendor)
T_o = Gas temperature uncertainty (± 2% per Rule 115 requirements)
P_o = Gas pressure uncertainty (± 5mm Hg per Rule 115 requirements is ~0.66%)
D_o = Pipe inside diameter uncertainty (± 0.5% per Shell Flow Meter Engineering Handbook [14])
Insertion of the above values into the equation results in an overall uncertainty of ± 2.75% to ± 4.25% for ultrasonic flow meters, depending on the gas velocity uncertainty.

For thermal mass meters, vendors quote 0.25% repeatability, ± 0.5% of temperature reading for velocities above 100 standard feet per minute (SFPM, velocity of air at standard temperature and pressure conditions) and with optional velocity/temperature/mapping an overall accuracy of ± [3% of the reading +(20 SFPM +0.25 SFPM/°C], above or below 25°C. Using the same values above for errors in temperature, pressure, and diameter together with the minimum ± 3% accuracy quoted for thermal mass meters, and neglecting the speed of sound term (does not enter in the uncertainty of thermal mass meters), results in a minimum overall error of ± 3.8% for thermal mass meters.

As mentioned earlier one vendor of pitot tubes claims overall accuracy of ± 1%. Using the same values above for errors in temperature, pressure, and diameter together with the quoted ± 1% accuracy and neglecting the speed of sound term (does not enter into the uncertainty of pitot tubes) results in a minimum overall error of ± 2.6%.

These uncertainties only represent the inherent uncertainty of the input variables measured to derive the flow measurement. For all the meters there is also an uncertainty associated with the composition of the gas being measured. For ultrasonic meters the uncertainty of the gas composition can be estimated directly from the input variables measured by the flow meter by using equation 6 and the speed of sound derived from the flow meter. However, for pitot tubes and thermal mass meters an independent gas composition measurement must be made, in order to correct these meters for varying gas composition. Correcting pitot tubes and thermal mass meters for varying gas composition will be addressed in more detail in the next section. (Additional uncertainties from flare destruction efficiency measurements would add to this, but estimates of this uncertainty are beyond the scope of this report.)

The Measurement Data Quality Objectives in the TCEQ Work Assignment 5 Work Order state that the overall desired accuracy, precision, and sensitivity is ± 20 percent. Specifically for flow rate, composition measurements, and the resulting calculated mass rate to the flare the desired accuracy, precision, and sensitivity should be ± 20% (never to exceed ± 5,000 pounds per hour of total VOC emitted from the flare). More experience is needed using these devices to ensure that this criteria can be met under all conditions. Currently, there is only limited operating data that can be used to evaluate compliance with these data quality objectives. While the ± 20% would seem doable for a well engineered system within the limitations of the individual meter, this may not be achievable in all cases for the following reasons:

- No single analyzer is capable of achieving the turndown ratios required to measure all possible waste gas flow rates. This may require the installation of multiple monitors to achieve this goal.
- Both ultrasonic time-of-flight meters and thermal mass meters have maximum flow rate limitations significantly below the design maximum flare waste gas flow rates.
- Using widely accepted root sum square error models and vendor-supplied parameters, calculation of overall measurement errors range between ± 2.6 to ± 4.25 percent.
- Pitots are not capable of accurately measuring flows below 10-15 feet per second. Figure 3 shows that typical flare waste gas flow rates are consistently in this range.

To illustrate the first and second points, ultrasonic flow meter vendors quote maximum velocity measurement capacities of 150-275 feet per second (fps). Thermal mass meter vendors quote maximum velocity measurement capacities of 200-300 fps. Flares can have waste gas flow rates ranging from almost zero up to design maximums of over 1000 fps.

For ethylene gas in a 36" diameter flare header at TCEQ Standard conditions, 300 fps equates to a flow rate of ~7,500,000 standard cubic feet per hour (SCFH) or ~555,000 pounds per hour. Large flares can be designed for flows as high as 2,000,000 pounds per hour during major emergencies. Thus, for maximum flows during emergency conditions, a thermal mass meter or ultrasonic time-of-flight meter will only measure ~28% of the potential waste gas flow rate for a large flare. However, many major emergency flows can be reasonably approximated based on process knowledge. For example, most flares are designed for a worst-case, maximum flow assuming a total power failure requiring complete shutdown of the facility. For example, by determining which parts of the process unit have been isolated, and de-inventoried the quantity and composition of the material sent to the flare can be estimated during these rare design case events. While instantaneous numbers may not have the desired degree of accuracy, event totals should be reasonably approximated.

2.3.2 Calibration Systems

Initial and Scheduled Calibration

Flow measurement quality assurance depends on the instrument and the desired service. Service considerations such as the characteristics of the waste gas stream and materials compatibility are essential considerations. For all the preferred flow measurement devices, thermal mass flow meters, pitot tubes, ultrasonic time of flight analyzers, accuracy is directly affected by flow profiles, gas stream temperature, gas stream pressure, and gas stream composition. Although ultrasonic time of flight analyzers are less affected by gas stream composition than pitots or thermal mass meters.

In order to compensate for the effects of service, it is important to select the appropriate calibration methods and frequencies. The portable thermal mass flow meters and pitot tubes used frequently for flare application generally are calibrated in methane or air in a wind tunnel or controlled chamber. A twelve to sixteen point calibration curve is generated and calibrations are certified and traceable to U.S. National Institute of Standards and Technology (NIST) standards. For quality assurance purposes, thermal mass meters and pitot tubes are sent out for an annual recalibration certification and a log of certificates and maintenance work is maintained to assure long-term accuracy and reliable performance relative to manufacturers specifications. Temporarily positioning two thermal mass flow meters in series is an option considered as a QA check. This can be especially useful if the certified factory calibrations are offset in time to determine relative drift and bias. Reproducibility under equivalent conditions is 0.5 to 1.0 % relative standard deviation (RSD). Ultrasonic time of flight analyzers being less dependent on stream composition and thus not factory calibrated to a given composition normally do not require being returned to the factory for calibration checks.

One additional test that can be performed to check both ultrasonic and thermal mass flow meters is the zero flow test[5]. The zero test can be performed by removing the sensors and covering them to isolate the sensor from any air currents. A zero flow reading should be obtained.

Compositional Impacts on Calibration

Particulates

For long duration measurements in flares that contain significant particulate matter, the probe should be periodically pulled and checked for deposits on the sensor elements. These deposits should be removed at a frequency that ensures minimal particulate buildup. By positioning the probe downstream of a wet gas knock out vessel, most deposition problems can be eliminated or minimized.

Thermal Mass Meters and Pitot Tubes

The vendor reported accuracies in flow measurement for thermal mass meters and pitot tubes are for situations where the calibration gas has the same composition as the gas being measured. Due to the wide potential variation in flare gas composition (from mostly ethylene or propylene to mixtures containing varying amounts of C_1-C_5s, hydrogen, nitrogen, hydrogen sulfide, and possibly other inert gases), correction of the observed flow meter reading to account for the actual gas composition versus that which the meter was calibrated on will be required to meet the data quality objectives of this study. Figure 9 shows the impact of gas composition and gas velocity on the correction factors for a thermal mass meter. As shown, the correction factors for converting measurements of a waste gas significantly different from the calibration gas are nonlinear with respect to observed velocity.

For example, Figure 9 shows that at a 1000 fpm velocity reading the correction factor for air is ~1.5 while the correction factor for hydrogen is ~2.0. Thus, at 1000 fpm for a meter calibrated on air the actual conversion factor for hydrogen is then 2.0/1.5 = 1.33. Figure 9 shows that at 5000 fpm the correction factor for air is ~2.0 while the correction factor for hydrogen is ~2.7. Thus, at 5000 fpm for a meter calibrated on air, the conversion factor for hydrogen is 2.7/2.0 =1.35. Thus at 1000 fpm using the direct reading for a meter calibrated on air as the hydrogen flow rate will give a 33% error and at 5000 fpm using the direct reading for a meter calibrated on air will give a 35% error, a 2% increase in overall error. Note that as the flow rate increases the difference between hydrogen and air also increases. Thermal mass meter vendors typically recommend using simple density and heat capacity ratios to estimate the correction factor for varying gas compositions. Since this method also does not vary with velocity, the inaccuracy associated with varying gas compositions also increases as the flow rate increases.

In recent discussions with technical experts from a thermal mass meter supplier, the supplier has stated that thermal mass meters are not recommended for flare waste gas flow applications where highly variable, high volume % (> 5 volume %) concentrations of hydrogen may be present.[30] Although the vendor's technical experts now state this, the author's experience has been that most local representatives are unaware of this recommendation. In the past, some vendor representatives told the authors that hydrogen, in particular, was a problem for thermal mass meters, and that hydrogen measurements would be off by a factor of 5 to 20. The value of this factor varied depending upon the individual representative.

The dual sensor pair thermal mass meter mentioned earlier in this report is an attempt to resolve the potential measurement inaccuracies associated with variable gas composition. Extensive laboratory studies using wind tunnels and flow chambers have been conducted measuring pure gases as well as various gas mixtures over a wide range of flow rates. The measurements have been conducted at velocities approaching zero up to 275-300 feet per second and the entire range in between. In essence, curves such as Figure 9 have been developed for an extensive array of gas compositions and these data used to develop exponential equations to describe the functional relationship. In recently developed thermal mass meters these laboratory-developed equations have been programmed into a minicomputer that is an integral part of the flow meter.

Since every compound has a distinctive thermal signature, the vendor claims that the dual sensor pair thermal mass meter is capable of correcting the measured flow rate for the actual gas composition in real-time. Having two pairs of sensors, one in the main waste gas flow stream and one near the walls, allows the meter to obtain a flowing stream waste gas velocity and a near zero waste gas velocity. One pair of sensors could conceivably give the same velocity reading for two or more widely varying gas mixtures. According to the vendor[29], no two gas compositions will have identical velocity readings at both the in stream velocity and at a near zero velocity. Thus, the meter is able to identify the actual composition of the waste gas by comparing the two readings and correct the velocity measurement for the actual composition in real time.

Thermal mass meters with two pairs of sensors have only recently been developed. The authors have no experience with these systems. According to the vendor several of these dual sensor instruments have recently (within the last year) been installed in flare headers.[29] If the gas composition varies from the extensive compositions in the on-board computer, the meter will still give a reading that may be suspect. The vendor of these meters (as well as the vendors of most other flow meters) asks for a list of the possible waste constituents and the potential range of constituents up front to ensure the accuracy of the measurements. Good process knowledge or field data will be required to design and implement thermal mass flow meters capable of making real time corrections for variable gas compositions. While these meters have the potential to be more accurate than traditional single sensor pair thermal mass meters, the user pays for this improved accuracy. A single sensor pair thermal mass meter costs on the order of $5,000 while the dual sensor pair thermal mass meters cost between $15,000-$20,000.

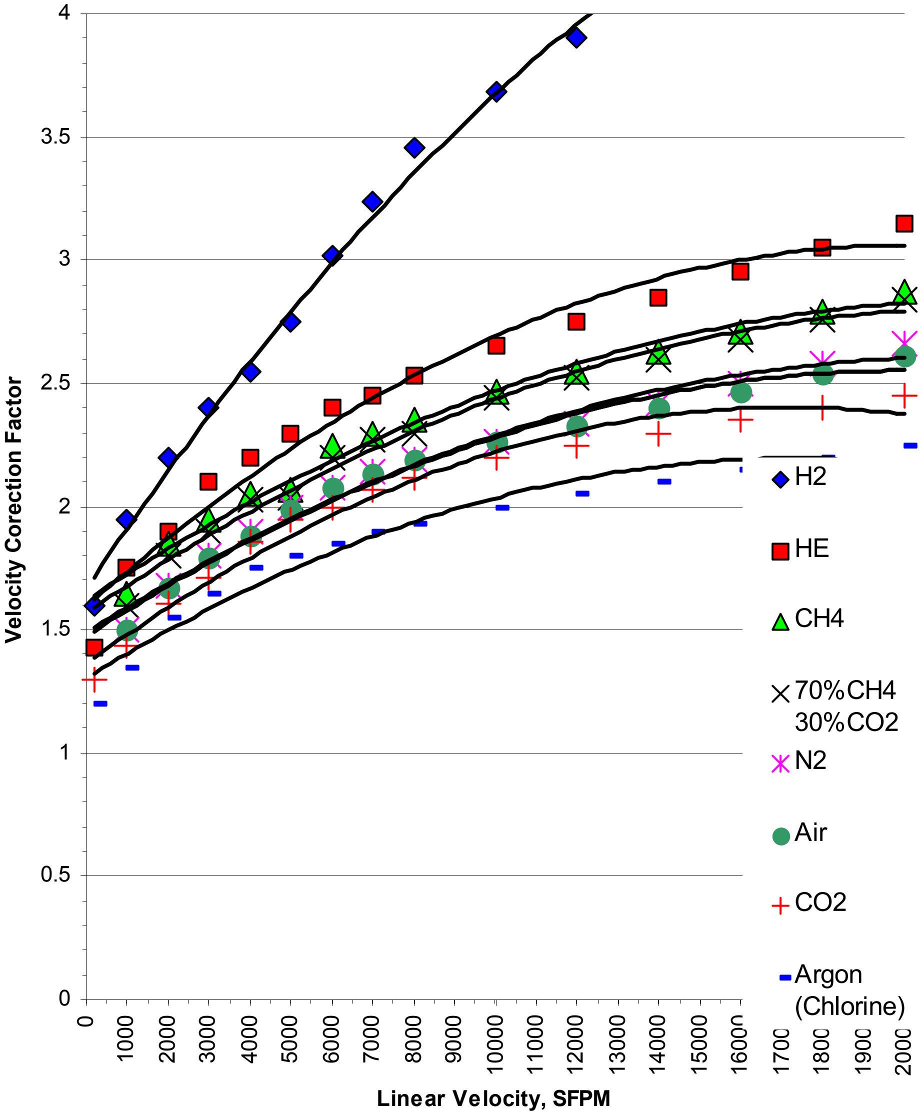

Figure 9. Example Gas Flow Meter Calibration Curve[6]

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[6] **Data Courtesy of Kurz Instruments, Irvine, California**

At the suggestion of a thermal mass meter supplier, the authors have started using the ratio of the Prandtl numbers for the gases being measured to the Prandtl number of the gas the meter was calibrated on to correct observed flow meter readings (see Figure 7). Using gas chromatography data to obtain composition data and to compute mole weighted average physical properties, the author's have observed Prandtl numbers ranging from 0.13 to 1.3 on the same flare during a 1-week timeframe. Therefore, depending upon the application, uncorrected thermal mass meter readings could be off by a factor of 0.13 to 1.3. However, even using a gas chromatograph to collect composition measurements is subject to inaccuracy simply due to time lag necessary to get the GC result (GC cycle times of 6, 12, or 15-minutes are commonly required to obtain one composition result).

The Prandtl number is a dimensionless number defined by the following equation:

Equation 7

$$N_{PR} = c_p(\mu)/k$$

Where:

N_{PR} = Prandtl Number
c_p = specific heat of the gas or gas mixture at constant pressure (BTU/lb F)
μ = absolute viscosity lb/ft-second
k = thermal conductivity BTU/ft-hr F

However, this method also calculates a constant correction factor independent of flow rate contrary to the data in Figure 9. Whether the waste gas is in plug flow, pulsed flow, turbulent flow, or laminar flow also impacts the correction factor for gases different than the gas the analyzer is calibrated on. The authors believe that getting accurate correction factors to correct for variable gas composition for pitot tubes and thermal mass meters currently requires laboratory or in-field calibrations. More information on calibration of gas flow meters is presented in this section.

The above information on calibration and composition correction is specific to pitot tubes and thermal mass meters.

Ultrasonic Time of Flight Meters

GE Panametrics, one of the primary suppliers of ultrasonic time-of-flight flow meters, states the following in their instrument literature; "The GF868 is the only meter on the market that uses Panametrics' patented method for calculating the average molecular weight of hydrocarbon mixtures. This proprietary algorithm extends the range for measuring average molecular weight, while improving accuracy and compensating for non-hydrocarbon gases better process control problems, and accurate plant balance."[5] The vendor's literature states that molecular weight accuracy is ± 1.8% for molecular weights ranging from 2 to 120 pounds per pound mole and should be optimized for other gas compositions.[5] For mass flow of hydrocarbon mixtures the vendor's literature states that typical accuracies are ± 3 to 7% for a 1-path system and ± 2.4 to 5% for a 2-path system.[5] The vendor's literature further states that the quoted accuracies are dependent on the accuracy of the temperature and pressure measurements needed for the proprietary algorithm.[5] Given that the algorithm is proprietary, it is not possible to objectively and independently assess ultrasonic time-of-flight meters overall accuracy when considering actual waste gas composition's impact on overall accuracy.

Multi Service Flares

For flares with multiple process units and multiple process streams tied into them, the accuracy of the calculated flow rate declines significantly for situations where the actual waste gas composition is significantly different than the gas composition the meter was originally calibrated on. Field calibration of these meters is difficult and it is not feasible to calibrate these meters for all the waste gas compositions they may see. Initial and periodic in-field calibrations of these flow measurement meters using tracer injection techniques can improve the overall accuracy of the results. Only ultrasonic flow meters have been demonstrated to correct for varying gas composition in real time, although recent developments in thermal mass meters may soon allow this capability for these meters.

Tracers for Field Calibration/Verification

In addition to laboratory calibrations traceable to certified standards, field measurements using tracer injection techniques can be used to field calibrate ultrasonic time-of-flight meters and thermal mass meters. Calibration here means comparison of the flow meter output to an independent reference flow measurement. Verification means observation of the flow meters operating characteristics and independent calculation of flow.

Metered Injected Gas Tracers

A chemical tracer gas may be used to calibrate /verify the flow rate. Helium is the preferred tracer gas for flare gas measurements. Because it is an inert gas, helium will not react chemically with any other waste gas constituent. In addition, it is non-toxic, mixes well, is readily available, and relatively inexpensive. Argon and sulfur hexafluoride are not as well suited principally because they do not act consistently as ideal gases when mixed into light gas streams, in particular hydrogen, and along unobstructed lateral sections of pipe. Cost and ease of analysis in the field are also considerations. The amount of Helium metered and injected will largely depend on total flare gas flow and lower detection limit of the downstream measurement instrument. An example of a typical test is a metered injection of one to ten liters of helium per minute through a rotameter. The rotameter is calibrated with the helium through a wet or dry test meter and pressure corrected with an in line pressure gauge. The injection point is selected upstream at a point that promotes mixing. Usually a bank or six-pack of full size cylinder is incorporated with a regulator set for a delivery pressure as low as reasonably possible to maintain a steady flow. Downstream gas is drawn into Tedlar™ bags and analyzed or a sample loop and on line micro GC may be used. Helium samples should be drawn at a frequency that permits plotting a concentration gradient tracked over a period of several hours. Helium lower detection limit (LDL) on a Micro GC using an argon carrier gas is below 100 parts per million by volume (ppmv). Calculation of flow is by simple ratio:

(Metered Helium rate injected * 100%He) / [He] downstream = flare gas rate.

Radioactive Tracers

Radioactive tracer flow rate measurement involves injecting a gas radioisotope into the waste gas stream. Testing involves monitoring the “time-of-flight” of the isotopes between two or more detectors placed a known distance apart. The results of the measurement are most accurate in “plug flow” applications. The measured velocity is used to calculate mass and volumetric flow rates, and to characterize different flow regimes (laminar or plug flow). Tracer flow rate measurements are commonly used to check existing flow measurement devices and to measure flow distribution between main headers and branch headers.

The radioactive tracers used have very short half-lives. Tests involving radioactive tracers are complex, and therefore require detailed planning and coordination. This measurement is contracted to licensed and certified specialty companies. Prior to using this technique, comprehensive safety reviews and permission from the facility radiation safety officer are required. [7]

Using radioactive Krypton 85 (a gamma emitter) and three external receivers equally spaced apart starting at 10 meters downstream of the injection point, measurements time the flow as a time-of-flight across the scintillation detectors (gamma ray collectors). By factoring the time-of-flight with a specific gravity and a cross-sectional area of the pipe at the receivers, a mass flow is calculated. By interpretation of the data (ratio of multiple areas), the degree of pulsed flow and back flow may also be determined. [8]

Figure 7 shows a specific example where a radioactive tracer was used to verify measurements from both pitot tubes and thermal mass meters. Each of the red squares in Figure 7 represents one radioactive tracer injection. Note that each injection yields a single point measurement, thus several measurements are required to accurately determine the flow rate. In the case of Flare J, the radioactive tracer injection confirmed that the flow was in pulse flow as measured by the thermal mass meter rather than the plug flow indicated by either of the single-point pitot tubes.

Other field validation measurements

Another test is to take a sample of flare gas at the same time the ultrasonic meter is recorded for its values of mass weight and/or sound speed. The calculated MW value from the chromatographic analysis is compared with the readings of the ultrasonic meter. Manufacturer specifications relating to this comparison verify proper spacing of the sensors, programming, and proper ultrasonic operation.

