TECHNICALREPORT

June 1, 2014

Trace Air Contaminants Study of Combustion Sources

Prepared For: *Petroleum Technology Alliance Canada (PTAC)*
Suite 400, Chevron Plaza, 500-5 Ave SW
Calgary, AB, T2P 3L5

Prepared by: *Clearstone Engineering Ltd.*
700, 900-6th Avenue S.W.
Calgary, AB, T2P 3K2

DISCLAIMER

EXECUTIVE SUMMARY

Alberta Environment is currently re-evaluating the ambient air quality objectives (AAQOs) for the province. This initiative includes reviewing the values of currently targeted substance and potentially adding additional substances to the list. A Stakeholder Advisory Committee (SAC) has been established to participate in this review and evaluation process. The first two substances to be reviewed are Acrolein and Arsenic.

The purpose of this study is to provide upstream oil and natural gas (UOG) industry with facility-related data that can facilitate defensible science-based decisions in this matter, and allow potential risks to the UOG industry to be assessed.

Accordingly, a series of source emission tests were conducted at facilities in various operational regions of Alberta covering a range of different UOG industry subsectors. The emission tests were conducted on a wide range of source types. Operational regions included the south east, central, north east and north. Industry subsectors included sweet gas, sour gas, conventional oil, cold heavy oil and thermal heavy oil production facilities. In total, thirteen combustion source samples were collected from six different combustion source types located at seven different facilities across Alberta.

Source sampling was completed using two types of sampling trains. Organic substances and inert gases were sampled using a canister sampling train and inorganics (metals) were sampled using a two stage impinger train. Canisters contents and impinger solutions were analyzed by Alberta Innovates. The sample line for the the impinger train was not rinsed at the end of the measurements; however, sample residue in the sample line was deemed to be minimal. The organics protocol quantified the target substance Acrolein, and approximately 187 other secondary substances. The specific organic compounds targeted by the analytical method are listed in Section 11 (Appendix D). Compounds targeted by the applied analytical method but not detected are not specifically highlighted in this report, but include 1,3-Butadiene (it was not detected in any of the samples). If a target compound was not detected in means that its concentration was below the lower detection limit of the applied analytical method (e.g., <10 $\mu g/m^3$ for C_{5+} compounds).

The inorganics protocol quantified Arsenic, and approximately 35 other substances; however, the protocol is applicable to non-volatile inorganic substances and while it is able to detect some volatile inorganic substances such as mercury, those results will understate actual values of volatile inorganic substances due to inefficiencies of the

sampling system in capturing the gaseous phase of inorganic substances. Accordingly, the results for mercury should be considered qualitative screening level results. Mercury was detected in most of the samples collected so this simply confirms it is generally present in detectable levels. For non-volatile inorganic compounds the results are accurate and quantitative.

The fuel gas associated with each combustion source was sampled for organic substances and inert gases using the same organics analytical protocol.

A rigorous material balance, considering all fuel and flue gas substances identified, was conducted for each combustion source to determine the actual air to fuel ratio, combustion efficiency and flue gas to fuel gas ratio. Based on the results of this material balance, emission factors for all compounds expressed in terms of mass emission per unit of energy input were determined.

Acrolein was observed in only one combustion source emission test and the determined emission factor was 9.09E-5 kg/GJ. This value is well above the detection limit of 7.91E-10 kg/GJ. The emission was associated with a compressor engine that was operating with a combustion efficiency of 95.6%, well below the average efficiency of 99.5% for all of the combustion devices samples. The emission factor determined for Acrolein was within the published range for 4-cycle Rich Burn, Natural Gas Internal Combustion Engines (1.13E-3 to 2.65 E-6 kg/GJ).

Based on these tests, it is appears that acrolein formation and emission from combustion sources may be associated with poor combustion efficiency and a follow up sampling program is recommended to potentially confirm this hypothesis. For combustion sources operating within the design specifications of good to excellent combustion efficiency, acrolein formation and emission does not appear to be an issue.