An oscilloscope can be used to monitor actual transit times and difference in transit times from test points on the ultrasonic meter. Calculation of the flow rate is then done by hand and compared to calculation of the rate by the meter. [9]

Online measurements to correct for composition changes

Given the potential variation in stream composition, online instruments may be added to improve overall measurement accuracy. The cost of using such equipment must be balanced against the gain in accuracy actually achieved. The two most common additions are densitometers and direct online composition measurement devices. The latter is discussed in detail in the next section.

Densitometers may be used as a means to collect real time data on the gas composition to correct thermal mass meters, or as an independent verification of the molecular weight determined by time-of-flight ultrasonic meters. Insertion probe gas specific gravity transducers are designed to give an output proportional to the molecular weight and consequently specific gravity of the gas. The most common type of densitometer is a resonating element, which references a fixed volume of reference gas at a constant temperature with the measurement gas. A diaphragm ensures that the pressure on the reference gas and measured gas are at the same pressure. Under conditions of equalized temperature and pressure and with super compressibility effects considered, the specific gravity and relative density are equivalent. Response time may be an applicability consideration when there are resonating pressure effects with a frequency faster than the diaphragm can respond to. Absolute reference pressure range must be able to track flare header pressure range, which can be below 14.7 psia. If a mass flow is desired without regard to composition, a densitometer may be used in conjunction with a thermal mass flow meter to determine a mass flow to the flare. [10,11]

While additional instruments to measure the waste gas density can improve the accuracy of the measured flow rate, the importance of these measurements being paired in time with the velocity measurements cannot be overemphasized. For, example the most accurate method of measuring the actual waste gas composition, and thus the physical properties of the waste gas may be online gas chromatographs. However, these traditionally have 6,12, or even15 minute cycle times, while the flow meters measure the velocity every minute. Figure 10 graphically illustrates the importance of pairing the flow and compositional measurements in time. Note that the hourly average flow measurements in Figure 10 tends to smooth out the short-term peak flows and would indicate that the flow is between 2000 and 3000 pounds per hour, while the actual peak flows vary from 1500 to as high as 7000 pounds per hour. By looking at the wide range of potential compositions shown in Figure 4 and the instantaneous vs. hourly averaged flow rates shown in Figure 10, it is apparent that using GC data collected on 6, 12, or 15 minute cycles to correct velocities measured at 1-minute intervals has the potential to miss concentrations shifts, which would then lead to the application of inadequate correction factors to adjust for these composition changes, resulting in potential flow rate measurement uncertainties that dwarf other potential measurement errors. More discussion of this issue is presented in the following Sections.

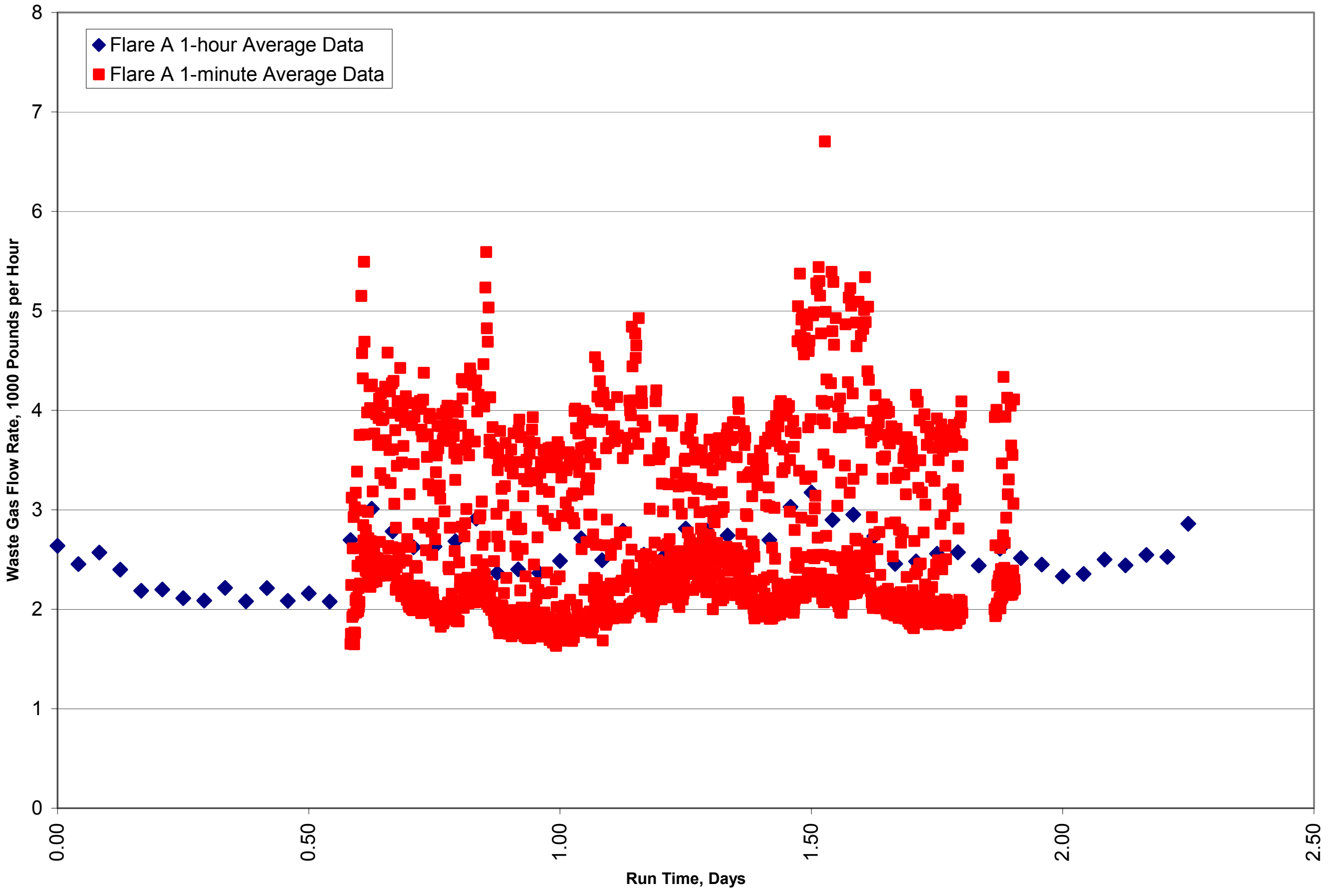


Figure 10. Effect of Averaging Time on Measured Flows

2.4 Summary Overall Results of Flow Meter Evaluation

Of all the flow measurement technologies evaluated, only pitot tubes, thermal mass meters, and ultrasonic time of flight meters satisfied all of the primary criteria for application to measurement of waste gases in flare systems. Pitot tubes are applicable across a much narrower range of flow velocities than thermal mass meters or ultrasonic meters, but this can be mitigated to some degree by having multiple meters to cover the full range of interest. While thermal mass meters and ultrasonic time of flight meters can quantify a considerably wider range of flow velocities, in flare applications they may not be able to sense the velocities that present during the extremely rare maximum design case event. While sensing the flow during a maximum design case event may be possible by using these meters in tandem with a high flow pitot tube or similar meter, the authors are not certain the added complexity and cost are warranted given the extremely rare occurrence of such an event, and the presence of other process data that would allow the quantity of material being flared to be estimated. As shown in Figure 3, flare waste gas velocities are infrequently seen above 40 feet per second. Additionally, infrequent upset events for the flares analyzed are in the 60-90 feet per second range, well within the optimal range for ultrasonic time of flight analyzers, thermal mass meters, and pitot tubes.

The inherent error of all three applicable measurement technologies in a standard gas service are similar (± 3-7%), however, the actual observed uncertainty of pitot tubes and thermal mass meters in flare service will be greater than that of ultrasonic time of flight meters, as the former technologies depend upon accurately assessing and correcting the observed flow for variation in waste gas composition. Ultrasonic meters are less sensitive to changes in gas composition, and by operating principle can assess changes in gas composition from the primary signals processed by the meter. Real time correction of pitot tubes and thermal mass meters for changes in gas composition, while possible in concept, have to only a limited degree been field demonstrated in real world applications on flare system. This is an area where additional development of thermal mass meters and pitot tubes would be warranted to demonstrate similar precision and accuracy to ultrasonic time of flight meters in waste gas service. While ultrasonic time of flight meters currently are the most accurate meter for use in waste gas service, they are also the most costly to install, being an order of magnitude more expensive than annubars and thermal mass meters. Currently, ultrasonic time of flight meters show the most promise of meeting the stated data quality objectives of this study in waste gas service. However, their cost probably limits their application to flow measurements at the terminal end of flare systems. Thermal mass meters offer a suitable alternative in services where the waste gas composition does not vary greatly, and as a sturdy portable instrument that can be used to troubleshoot flare systems (e.g. identify stray flows in complex flare headers).

3.0 FLARE WASTE GAS COMPOSITION MEASUREMENT

3.1 Fundamentals

To meet the data quality criteria laid out in the objectives of this study for the measurement of waste gas mass flows, it is obvious that reasonably accurate and precise waste gas flow composition measurements are required. This section of the report lays out basic considerations for obtaining representative samples and performance criteria necessary to achieve the data quality objectives, discusses the basics of operation for analyzers of interest in waste gas systems, presents the key performance criteria for both offline and online analytical methods and techniques deemed to be appropriate for flare service, summarizes the current state-of-the art of available methods/techniques, briefly discusses emerging techniques, and suggests areas where technical improvements could have a significant impact on the cost effective measurement of waste gas compositions in flare systems.

3.2 Analytical Performance Criteria Applicable to Flare Systems

3.2.1 Representative Sampling

The most accurate and precise analytical measurement is of absolutely no value in meeting the stated data quality objectives, if it is not done on a representative sample. Given the potential for significant variability in flare gas composition and the fact that many flare headers are elevated, making accessibility more difficult, at grade flow loops are frequently advisable. Since flare systems are operated at minimal pressure (1-5 psig), sample pumps or ejectors are usually required. A detailed discussion of sample systems is beyond the scope of this report. However, the interested reader is referred to Appendix B, which discusses in more detail key technical considerations in the design and operation of sample systems for the delivery of representative samples.

3.2.2 Constituents of Interest

One of the key data quality objectives of this study is to achieve 90% speciation of individual VOC, with special interest in being able to characterize highly photochemical reactive VOCs, including but not limited to: ethylene, propylene, all butenes (butylenes), all pentenes, 1,3-butadiene, isoprene, toluene, xylenes, ethyltoluenes, trimethylbenzene, formaldehyde, and acetaldehyde. As a practical consideration in many flare systems, in order to assess whether this 90% VOC speciation requirement has be met will require also analyzing for or knowledge of fixed gases (hydrogen, methane, carbon dioxide, carbon monoxide, oxygen, and nitrogen), as well as light alkanes (C_2-C_7). Analysis of compounds such as hydrogen sulfide, mercaptans, ammonia and light amines, while perhaps not needed to meet the stated data quality objectives, may be of interest as they may have an impact on safe, representative sample handling, conditioning, and disposal. This list is not comprehensive. Constituents of interest required to meet the 90% speciation of VOC in chemical plant flare applications could be quite varied and may have to be assessed on an application-by-application basis. For the purpose of this report, analytes have been grouped by classes for assessment of applicable analytical techniques as follows: hydrocarbons (alkenes, alkanes, and aromatics), fixed gases (hydrogen, methane, carbon monoxide, carbon dioxide, nitrogen, and oxygen), aldehydes, and others.

The analysis of aldehydes presents some unique challenges not encountered with the other compounds specifically identified in the data quality objectives. Formaldehyde and acetaldehyde are not expected to be present in reduced waste gas streams from refineries or olefins plants. They may be present in trace quantities in waste gas streams from a few chemical process units that employ oxidation such as the production of phenol, acetone, methyl ethyl ketone, ethylene oxide, propylene oxide, and urea-formaldehyde resins, to name a few. Because aldehydes are not expected to be encountered in significant quantities in most flare gas applications, the special analytical techniques and considerations required for this class of compounds have been placed in Appendix C, and will not be discussed explicitly in the body of this report.

3.2.3 Dynamic Range

Analytical techniques used to analyze waste gas steams in flare system must possess a wide dynamic concentration range due to the variable nature of waste gas sources. Generally, these analytical techniques must be able to detect analytes at concentrations from 100 ppmv to 100% in waste gas streams (10^5 dynamic range). The lower concentration limit is based on both achieving the data quality objectives and practical lower detection limit for most thermal conductivity detectors. Use of online dilution equipment or multiple sample loops (e.g. vary sample size introduced to analyzer on the order of 10x to 50x) can be used with some analyzers to effectively extend the dynamic range of the instrumentation. Parallel systems or programmed logic loops may be required to make these alternatives effective options for continuously speciating waste gas streams. The more complex the system needed to achieve the required dynamic concentration range, the more likely there will be additional expense to install and maintain the system, as well as the potential for more system reliability issues.

3.2.4 Separation

Because speciation is part of the data quality objectives, the ability to cleanly separate the constituents of interest is an important performance criterion for analytical systems used in flare service. Co-elution and poor separation of constituents can be a significant problem in flare systems due to the large number of possible components and the dynamic range of those components. In order to meet cycle time requirements and simultaneously achieve adequate component separation, hardware options must be critiqued not only for their ability to achieve the desired separation in a given service, but also for their adaptability for changing conditions and sources. While not explicitly addressed in this study, software (e.g. advanced GC column temperature programming, assessment of peak retention time shifting, etc.) can also be used to enhance the separation of constituents of interest. While component separation is clearly a performance criterion that must be evaluated for analytical systems applied to the measurement of components in flare systems, there is no absolute measure for this performance criteria. Rather it is a relative scale related to flexibility and adaptability to field applications.

3.2.5 Quantification

Lower detection limits as defined by signal to noise ratio, linearity of response, electronic gain, detector overload, carryover or cross contamination, detector drift, bias, and loss of detector sensitivity are all quantification performance criteria that need to be considered. Column selection, contaminants, retention time shifting, peak distribution, integration width, and sensitivity parameters all effect quantification and consequently impact performance specifications. The quantification standards set forth in EPA Performance Specification 8 for continuous VOC analyzers,[24] Performance Specification 9 for continuous speciated analyzers,[25]and the performance specification in EPA method 18[18] for offline or grab analyses were used to evaluate the level of quantification achievable by each of the analytical techniques assessed for use in flare systems.

3.3 Basics of Analytical Instrumentation Applicable to Flare Systems

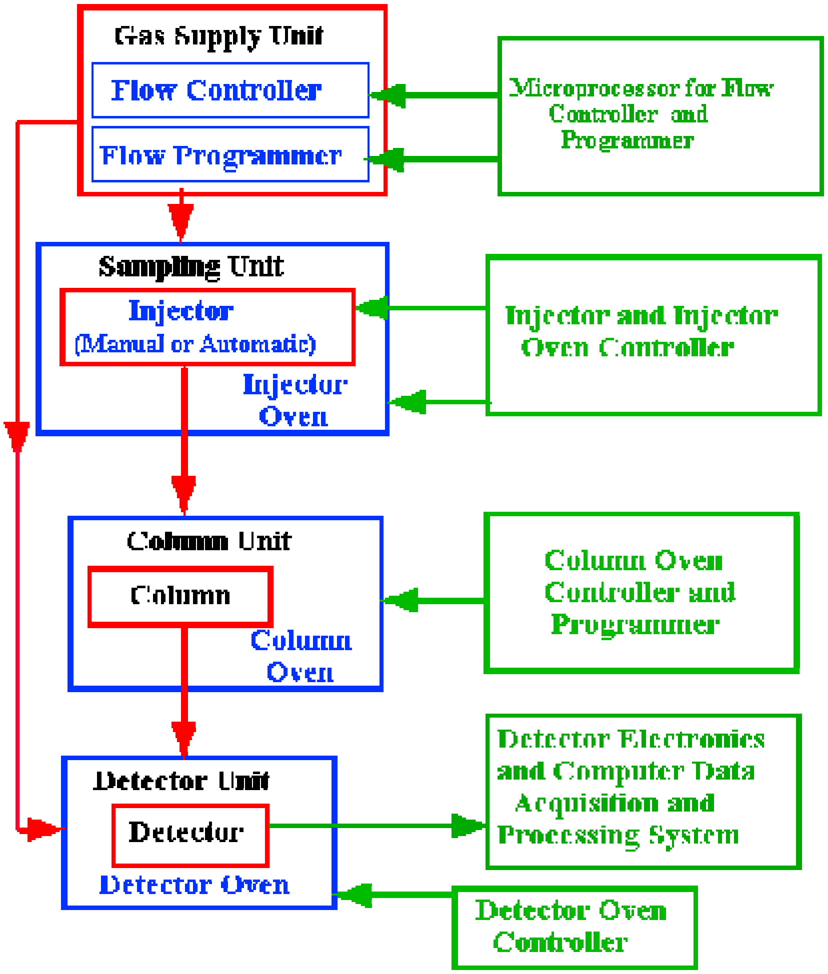
3.3.1 Gas-Solid Chromatography

Gas chromatography is the most common method for analysis of industrial waste gas streams. It is essentially a physical method of separation where the components to be separated are distributed between two phases, a stationary phase contain within the column and a mobile fluid which travels through the stationary bed. The chromatographic separation of the gas components occurs as a result of the varying affinity of each component for the stationary phase selected. Due to the difference in retention time of the various components on the stationary phase, the sample is separated into discrete peaks of the constituents of interest. The mobile phase then conveys these peaks to a detector for quantification.

A gas chromatograph consists of essentially three integrated functions, sample introduction (injector), separation (column), and detection. The detector signal is sent to a recording instrument where identification is determined by retention time or elution time, and quantitative values are obtained by signal strength over time (peak height or area counts). The relationship of these three functions is depicted in Figure 11. Many types of columns are available to achieve the desired separation based on composition of the waste gas stream. Often, multiple columns are required for complex separations and temperature control is often used to enhance separations.

Following separation in the column, individual components emerge from the column and are conveyed to the detector by the carrier gas. There are many detectors available, however, the most common associated with waste gas streams are thermal conductivity detectors (TCD), flame ionization detectors (FID), and photoionization detectors (PID). The TCD measures the difference in thermal conductivity of the eluting component with the pure carrier gas. It is considered a universal detector since it measures all components relative to the carrier gas. The FID combusts the sample components in hydrogen flame, producing ions that are collected and converted into a signal. The FID measures only ionizable components. The PID measures ionization radiation based on the photoionization potential of the components. Excitation energy is supplied by an ultraviolet lamp. The PID measures only components that have an ionizing activation energy equivalent to or below that supplied by the lamp employed. It has a good response to many compounds containing double bonds. [2] While the above detectors are the most broadly applicable to the class of compounds normally found in flare systems, there are a variety of other chemical or class specific detectors (helium ionization, thermal ionization, flame photometric, nitrogen phosphorous, electron capture, catalytic combustion, etc.) that may be used in conjunction with gas chromatography in particular flare applications. The interested reader is referred to Appendix D for a more detailed description of these detectors.

Figure 11. Typical Gas Chromatographic Schematic



3.3.2 Non-Dispersive Infrared (NDIR)

Non-dispersive infrared spectroscopy is based upon the principle that individual compounds and classes of compounds adsorb infrared light at characteristic wavelengths. The attenuation of the IR source at this characteristic wavelength within the sample cell versus the attenuation in the reference cell can be related to the concentration of the compound or class of compounds in the sample cell. In NDIR spectroscopy the source emits light at all IR wavelength, and thus is a non-dispersed source. An optical filter is used to focus the IR light to the sample to the desired wavelength. The detector then senses the attenuation of the characteristic wavelength in the sample cell versus the reference cell. The infrared detector that is combined with the filter is sensitive only to the infrared rays that have wavelengths within a narrow range depending on the wavelength and filter selected.

Historically, NDIR techniques have been used for the measurement of CO, CO_2, NO_x NO_2, and SO_2. Within the past several years several portable NDIR instruments for the analysis of hydrocarbons have been marketed. Several companies now offer a custom configurable multi-channel instrument for the detection of hydrocarbons. There are commercially available NDIR systems available for the analysis of methane, propane, C_1-C_6, CO, CO_2, NO_x, NO_2, and SO_2. Since these analyzers can not speciate, individual compounds they can not meet the data quality objectives of this study, but may be useful in troubleshooting flare systems or collecting preliminary data prior to the design of online GC systems.

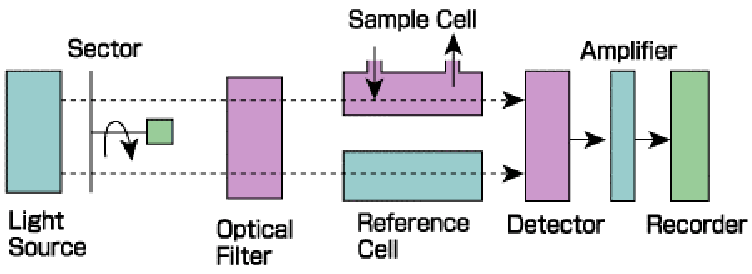
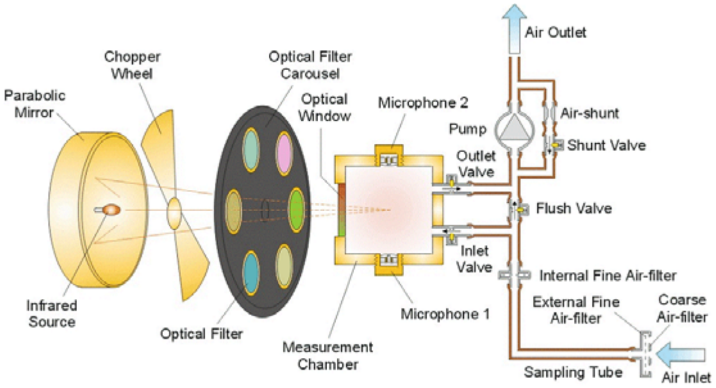


Figure 12. Non-Dispersive Infrared Gas Analyzer

3.3.3 Photoacoustic Sensor

When a gas is irradiated with IR light it absorbs incident radiation within its own characteristic absorption spectrum. The amount of absorbed radiation, which follows the Beer-Lambert absorption law, is a function of the gas concentration, the path length and the specific absorption coefficient of the gas. This absorbed radiation, which for a very short period of time is stored as intramolecular vibrational-rotational energy, is quickly released by relaxation to translational energy. Translational energy is equivalent with heat and, when the absorption chamber is sealed, this will causes the pressure to rise. Each gas has a unique IR spectrum, and strong absorption takes place only at certain wavelengths. When the incident light is modulated at a given frequency, a periodic pressure change is generated in the absorption chamber. This photoacoustic pressure signal can be measured with a sensitive pressure sensor, usually a microphone. In a conventional photoacoustic sensor, the gas to be analyzed is pumped into an absorption chamber that is sealed with mechanical valves during the measurement. The cell is irradiated with modulated IR light filtered at the wavelengths at which the gases of interest absorb strongly. [13,14] Photoacoustic instruments are an emerging technology. Instruments that can speciate specific organic compounds are just starting to enter the marketplace. They are mentioned here for completeness, but at this juncture they are not mature enough to be considered as being able to meet the data quality objectives of this study.



1. An air sample is drawn into the measurement chamber and the chamber is sealed by the valves.

2. Radiation from the IR-source passes through a chopper and optical filter into the chamber, where it is absorbed, generating heat and pressure variations.

3. The pressure variations correspond to the chopper frequency, creating a pressure wave which can be detected by the microphones.

4. The microphone signal, proportional to the gas concentration, is post processed and the measurement result is calculated.

Figure 13. The Principal Components of a PAS Detector

3.4 Offline Techniques for Measurement of Flare Gas Compositions

This section reviews methods and analytical techniques applicable for the offline analysis of waste gas samples from flare systems. Each method or technique is reviewed based upon its ability to analyze the constituents of interest, ability to analyze over the dynamic range encountered in flare systems, flexibility and adaptability to deal with separation issues, and against applicable quantification performance standards.

3.4.1 EPA Method 18

Constituent of Interest

Since EPA Method 18 is not a unique analytical method, but rather a collection of techniques designed to meet specific performance test objectives, this method has the flexibility to analyze for all of the constituents of interest in the data quality objectives of this study. However, depending upon the specific flare waste gas application, multiple analytical configurations and/or instruments may be needed to speciate all compounds of interest.

Dynamic Range

For EPA Method 18 the low end of the dynamic range is usually determined by the sampling system. An adsorbent trap can extend the lower detection limit to below 1 ppmv for most VOCs. Direct interfacing or bag samples can typically achieve 1-ppmv lower detection levels. GC detector saturation or column overloading governs the upper detection limit. The upper range can be extended by dilution of sample with an inert gas or by using smaller volume gas sampling loops. The upper limit can also be negatively impacted by condensation of high molecular weight compounds. For VOC above the molecular weight of benzene, one can extend the upper detection limit range by heating the entire sample line and injection system to a temperature where condensation does not occur for the analytes of interest. Heating of grab bag samples may be done in a temperature-controlled environment to vaporize condensates simultaneous with sample introduction.

The following are generally accepted dynamic ranges for detectors commonly used with EPA Method 18: TCD, 10^3; FID, 10^7; PID, 10^{4-5}. With miniaturization technology and three gain settings, the dynamic range using a micro GC TCD detector can be extended to 10^6. As previously stated, for waste gas applications the dynamic range encountered can be from below 1 ppmv to 100% for any of the VOCs listed in the data quality objectives. Since adsorbent traps are generally not applicable in waste gas service, due to the high potential for overloading of traps and poor retention of lighter molecular weight components, the dynamic range is then a function of the detector employed and any sample dilutions or variable sample loops employed.

Separation

Separation using EPA Method 18 criteria are based on analysis development, selection of GC parameters including temperature programming, and column choice. Preliminary GC adjustment is done using the standards and selected column(s) to perform initial tests to determine appropriate GC conditions that provide good resolution and minimum analysis time for the compounds of interest. Based upon the data quality objectives set forth in this study, separation of the VOCs of interest can be performed on a 30 meter non-polar methyl silicone type PLOT (Porous Layer Open Tubular) columns with a resolution down to baseline at a signal to noise ratio of 3.

Quantification

EPA Method 18 identifies compounds based upon peaks in the samples eluting at the same retention time as known standards. Any unidentified peaks that have areas larger than 5% of the total area are identified using GC/MS, or by matching the peak with additional known standards, with confirmation by further GC analysis. Secondly EPA Method 18 relies on a three-point calibration of each target analyte to generate a response factor. If this response factor deviates from linear by more than 5% over the expected concentration range, then a calibration curve is required. Method 18 establishes precision and accuracy criteria for field audit samples. Precision of triplicate analyses of calibration standards must fall within 5% of their mean value. The accuracy of the prepared audit samples must fall within 10% of their prepared values. Recovery is checked to meet a ± 30% recovery of the prepared values for the sampling techniques employed, typically direct online sample loops or bags for waste gas steams. Based upon the recovery tests, a recovery correction is applied for each sampling system used.

Summary Statement

Method 18 is a compilation of many gas chromatographic methods used for the measurement of gaseous organic compounds emitted from industrial sources. This method is most applicable to low level organic emissions from vents, scrubbers, or post combustion emission points. The method is also suited for emissions from individual sources that have relatively steady operation and subsequently steady flow and composition relative to what is typically encountered in waste gas streams in flares. While the adaptability and flexibility provided in the method is sufficient to say that Method 18 can analyze for the compounds of interest, across the dynamic range encountered in flare systems, with an acceptable level of precision and accuracy to achieve the data objectives of this study, this can only be achieved by tailoring the specific method to the specific application. For many flare applications this may require multiple methods and analyzers to achieve the desired result.

Method 18 is not broadly applicable to waste gas streams due to the component and compositional variability that can be encountered during monitoring of uncontrolled (per-combustion) waste gas streams. Offline sampling methods, as detailed in EPA Method 18, with subsequent analysis are not well suited for waste gas measurements because of cycle time constraints to achieve adequate characterization of the waste gas stream. The nature of flaring events is such that episodic events can occur over the order of minutes with sampling and subsequent analysis estimated to require on the order of hours. Due to the range of constituents and concentrations that can be encountered in flare systems, achieving the data quality objectives may require multiple analyses on multiple instruments of the same sample. This potential time lag is even more problematic if the composition data is to also be used to correct the flow meter for composition changes from that on which the meter was calibrated.

3.4.2 ASTM D-1945 and D-1946

Constituent of Interests

ASTM D1945 (Standard Test Method for Analysis of Natural Gas by Gas Chromatography) is a standard method used for natural gas applications. ASTM D1946 (Standard Practice for Analysis of Reformed Gas by Gas Chromatography) is essentially similar but with the addition of carbon monoxide and has the ability to quantify light olefinic compounds. These methods are not applicable to waste gas streams containing significant quantities of aldehydes, ketones, or alcohols. These methods are not specifically configured for detection and resolution of olefinic components or higher molecular weight components, including but not limited to all pentanes, trimethylbenzenes, xylenes, and ethyltoluenes.

Dynamic Range

This method is useful to characterize simple natural gas streams relative to possible waste gas compositions and ranges. Natural gas and reformer gas have by comparison a relatively narrow range of compositions relative to many waste gas streams. The TCD used in these methods offers adequate linearity of response for hydrocarbons over a 10^3 range, however this range may not be large enough for many waste gas applications, which can have a dynamic range of 10^5. The sensitivity of the traditional TCD used in this method is questionable for applications where the minimum detection requirements are at or below 100 ppmv and linearity is desired over a large dynamic range.

Separation

The permanent gases hydrogen, methane, oxygen, nitrogen, carbon dioxide and carbon monoxide are measured using a molecular sieve (5A or 13X column) with thermal conductivity detection. Simultaneously, light hydrocarbons methane through hexane are measured using a Porplot Q column with a thermal conductivity detector and back flush of all higher mass components is performed to give a C_6^+ value.

This separation does not give adequate resolution of C_4 and higher mass components as required by the data quality objectives of this study. These methods are unable to adequately separate aldehydes, ketones, or alcohols.

Quantification

In the ASTM 1945 Method, reference standards are prepared from pure components. Precision is checked by confirmation of two consecutive checks of reference standards that agree within 1% for each component. Linearity of response is checked by injection of a series of standards of increasing mass by way of partial pressure increments through a fixed loop. Linearity is checked with major components. Repeatability and reproducibility are set on sliding scales found in the comparison table. Relative accuracy is checked by normalization of the molar values obtained in the analyses and comparison with the original values. The sum of the original values should not differ from 100% by more than 1 percent.

Summary

ASTM methods D1945 and D1946 do not have the ability to analyze all the constituents of interest, nor do they have the dynamic range required for many waste gas applications. While these methods may be applicable to flare applications with relatively constant compositions and constituents, they generally are time intensive (estimate >10x factor), less accurate, and do not offer the degree of speciation and resolution other methods offer. Also, the method does not address determination of hydrogen sulfide. The significance and use of ASTM D 1945 as stated in section 4.1 of the method is that it provides data for calculating physical properties of the sample, such as heating value and relative density, and for monitoring the concentrations of one or more of the components in a mixture.

3.4.3 GPA 2261 and 2177

Constituent of Interest

Gas Processors Association Method 2261 is a natural gas method used primarily to determine the calorific value of fuel gas. It measures C_1–C_6^+ hydrocarbons, inert gases oxygen, nitrogen, carbon dioxide, and hydrogen sulfide. It typically uses a two-column system with one 10-port valve or three valves to allow analysis from both columns with back flushing to get a C_6^+ value and utilizes a single TCD detector. These methods are not applicable to aldehydes, ketones, or alcohols. Similar to the ASTM methods, these methods are not specifically configured for detection and resolution of olefinic components or high molecular weight components, including but not limited to pentenes, trimethylbenzenes, xylenes, and ethyltoluenes. Separation of aldehydes, ketones, and alcohols are not achieved with this method. While these methods may be applicable to some waste gas streams, they do no have the flexibility to analyze for all the constituents of interest for this study.

Dynamic Range

The dynamic range for GPA Methods 2261 and 2177 covers the typical range encountered in natural gases. These molar volume ranges are defined as 0.01-100% methane, 0.01-100% ethane, 0.01-100% propane, 0.01-10% N-butane, 0.01-10% isobutane, 0.01-2% isopentane, 0.01-2% N-pentane, 0.01-2% hexanes and heavier, 0.01-10% helium, 0.01-20% oxygen, 0.01-100% nitrogen, hydrogen sulfide 3.0-100%, and 0.01-20% carbon dioxide. The dynamic range encountered in waste gas streams is much wider than the range demonstrated by these methods. GPA 2261 uses varying partial pressures to determine calibration and linearity. With the wider dynamic range encountered in waste gas streams, errors can be introduced due to unknown degrees of compressibility with different compositions.

Separation

Separation of natural gas components in GPA 2261 is achieved with an adsorption molecular sieve column and one or two partition columns (Porpack Q and/or silicone). This serial configuration separates out non-condensable gases, including CO and natural gas components, with a reverse flow to group hexane and heavier components. For waste gas streams, separation of alkanes from alkenes may not be adequately resolved with this configuration. Resolution and determination of hydrogen sulfide is included.

Quantification

In the GPA methods, calibration is achieved with response factors derived from reference standards of known composition or from duplicate injections of pure components that agree within ± 0.5% of the average areas. Precision data is specific for each component in terms of both reproducibility and repeatability and specifications are presented in the table below. Linearity is checked by sequentially increasing the partial pressure of a pure component standard gas of the major component of interest. Any linearity deviations indicate the sample loop is too large. For waste gas streams, this linearity method has the potential to increase the lower minimum detection level, as it may result in a sample loop size too small to detect some low concentration VOCs of interest. Additionally, hydrogen linearity and subsequently quantification is unacceptable using helium as a carrier without modifications and adding an alternative carrier gas. Multiple injections and use of special supplementary procedures with additional columns and valve switching would be required to meet the data quality objectives of this study on many water gas applications. Such serial type column configurations are not well suited for quantification of waste gas streams, as large concentration variations could lead to column overloading, resolution, and long cycle times relative to parallel configurations.

Summary

The GPA methods cover the determination of natural gas and similar mixtures within a limited range. The GPA methods do not offer the versatility and resolution required to meet the data quality objectives of this study for all waste gas stream applications. These methods may be applicable in a few waste gas applications with limited constituents and relatively narrow composition ranges.

3.4.4 Multichannel Micro GCs.

Transportable, multi-channel, micro GCs are well suited for waste gas flare measurements because of the adaptability and dynamic range allowed for an extended range of fixed gases and hydrocarbons, as well as many other components of interest in waste gas streams. These micro GCs typically contain four channels. Each channel contains a micro-machined injector, a high resolution GC capillary column, and a micro-thermal conductivity detector, thereby making each channel essentially a self-contained GC. As a result, simultaneous analyses of samples on up to four different columns using four different sets of operating conditions can be used. Digitally controlled pneumatics and an extended detector range enable analysis of gas streams containing multiple components over a wide range of concentrations with a good degree of precision and accuracy.[15,16] Agilents' 3000 Micro GC and Varian's CP-4900 are examples of transportable, multi-channel, micro gas chromatographs.

Constituents of Interest

The micro-machined thermal detectors allow for near universal detection of gases, which in many cases makes obtaining a compositional material balance possible. Four channels are used to analyze complex samples quickly and easily. Pre-configured models are available for refinery gas analyses that are directly applicable with minimal modification to waste gas applications. Table 3 illustrates the constituents commonly analyzed on each channel. Of the constituents of interest listed in the data quality objectives, only formaldehyde and acetaldehyde cannot be measured with these instruments.

Table 3. Typical Micro GC Configuration

Suggested Micro GC Instrument Settings for Initial Testing are:

	Channel A	Channel B	Channel C	Channel D
Column	12 M molecular sieve 5A	Porplot U 8M	alumina 10M	OV-1 !0M 2um
Column Temp C	100	105	100	125
Run Time (sec)	160	160	160	160
Sample Time (sec)	40.0	40.0	40.0	40.0
Inject Time (sec)	30	30	30	30
Detector filament	on	on	on	on
Detector auto zero	on	on	on	on
Detector sensitivity	low	medium	medium	high
Peak Attribute	area	area	area	area
Calibration fit (3 minimum)	point to point	point to point	point to point	point to point
Calibration Type	external std	external std	external std	external std
Column head pressure	20-30psig	20-30psig	20-30psig	20-30psig
Components	hydrogen	carbon dioxide	ethylene	n-pentane
	helium	ethane	propylene	1-pentene
	oxygen	acetylene	n-butane	collective C5 s
	nitrogen	propane	isobutene	benzene
	methane	hydrogen sulfide	1-butene	toluene
	carbon monoxide	carbonyl sulfide	isobutylene	ethylbenzene
		methyl mercaptan	cis-2-butene	xylenes (collective),
			trans-2-butene	n-heptane
			1,3 butadiene	
			ethyl acetylene	

Dynamic Range

Typical lower detection limits are 10-20 ppmv for most components. A low, medium and high electronic gain may be used as a 10x to 100x step change in signal and increases the dynamic range of the detectors from 10^3 to 10^6, and is selective by channel. Dynamic range with sensitivity gain and linearity are superior to traditional GC Thermal Capture Detectors (TCD). Due to this extended detector range, there is no need for dilution interfacing or complex valving configurations, and the risk of detector saturation is low. All components can be measured up to 100% molar concentrations, with the assumption that heated injectors are used and no vapor condenses. [15,16]

Separation

Separation can be achieved for all components listed in the data quality objectives, with the exception of formaldehyde and acetaldehyde. Resolution is best for compounds with a carbon number of five and lighter. Software controlled alternate conditions may be required for applications where toluene, xylenes, ethyltoluenes, or trimethylbenzenes are present at the percent level.

Quantification

A full multipoint calibration using three or more points over the expected range of concentrations can be performed in the laboratory or field. Multi-channel micro GCs are capable of meeting US EPA Performance Specification 9 calibration criteria for continuous monitors with one exception, the linearity criteria. Calibration type is user selected, based on area count, with the options to use point to point or linear regression, without forcing the intercept through zero. Relative reproducibility and drift of all components in standard gases using the micro GC has been superior to traditional methods when compared with GPA 2261 specifications. This can be attributed to digital control of the injectors and detectors; as well as precision silicon based micro machining. Refer to Table 4 for detailed performance specifications, relative accuracy, and precision specifications.

Table 4. Summary of Offline Waste Gas Composition Measurement Techniques

Waste Gas Composition Measurement Technique Selection	Oven Temperature Range C	Cycle Time	Flow Range cc/m	Calibrations Standards QA/QC	Columns	Injectors	Detectors	Performance Specifications
Manual Techniques								
Portable Micro GCs, Agilent 3000 Micro GC , Varian CP-4900 *	4 independent set from 35-180, isothermal	~ 3 minutes	3 to 12, column specific	External reference stds, multiple stds point to point or best linear fit daily checks single point for each module	4 parallel	Single pump through with 4 electronic timed injectors, fixed volume injectors, backflushed timed mode or fixed mode injectors, splitless sample, direct interface with flowing gas or collected bags attached manually	(4) TCD thermistor type	3 point linear fit or >3 point point-to-point calibration. Less than 5 % variance from average of 3 injections, 106 dynamic linearity +/- 10%, repeatability is ~1% RSD
EPA method 18	Not specified, generally temperature programmed for appropriate resolution	Not specified, generally 3 analyses /hour possible	30-100 for appropriate resolution	External reference stds for each target analyte, multiple gases and points, recovery tests, multipoint calibration with regression analysis to obtain a least square line,	1 with loop inject	Single fixed volume loop, direct interface, bags, dilution interface, single loop volume	TCD, FID, (not specified)	Collection efficiency, Recovery of direct or dilution, recovery for bags and tubes, standards certified to +/- 2% accuracy, calibration curves based on at least three points with dilution as an option, regression analysis and least square line.
ASTM D-1945	Not specified, generally temperature programmed for appropriate resolution	Not specified, generally 3 analyses /hour possible, longer if speciation of C6 or C7 components	Variable, as appropriate for resolution	External pure components or reference stds., relative response factors, linearity, reproducibility and repeatability checks	2 in parallel, 13X molecular sieve and silicone 200/500	Single fixed volume loop	Single.TCD Filament type	Known linearity for each component over the range of interest, dry reference standards or blended pure components, repeatability with two consecutive samples within 1%,
ASTM D-1946	Temperature programmed as feasible	Not specified, generally 3 analyses /hour possible	Variable, as appropriate for resolution	External pure components or reference stds., relative response factors, linearity, reproducibility and repeatability checks	2 columns, an adsorption column for H_2, O_2, N_2, CH_4, CO and a partition column for C_2H_6, CO_2, C_2H_4	Single fixed volume loop	Single or Dual TCD Filament type	Known linearity for each component over the range of interest, dry reference standards or blended pure components, repeatability with two consecutive samples within 1%.
GPA 2261and GPA 2177	40 isothermal	Not specified, generally 3-4 analyses /hour possible	Variable, as appropriate for resolution	External pure components or reference stds., relative response factors, linearity, reproducibility and repeatability checks	2 in parallel, silicone and molecular sieve and pre-cut for C6+ group	Single fixed volume loop, pressure dependent	Single.TCD Filament type	Linearity check with methane based on partial pressure and fixed loop,. Response factors or response curves from gas reference standards, , unnormalized value total should not vary more than +/-1% from 100%, relative response factors OK., retention times.