Arsenic was observed in all combustion source emission tests and the average emission factor was determined to be 4.16E-06 kg/GJ, approximately two orders of magnitude above the lower detection limit of 3.24E-08 kg/GJ. Based on evaluations of combustion air and fuel gas as the potential source of arsenic in the flue gases, it was concluded that fuel gas was the most likely source. Calculated theoretical concentrations of arsenic in the fuel gas were within the range noted by others for arsenic in natural gas.

A sampling program to quantify arsenic and potentially other metal substances in raw natural gas, process fuel gas and sales gas in various Canadian regions is recommended.

In addition to acrolein and arsenic, numerous other organic and inorganic substances were identified and quantified. Each source was characterized by its own suite of substances with some substances being associated with several sources. Emission factors were determined for all substances for each source sampled. These results serve as a database for future assessments of trace contaminant emissions.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ACRYNOMS

AAQO	Ambient air quality objectives
AAAQO	Alberta ambient air quality objectives
AFR	Air to fuel ratio (Volume basis)
AI	Alberta Innovates Laboratory
As	Arsenic
C1C4	C_1 to C_4 hydrocarbon identification and quantification
CAPP	Canadian Association of Petroleum Producers
CE	Combustion efficiency
CEL	Clearstone Engineering Ltd.
CEMS	Continuous Emission Monitoring System
CH4	Methane
GC	Gas chromatograph
GC/MS	Gas chromatograph/mass spectrometer
GJ	Giga Joule
kg	kilogram
L	Litre
LDL	Lower detection limit
mg	milligram
NA	Not applicable
ppm	part per million
ppb	part per billion
PTAC	Petroleum Technology Alliance Canada
RSC	Reduced sulphur compounds
SAC	Stakeholder Advisory Committee
THC	Total hydrocarbon
TOC	Total organic carbon
ug	microgram
UOG	Upstream oil and gas
VOC	Volatile organic compound

ACKNOWLEDGEMENTS

The development of this report has been sponsored by CAPP and conducted through PTAC. The support and direction provided by each of the participating companies and agencies involved is gratefully acknowledged. Special thanks are given to the following individuals and companies who participated on the project steering committee and/or provided review comments.

1 INTRODUCTION

Provincial ambient air quality objectives (AAQOs) are currently being re-evaluated by Alberta Environment. This initiative includes reviewing the values of currently targeted substance and potentially adding additional substances to the list. A Stakeholder Advisory Committee (SAC) has been established to participate in this review and evaluation process and the first two substances to be reviewed are Acrolein and Arsenic.

The upstream oil and natural gas (UOG) industry strives to prepare objective input regarding the technical achievability of a proposed/lowered standard for both substances and the purpose of this study is to establish relevant UOG facility data that can facilitate defensible science-based decisions in this matter, and allow potential risks to the UOG industry to be assessed.

Acrolein may be formed from the breakdown of certain pollutants found in outdoor air, from the burning of organic matter including tobacco, or from the burning of fuels such as gasoline or oil (http://www.epa.gov/ttn/atw/hlthef/acrolein.html).

Inorganic arsenic is found throughout the environment; it is released into the air by volcanoes, the weathering of arsenic-containing minerals and ores, and by commercial or industrial processes (http://www.epa.gov/ttn/atw/hlthef/arsenic.html). Mining, metal smelting and burning of fossil fuels are the major industrial processes that contribute to arsenic contamination of air, water and soil.

The objective of the proposed study was to conduct a screening-level assessment of acrolein and arsenic emissions by the upstream oil and gas industry for use by stakeholders in discussions with Alberta Environment regarding new or revised AAQOs.

2 SCOPE OF WORK

The proposed work consisted of a screening-level measurement program designed to determine emission factors for a range of fossil-fuel/waste-gas combustion sources and a range of waste-gas and fossil-fuel qualities and geological sources in the UOG industry. The types of combustion sources considered included natural gas-fuelled reciprocating compressor engines, natural gas-fueled turbine engines, small and large process heaters and boilers, tail gas incinerators and flares. For practical purposes, flare testing needed to be restricted to enclosed flares where safe access to the post-flame combustion products was achievable. The range of fuel-gas and waste-gas types included raw field gas at conventional and heavy oil production facilities; produced gas used as fuel, and processed natural gas from sweet and sour gas fields.

An allowance was made for up to 16 sources to be sampled as indicated in the Proposed Sample column in **Table 1**. Final results presented are indicated in the Actual Sample column. The proposed sample included the noted ranges of fossil fuel/waste gas combustion sources, waste-gas combustion sources, waste gas and fossil fuel qualities and geological sources in upstream oil and gas industry. However, due to the safety issues and weather constraint, some of the sources were eliminated.

Table 1: Proposed and actual sources surveyed for trace air contaminants.

	Industry Subsector	**Source**	**Proposed Sample**	**Actual Sample**
Location 1	Sweet Gas Gathering System (Plains Region)	Reciprocating Engine	X	√
		Process Heater	X	√
Location 2	Sweet Gas Gathering System (Foothills Region)	Reciprocating Engine	X	√
		Process Heater	X	√
Location 3	Sweet Gas Processing Plant	Reciprocating Engine	X	√
		Process Heater	X	√
Location 4	Thermal Heavy Oil Production	Treaters	X	√
		Steam Generators	X	√
Location 5	Cold Heavy Oil Production	Tank Heaters	X	√
		Screw Pump Engine	X	√
Location 6	Sour Processing Plant	Tail Gas Incinerator	X	X
		Turbine Engine	X	X
		Steam Boiler	X	√
Location 7	Conventional Oil Production	Treater	X	√
		Reciprocating Engine	X	√
		Enclosed Flare	X	X

3 STUDY METHODOLOGY

Sampling, analyzing and assessing these sources required the application of appropriate sampling systems and the use of appropriate tools to analyze the samples. The results generated were used to develop the applicable emission factors.

3.1 SAMPLING SYSTEMS

Two sampling methods were required to achieve the objectives of the study. For arsenic and other metals, an impinger sampling train was employed with an acid solution added to the first impinger. For acrolein, other organic compounds and inert gases, an evacuated canister sampling train was employed. In both cases, the field collected samples were returned to the laboratory for detailed analyses. The two methods are briefly described below and detailed sampling protocols are presented in Appendix C

3.1.1 IMPINGER METALS SAMPLING TRAIN

The impinger sampling train is shown in **Figure 1**. It includes a sample probe for insertion into the source, followed by two impingers, immersed in an ice bath. Each impinger contained a 1.0 %vol nitric acid solution. After the metals are removed in the acid solution, the gas flows through a meter and vacuum pump, and is discharged to the atmosphere. The initial and final volumes of the nitric acid solution are measured in order to assess the moisture content of the sampled gas stream. Gas temperature and pressure are measured at the meter location to provide for volume corrections to standard conditions.