Table 4. Summary of Offline Waste Gas Composition Measurement Techniques (Continued)

Waste Gas Composition Measurement Technique Selection	Detection limits/Ranges (volume)	Accuracy / Precision Expected +/- %	Potential Interferences	Sample Conditioning	Data Management	Advantages	Limitations	Additional Comments	Recommendations and Summary Statement
Manual Techniques									
Portable Micro GCs, Agilent 3000 Micro GC, Varian CP-4900 *	100 ppm-100%	5% for GC precision of 3 injections, 10% relative accuracy for sample train over dynamic range (dual standards, from same supplier), manufacturer specs <1% RSD precision. RSD daily over 2 months 2 components 3%. Preceeding based on authors testing over 1,600 hours and 20 flares. A * Manufacturer specs <1% RSD repeatability, linear range 106 +/- 10%, .	NH_3, amines	Membrane, filters	Windows EZChrom™, stand alone	160 second cycle time, portable, compact	Transferring data time consuming, not for classified areas, weather, sieve column needs periodic regeneration	Versatile, field adjustments easy, laptop required, duration of testing must be aligned with waste gas composition variability	Good for testing to generate design data or data for online analyzer variables, Easily portable, easy calibration and setup, good dynamic range for surveys and testing to acquire exemption or CEMS design data
EPA Method 18	For ppm sources, generally 1 ppmv-1%vol	+/- 5% for GC precision for triplicate injections, +/- 10% accuracy for prepared audit samples, +/-30% for tube recovery, +/- 30% for bag sampling. Audit analysis +/- 10% of certified concentration. Based on Method 18 criteria	High % components, detector saturation	Externally collected, Tedlar™ bags, sorbant tubes, pumps, water needs managed	Variable, recorder and integrator, cumbersome	EPA Protocol	Limited at % levels, principally used for post combustion vents, many alternatives and multiple variables impact accuracy and precision, long cycle times because of manual sampling	Time consuming, not enough chromatography details, duration of testing must be aligned with waste gas composition variability	Traditional stack source sampling, not recommended for waste gas streams without modifications. Criteria referenced in a variety of regulations, however not easily or practically transcribed for speciated waste gas measurements
ASTM D-1945	100 ppm-100%, except hydrogen sulfide 300 ppmv-30%, typical calibration follows natural gas ranges	1% for all components basis deviation from 100% normalized results, relative response factors acceptable. Sliding repeatability scale: mole % (0.1-1) R</= 0.04, (1-5) R</=0.07, (5-10) R</= 0.08, over 10 R</= 0.1. S Basis re-approved method literature 2001.	High water content and natural gas liquids	% a column for interfering hydrocarbons, drier in front of sample valve	Variable, recorder and integrator, cumbersome, manual calculations of physical properties	Good for natural gas samples, acid gas samples, supplemental methods for heavier components	Limited application for complex waste gas streams. Resolution and run time concerns Groups all C5+, C6+, or C7+ components, long cycle times	Supplemental procedures for heavy ends	Needs updating, antiquated, too long cycle times, not recommended because of single detector and configuration. Some learnings but not generally directly applicable for waste gas streams
ASTM D-1946	100 ppm-100%, including carbon monoxide, typical calibration follows reformer gas ranges	Sliding repeatability scale: mole % (0-1) R</= 0.05, (1-5) R</=0.1, (5-25) R</= 0.3, over 25 R</= 0.5. Sliding reproducibility scale: mole % (0-1) r</=0.1, (1-5) r</=0.2, (5-25) r</=0.5, over 25 r</= 1.0 Basis re-approved method literature 2000,	High water content and natural gas liquids		Variable, recorder and integrator, cumbersome, manual calculations of physical properties	Suited for reformer gas containing carbon monoxide	Limited application for complex waste gas streams. Resolution and run time concerns	Supplemental procedures for heavy ends	Needs updating, antiquated, too long cycle times, not recommended because of single detector and configuration. Some learnings but not generally directly applicable for waste gas streams
GPA 2261and GPA 2177	100 ppm-100%, typical calibration follows natural gas ranges	Based on published Methods revised 2000. Relative precision over expected molar ranges are: Nitrogen:(1.0-7.7) repeatability 2% reproducability 7%, CO2 (0.14-7.9) repeat 3% reproducability 12%, Methane (71.6-86.4) repeat 0.2% reproducability 0.7%, ethane (4.6-9.7) repeat 1% re	High water content and natural gas liquids	Phosphorous pentoxide or magnesium perchlorate tube dryers	Variable, recorder and integrator, cumbersome, manual calculations of physical properties	Good for natural gas samples, acid gas samples	Groups all C6+ components, long cycle times	Good relative response factor table	Needs updating, antiquated, too long cycle times, not recommended because of single detector and configuration. Some learnings but not generally directly applicable for waste gas streams

The authors have used portable, multi-channel micro GCs extensively to do diagnostic studies on flare systems. When using a portable micro GC, it may be restarted (rebooted) daily and a GC verification program is typically run to ensure there are no error conditions in the embedded computer system firmware. Column and detector performance is checked daily and logged by running a standard that contains a particular surrogate component on each channel. If the relative standard deviation varies on any channel by more than 5%, a bake-out conditioning method is run for 1 hour, after which the operating medium is opened and the standard is rerun. If the standard deviation remains above 5 %, a complete calibration is performed and logged. [17,18,19,20]

Retention time shifting is checked daily but has not required frequent corrections (e.g. less than monthly based upon continuous use 24 hours a day, 5 days a week), with the exception of the molecular sieve column. Due to the accumulation of water on the molecular sieve, the molecular sieve column contains a feature to update the retention time after each analysis. This feature reduces elution time as a function of water load. The molecular sieve needs to be regenerated at a frequency determined by the water content in the waste gas and resulting loss of peak separation. This typically takes two hours every two days. In the event retention time shifting does occur, flows are rechecked and adjusted as necessary. Formation of ammonium salts is one common cause for retention time shifting. These salts can generally be removed by running frequent short duration runs with hot columns and injectors using humidified air.

Summary

Transportable multi-channel, micro gas chromatographs are well suited for waste gas flare measurements because of the adaptability and dynamic range available for an extensive list of fixed gases and hydrocarbons, as well as many other components typically found in waste gas streams. The micro-machined thermal detectors allow for near universal detection of gases across a 10^6 dynamic range that makes a compositional material balance possible on many waste gas streams. Precision and accuracy performance in most cases is sufficient to meet typical performance specifications for continuous analyzers, such as USEPA Performance Specification 9.

3.4.5 Summary of Offline Methods

EPA Method 18, ASTM 1945 and ASTM 1946, as well as GPA Methods 2261 and GPA 2177 all have limited applicability for waste gas measurements. EPA Method 18 requires detailed interpretation and selection of various options to be successfully deployed in waste gas service. The ASTM and GPA methods cover a narrow range of concentrations and a limited number of components pertinent to waste gas streams. Consequently, these methods require extensive interpretation and modification to become broadly applicable for waste gas stream analyses. All of the above referenced portable methods have longer cycle times than is desirable for waste gas stream measurements and have the potential to be labor intensive for field deployment. Transportable, multichannel, micro gas chromatographs are well suited for waste gas flare measurements. Due to the extended range of the micro TCD and the universal nature of this detector for gas species, most of the fixed gases and hydrocarbons of interest in waste gas streams may be analyzed. In many cases this allows a fairly complete compositional material balance to be completed. Field deployment and implementation is relatively easy and may be less labor intensive than the other traditional methods reviewed. Table 4 summarizes the performance statistics for each of these methods. While the standard methods can meet the data quality objectives for some applications across narrow concentration ranges, only the multichannel, micro GCs appear to be broadly applicable to most waste gas flare applications. All of these methods would require considerable modification if formaldehyde and acetaldehyde are present to any significant degree.

3.5 Online Techniques for Measurement of Flare Gas Compositions

This section outlines some general considerations that must be taken into account for any permanent online analyzer in flare gas service. Commercially available online analyzer systems are evaluated as to their ability to meet the data quality objective of this study on a continuous basis (per EPA definition, must be able to analyze the flare gas at least once every 15 minutes). Online VOC analyzers were included for completeness even though their inability to speciate VOCs precludes them from being able to achieve the data quality objectives of this study. At the current time the only available online analyzers with the potential to meet the data quality objectives laid out in this study are online GC analyzers. We have summarized the currently available online techniques, along with recommendations where improvements could significantly impact the ability to consistently achieve the data quality objectives set out for this study. In addition, a brief description of several emerging analyzer systems is given. However, at this time insufficient information is currently available on these emerging analyzers to assess their ability to continuously meet the data quality objectives of this study.

Table 5. Online Non-Speciated Waste Gas Composition Measurement Techniques Evaluation

Waste Gas Composition Measurement Technique Selection	Oven Temperature Range C	Cycle Time	Flow Range cc/m	Calibrations Standards QA/QC	Columns	Injectors	Detectors	Performance Specifications
Manual Techniques								
Continuous VOCs (FID - Generic)	Temperature controlled detector block	Continuous, response time < 2 seconds for 90% full scale	Variable Nominally 0.5 lpm	Serial dilutions of a single VOC or mixture that tracks waste gas stream composition averages. Single point for each range.	None	Continuous flow through	FID	VOCs reported as relative to a methane standard or a mixed gas proportional to a source average as per PS8, Hydrogen not counted, so not reliable for BTU if H2 present. Instruments follow EPA Method 25A Criteria.
Continuous Hydrogen (TCD - Generic)	Temperature controlled detector block 60 C	Continuous, response time < 10 seconds for full scale	Variable, 0.5-1.5lpm with reference gas flow also	Pure hydrogen /pure nitrogen composites	None	Continuous flow through	TCD	Potential use for waste gas streams with routinely high hydrogen content >90% molar and noble gases, up to 5% error and zero offset of 2% with 5% residual hydrocarbon interferent. Specific scenario will not meet PS8 criteria.
Continuous VOCs (NDIR Generic)	Temperature controlled detector block	Continuous, response time < 2 seconds for 90% full scale	Variable, generally 0.5 lpm or less through drier, 0.6-1.5bar absolute with pressure switch	Dependent on wavelength range of 2-9 um. Propane used for conditions that track EPA method 25B	None	Continuous flow through	IR dual beam double layer detector / optical coupler	Performance effected by density of gas relative to reference gas density.

Table 5. Online Non-speciated Waste Gas Composition Measurement Techniques Evaluation (Continued)

Waste Gas Composition Measurement Technique Selection	Detection limits/Ranges (volume)	Accuracy / Precision Expected +/- %	Potential Interferences	Sample Conditioning	Data Management	Advantages	Limitations	Additional Comments	Recommendations and Summary Statement
Online techniques (non speciated)									
Continuous VOCs (FID - Generic)	0.5ppmv to 10% or 50ppmv to 100%	Basis compiled product literature, Linearity of 10 7 as per FID characteristics, Carbon atom counter, drift and accuracy tested required as per PS8. Basis compiled product literature, Beckman, Siemens, California Analytical. (All EPA Method 25A compliant)	None known	Filters	Windows Ezchrom™, ethernet RS485 tie in to distributed control system for recording and record keeping	Reliable, simple, industry standard	Unable to detect hydrogen.	Can likely meet PS8 criteria	Several good simple systems to select from.
Continuous Hydrogen (TCD - Generic)	0.1-10% as hydrogen over 4 ranges	Thermal conductivity measured for binary gas systems only, multi point hydrogen calibration, four ranges all linear, auto ranging, drift < 1% /week of smallest span, repeatability <1% of respective span, linear error <1% of respective span. Basis Siemens product literature	None known	Filters, Cooler, pump,	RS485 Ethernet TCP/IP	May be useful for some hydrocracker or hydrotrater units when hydrogen is >90% of waste gas.	Significant errors with more than binary waste gas or periodic/random venting of VOCs.	Not a measure of VOCs	Specialty use only.
Continuous VOCs (NDIR Generic)	Single / multiple ranges with autoswitching possible for 1 ppmv-100% range as propane	Zero drift < +/- 1% of measurement range weekly, Span drift < +/- 1% of measurement range weekly, Repeatability < 1% of respective measuring range, linear deviation < 0.5% of full-scale value. Basis Siemens Product literature, other vendors near equivalent specifications.	Filter and wavelength dependent	Filters, RH < 90%	RS485 Ethernet TCP/IP	Low maintenance, only 4 gases max. Can be stacked	Specific limited number of chemicals or groups of chemicals.	PS8 criteria may apply, but may be selection dependent (single components vs. groups of components)	Possible configuration is: C1-C6 on one channel, Methane wavelength on another channel. Less common that FID configuration.

3.5.1 Total VOC Analyzers

Since TOC analyzers do not speciate individual compounds, they by definition cannot meet the data quality objectives of this study. However, a brief description of available VOC analyzers is given here, as they may be useful in providing load variability and range finding capability for more refined methods. There are many suppliers of continuous VOC analyzers with flame ionization detectors. Specifications for the following commercial analyzers were reviewed: VIG Ratfisch, Signal 300HM, Siemens Fidamat 5E, Beckman 400, Moncon 8800 H, and others. Based on Performance Specification 8 (Performance Specifications for Volatile Organic Compound Continuous Emission Monitoring Systems in Stationary Sources) and specifications literature, it appears that most instruments of this type meet the drift specification of 2.5% of the span value and relative accuracy tests. The analyzers also meet criteria set in EPA 204 (Volatile Organic Compounds Emissions in Captured Streams). Those specifications are: zero drift of less than ± 3 % of the span value, calibration drift of less than ± 3% of the span value, calibration error of less than ± 5% of the calibration gas value, and response time of less than 30 seconds.

Factors affecting performance are relative response to various hydrocarbon species as a function of carbon content and structure, as well as the presence and arrangement of other heteroatoms in the molecule. Response factors express the variance from the carbon count and are usually given in terms of a reference species such as propane or methane. In some applications, the composition of the waste gas may differ significantly from that of gas used to calibrate the analyzer. Because of the difference in relative response factors, variation in actual gas composition from that the instrument was calibrated on may lead to greater uncertainty in the observed VOC value.

3.5.2 NDIR Analyzers

As mentioned earlier, non-dispersive infrared detection has until most recently only been used for trace hydrocarbon analysis. These analyzers are generally more expensive and complicated than FID detectors, but may offer reduced maintenance and lower drift than FID continuous VOC instruments. However, this analyzer has an extremely narrow response range for the range of components anticipated in waste gas streams, and consequently is not expected to be useful in measurements on systems containing aromatics, olefins, oxygenated species in addition to saturated hydrocarbons.

The authors have used an NDIR hydrocarbon analyzer which is as part of a commercially available portable emissions monitoring analyzer (Enerac 3000E). The application was not on a waste gas stream but rather on vents from 2 and 4 cycle internal combustion engines. Drift, zero and span were less than ± 3% when tested against calibration gas (0.5% volume propane) in the field and hydrocarbon in instrument air. The detector meets EPA's Reference Method 25B "Determination of Total Gaseous Organic Concentration Using a Non-dispersive Infrared Analyzer" and measures hydrocarbons as propane using the latest state of the art pulsed infrared LED emitter and dual lead selenide detector technology. Methane and ethane are not measured. The manufacturer's recommendation is for a single point calibration with propane. A second point can be run and linearity checked for EPA compliance as a conditional test method. The manufacturers performance specifications are: concentration range: 0-5% or 0-1% by volume accuracy: ±5% of reading or 0.01% volume (whichever is greater); repeatability: ± -2% of reading or 0.01% volume; maximum zero drift (per year): ± 0.02% volume; response Time: <10 sec; warm up time (@22 deg. C): 60 seconds; operating temperature range: -10 to 40 °C. Another instrument with similar capabilities is the Greenline 8000 from E Instruments Group. [79] Several companies offer a configure-your-own multi-channel instrument with a wide bandwidth of 9μm. This will generally detect all C_1-C_6 straight chain hydrocarbons, but results may be biased low on streams with significant aromatic content. [78]

Pertinent information for online non-speciated VOC analyzers reviewed is summarized in Table 5.

Table 6. Online Speciated Waste Gas Composition Measurement Techniques Evaluation

Waste Gas Composition Measurement Technique Selection	Oven Temperature Range C	Cycle Time	Flow Range cc/m	Calibrations Standards QA/QC	Columns	Injectors	Detectors	Performance Specifications
Online Techniques Speciated								
Siemens Maxum 11 (HRVOC flare base package configuration)*	Isothermal, not specified	Stream dependent, either 7.5 minutes or 15 minutes.	10 to 40, column specific	External reference stds initially, internal use of methane and relative response factors on line, spec 9 performance quarterly	4 in parallel	Four 10-port valves with backflush, heated, direct interface	Four TCD thermistor type	LDL 0.5% mole H_2, O_2, N_2, CH_4, CO, CO_2, C_2H_6, C_2H_4 all 0.01% mole, all others 0.02% mole, range 0.01-100% mole all components, linearity +/- 2% for hydrogen up to 50%, linearity for other components to +/-2% multipoint calibration likely required.
Process Analytical Applications Inc PAAI - (flare base package configuration) *	Isothermal 140	Generally under 12 minutes	Not specified	External reference stds initially, linearity checks on ethene and propene, spec 9 performance quarterly not fully verified at this time, uses 4 separate calibration standards and employs single point calibration	9 columns with three trap columns	Two 6-port valves, two 10-port valves, direct interface, splitless injection	Single TCD Filament type	Linearity tested for ethene and propene and meets 0.5% repeatability. Multipoint calibration likely required for PS9 r2 requirements. Calculated BTUs, not tested with all target analytes,
Star Instruments VOC Analyzer	Unknown	Under 15 minutes based on literature.	Not specified	Star claim is not specific but states QA/Validation protocols are EPA QA / R-2 & R-5, 40CFR Chapter 1 part 60, Appendix F, and TCEQ compliant. No supporting tests data.	Single column	Single injector, splitless	PID with FiD option. PID has one-year life with auto lens cleaning capability.	Basis Star Instrument TCEQ Monitoring Guide (HGA) . Inboard QA and QC requirements maintained automatically through onboard computer control and data archives. Star developed a comprehensive QA plan and Validation Protocols, with defensible reporting on a continuous basis.

Table 6. Online Speciated Waste Gas Composition Measurement Evaluation (Continued)

Waste Gas Composition Measurement Technique Selection	Detection limits/Ranges (volume)	Accuracy / Precision Expected +/- %	Potential Interferences	Sample Conditioning	Data Management	Advantages	Limitations	Additional Comments	Recommendations and Summary Statement
Online Techniques Speciated									
Siemens Maxum 11 (HRVOC flare base package configuration) *	100ppmv-100% for permanent gases, 200 ppmv to 100% for Carbon 3 or > #C components, 0.5%vol-50%vol hydrogen	From Siemens Draft Product Bulletin HR-VOC using Maxum ll, overall accuracy 5% for all components except 10% for hydrogen, repeatability +/-1% all components except Hydrogen at 5%.	NH_3, amines	Filters, pre-columns, and backflushing, non-condensing	Windows Ezchrom™, ethernet RS485 tie in to distributed control system for recording and record keeping	Excellent range and applicability, 7.5 minute cycle times	Hydrogen looses linearity above 50% volume	BTU calculation imbedded, FID as an additional option may help with performance testing linearity requirement	Good option for continuous monitoring, dual system has redundant for two sources or backup system. Multiple parallel "appellets" allow for analysis of complex waste gas streams over a wide dynamic range and with a relatively fast cycle time. Considered a versatile system.
Process Analytical Applications Inc PAAI - (flare base package configuration) *	130ppmv - to 100%	Analyzer repeated within 0.5% for 3 of 5 runs with ethene. Analyzer repeated within 0.75% 3 of 5 runs for propene. LDL demonstrated at 130 ppmv for ethene and propene. Based on PAAI presentation data.	Unknown	Filters, pre-columns, and backflushing	ABB Vista, Emerson-Rousmount, or Yokagawa platform using their preferred software	Single injection and detector configuration with isothermal conditions, 11.5 minute cycle time, EPA Method 301 Field Validation service offered	QA protocols are not well established, not field proven, no internal calibration capabilities in base package.	New instrument, first environmental application, maintenance and retention time shifting due to complexity yet to be determined.	Expandability and versatility questionable because of complexity of valve switching and timing. Uses a single TCD detector and very complex valve and column arrangement.
Star Instruments VOC Analyzer	Unknown for flares	No information for flares.		Unknown	Windows CE Computer with touch screen, RS-232 and RS485 for network connectivity.	PID specific and selective for olefins and aromatics at low ppm levels, however not essential for flare waste gas measurements	Unable to detect hydrogen, or fixed gases such as CO_2, CO, nitrogen, or oxygen with these detectors. Limited range with PID.		Needs further development for flare applications. All application literature is focused on cooling water towers. Literature states "Identical hardware and software may be used for flare gas analysis, less the water sampling components".

3.5.3 Permanent Online Monitoring Gas Chromatographs

Development of an unattended analytical method to achieve 95% on-stream time and meet reporting requirements including cycle times of less than 15 minutes requires these additional considerations:

Validation of Components and Ranges – Representative data must be obtained during the pre-design survey to encompass the full range of waste gas stream components and compositions. Representative pre-design survey data may be collected for as little as little as a few hours to as long as several weeks. Statistical methods may be applied to aid in assessing the required duration of pre-design survey testing. Pre-design surveys should also include review of process feeds, process upsets, and flaring event reports.

Online Calibration – While perhaps being the closest continuous online analyzer performance guideline for analyzers on flare systems, Performance Specification 9 (Specifications and Test Procedures for Gas Chromatographic Continuous Emission Monitoring Systems In Stationary Sources) was written for emission monitoring applications. This fact leads to several problems when applied to waste gas applications. Due to the potential large number of analytes of interest and the wide range of “expected” concentrations, running calibration standards at the low, medium, and high concentration ranges could be impractical from both a time and feasibility of obtaining the required calibration gases. A more practical approach might be to pick a manageable number of surrogate HRVOCs to calibrate and assess performance against PS 9 for these compounds, and use relative response factors for other compounds. Including gases such as light alkanes, nitrogen, oxygen, hydrogen, carbon monoxide, carbon dioxide, and other significant gaseous components based upon their likelihood of occurrence in units discharging to the flare system being monitored is advantageous to assess whether the 90% VOC speciation target is met.