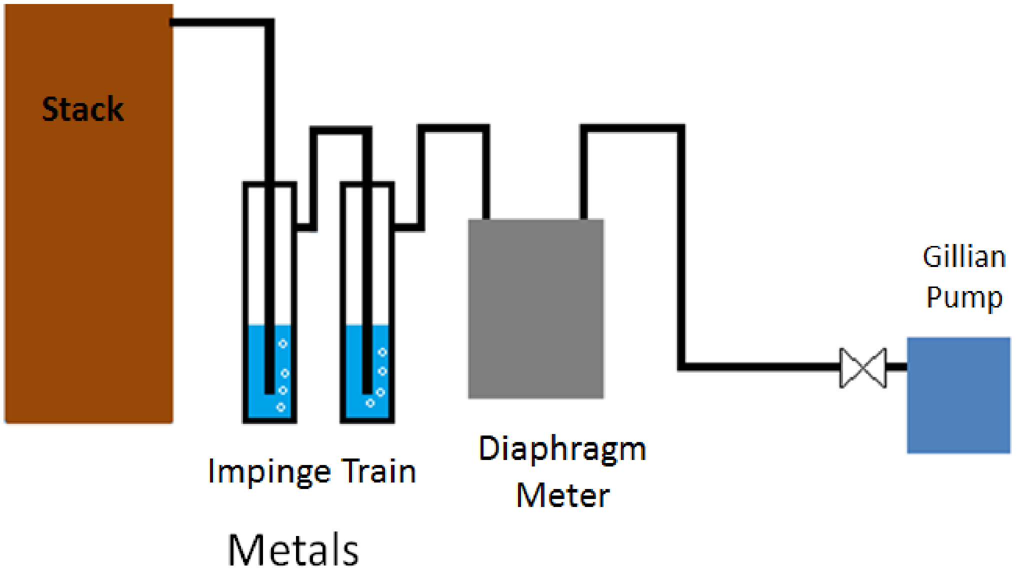

Figure 1. Schematic diagram of impinger sampling train used for metals.

3.1.2 ORGANICS SAMPLING TRAIN

The canister organics sampling train is shown in **Figure 2**. It includes a probe, for insertion into the source and an evacuated canister. The whole canister is returned to the laboratory for analytical work based upon the prescribed protocol. The sample train is based upon NCASI Method IM/CAN/WP-99.02 but does not include the impinger gas conditioning components.

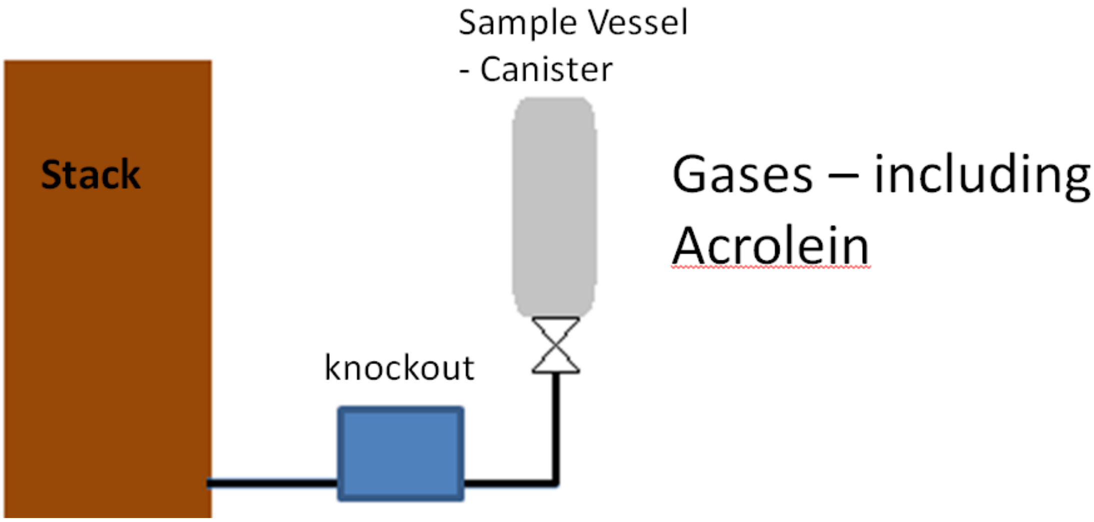

Figure 2. Schematic diagram of canister sampling train used for organics.

3.1.3 FIELD SAMPLE PROTOCOL

In general, fuel gas and flue gas were sampled at each of the selected sources. Fuel gas was sampled for gaseous organic compounds and inert gases using the organics sampling train and flue gas was sampled for organics and metals using both sampling trains.

For each site visited method blanks were also collected for quality control purposes.

- Travel Blanks remained with the project cooler from the laboratory to the sampling site and back to the laboratory without being opened. Sample train travel blanks were included for all applications of the metals sampling train.
- Method Blanks were used for each source. The method blank was handled similar to the actual sample with the same reagents being added, with contact to the same type of vessels and with the same handling procedure. The method blank was used to address potential contamination associated with every step in the procedure not related to the actual sample collected. The method blank analytical results were used to correct sample analytical results.

Actual sample collection at each location and relevant field information pertaining to the source, sampling conditions and or field issues encountered are summarized in **Table 47** of Appendix B.

3.2 ANALYTICAL PROTOCOLS

Analytical work completed by Alberta Innovates followed prescribed protocols as outlined below.

3.2.1 METALS PROTOCOL

The metals analytical work included the quantification of arsenic and numerous other metals. The analytical procedure applied a full metals scan by ICP-MS quantification. The LDL specified for Arsenic was 0.1 µg/L (of impinger solution) and for the remaining compounds the LDL values were between 0.1 µg/L to 2.0 mg/L. **Table 2** summarized the inorganic components LDL values in the impinger solution and the LDL when converted to an emission factor. The later varies by source specifics and the nominal values shown are based on average volumes of gas sampled.

Table 2: Summary of the inorganic components LDL values.

Component	LDL	LDL for Emission Factor
	µg/L	kg/GJ (Fuel)
Aluminum	3	2.10E-06
Antimony	0.05	3.50E-08
Arsenic	0.1	6.99E-08
Barium	0.1	6.99E-08
Beryllium	0.1	6.99E-08
Bismuth	0.1	6.99E-08
Boron	0.8	5.59E-07
Cadmium	0.01	6.99E-09
Calcium	100	6.99E-05
Chlorine	300	2.10E-04
Chromium	0.3	2.10E-07
Cobalt	0.1	6.99E-08
Copper	0.1	6.99E-08
Iron	4	2.80E-06
Lead	0.1	6.99E-08
Lithium	0.2	1.40E-07
Magnesium	10	6.99E-06

Table 2: Summary of the inorganic components LDL values.		
Component	**LDL**	**LDL for Emission Factor**
	µg/L	**kg/GJ (Fuel)**
Manganese	0.1	6.99E-08
Mercury	0.05	3.50E-08
Molybdenum	0.1	6.99E-08
Nickel	0.1	6.99E-08
Phosphorus	5	3.50E-06
Potassium	20	1.40E-05
Selenium	0.3	2.10E-07
Silicon	0.8	5.59E-07
Silver	0.01	6.99E-09
Sodium	20	1.40E-05
Strontium	0.1	6.99E-08
Sulphur	2000	1.40E-03
Thallium	0.1	6.99E-08
Thorium	0.1	6.99E-08
Tin	0.1	6.99E-08
Titanium	0.1	6.99E-08
Uranium	0.1	6.99E-08
Vanadium	0.1	6.99E-08
Zinc	0.2	1.40E-07

Notes: The LDL Emission Factors were calculated using the following conditions: Impinger solution : 21.62 ± 0.81 ml, STP Gas volume: 0.018 ± 0.0011m^3, Estimated Dry Flue Gas Flow rate: 21.84 ± 13.84 m^3/h, Dry Fuel Gas: 1.00 m^3/h, and High Heating Value: 37.51 ± 1.85 GJ/ (m^{3}fuel).

3.2.2 ORGANICS PROTOCOL

The organic compound analytical work included the quantification of acrolein and numerous other organic compounds. The organic components LDL are shown in, **Table 9** of Appendix A. The analytical procedure used RSC/VOC/C1C4/Inert scans.

- RSC scans identified and quantifies reduced sulphur compounds by GC
- VOC scans identified volatile organic compounds with by GC/MS
- C1C4 scans identified and quantified C1 to C4 hydrocarbons by GS/MS
- Inerts scan identified and quantified all inert gases by GC

3.2.3 RAW ANALYTICAL DATA PROCESSING

All fuel gas results reported by AI were corrected for potential air in leakage by subtracting out the appropriate quantities of nitrogen and oxygen in order to make the oxygen content of the final analytical result equal to zero. Flue gas samples were reviewed and where independent flue gas oxygen content was available, appropriate corrections were applied.