Data Management and Reporting - Significant quantities of data will be generated by these online systems. Depending upon applicable regulatory requirements, significant amounts of data manipulation, retention and reporting may be required and appropriate data management systems can make these data much more usable.

Bias and Drift – These are addressed in the calibration protocols and linearity requirements and often present no problems with properly functioning flame ionization detectors, however signal degradation should be considered when using a TCD in corrosive waste gas service and when using a PID. The PID lamp signal should be checked on a weekly basis because of lamp fogging and intensity decay.

3.5.4 Permanent Online Monitors: Commercially Available Systems

In this section we review three online GC analyzers currently being marketed for analysis of HRVOC in flare systems. The strengths, weaknesses, and problems cited are deemed to be representative of those that will be present when trying to apply virtually all available GC methods to flare systems. These suppliers sell generic configurations that are evolving and potentially can be custom configured to meet the 90% speciation of VOCs requirement in the data quality objectives of this study. As configured these instruments have limitations, and all rely on front-end engineering design and services to build a system for a specific flare application. Consequently, the generic versions presented here are considered basic platforms and work in progress. Each specific flare application will most likely require additional modifications to meet the present PS9 requirements, or require approval of specific variances.

Siemens, a major industrial supplier of GC analyzers, markets a basic packaged system that measures ethylene, propylene, butylenes, and 1,3-butadiene. The cycle time to measure the above referenced HRVOC and other flare gas constituents necessary to calculate the BTU content of the gas is 450 seconds. Therefore each analyzer can analyze up to 2 sample streams and still satisfy the continuous analysis requirement of one analysis every 15 minutes. Sample lag time target should be in the 60-second range.

The separation of flare gas components utilizes 4 independent “appelets” configured in parallel. Each appelet consists of a 10-port valve for injection and backflush, a pre-column, a separation column, and a TCD detector. One single stream from the flare feeds the separation system and all components are analyzed simultaneously. One appelet measures hydrogen, oxygen, nitrogen, carbon monoxide, and methane. Water is removed in the pre-column, which effectively eliminates peak shifting associated with separations using molecular sieve columns. Since helium is used as the carrier, there are some range limitations with hydrogen analysis that may or may not be acceptable, basis actual or expected waste gas hydrogen content. Minimum detection of hydrogen is 0.5% volume and linearity is 2% up to a maximum of 50% volume hydrogen. A separate additional carrier gas can be custom configured for higher hydrogen levels and linearity response, but it is not part of the basic platform configuration.

A second appelet measures carbon dioxide, ethane, acetylene, and ethylene. A third appelet measures propane, propylene, trans- and cis– 2 –butylene, and C_5^+. This generic platform does not speciate C_5^+ components. While custom configuration to speciate beyond C_5 is possible, such customization may have a negative impact on cycle times. The fourth appelet measures isobutylene and 1- butylene.

Electronic pressure control is part of a reliable sample delivery system when used in conjunction with a pump, since it is common for pressures to fluctuate below ambient in some flare waste gas streams. The system using TCD detectors offers good reliability and about 2% linear deviation over a range from below 100 ppmv to high percent levels.

The manufacturer suggests using only a bottle of pure methane for calibration combined with the use of relative response factors, which is a well-established practice for flame ionization detection. However, it is clear this calibration method does not meet Performance Specification 9 requirements, (Section 10.1 of 40 CFR Part 60 Appendix B) as a calibration for "each target analyte" is not conducted. Full multipoint calibrations must be run monthly using representative gases containing all "target analytes" as stated in PS9 Section 7.1.

Based on the manufacturer's literature, calibration error meets the 10% response variance of calibration gas at each level after 24 hours, and meets the linearity precision of 5% for each triplicate injection at each concentration level. The linear regression specification for each target compound at all three levels must have a r^2 value ≥ 0.995. This may not be achievable for all applications; given the linear dynamic range of a TCD detector (10^3) is not as wide as for an FID detector (10^7). Combined with the potential for 10^5 swings in actual concentration for some flare applications, the linear regression curve fit requirement of PS9 may be difficult to meet for many applications. It is possible that equivalency testing using a multipoint calibration and corresponding Method 301 protocols can be performed to satisfy the calibration requirements. Additionally, meeting the linearity requirement for any flaring application where hydrogen can be a major contributor to the waste gas composition at greater than 50% volume will be an issue.

In order to meet the performance requirements of PS-9, additional hardware may be needed if linearity over the tested range does not meet PS9 and alternate Method 301 validation protocols are not performed or not met. Other means of addressing this potential problem are a FID detector in parallel with the (TCD) using a molecular sieve column or a parallel TCD train are two possible configurations. The additional detector may also require additional data handling and reporting considerations for calculation of rolling HRVOCs hourly average mass emission rates. [2]

Process Analytical Applications, Inc., who has principally been a supplier of process analytical instruments, has developed a basic packaged system for HRVOC flare applications. Their system uses one of three gas chromatographs (ABB Vista, Emerson-Rosemount, or Yokagawa) equipped with a single TCD and a complex valving arrangement using two10-port valves, and two 6-port valves, with nine columns and three traps to detect 15 peaks with a cycle time under 12 minutes. The basic configuration for this application detects 15 peaks (nitrogen, oxygen, carbon monoxide, carbon dioxide, hydrogen, methane, ethane, ethylene, propane, propylene, n-butane, isobutane, n-pentane, isopentane, and C_6+). Another application uses two TCD detectors in parallel to detect 25 components including all the butylenes and 1,3- butadiene. Hydrogen is handled as a stand-alone component using nitrogen as a carrier gas. Helium is used for all other components as a carrier. The exact valving, trap, column selection, and overall separation configuration is proprietary. The vendor claims a range from 130 ppmv to 100% for the components analyzed. Their application uses an isothermal oven temperature of 140°F. Their linearity testing protocol used four validation gases that were customer specified and an accuracy of ± 2% relative standard deviation (rsd) was achieved over the range tested. The basic configuration does not include an automated calibration protocol and complete Performance Specification 9 testing has not been conducted. Performance data as presented used only a single or dual point calibration and low-end bias was 34% for ethylene and 12% for propylene. These performance statistics may be improved significantly with more calibration effort (more points and more repetitions of multiple standards). Further concerns with this system are that the butylenes are not separated, and the C_6^+ peaks are lumped and reported together. The vendor offers a service to conduct Method 301 validation as an alternative test method. As with the previous online analyzer discussed, PS9 requirements would not likely be met because of the TCD detector linear range capability, combined with the expected range of compounds encountered in many waste gas applications. With the complexity of the column switching employed, retention time shifting of components is also a concern. This is a newly developed system and has yet to be proven under field conditions. [14]

Another gas chromatograph instrument from Star Instruments Inc. is marketed as an HRVOC online instrument. While the design and quality assurance approach focuses on cooling water tower applications, the literature provided by Star and conversations with a Star officer indicate that this system is also applicable to waste gas streams. It is essentially a dual platform with a continuous VOC analyzer monitoring VOC levels, and when a predetermined VOC threshold is exceeded, a single GC column and GC switching valve are automatically activated for speciation of the sample. The vendor's literature states that identical hardware and software may be used for flare gas analysis as is used for cooling water analysis. The principal detector is a photoionizaton detector (PID) with an extended life design and an automated lamp lens cleaner. FID and TCD detectors are available depending on the specific application. No performance data is available with reference to waste gas applications, although TCEQ operating permit compliance program documentation for one installation in the Houston-Galveston ship channel area lists only ethylene, propylene, butylenes, and 1,3 butadiene for that facility. Based on the data quality objectives for this study, this combination of a VOC analyzer and a single column, single switching valve, single detector GC would not meet the objectives without significant modifications, consisting of additional detectors, columns, injectors, and valve switching. A single PID may pass PS9 criteria for the listed olefins however because of poor response to alkanes it would likely not pass range or linearity criteria. Also, the PID detector generally has an upper detection limit that is likely below the range that will be encountered in many waste gas applications without additional dilution equipment or variable sample loop configurations.

Pertinent information on the online GC instruments reviewed for use in waste gas service in flare systems has been summarized in Table 6.

Emerging Technology

Siemens has recently developed a process multichannel micro GC that has six modular configurations, and capabilities as versatile as the portable multichannel micro GC described previously for offline testing. The same micro-machining technology and a combination of serial and parallel TCD micro detector arrays are employed. The chromatograph uses a single valveless injector and contains valving for backflushing of pre-columns and heart-cut valving. Three columns are used for separation, and an array of up to eight TCD detectors is used in a smart mode to range samples and speciate the HRVOC of interest. A BTU calculation is integrated into the data analysis.

The same EZChrom™ software is employed as with the portable micro GCs and the instrument is packaged for permanent service in classified areas. Additionally, since the instrument is small ("size of a soccer ball"), the manufacturer claims it can be installed at the sample tap with protection from direct sun and rain. This online GC potentially has the same advantages as those previously cited for the portable micro GCs. Precision, accuracy, resolution, and detection limits are similar. Cycle times are also fast (under 240 seconds) with the standard configuration. Offline calibration is the anticipated mode of calibration with methane used for each TCD micro array to adjust relative response factors after initial multipoint calibration. Interfacing to distributed control systems and data management for reporting and recording may present some challenges, however communications are standard Ethernet or RS485 using TCP/IP or MODBUS RTU protocols. This instrument is a new product and has not been field tested or marketed for HRVOC flare waste gas applications. There are a few process installations in Europe and the first one is now being installed in the USA. It warrants further consideration for flare waste gas applications as more systems are installed in the field. [2]

3.5.5 Photoacoustic Spectroscopy

A portable, photoacoustic multi-gas instrument is available that can measure up to five components and water vapor in gas mixtures. The measurement principal is based on a photoacoustic infrared detection method. Most gases that can absorb infrared light are measurable. Five specific optical filters selectively measure the five components. Response is linear. Lower detection limits are molecule dependent and are typically in the 10 to 100-ppbv range. The dynamic range is 10^5 times the detection limit. Applicability for flare waste gas streams is problematic since the dynamic range, although adjustable, may be too low and there are potential interference considerations with matrix effects in complex mixtures. This instrument is probably more applicable to cooling water tower emissions in conjunction with a permeable membrane than to flare applications. There may be potential applications for this technology for waste gas streams where five or fewer HRVOCs may be measured using a single instrument. Applications associated with flares from a single source on a simple process unit may be good candidates for this technology. Also, if the waste stream contains more than five components of interest, the instruments can potentially be stacked with different target analytes filtered for each instrument.[13] This instrument is too early in its development to be realistically considered as a candidate to meet the data quality objectives of this study. Pertinent information on emerging online instrumentation is summarized in Table 7.

All the systems considered for permanent installations have inherent limitations with regard to complete speciation as configured in the basic generic HRVOC packaged system. Both the Siemens and the Process Analytical Applications systems appear to have the capability of modification to include additional detectors and column configurations. Since both use conventional TCD detectors, questions remain as to whether they possess the dynamic range sufficient to handle many waste gas applications. Both systems using TCD appear to adequately address separation of analytes, interferences, GC hardware, sampling system, seven-day calibration error tests of <10%, and data acquisition and reporting criteria with the basic configured system. The Star Instrument Inc. online VOC analyzer as presently configured appears will have significant problems consistently meeting the speciation requirements of the data quality objectives of this study.

3.5.6 Summary of Online Methods

The potential number of components present and the large dynamic range of concentrations potentially encountered make continuous online analysis of waste gas composition in flare systems an extremely difficult challenge. While online VOC instrumentation is available, it will have limited use in achieving the data quality objectives of this study, as not speciation can be done for specific HRVOC. Existing GC techniques have the ability to analyze for the majority of the compounds specifically listed in the data quality objectives and other key components of interest needed to obtain a 90% closure on VOC. The notable exceptions to this are formaldehyde and acetaldehyde, which will require significant additional hardware to be able to quantify. However, it is doubtful that aldehydes will be present in most waste gas systems at significant quantities that would compromise achieving the data quality objectives.

One can custom design a multi-detector, multi-column gas chromatography analyzer using commercially available systems that can measure many of the components that can be in waste gas streams to flares with the precision and accuracy required to meet the data quality objectives. In fact, there are some vendors developing single-detector, multi-column gas chromatograph-based instruments that may be able to sequentially measure most flare waste gas constituents. However, the use of a single detector complicates the ability to achieve speciation of all possible components with adequate resolution and accuracy within the required analysis cycle time. The complexity of the GC system required will be a function of both the number of compounds of interest in each flare application and the dynamic concentration range of these compounds encountered in the specific application. Considerable data collection will be required prior to design of the online analyzer system to be able to meet the data quality objectives for many flare applications.

Online micro-machined, multi-channel, micro GCs, similar to those discussed in the offline section, offer great promise of analyzing the greatest number of compounds of interest over the largest dynamic range with the simplest GC configuration. However, these systems have yet to be applied in a permanent online flare application.

The only performance specification available for continuous speciating analyzers is Performance Specification 9. This specification was developed for emission monitors with a limited number of target analytes over a limited concentration range. The number of "compounds of interest" and the dynamic range of these compounds in flare systems will make achieving the calibration and linearity requirements of PS9 a formidable challenge for many flare applications. In particular, the requirement to achieve ± 2% accuracy from predicted values using calibration gases and re-calibration once a year using NIST traceable primary flow standards with an uncertainty of < 0.25% will be difficult to meet, given the number of compound of interest in flare system. It is not clear to the authors that achieving compliance with PS9 for online GCs is a necessary requirement to meet the data quality objectives of this study.

Some suggestions to meet PS9 linearity requirements or to demonstrate equivalency to PS9 linearity requirements include: smart injection systems that incorporate multiple loops of different volumes and online dilution sampling equipment that meets EPA Method 205 verification requirements for gas dilution systems. Multiple detectors specific for different ranges of gases can also be incorporated to narrow the range for each detector to meet linearity requirements. Additionally, another approach might be to generate a multipoint calibration curve for each target analyte, generate a quadratic regression equation and have a requirement that all points fall within an error band relative to that calibration curve. Then EPA Method 301 criteria can be applied to demonstrate equivalency.

Table 7. Emerging Waste Gas Composition Measurement Techniques

Waste Gas Composition Measurement Technique Selection	Oven Temperature Range C	Cycle Time	Flow Range cc/m	Calibrations Standards QA/QC	Columns	Injectors	Detectors	Performance Specifications
Emerging Technologies								
Siemens MicroSAM - Micro Single Analytical Module *	50-200	Under 15 minutes based on literature.	Not specified	External reference stds, multiple stds point-to-point or best linear, spec 9 performance tests quarterly	2 or 3 columns with a pre-column and backflushing	One injector port, smart switching based on detector array and heart cut valve, and backflush	Four TCD thermistor type, logic loops	Unknown for waste gas applications
Innova 1314 Photoacoustic Multi-gas Monitor *	Isothermal 40	Continuous, response time 75 seconds	100-140	Zero point, humidity - interference, humidity-span, and gas calibration performed quarterly, water vapor compensation, self checks	Five chemically specific optical filters and a compensating water filter	Flow through photoacoustic cell, normal 75 second response	Photo Acoustic	Unknown for waste gas applications

Table 7. Emerging Waste Gas Composition Measurement Techniques (Continued)

Waste Gas Composition Measurement Technique Selection	Detection limits/Ranges (volume)	Accuracy / Precision Expected +/- %	Potential Interferences	Sample Conditioning	Data Management	Advantages	Limitations	Additional Comments	Recommendations and Summary Statement
Emerging Technologies									
Siemens MicroSAM - Micro Single Analytical Module *	2ppmv-100% over variable settings	Overall accuracy 5% for all components except 10% for hydrogen, repeatability +/- 1% all components except Hydrogen at 5%. Basis Siemens Product Literature.	any liquids	membrane, filters, backflushing	Windows Ezchrom™, ethernet RS485 tie in to distributed control system for recording and record keeping	Fast cycle times, good range, small and good for installation at sample tap, low relative cost, BTU in 140 seconds	Not marketed or proven for waste gas applications although no apparent obstacles	Few installations in Europe, only one new installed in USA, something to watch	May have potential for low cost simple waste gas applications, observe performance Not proven yet. Only one US installation, concept good, outstanding concerns about use with complex streams and accuracy /precision.
Innova 1314 Photoacoustic Multi-gas Monitor *	Variable basis LDL, nominally~10ppmv- 10% volume	~2% on detector, repeatability 1% measured value, drift 2.5% measured value/3 months. Based on Innova Air Tech Instruments Model 1314 specifications.	Variable density, condensables, strong vibrations at 20Hz	coarse and fine particle filters	Windows 95,98, 200, NT stand alone display, RS232 to ASCII files, or IEEE 488 or CAN interfaces, 7300 application software for sequential monitoring	Fast cycle times, low maintenance, no carrier gases	limited to 5 HRVOCs per instrument, accuracy density dependent, few proven field applications - none on flares, not for classified areas	Selectivity unproven, portable	Possible application on vents or single source flares May work well for specific HR-VOCs, not good for >90% speciation<BTU, or compositional closure

4.0 FLARE GAS EMISSION CALCULATION ERROR ANALYSIS

4.1 Overall Error in Calculated Emissions

The Measurement Data Quality Objectives for this study were to assess the waste gas flow to flares with an overall accuracy, precision, and sensitivity of ± 20 percent. Specifically for flow rate, composition measurements, and the resulting calculated mass rate to the flare the desired accuracy, precision, and sensitivity is ± 20% (never to exceed ± 5,000 pounds per hour of total VOC emissions). Sources of error in computing this mass flow include the inherent error of the flow meter, the error in the flow measurement associated with measuring a gas different from that used to calibrate the meter, the error introduced by measuring a non-representative velocity or flow distribution (e.g. errors introduced by placement of the meter), and the error associated with determining the composition of the waste gas. The relative contribution of each of these sources of error will be discussed in regards to their impact on meeting the stated data quality objectives.

As stated in the flow measurement section, the inherent flow meter error associated with all three applicable flow measurement techniques (pitot tubes, thermal mass meters, and ultrasonic time of flight meters) will typically be in the range of 2-5%, depending upon the type and quality of the meter. The impact of varying gas composition on the accuracy of the flow measurement is a function of the type of meter. As discussed previously, ultrasonic meters can assess gas composition changes in real time and adjust for changing gas compositions, and therefore this source of error for ultrasonic meters is typically less than 1% of the flow measurement.[37] Pitot tubes and thermal mass meters have yet to demonstrate that they can be corrected in real time for variable gas compositions. If not corrected for changing compositions, these flow measurements could be off by 50-100% in applications with large variation in gas composition. Based upon limited field data, the authors estimate that correcting thermal mass meters with independently collected, periodic composition data can reduce this source of error down to 5%-10% of the measured flow.

The level of error introduced to the measurement by incorrectly sensing the real flow profile (e.g. flow channeling, stratified flow, poor sensor placement, etc.) in the pipe is not easily estimated. However, recent petroleum industry discussions with technical experts from the major flow measurement vendors indicate that this can be a significant source of error that is often overlooked.[28] With proper straight runs of pipe upstream and downstream of the meter, or with the use of flow conditioners, this source of error can be kept under 1% for custody transfer flow meter applications.[37] However, since flow meters added to flare systems will generally be added to existing piping systems, and because safety concerns may limit the use of flow conditioners, this source of error will undoubtedly be higher. For illustration purposes, we assume this source of error to be ~2 percent.

Getting a single error estimate for the gas composition to be used in the mass flow calculation is also somewhat difficult. Based upon the analyzer specification given in the flow composition section of this report, the accuracy for any given component should be approximately ± 5 percent. The relative error for components at or near their detection limit could be higher, perhaps approaching 30-35 percent. However, it is error associated with the major components that will have the largest impact on the calculated mass flow. The errors for individual components will be somewhat self-correcting, as the data quality objectives requiring a 90% closure on VOC will force a mass closure. Therefore, while the relative error for individual components may be higher, the error associated with the total mass flow should be within ± 5 percent.

Assuming that these sources of error are independent, one can use the root sum square model presented previously Equation 6 to estimate the sum of these errors on the mass flow of waste gas to the flare. For illustration assume that the inherent flow meter error is ± 3%, the impact of variable gas composition on the flow meter is ± 2%, that the non-ideal flow profile error is ±2%, and the gas composition error is ± 5 percent. The resulting root sum error for the mass flow would be ± 6.5 percent. In the authors view this represent about the minimum error that can currently be achieved under ideal conditions. However, this is just illustrative of the sum of errors that may be present in flare measurement systems. The rollup of error in non-ideal flow meter installation applications and with highly variable gas compositions could result in considerably larger error estimates.