Table 3 compares the typical fuel gas composition provided by the facility operators at each location and the fuel gases results reported by AI (after appropriate corrections were applied) based on samples collected at the device indicated. The gases analysis reported by AI after appropriate corrections agreed reasonably well with the typical analysis provided by operators at different sources. However, differences were noted between typical results and the AI results and between AI results for more than one fuel gas sample taken at the same facility.

The methane content in the Location 7, a conventional oil production site was determined to be 66 mole percent considerably lower than all other locations. Location 6 also exhibited a relatively low methane concentration. For the remaining locations methane concentrations were greater than 90 mole percent.

Table 3: Comparison typical fuel gas analysis and extended gases analysis for samples at specific device locations.

	Sources	Methane mole%	Ethane mole%	Propane mole%	Butane mole%	Carbon Dioxide mole%	Nitrogen mole%	Total[3] mole%
Location 1	Typical Gas analysis[1]	96.23	0.26	0.03	0.00	0.11	3.25	99.88
	Reciprocating Engine[2]	95.29	0.27	0.03	0.00	0.23	4.18	100.00
	Reboiler[2]	95.39	0.27	0.03	0.00	0.24	4.07	100.00
Location 2	Typical Gas analysis[1]	93.76	0.45	0.20	0.12	1.11	3.91	99.55
	Reciprocating Engine[2]	93.78	0.78	0.27	0.09	0.94	3.82	99.67
	Reboiler[2]	93.76	0.74	0.21	0.06	1.20	3.79	99.75
Location 3	Typical Gas analysis[1]	93.43	0.34	0.05	0.01	0.08	5.87	99.78
	Reciprocating Engine[2]	92.38	0.44	0.06	0.01	0.08	7.02	99.98
	Reboiler[2]	93.71	0.44	0.06	0.01	0.06	5.70	99.98
Location 4	Typical Gas analysis for Steam Generator[1]	92.98	1.81	0.66	0.31	1.77	1.06	98.59
	Steam Generator[2]	93.03	3.20	0.99	0.31	1.71	0.15	99.38
	Typical Gas analysis for Treater[1]	94.86	2.22	0.68	0.14	0.97	0.90	99.77
	Treater[2]	93.46	3.72	1.14	0.21	0.85	0.30	99.68
Location 5	Typical Gas analysis[1]	95.01	0.60	0.20	0.03	3.59	0.35	99.78
	Tank Heater[2]	94.16	0.72	0.00	0.04	4.60	0.21	99.73
	Pump Engine[2]	95.25	0.72	0.24	0.04	3.20	0.28	99.73
Location 6	Typical Gas analysis[1]	87.82	5.43	2.12	0.60	0.01	3.41	99.39
	Steam Boiler[2]	88.44	5.88	2.15	0.53	0.00	2.30	99.30
Location 7	Typical Gas analysis[1]	66.25	7.89	4.50	1.53	13.83	3.03	97.03
	Treater[2]	68.71	9.16	0.00	1.71	16.21	0.81	96.61
	Reciprocating Engine[2]	66.28	8.84	4.90	1.65	15.63	0.19	97.50
Note:	[1] Typical Gas analysis provided by operator and included: argon, hydrogen, helium, nitrogen, oxygen, carbon dioxide, hydrogen sulphide, methane, ethane, propane, butane, iso-butane, pentane, iso-pentane, hexane, heptane, octane, nonane. [2] Extended gas analysis obtained by sampling fuel at location of device indicated. [3] The sum of top 6 components in fuel.							

3.3 EMISSION FACTOR DEVELOPMENT

For all simple combustion processes, a material balance methodology was applied to develop emission factors based on energy input. This methodology was applied to all sources except the tail gas incinerator. Through the material balance methodology, the flue gas emission was explicitly linked to the fuel gas input and emission factors were determined for all organic and inorganic contaminants. These were expressed in terms of mass emission per unit of higher heating value energy input.

The tail gas incinerator is a complex combustion process as it includes additional input streams other than fuel gas and combustion air. Tail gas incinerator input streams include one or more waste gas streams and, in some cases, process generated waste gas or flash gas that is used as fuel in the incinerator. The tail gas contains combustible compounds as well as oxygen, nitrogen and carbon dioxide. A material balance would require relative or actual flow rates of all input streams and stream analyses. Although preparations were made to meet these requirements, a tail gas incinerator was not sampled and no calculations were performed for tail gas incinerator.

3.3.1 SIMPLE COMBUSTION PROCESS MATERIAL BALANCE

A simple combustion process was defined as one where the only input streams were fuel gas and combustion air and the only output was a single flue gas stream. For this process a material balance calculation was completed for all organic compounds identified in the fuel gas and the flue gas. Typically the fuel gas contained 25 to 50 compounds, some of which were present in the flue gas. Typically the flue gas contained 30 to 60 compounds, some of which were not present in the fuel gas and assumed to be manufactured in the combustion process. Air was assumed to be pure oxygen and nitrogen with no organic or metal compound contamination.

The EXCEL spreadsheet based material balance program balanced flue gas oxygen content with measured oxygen content. The material balance program allowed for partial destruction of all fuel gas compounds and the creation of new compounds measured in the flue gas. The program was manually managed though two or more iterations to produce the final material balance.

3.3.1.1 EMISSION FACTOR RESULTS

Once the balance was established, organic compound emission factors were automatically determined. Subsequently, metal substance emissions factors were determined using the material balance established from the organics data material balance.

3.3.1.2 OTHER RESULTS

Other relevant information including flue gas THC and combustion efficiency were determined by the material balance program and presented for each source assessed.

3.3.2 COMPLEX COMBUSTION PROCESS

As noted, the tail gas incinerator was considered to be a complex combustion process.

To facilitate an assessment of this type of emission source, the following supplemental field data collection is required.

- CEMS data
- Tail Gas flow and composition data from a recent sulphur plant test
- Incinerator discharge temperature
- Supplemental waste and flash gas fuel input compositions

As noted in section 2, the tail gas incinerator was not sampled due to safety issues and proposed calculations related to this source were not completed.

4 STUDY RESULTS

Although the study was focused on acrolein and arsenic, the methodology resulted in the identification and quantification of numerous other organic and metallic substances in addition to acrolein and arsenic. Acrolein and arsenic results are analyzed in some detail while the results for the other substances are simply noted as screening level results for further consideration.

4.1 ACROLEIN AND ARSENIC

Table 4 provides a summary the combustion efficiency and emission factors for acrolein and arsenic for all sources sampled. Emission factors determined for all other components observed in the flue gases for each device are presented individually for each source in the detailed results tables in Appendix A.

Of the 13 sources evaluated, only the compressor at Location 1, with a combustion efficiency of 95.6 %, exhibited acrolein in the flue gas. The determined acrolein emission factor for this source was 9.09E-5 kg/GJ. The average combustion efficiency of the other 12 sources was greater than 99.0% and none exhibited acrolein in the flue gas. The lower detection limit of acrolein, in terms of an emission factor, was determined to be 7.91E-10 kg/GJ. This corresponds to an analytical LDL of 0.2 ppbv in the flue gas. The low LDL of acrolein suggests that the result for the compressor at Location 1 was real and not just measurement noise. The potential relationship between the emission of acrolein and combustion efficiency of the compressor engine is noted as a possible reason for acrolein formation in the combustion process.

Arsenic was detected in all sources and the average emission factor for all sources tested was 4.16E-06 kg/GJ. The average LDL of arsenic, expressed in terms of emission factors, was determined to be 3.24E-08 kg/GJ. This value corresponds to 11.1 µg/m^3 in the dry flue gas. For all emission sources, the calculated emission factor was one to three orders of magnitude higher than the LDL.