The illustrative calculations above would seem to indicate that the ± 20% data quality objective should be achievable with existing technologies. Assessment of the ± 5000 lb/hr absolute limit on emissions requires one to estimate a destruction efficiency across the flare. A detailed study of factors affecting flare destruction efficiency is beyond the scope of this work. For our assessment, we have assumed a constant destruction efficiency of 98 percent. A 3-inch diameter flare header flowing at 200 fps with waste gas of specific gravity 0.44 would result in 168,621 lb/hr of gas to the flare. A ± 20% uncertainty in this flow results in ± 33,724 lb/hr uncertainty on the flow to the flare, and at 98% destruction efficiency ± 675 lb/hr uncertainty on the emissions from the flare. Even at a design case event that might be at 1,000 fps, the absolute uncertainty in the emissions from the flare should still be under ± 5,000 lb/hr. Except for all but the very largest flares achieving the ± 5,000 lb/hr absolute uncertainty should be achievable. As stated previously, the issue with meeting the uncertainty at the design case will be the inability to measure the high flow velocity, probably not the ability to meet the ± 5,000 lb/hr criteria. Obviously, this conclusion is a strong function of the assumed destruction efficiency. Assuming a lower destruction efficiencies would make obtaining this absolute mass uncertainty on emissions from flares much more challenging.

5.0 CONTROL OF GAS ASSIST RATIO ON OPERATING FLARES

5.1 Introduction

Several pioneering studies in the 1980s demonstrated that when operated properly, flares should have destruction efficiencies between 98 and 99 percent. Several studies have shown that entrained liquid in the waste gas being flared can significantly reduce flare combustion efficiency to levels approaching 70-80%, thus increasing emissions.[21, 22, 23, 24, 25] Liquid knockout pots and water seals prior to the flare stack are designed to minimize the presence of entrained liquids from either the process or condensation of the heavier waste gas components. To maximize flare combustion efficiency as well as waste gas destruction efficiency, proper operation of these liquid collection systems cannot be overemphasized. Besides significantly reducing the flare combustion efficiency, entrained liquids in flared waste gas can also cause rain out of hydrocarbon materials, which can lead to unsafe situations from both a safety and an environmental perspective. [1, 26, 27]

Also, with respect to the flared waste gas composition, significant quantities of low-BTU (<300 BTU/SCF) materials can result in reduced combustion efficiency, thereby increasing waste gas emissions. For these situations, auxiliary fuel gas with a substantially higher heating value (~1,000BTU/SCF) is combined with the waste gas to ensure complete combustion. The US EPA New Source Performance Standard addresses the burning of low-BTU waste gas. This regulation (40CFR60.18) requires specified flare tip velocities, monitors to ensure the pilot light is lit at all times, and other aspects of flare operations to ensure minimized air emissions during flaring conditions.

Assist gas is supplied to the flare tips of many large, high capacity flares to minimize flare noise, smoking, soot formation, and to further maximize combustion efficiency. Normally, either steam or air is used as the assist gas. Injection of assist gas at the flare tip increases the mixing of waste gas with air, as well as the residence time of the waste gas constituents into the flame zone, thereby increasing combustion efficiency. The choice of steam or air is primarily dictated by economics, such as the availability of excess steam at the facility, the costs associated with producing steam vs. air, etc. Using steam as the assist gas gives some improvement in combustion efficiency versus air, as steam has a lower activation energy for the production of H and OH radical needed in combustion reactions versus that required to produce O radicals from air. [1, 26] In fact, one of John Zink's many technical papers on the basics of flare design and operation[1] specifically states, "Steam injection is the most common technique for adding momentum to low pressure gases. Steam itself provides an additional smoke suppression benefit as it interacts in combustion chemistry. Low-pressure air can be utilized in cases where gas pressure is low and steam is not available."

Limited data indicate that steam injection rates that yield a steam to waste gas mass ratio of 0.15 to 0.5 and higher are typically required to achieve smokeless operation and maximum combustion efficiency. [1, 21, 22, 23, 24, 25, 26] Since air does not enter into the flame zone chemical reactions as easily as steam, higher ratios of air to waste gas are typical. Steam or air injection does reduce the smoking nature of flaring events by significantly reducing soot formation. However, assist gas injection may also reduce the overall combustion efficiency by cooling the flame to below optimum temperatures for destruction of some waste gas constituents, and in severe cases may even snuff out the flame, thus significantly reducing combustion efficiency and significantly increasing flare exhaust gas emissions.

Figures 14 and 15 graphically illustrate this point. Figure 14 shows the optimum steam to waste gas mass ratios to maximize combustion efficiency to be in the 0.5 to 1.5 range. Slight reductions in combustion efficiency occurred at assist to waste gas ratios of 3-4, and significant reductions in combustion efficiency occurred at assist to waste gas ratios above 5.5. Figure 15 shows similar results with optimum soot destruction at assist gas to waste gas ratios from 0.25 to 1.0. However, Figure 15 shows reductions in combustion efficiency for HC, CO, and total waste gas below assist gas to waste gas ratios of 0.3 and above assist to waste gas ratios of 0.8. There are insufficient data currently available for assist gas to flare waste gas ratios between 1.0 and 5.5 to definitively establish the critical ratio where the combustion efficiency declines sharply.

The above discussion indicates that the effect of assist gas to waste gas ratio on flare combustion efficiency, as well as destruction efficiency, requires further investigation. Over aerating or over steaming of the flare flame has the potential to significantly reduce combustion efficiency.

5.2 Examples of Assist Gas Ratio Control Techniques

As noted previously, one of the objectives of this report is "to evaluate current methods of controlling assist gas (steam or air) to waste gas ratios to assure that ratios are maintained within a known certainty." The authors reviewed current practices for controlling assist gas to waste gas ratios during flaring events.

There are three commonly used techniques for controlling assist gas to waste gas ratios; manual control, distributed control system (DCS) auto set point control, and infrared sensor feedback control. In the authors' experience, a comprehensive review of approximately 50 flares in U.S. refineries and chemical plants, informal discussions with representatives of several other petrochemical companies, and some published references [5, 6, 42] indicate the following:

Manual Control

The first and most widely practiced method of controlling the assist gas injection rate is manual adjustment by the operator based on flame observations (either directly or on a video monitor). Where manual adjustment is used, some facilities have flow meters on the assist gas and the operators are trained to minimize the use of the assist gas for economic reasons. Of the approximately 50 flares in refineries and chemical plants of which the authors have knowledge, roughly 90% use this method. Discussions with representatives of other petrochemical companies indicate this high percentage of manual assist gas control is representative of the industry as a whole, with one or two companies being exceptions, and using a lower percentage of manual vs. automated controls.

Distributed Control System (DCS) Auto Set Point Control

The next most practiced method of controlling the assist gas injection rate consists of continuous assist gas and waste gas flow meters tied into a distributed process control system with automatic control to a set ratio. Of the approximately 50 flares investigated, roughly 10% use this method. Discussions with representatives of other petrochemical companies indicate this low percentage of DCS auto set point control assist gas controls is representative of the industry as a whole, with one or two companies being exceptions using a higher percentage of automated vs. manual controls. The waste gas flow meters used for these measurements vary from flare to flare and company to company. The assist gas meters used for these measurements also vary from flare to flare and company to company. However, there should be more commonality in steam/air meters since the assist gas is at high pressures (100-600 psig), and is of constant, known composition. The control systems used to adjust the assist gas flow rate based on the waste gas flow rate are a very small part of a much larger process control system that varies from company to company and facility to facility. In addition to controlling the assist gas ratio for the flare(s), these control systems also control all the process temperatures, pressures, and flows. A discussion of the design and operation of distributed process control systems is outside the scope of this report.

Infrared Sensor Feedback Control

The least practiced method of controlling assist gas injection rate consists of infrared sensors that sense the flare flame characteristics and automatically adjust the assist gas flow rate to maintain smokeless operation. Of the flares the authors have knowledge, less than 2% of the flares use this method. Discussions with representatives of other petrochemical companies indicate this very low percentage of flares using infrared sensors to control the assist gas ratio is representative of the petrochemical industry as a whole. Where these systems are used, the sensors are primarily infrared radiation cameras. There are numerous vendors of infrared radiation cameras for measuring flare smoke, including Raytheon®, Mikron®, and many others. As with all infrared systems, the accuracy of these systems is affected by interferences (primarily CO_2 and water vapor), emissivity, and luminosity.

5.3 Assist Gas Ratio Technique Performance

With respect to the stated data quality objective of assuring that assist gas to waste gas ratios are maintained within a known certainty, the authors reviewed available data from several flares. Figures 16, 17, and 18 show data from 4 flares each using one of the above three assist gas control techniques.

Figure 16 indicates that for the flares in question, manual control appears very similar to an on/off switch. The majority of data in Figure 16, and the median value for all the points in this figure are essentially zero meaning that very little steam is actually flowing to the flare tip. Figure 16 also shows that when the steam valve is opened to the flare, the actual assist gas to waste gas ratio can vary widely from around 2 to above 50. Note that the average deviation from the mean for all the points in Figure 16 is 13. The authors were unable to obtain sufficient data to assess whether this performance is indicative of all manually controlled assist gas systems, or merely an outlier. However, given the previous discussion on the potential impact of assist gas ratio on combustion efficiency it does warrant further investigation.

Figure 17 shows that DCS auto set point control, with the steam flow controlled by the actual waste gas flow, has the potential to maintain the assist gas to waste gas ratio with greater certainty. Figure 17 shows data from 2 different flares using DCS auto set point assist gas to waste gas ratio control. Figure 17 shows that the median for Flare C is 0.7 with an average deviation from the mean of 1.4 while the median value for Flare E is 0.7 with an average deviation from the mean of 0.9. Figure 17 also shows that the assist gas ratios were consistently maintained around 1 for eight of the nine months, with Flare E maintaining an assist gas ratio around 4.5 for the first month prior to being reset to a lower set point. The outlier points shown in Figure 17 are thought to be due to the time lag between the waste gas flow meter sending a signal to the steam valve and the steam valve opening. Since the points in Figure 17 are 1-hour averages, short-term spikes in the waste gas flow rate accompanied with a time lag until the steam valve opens can result in some hourly averages appearing much higher than the mean.

Figure 18 shows that infrared sensor feedback automated assist gas ratio control using a smoke monitor can also result in effectively controlling the assist gas ratio. Figure 18 shows that prior to the associated process unit being down for a process turnaround, no attempt was being made to control the % smoke to a value by adjusting the assist gas. After the turnaround, assist gas adjustments were used to control the observed % smoke. As a result the average deviation from the mean dropped from 8.6 % smoke to 1.8 % smoke, with the smoke consistently being maintained in the 0 to10% range.

5.4 Summary Results of Assist Gas Control Techniques Evaluation

Assist gas is used to improve mixing in the flare flame zone, thereby reducing visible smoke and improving overall combustion efficiency and destruction. Air or steam is traditionally used as the assist gas with the majority of facilities using steam. Earlier 1980's vintage studies demonstrated that assist gas to waste gas mass ratios between 0.4 and 4 were effective in reducing soot while ratios between 0.2 and 0.6 achieved the highest hydrocarbon destruction efficiency.

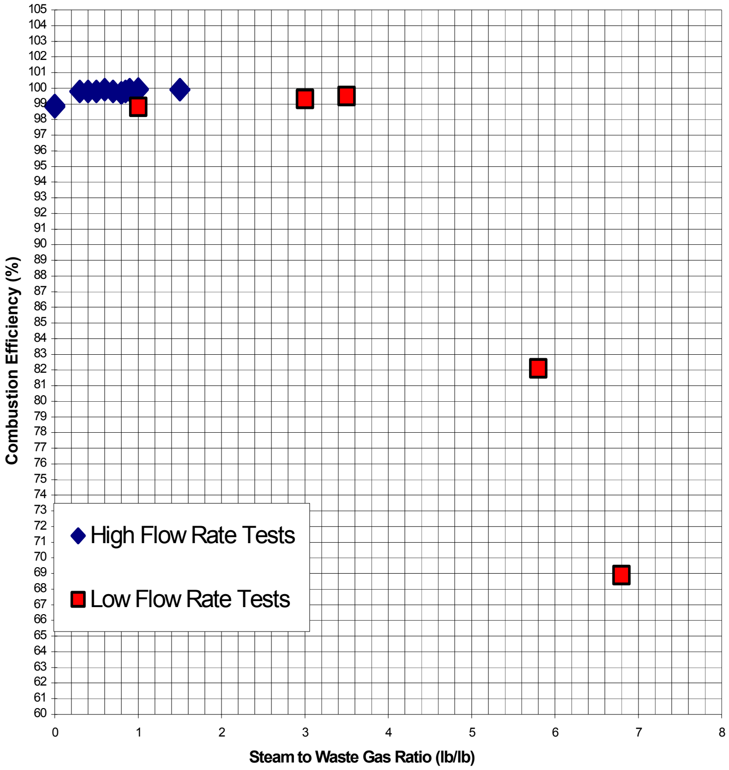
Manual control consisting of adjusting the steam flow based on visual observations, DCS auto set point automated ratio control consisting of automatically adjusting the assist gas flow based on the waste gas flow, and infrared sensor feedback automated control consisting of automatically adjusting the steam flow based on the [% smoke] measured by a smoke monitor were identified as techniques currently used for controlling the assist gas ratio. Of the 50 flares reviewed for this report, < 2% are using the smoke-based automated control technique, < 10%

are using the DCS auto set point waste gas flow based automated control technique, and approximately 90% are using manual control based on visual observations.

Both the infrared sensor feedback smoke-based automated control and the DCS auto set point waste gas flow-based automated control techniques appear capable of meeting the TCEQ Data Quality Objective of maintaining the assist gas ratio within a known certainty. The results for manually controlled assist gas systems exhibited considerably more uncertainty, but the amount of data available were not sufficient to make strong conclusions on all manually controlled assist gas system. However, the degree of uncertainty that was observed warrants further investigation of manually controlled assist gas systems.

5.5 Developmental Recommendations

The limited data sets examined for this study would indicate that controlling assist gas rates using DCS auto set point control based upon waste gas flows or infrared sensor feedback control based on smoke observations of the flare is significantly more effective than manual control for controlling the assist gas to waste gas ratio within a known certainty. While previous investigators' data on destruction efficiency versus assist gas ratio obtained under controlled conditions would suggest that poor assist gas control might negatively impact destruction efficiencies, there are little to no data available on the impact of assist gas ratio control on destruction efficiency of operating flares. The effect of assist gas to waste gas ratio on flare combustion efficiency as well as destruction efficiency of operating flare systems requires further investigation, since over aerating or over steaming of the flare flame could significantly impact combustion efficiency.



EPA-600/2-83-052, Flare Efficiency Study, M. McDaniel, Engineering-Science, Inc., July, 1983

Figure 14. Effect of Assist Gas on Combustion Efficiency

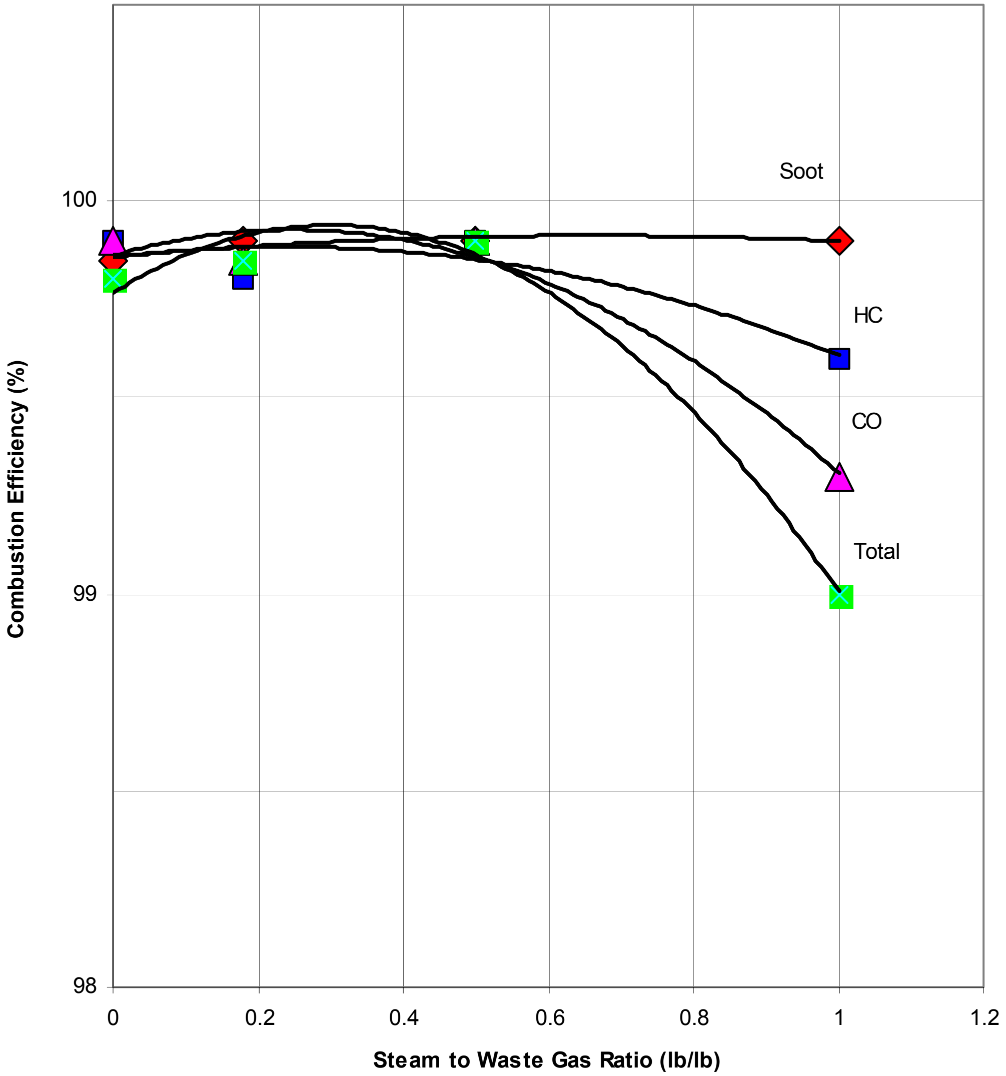


Figure 15. Influence on Steam on Global Efficiency[7]

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[7] US EPA/600/2-84-095, Evaluation of the Efficiency of Industrial Flares: Test Results, J. H. Pohl, R. Payne, and J. Lee, Energy and Environmental Research Corporation, May, 1984

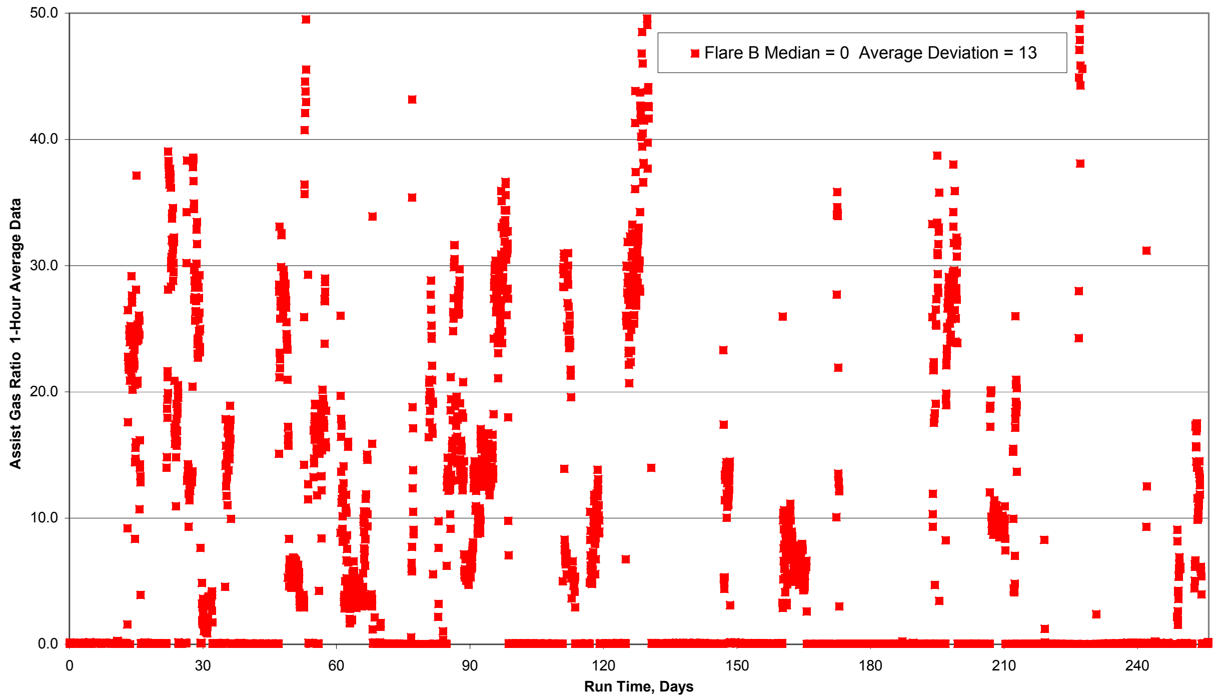

Figure 16. Manual Assist Gas Ratio Control Example

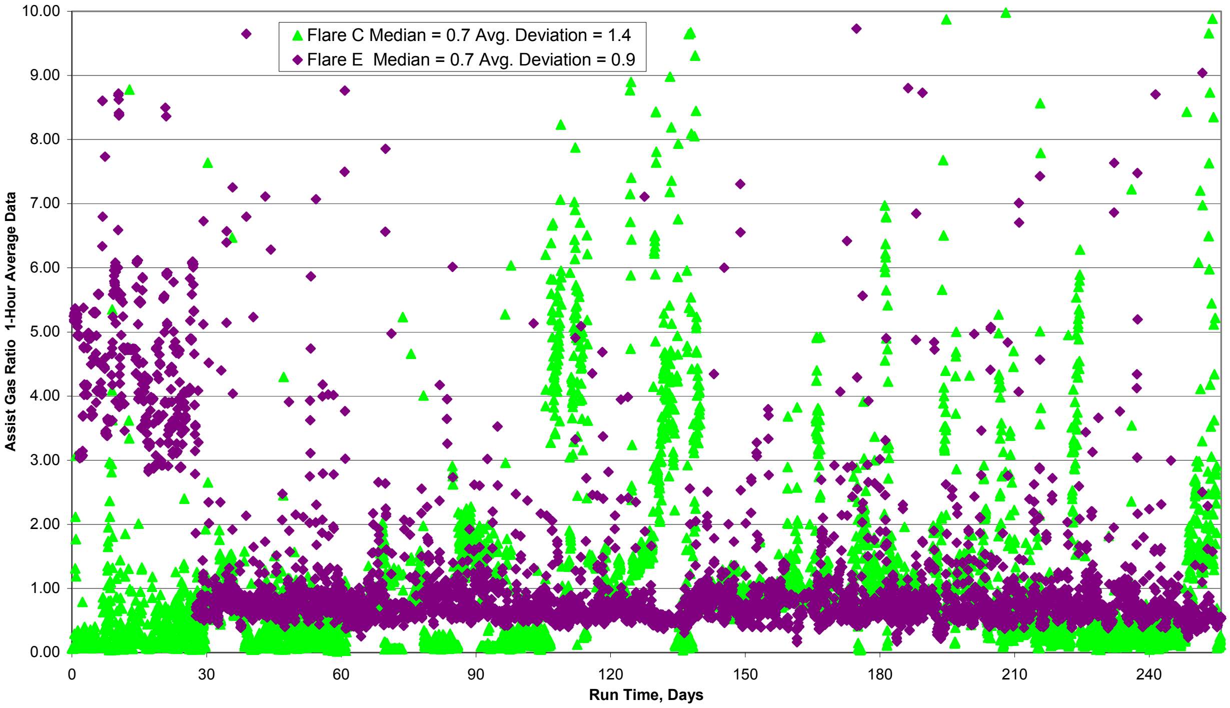

Figure 17. DCS Auto Set Point Assist Gas Ratio Control Example

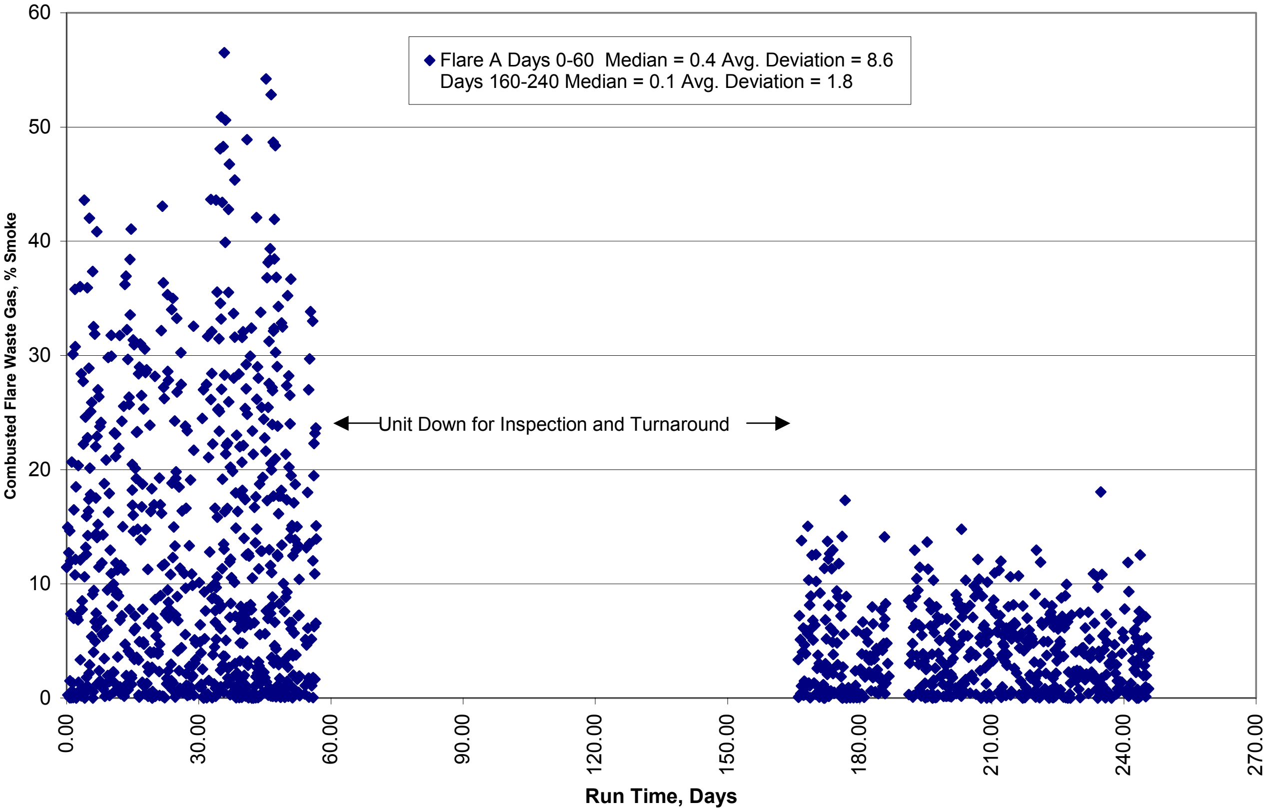

Figure 18. Infrared Sensor Feedback Assist Gas Ratio Control Example

6.0 CONCLUSIONS AND RECOMMENDATIONS

Due to the unique requirements of flare systems (low pressures, large pipe sizes, and 1000:1 turndown on flows) only multi-ranged pitot tubes, thermal mass meters, and ultrasonic time-of-flight meters are broadly applicable to the measurement of flows in flare systems.
Ultrasonic meters and Thermal mass meters can measure a greater range of gas velocities, and therefore are easier to apply to flare systems than pitot tubes.

For the flares examined, all flows were below velocities of 300 fps, the high end measurable by ultrasonic and thermal mass meters. However, many flares are designed for worst-case events that will exceed this measurement capability.

Flow measurement systems that combine multiple measurement techniques can measure this design worst case. Using multiple measurement techniques increases the costs associated with purchase, installation, calibration, and maintenance of dual meters. Design worst-case events are infrequent and rarely occur. Typically, design worst-case events are associated with emergency, unplanned shutdowns of a complete process unit or the shutdown of several process units serving a flare due to a power failure. Other process data usually exist which can be used to estimate the mass flow during such events. Thus, the additional expense of installing multiple measurement systems may not be warranted due to the relative infrequency of such events and the availability of process data that can be used to estimate mass flow during worst-case design events.

Ultrasonic time-of-flight meters have greater accuracy and precision for measuring flows in flare gas systems, because they are less sensitive to changes in gas composition and can correct for variable gas composition using only flow meter inputs.

Thermal mass meters and pitot tubes need significant correction for changing gas compositions. Currently, real time correction for gas composition changes has not been demonstrated in field applications with thermal mass meters or pitot tubes, although vendors claim such meters are available. Correcting with periodic composition data adds to the uncertainty of the flow measurement of thermal mass meters and pitot tubes used in flare applications.

Measurement of flows in flare systems can be made with an uncertainty in the range of ± 5-10 percent. However, obtaining this accuracy in flare systems with highly variable compositions or where the meter cannot be located in a section of pipe with a representative flow profile will be a challenge.

Measurement of the gas composition in flare systems on a continuous basis will be a challenge due to the number of compounds of interest and the dynamic range of concentrations, that may be present for the compounds of interest. To design and implement a continuous monitoring system capable of detecting the full range of compounds of interest across all concentrations of interest using conventional GCs will require considerable up-front data collection, and fairly sophisticated combinations of columns and detectors.

If aldehydes happen to be present at quantities that would impact achieving the data quality objectives, the GC system required to analyze for them will become even more complex.

Portable multichannel, micro GCs have proven extremely capable of detecting most compounds of interest in flare systems across an extremely large dynamic range (10^5). Application of such instruments in online applications will significantly reduce the complexity of the GC instrumentation needed to achieve the data quality objectives of this study. However, online versions of these instruments have yet to be demonstrated in flare applications.

While online GC systems can be designed to meet the data quality objectives of this study a high percentage of the time, the actual percent of time the data quality objectives can be met will be a strong function of the specific flare system, in particular the variability of the waste gas composition. There is insufficient data available to make a fact-based estimate on this percentage.

Application of US EPA Performance Specification 9 to online GCs in flare service is problematic given the potential number of compounds of interest and the dynamic range potentially encountered for these compounds. The linearity requirement will be extremely difficult to meet and the calibration procedures impractical.

Picking a few representative compounds with which to calibrate and using relative response factors for other compounds of interest seems a practical solution. Due to the large dynamic range, the linearity requirement of PS9 may need to be relaxed in favor of a multipoint calibration curve.

Under ideal conditions the mass flow in flare systems can be measured with an uncertainty in the ± 5-10% range. However, problematic applications with widely varying gas compositions and poor meter installation geometries will have difficulty meeting the ± 20% data quality objectives of this study. Obtaining measurement of flare emissions within an absolute uncertainty of ± 5,000 lb/hr appears doable for all but the very largest flare. However, this assessment is strongly influenced by the 98% destruction efficiency assumption used in this study.

Controlling the assist gas to waste gas ratio by measuring waste gas flow to the flare appears to be more effective at controlling this parameter at a desired value than manual control, but there was very little data available from which to make this conclusion. Additional data collection on the effectiveness of manual control would be warranted.

The authors assessment is that current flow and measurement technologies are capable of meeting the stated data quality objectives a high percentage of the time in most flare applications. However, the extremely limited amount of data on real world applications and the high degree of variability in flare applications make it impossible to assess what percentage of the time these data quality objectives can be met, and on what percent of flare systems they may be met. Both flow and gas composition measurement vendors have responded to the added interest in measurement of waste gas flow and composition. Significant recent developments have been made in both flow and composition measurement techniques. Demonstration of these advancements could significantly enhance the ability of sources to meet these data quality objectives in the near future.

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Appendices

Appendix A

Description of Flow Measurement Devices not Applicable to Flare Systems

A.1 Differential Pressure Techniques

Orifice Plates

Orifice Run with Differential Pressure Taps

Principle of Operation

Orifice plates operate on the principle that the pressure drop caused by constricting flow is proportional to the velocity. In a typical orifice plate application, fluid flows through a pipe and nears the constriction in the plate. The pressure begins to drop and the velocity increases as the fluid flows through the smaller opening. As the fluid exits, the velocity decreases and the pressure increases, but not back to the original pressure. Pressure loss occurs due to friction from the orifice plate and turbulence losses from the flow. Pressure taps located upstream and downstream of the plate measure the pressure differential and using orifice plate equations provide a flow rate. The pressure differential is proportional to the velocity squared.

Applicability to Flares

Although orifice plates are explicitly referenced in 40 CFR 60.18 Method 2D, they are not used in flare or waste gas service. They may be used to measure stack flows in situations in which pressure drop and the limitations in the flow meters range are not an issue. In flares, orifice plates have the potential to serve as an obstruction to the flow and often induce a large the plate pressure drop due to. Both of these situations are potential problems for flare lines due to safety considerations. Additionally, the turndown ratio of orifice plates is typically a 3:1 ratio but may be extended in some circumstances to 10:1. This range of turndown ratios is not suited for flare flow measurements that may fluctuate considerably.

Venturis:

Venturi Run with Differential Pressure Taps

Principle of Operation

Venturi flow tubes operate on the same principles as orifice plates, constricting the flow through a known opening and equating the pressure drop to a velocity. Instead of using a plate and an orifice, venturi flow tubes use a flow channel that has a tapered inlet and a flared outlet. The basic underlying principle remains the same: as the area decreases through the venturi opening, the pressure of the fluid decreases. As with the orifice plate, there is a head loss associated with the venturi models due to friction and turbulence. However, overall pressure loss is less than in orifice plate applications.

Applicability to Flares

Venturi meters are not mentioned outright in 40CFR60.18 Method 2D, but it is eluded to in being a pressure drop measuring device. While they may be used to measure stack gases in similar situations as orifice plates, Venturis are seldom used in flare applications. Reasons include obstruction concerns, large pressure drops, and low turndown ratios. The biggest driver being the pressure drop, as flare lines are generally pressured slightly above atmospheric and therefore cannot have a large pressure drop across the flow measurement device.

Rotameters

Variable Area Rotameters

Principle of Operation

The operation of a rotameter is quite simple, as fluid flows through the device a float is raised that indicates fluid velocity. The basic components consist of a tapered tube, a float that is the same size as the inner diameter of the smaller end of the tapered tube, and a scale that measures the flow rate in proportion with the float height.

Rotameters are often mounted vertically, with the fluid passing upward through the smaller end of the tapered tube to the larger opening. As the fluid enters the tube the float is raised, increasing the size of the area around which the fluid can flow. As the float raises and the area increases, the differential pressure around the float decreases. The float equilibrates when the force exerted by the fluid is equal to the weight of the float. For this reason, floats and the tubes are often designed specifically for the fluid involved in the process.

Applicability to Flares

Rotameters are referred to in 40CFR60.18 Method 2D, but have never been used in flare applications. Flares often have a tendency to have a wide range of flows while rotameters are ideal for small volumes of known flows. In most flare applications the sheer size needed to capably handle the potential flare flows rules out this technology.

Mechanical Techniques

Turbines

Principle of Operation

Turbine flow meters operate simply by counting the rotations of a bladed rotor. Generally the rotor is suspended into the fluid flow and the rotor is slightly smaller than the actual metering chamber. As fluid enters the chamber it rotates the blades of the rotor. Each rotor pass corresponds to a calibrated amount of fluid. Rotor passes are counted through the use of pulses generated from magnets in the coils or in the rotor blades themselves.

Applicability to Flares

Turbine meters are referred to in 40CFR60.18 Method 2A, but are not generally used to measure flare flows. In the past, some forms of insertion turbine meters have been used to measure flare flows, but recorded accuracies were very poor[1]. They are not considered a reliable, accurate option for measuring waste gas flare flow. In the slim chance of mechanical failure, the turbine itself could act as an obstruction in the flare line and therefore would pose a safety risk. Turbines generally also incur a moderate to high-pressure drop in the line once installed, which is unacceptable in flare line flows.

Pistons/Discs/Impellers

Principle of Operation

Piston, disk, and impeller meters operate similarly to turbines in that they equate the device's rotations or oscillations to a velocity. All three rely on the force of the fluid to operate the flow meter. Piston meters use the fluid flow to power an oscillating or reciprocating piston. The piston's oscillations or strokes are counted by a magnetic transmitter or, in less sophisticated models, a mechanical register. Disk meters work very similarly to turbines except a disk-like plate is used instead of bladed rotors. The disk may have fins to help catch the fluid used to power the plate. A magnetic transmitter counts the disk's rotations similarly to a turbine or by mechanical means. In an impeller meter, the fluid rotates an impeller that is linked to mechanical registers.

Applicability to Flares

Pistons, disks, and impellers are not explicitly mentioned in 40CFR60.18 Method 2A, but they are devices capable of measuring volume. However, pistons, disks, and impellers are not used in flare or waste gas services. For all three of these flow meters, the energy of the fluid is used to operate the device by rotating the piston, disk, or impeller. This is unattractive for measuring waste gas flows to flares since impedances in the gas flow can lead to process upsets or safety concerns. Using the force of the fluid to power the flow meter often leads to pressure loss, which is unacceptable in flares.

Dry and Wet Test Meters

Principle of Operation

Dry and Wet test meters operate similarly to other mechanical meters in that the fluid powers some form of driver that is counted by a magnetic transmitter or mechanical register. Dry test meters are used in many stack-sampling applications. They consist of chambers that are alternatively compressed and expanded by the gas. The compression/expansion action drives the device and also turns a mechanical register that measures gas usage. Wet test meters are also used in many stack-sampling applications. A typical wet test meter consists of a mutating disk that wobbles as water flows through the device. As the disk wobbles it rotates a spindle that is connected to the mechanical register. The velocity of the fluid is proportional to the rotations of the spindle.

Applicability to Flares

Dry and wet test meters are not mentioned explicitly in 40CFR60.18 Method 2A, but they are devices capable of measuring volume. Dry and wet test meters are used in many stack sampling applications but are not used in flare applications. As with all mechanical meters, dry and wet test meters have the possibility to act as obstructions in the pipeline, which could lead to safety issues. Additionally, these meters are not designed to handle the large flow rates or the wide ranges of flow rates associated with waste gas flows to flares.

Direct Mass Measurement Techniques

Coriolis Mass Meters

Principle of Operation

Coriolis meters operate on the principle of the Coriolis effect and Coriolis acceleration. The instrument achieves this by using one or two tubes that are anchored and equipped with a coil and a magnet. Current is sent through the coil, which causes the tubes to vibrate at a set frequency. At zero flow, magnetic sensors pick up the vibrations and compute to an even sine wave. When fluid is flowing through the pipe, the vibrations cause a force to act on the fluid due to Coriolis acceleration and an equal force is imparted on the tube. This force causes the tubes to slightly twist, which is measured by the magnetic sensor. The resulting sine wave becomes slightly out of phase, which is an indication of the mass flow. Additionally, the resonant frequency of the vibrations, or period of the sine wave, is an indication of the density of the fluid.

Applicability to Flares

In flare applications, Coriolis meters are not a viable option due to the size constraints and pressure loss through the instrument. As previously stated, flare lines can be sized up to 48". Coriolis meters typically are not available in sizes over 6", creating an obvious problem in measuring such large flows. Additionally, the cost of Coriolis meters increases dramatically the larger they are sized. The expected pressure loss through the device is also a concern, as Coriolis meters can have a head loss of 10psig. This will be an issue in many flare applications since flare header lines are usually pressurized slightly above atmospheric conditions.

Electronic Flow Meters

Magnetic Meters

Principle of Operation

The major principle of operation for magnetic flow meters is Faraday's Law. Essentially, coils located in the flow meter produce a magnetic field across electrodes. As the fluid, which must be slightly conductive, flows through the magnetic field, a voltage is created. Transmitters relay the voltage, which has been converted into a current or a frequency output, to a control system that infers a mass flow rate.

The underlying Faraday's equation is:

Equation 1

$$E = kBDV$$

Where:
k = Faraday Constant
E = Induced Voltage Generated by the Coils
B = Magnetic Field Strength
D = Distance Between Electrodes
V = Velocity of Conductive Process Fluid

Applicability to Flares

Magnetic Flow meters are not recommended for use in flare or waste gas streams. Magnetic flow meters must always be full of liquid while in service, consequently this is impossible to achieve in flare lines. Flare flows, aside from not being liquid, also are not inherently conductive, thus negating the instrument and technology.

Vortex Meters

Principle of Operation

Vortex flow meters incorporate a bluff body, which is an obstruction with a flat, broad front facing into the fluid stream. As the fluid flow impacts the bluff body, a vortex is formed on one side of the bluff body. On the side of the vortex formation, velocity increases and pressure decreases. As the vortex grows downstream it eventually detaches, the same pattern is then repeated on the opposite side of the bluff body. Sensors determine the flow velocity by measuring pressure oscillations or through temperature differences. Additionally, external sensors are also used to determine the flow rate by measuring the force impacted on the bluff body.

The flow velocity is proportional to the frequency of the vortex formations. The relationship used to calculate velocity is:

Equation 2

$$\mathrm{V} = \mathrm{f}\left(D / St\right)$$

Where:

V = Fluid velocity
f = vortex shedding frequency
D = width of bluff body
St = Strouhal Number (a dimensionless number normally approximated as 0.2 for vortex shedding purposes)

Applicability to Flares

Ideal conditions for Vortex meters are clean, high-speed flows that are relatively free of turbulence. Steam flow lines are one ideal service for Vortex use. Flare flows, on the other hand are not clean flows and can have very low flow conditions as well as very high flow conditions. Corrosive services and those with particulates present problems to vortex meters. Additionally, vortex meters do not have the required turndown ratio to handle the range of flows present in flares. Additional issues are the pressure drop and obstruction that the bluff body presents. Both are capable of presenting enough concern to make vortex meters unacceptable for measuring waste gas flow rates to flares. (Authors' note: A new generation of vortex meter, which does not use a bluff body, is in the final stages of development and may soon enter the market. Vendors have indicated that this new type of vortex meter may be applicable to flare applications. Insufficient data on this new meter was available at the time of this writing to include a meaningful evaluation of this type meter.)

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Appendix B

Technical Considerations for Design and Operation of Sample Systems for Flare Service

Real time representative compositions are necessary for three reasons. First factors are calculated based on composition to generate a pseudo specific heat capacity, thermal conductivity, and dynamic viscosity. These factors are used to adjust measured values from thermal mass flow meters or time-of-flight meters for improved accuracy and precision. Second, the compositions may be required to estimate HRVOC emissions using flow rate, composition, and destruction efficiency. Third, the composition may be used to determine heating value that factors into destruction efficiency. [1,2,3,4]

Flow Loops

Continuous flow loops to obtain representative waste gas samples at grade or easily accessible points are advisable, especially for waste gas streams where variable compositions are anticipated such as may be encountered where multiple unit operations are manifold into one flare header or where unit batch operations exist. The selection of a sample draw location that minimizes liquid or condensable entrainment as well as promotes collection of a time weighed sample is preferred. Avoid draw locations where there is a potential to sample stagnant gas or entrained liquids. An example of a suitable location is a high point gate valve on top of the final wet-gas knockout drum downstream of any baffles or weirs. Ideally, the sample loop configuration runs over to the measuring instrumentation where a low volume tee allows sample introduction and then the loop is completed by return into the flare header, preferably but not essentially downstream of where the sample is drawn off.

Pumps

Since most elevated flare systems operate very near atmospheric pressure, a pump is necessary to drive the gas through the loop. A small, portable instrument air-driven impeller pump with four vanes is one option successfully demonstrated. Since there is only very small pressure differential under most conditions, a low powered, moderate velocity pump works well for this application. The pump is positioned upstream of the filters and upstream of the sample introduction tee. This insures the necessary positive pressure required for sample introduction. The drive for the pump can be a regulated facility instrument air in the 30-100 psig range.

A high flow back pressure regulator with a regulating valve may be installed to drive the flow in many ground flare designs, however it is important to determine if there is sufficient pressure drop at the return line for an adequate and reliable measured flow.

Ejectors

For permanent installations, a steam or nitrogen ejector positioned downstream of the sample introduction may be a good alternative to pumps. Jet ejectors are gas or steam-driven venturi jet devices that use the energy in compressed gas or steam to create a vacuum that can entrain or mix another gas stream. Ejectors offer less maintenance and less potential for contaminants but may also prevent an easy return of the stream back into the waste gas header. Aspirators or ejectors using air for the motive fluid should never be sent back into the flare header. Ejected waste gas should not be vented to atmosphere because of flammability, toxicity, and environmental impact.

Tubing and Valves

Nominal bore one-quarter inch outside diameter (OD) 316 stainless steel tubing is typically used for loop runs of less than 100 feet. Three-eighths inch to one-half inch tubing can be used for longer loops if required. This addresses most safety concerns associated with flammable gas and toxic gas. Polyethylene, Teflon, Tygon or other plastic tubing is not suitable. Additionally, small diameter tubing minimizes volume, resulting in more representative real time sampling. Some locations may also require installation of a backflow check valve. If this is necessary, a one- third pounds per square inch gage (PSIG) cracking pressure valve is usually sufficient. Plugging with wet sulfur can cause check valves to become obstructed. Block valves at the sample draw and return is a good safety measure. Block valves and by-pass tubing around the instrumentation, the pump, the filters, and the rotameter are used for isolation to perform any necessary maintenance.

Sample Conditioning

Pre-analysis sample conditioning typically includes dual series in-line coalescing filters placed downstream of the pump and before the rotameter. A protective gas selective membrane filter on the instrument inlet and a sintered metal particulate filter on the instrument inlet help prevent any fouling or plugging of the analyzers.

Rates an Synchronizing Cycles

Rates should be set so that loop throughput is a minimum of 10 volumes of waste gas per sampling cycle. For most applications a rotameter is placed in line to gauge the flow settings. Typically 10 Standard Liters Per Minute (SLPM) is sufficient for most conditions. The flow meter also acts as a flow indicator to alert the operator to any plugging issues or liquid entrainment. A small in-line coalescing type filter is also advisable to trap sour water, sulfur or other condensable hydrocarbons. A low point drain can be used to periodically collect fractions of condensed liquids for laboratory analysis or to manually drain any collected material into a waste collection container for tracking volume or simply proper disposal.

Materials Compatibility, Conditioning, and Sample Integrity Assurance

All wetted materials should be compatible for wet corrosive service and rated for the design pressure of the flare, which is typically from 30 to 50 psig. The loop system should be run for several hours to condition any new tubing for hydrogen sulfide service and deactivate any surface effects associated with new tubing. 304 or 316 stainless steel works well for most applications. A sample loop recovery test may be performed to insure acceptable reactive or sorbable species losses. This can be done by injecting a flowing gas standard of a trace amount of a chemical of interest such as 1-butene at the point where the sample is drawn and then running samples over time and comparing those values with samples directly taken from the standard and injected into the instrument. Fraction recovery criteria as per EPA Method 18 are considered validation, $0.70 < R < 1.30$. Starting concentrations should be low enough such that small losses can be recognized; a suggested working standard of 100 ppmv to 1000 ppmv is an appropriate range for levels of concern. Because the temperatures of the waste gases at the knock out drums are generally near ambient temperatures, no heat tracing of the sampling lines is required under most conditions.

Grab Samples

Grab samples may be taken when the duration of testing is short, such as verification testing done to determine an exemption or the need for continuous compliance monitoring when it is well established by analysis or other means that the composition of the waste gas does not significantly change. Multiple samples may be collected over several hours to demonstrate performance or compliance. This would typically be used in a scenario where steady state conditions are expected by design or historical documentation. Generally, three types of grab samples are available: Tedlar Bags, evacuated stainless steel Department of Transportation

(DOT) sample cylinders, and evacuated Summa or silanized canisters for more reactive chemicals such as H_2S and 1,3-butadiene. Some considerations when using these containers are: exposure potential and safety considerations of a rupture using Tedlar bags with toxic concentrations of hydrogen sulfide, evacuation of dead space from the sampling ports, driving force needed to fill the containers, driving force needed to introduce the collected sample into the instrument for analysis, hold times, proximity and reliability of the laboratory, and reactivity. Since the waste gas streams will be very near atmospheric pressure a Vac-U-Tube or Vac-U-Chamber may be required to fill an evacuated bag. These devices act by applying a negative pressure around the outside of a Tedlar bag and help eliminate the risk of contamination associated with dirty pumps. [5]

Tedlar bags should be clean, evacuated, and analyzed within 48-hours. Canisters and cylinders should be clean and evacuated. Canisters and cylinders generally have longer hold time than bags, however it is good practice to have the samples analyzed as soon as reasonably possible. Use a chain of custody form to record sample position, start and stop times, beginning and ending pressures, and cylinder or canister identification.

Samples should be taken in duplicate during each sampling event as a minimum and analyzed in duplicate. Using a travel blank of a standard in the same collection media and treating it as a sample can obtain a degree of quality assurance. A travel blank containing air can identify any dirty or contaminated sample media. Generally follow evacuated container sampling procedures are listed in EPA Method 18 for details and variants.

Pressure Considerations

Many elevated flares are operated at or very near atmospheric pressure. Care should be taken to expect pressure fluctuations and increases up to design pressures due to unexpected releases. Many ground flares operate at some positive pressure, typically 2-15 psig. Additionally many ground flares are staged such that secondary and tertiary burners are activated when a set flow threshold is reached. This can cause pressure spikes and dips. In some designs of flares used solely for emergency service, it is important to recognize that under routine operating process conditions there may be rupture disks or water seals that prevent any waste gas flow while only supplemental fuel or inert sweep gas may be present.

The delivery pressure at the injector port to multi channel micro gas chromatograph (GC) instruments can range from 0 psig to 7.5 psig without affecting mass injected into the analyzer. An internal pressure transducer equalizes the pressure with ambient barometric pressure before the sample is introduced on the columns. The sample is drawn through a filtered and heated inlet system by a timed vacuum pump. By minimizing the tee volume using 0.125" OD tubing and a <4" long tube connector and with consideration of the filter housing volume, a 40-second sample pump time is sufficient to obtain representative samples. It is important to maintain a fixed pressure in sample loops that may be used with continuous emission monitoring systems or periodic emissions monitoring systems High flow backpressure regulation may be required. [6,7]

Performing an analysis to measure oxygen with the sample loop system open to the waste gas can serve as a good check for leak integrity in a nearly atmospheric system, since the waste gas should not have any oxygen and any oxygen detected would consequently come from a breach in the sampling system or a breach internal to the analyzer. Traditional static leak checking of the sample loop using pressurized nitrogen and soap bubble solution is recommended before startup.

Frequency and Cycle Considerations

Some pressure surge or resonance is common on many flare systems. It is not uncommon for waste gas streams to cycle rapidly from several inches of water vacuum to several inches of water pressure. Sources of pressure fluctuations can include: sizing and seal design of wet knock out vessel internals (sloshing); [3] mismatched manifold sources from different unit operations; lack of pulsation dampening from compressor or plunger pump operations; extent of, size, and position of dry knock out drums; and internals design with water and level interface considerations in the wet gas knock out drums. Frequencies of pressure cycles have been observed in the range of less than 2-second to 30-second periods. [8,9]

Condensate

Condensable water can be minimized in the sample loop by selecting an elevated point off the knock out vessel. Most permanent continuous installations will be heat traced to minimize condensate. An in-line vessel with inert demister material such as glass wool can also be used in extreme conditions.

The presence of ammonia gas in the waste gas can be problematic, as salting out can occur. This can result in plugging of fine capillary tubing in instrumentation, or fouling of pumps and rotameters. Larger-bore tubing, lower gas rates through the loop, back flushing with nitrogen, and heated instrument regeneration are remedies used with varying degrees of success in conditions favorable to salting out phenomena. Under extreme salting conditions, addition of an ammonia scrubbing device may be required. Ammonia and low-mass amines are usually checked prior to continuous sampling using an electrochemical cell type instrument or colorimetric indicator tube from a collected grab sample. [8]

Particulates

Particulates can be a plugging and fouling issue especially when tying into lines that have not been in service for years. Pulsed low-pressure nitrogen from a regulated cylinder can help free lose iron sulfide and other metals from the sampling loop. Sticky sulfur buildup can also be a cause of plugging. [8]

The loop sampling systems will not collect any significant condensable hydrocarbon since any slugs of liquid hydrocarbon are trapped at the unit boundary knockout drum or condensed in the wet knockout drum. Any condensate trapped in the coalescing filter drop out can be collected, weighed and analyzed by the refinery lab or third party lab if desired. [8,9]

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Appendix C

Analytical Techniques for Aldehydes

Formaldehyde and acetaldehyde are not expected to be present in reduced waste gas streams from refineries or olefins plants. They may be present in waste gas streams from a few process units that employ oxidation such as production of the solvents acetone or methyl ethyl ketone, intermediates such as ethylene oxide, propylene oxide, and phenol, or secondary processes such as urea-formaldehyde based resin productions.

Manual Testing Methods for Aldehydes

The authors experience with aldehydes in waste gas streams is limited. The authors have done screening on five refinery waste gas streams using a Kitagawa colorimetric detector tube #171SB and have not detected any formaldehyde or acetaldehyde in the 1-35 ppmv measurement range using this technique. These tubes use a pretreatment tube to neutralize interfering reactants. In each of these tests, none of the listed interfering compounds were expected to be present basis the process. These tests were performed on a composite three-liter Tedlar bag sample using a fixed volume plunger pump.

A modified EPA TO-11A method[1] was used to determine the presence of formaldehyde and acetaldehyde on the inlet and outlet to a catalytic oxidizer on the vent gas from a Phenol Acetone Unit. Modifications involved shorter duration sample times of 1, 10 and 20 minutes since concentrations from a process vent were unknown but were expected to be greater than ambient air concentrations.[2] With this distributed sampling technique employed, validity of data is better ensured in terms of matrix effects, retention volumes, and breakthrough volumes. Results achieved using this technique were +/- 30% for duplicate samples and replicate analyses. All results were in the low ppmv range.

Metered active sampling with before and after flow checks using primary flow calibrators was used as well as additional tubes in series to assure validity by demonstrating no breakthrough. Silica gel coated 2,4- dinitrophenylhydrazine (DNPH) tubes from SKC were used as well as an ozone scrubber tube to form stable hydrozone derivatives. Blank DNPH cartridges were analyzed but no spiked sample or round robin testing was performed as the testing was not for compliance demonstration. Analysis was performed by HPLC with UV detection. TO-11A quality assurance and quality control criteria limits were met for flow calibration, leak check, sampler blank, back up cartridges, trip blanks, field blanks, continuing calibration standard, and replicate injections.

Use of EPA Method TO-5[3] that employs midget impinges containing the DNPH derivitizing reagent is applicable but not recommended. We are in agreement with the EPA Method 11A summary statement which outlines the drawbacks to EPA TO-5 as labor intensive, uses acidic and hazardous reagents, lacks sensitivity, prone to interference's, and poor reproducibility at ambient concentration levels.

Use of OSHA Method 52 which employs a 2-(hydroxymethly) piperidine (2-HMP) derivitizing agent on solid XAD-2 resin may be applicable to flare applications. However, it is generally not recommended because it specifies use of a relatively uncommon nitrogen phosphorus detector (NPD). It is an industrial hygiene ambient air / workplace method. We have no experience with this method.

Other essentially similar specific ambient air method for aldehydes include EPA Method IP-6A (Formaldehyde and Other Aldehydes in Indoor Air), NIOSH Methods 2016 and 2532, and ASTM method D5197. These methods all use Silica gel treated with 2, 4-dinitrophenylhydrazine (DNPH).

There is a hand held electrochemical cell based aldehyde meter available, the "Formaldemeter 400" introduced by PPM Technology in 2000.[5] It is battery operated with a 10 second response time, and with a range of 0.05-10 ppmv with an option to extend the range to 100 ppmv. This instrument is unproven, and interferences in waste gas streams are unknown. The product is focused on applications for industrial hygiene in medical and industrial environments, but may be a potential technology for waste gas stream screening. It will non-selectively detect formaldehyde, acetaldehyde, propylaldehyde and glutaraldehyde.

Online Monitoring of Aldehydes

Formaldehyde and acetaldehyde are not expected to be present in reduced waste gas streams from refineries or olefins plants. They may be present in waste gas streams from a few process units that employ oxidation such as production of the solvents acetone or methyl ethyl ketone, intermediates such as ethylene oxide, propylene oxide, and phenol, or secondary processes such as urea-formaldehyde based resin productions.

Traditional chromatographic techniques have proven less than desirable for formaldehyde with direct injection. Poor recoveries and detector response are generally encountered. For practical use online, a separate stand-alone gas chromatograph with FID may be used in conjunction with a DB-5 column, heart cut valve or two if both formaldehyde and acetaldehyde are present and a methanizer for conversion to optimize FID response. This may be included in a single instrument with a parallel FID detector, however it may also add complexity such that cycle times are increased to an unacceptable level.

"Heart cutting" can be characterized as use of a mulitiport valve to directly remove selective components based on retention time after they have been resolved from the other components and before they reach the detector. The components are then either held in a sample loop, held on a trap or placed on another column for further resolution and speciation. In this scenario, formaldehyde and acetaldehyde can be sent to a "methanizer" FID which reduces the aldehydes to methane so they can be detected over a range comparable to methane.

A Siemens Maxum ll GC/FID was recently brought online in a mobile van used for EO process gas monitoring. This configuration uses a methanizer for formaldehyde and acetaldehyde. The Methanizer option enables the FID to detect low levels of aldehydes or other combustible oxygen containing chemicals. It is installed as the removable jet in a special FID detector assembly. The Methanizer is packed with a nickel catalyst powder. During analysis, the Methanizer is heated to 380°C with the FID detector body. When the column effluent mixes with the FID hydrogen supply and passes through the methanizer, aldehydes are converted to methane. Due to the chemical relationship between nickel and sulfur, the methanizer can be poisoned by large quantities of sulfur gas. Recovery, linearity and, response was determined to be adequate for levels of acetaldehyde normally encountered, however, for the smaller amounts of formaldehyde normally generated (<10ppmv), there were significant problems encountered in reproducibility of standards on the order of +/- 30% volume. Since this application does not involve emissions, no comparative PS9 testing data is available.[6]

After speaking with at least two vendors who are promoting their online HRVOC analyzers for waste gas streams, it appears that a requirement for analysis of aldehydes or ketones is not a primary consideration in the HRVOC first tier design, but rather is viewed as a potential secondary ancillary add-on.

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Appendix D

Gas Chromatography Detectors

D.1 Thermal Conductivity Detector

Because it detects all molecules, the Thermal Conductivity Detector is commonly used for fixed gas analysis (O_2, N_2, CO, CO_2, H_2S, CH_4, etc.) where the target analytes do not respond well on other, more sensitive detectors. The TCD can detect concentrations from 100 ppmv up to 100 % volume on a flat baseline with sharp peaks. Where the peak is broad or the baseline is not flat, detection limits of 300ppmv are more realistic.

The TCD consists of four tungsten-rhenium filaments in a Wheatstone bridge configuration. Electric current flows through the filaments, causing them to heat up. Carrier gas (usually helium, which has very high thermal conductivity) flows across the filaments, removing heat at a constant rate. Two of the filaments are exposed only to carrier gas (reference), and two are exposed to the carrier/sample flow. When a sample molecule with lower thermal conductivity than the carrier gas exits the column and flows across the two sample filaments, the temperature of the filaments increases. This temperature increase unbalances the Wheatstone bridge and generates a peak as sample molecules transit through the detector. Sensitivity may be adjusted by the filament temperature, the detector temperature, and the signal amplification.

The TCD is widely employed in many standard methods of analysis for gas streams, and is widely available on portable and permanent gas chromatographs. [1]

Helium Ionization detectors

The helium ionization detector or HID is a universal type detector that responds to all small molecules except neon. It is not widely employed on continuous or portable analyzers. It is especially useful for volatile inorganics like NOx, carbon monoxide and ammonia. The HID needs no hydrogen or air and requires only helium and makeup gas. Sensitivity is in the low ppmv range. The HID incorporates electrodes, which support a low current arc through the helium make-up gas flow. This elevates the helium to a metastable state. When the metastable helium molecules collide with sample molecules as they elute from the column, the sample molecules are ionized and attracted to a collector electrode, amplified, and output to the data system. A useful application of HID in analysis of waste gas streams is in conjunction with a TCD for determination of ammonia. The detector becomes saturated in the low % ranges. [1]

Photoionization Detectors

The Photoionization detector or PID is a non-destructive detector used to quantify gases that have excitation energy above a constant voltage supplied by an ionizing UV lamp. The PID responds to molecules with carbon double bonds and is principally used for unsaturated olefinic or aromatic compounds. The response is poor for saturated hydrocarbons, especially lighter alkanes that would be commonly found in waste gas streams. This detector has applicability as an ancillary detector for specific determination of HRVOCs with customized chromatographic configurations. There are maintenance and quality assurance issues related to the PID lamp. The lamp has a limited life of typically two months, the lamp sensitivity decays non-uniformly over time, and the window becomes fogged over time. [1]

Flame Ionization Detectors

Flame ionization detectors are commonly used in Method 18 and for many hydrocarbon applications. The FID has good linear response over low ppmv to high % ranges and can act as a carbon counter for unknowns. The FID responds to molecules with a C-H bond. One accessory that can be used with an FID is a “methanizer”. The methanizer reduces CO and CO2 to methane using a special catalyst jet. The FID has traditional applicability for waste gas streams, but is unable to detect inert gases, hydrogen, oxygen, carbon monoxide, and carbon dioxide. The FID is widely employed in many standard methods of analysis for gas streams, and is widely available on portable and permanent gas chromatographs. [1]

Catalytic Combustion Detectors

The Catalytic Combustion Detector or CCD

The CCD detector consists of a coil of platinum wire embedded in a catalytic ceramic bead. A small electric current flows through the platinum coil, heating the ceramic bead to around 500^{o}C. The CCD is maintained in an oxidative environment by using air carrier gas. When a hydrogen or hydrocarbon molecule impacts the hot bead, it combusts on the surface and raises the temperature and resistance of the platinum wire. This resistance change causes the detector output signal to change, thus producing a peak. The CCD is selective as an FID but has about a 50x less sensitive lower detection limit. The CCD is operated on air alone as a required gas source. The CCD is generally not applicable to HRVOCs in waste gas streams and is not widely employed. [1]

Thermal ionization Detector

TID Thermionic Ionization Detector – An electrically heated thermionic bead causes a catalytic surface reaction with nitro functional groups and the resulting ions are attracted to a collector electrode and amplified. Since the TID is extremely selective, having little or no response to most aromatic and aliphatic hydrocarbons, it has low applicability for waste gas flare measurements. [2]

Flame Photometric, NP, and Electron Capture Detectors

Flame photometric, nitrogen phosphorous (NP), and electron capture detectors are chemical class specific detectors and not directly applicable to waste gas measurements. The electron capture detector offers extreme sensitivity for electronegative compounds (parts per trillion for SF6) and is a good detector of tracer testing when performed with sulfur hexafluoride.

References

1. Loos, K.R., Shell Global Solutions US. Petroleum Environmental Research Forum Presentation on "Refinery Flaring Revisited or *my old Flame"* in Paris, France, June 3-4, 2003.

2. SRI Instruments, "GC Detector Overview" http://www.srigc.com/index.htm 08/06/03.