Arsenic is not typically released from the materials, such as mild and stainless steel, used to manufacture the combustion devices. Therefore, the source of arsenic must originate from the combustion air or from the fuel gas or both. Based on the material balance method, theoretical arsenic concentrations in the combustion air and the fuel gas were calculated based on the air to fuel ratio (AFR) determined for each sample and the concentration of arsenic measured in the flue gas. AFR is expressed on a volume basis for these calculations. No estimates were made for the option of arsenic being present in both input streams.

The results of these calculations are presented in **Table 6**. Considering all locations and all thirteen sources sampled, the theoretical concentrations of arsenic in the combustion air were slightly more than the concentration in the dry flue gas based on the ratio of (1+AFR)/AFR. The theoretical concentrations of arsenic in the fuel gas were determined to be significantly more than in the dry flue gas by the ratio of (AFR-1)/1. The calculated average theoretical concentration of arsenic in combustion air is 18.3 µg/m^3 with a standard deviation (STDEV) of 19.5 µg/m^3 while the calculated average theoretical concentration of arsenic in fuel gas is 546.3 µg/m^3 with a STDEV of 767.6 µg/m^3.

Comparing the results, source to source at the same location, calculated theoretical arsenic concentrations in combustion air and fuel gas showed considerable variability at Locations 1 and 5. At Location 5, the reason is most probably due to a suspect low emission associated with sample line freezing associated with the Tank Heater source. At locations 2, 3, 4 and 7, the variability source to source is minor. At Location 6 only one sample was analysed. One result at Location 5 and both results at Location 7 exhibit very high arsenic concentrations relative to all other location results. Adjusting the averages, by removing the one high result and one suspect result at Location 5 and both high values at Location 7, yields average arsenic concentrations of 10.3 µg/m^3 for combustion air, and 165.1 µg/m^3 for fuel gas.

Other noteworthy observations include:

- At Location 5, the high arsenic result was associated with a screw pump engine even though the fuel gas contained 95% methane for both sources and appeared to be typical. The tank heater emission exhibited low arsenic results and this is most likely associated with sample line freezing problems experienced during source sampling.
- At Location 7, the high arsenic concentrations were associated with a fuel gas that contained about 67% methane and 9% ethane. This fuel gas composition was quite different from all others samples and appears to be characterized with higher than normal arsenic concentrations.

Table 4: Combustion efficiency and determined emission factors for acrolein and arsenic for different types of sources.

Industry Subsector	Source	Combustion Efficiency	Acrolein Emission Factor	Acrolein Emission Factor LDL	Arsenic Emissions Factor	Arsenic Emissions Factor LDL	Comments
		%	kg/GJ (fuel)	kg/GJ (fuel)	kg/GJ (fuel)	kg/GJ (fuel)	
Location 1 Sweet Gas Gathering system	Reciprocating Engine	95.649	9.09E-05	8.62E-10	1.70E-05	3.58E-08	White Superior; Engine Model: 8GT-825
	Reboiler	99.999	0	1.16E-09	3.32E-06	2.77E-08	Flameco Industries - FAH24-XXA2C; Serial #: 1109 82E
Location 2 Sweet Gas Gathering system	Reciprocating Engine	99.782	0	1.45E-09	8.63E-07	2.21E-08	Caterpillar; Model: G3512TAW; Serial #:4KL00571; Rated: 810 HP
	Reboiler	99.933	0	5.58E-10	2.68E-06	5.51E-08	Well-Hall Fabrication; PO #: F94P621;Work Order:94-7620/112/3;
Location 3 Sweet Gas Processing Plant	Reciprocating Engine	99.03+	0	1.15E-09	8.80E-07	2.92E-08	Waukesha; Model F3521GS1; Serial : 317511; Rate Power:738 HP
	Reboiler	99.997	0	1.15E-09	1.72E-06	2.94E-08	Rated Capacity: 429,000BTU
Location 4 Thermal Heavy Oil Production	Steam Generator	99.994	0	1.21E-09	4.38E-06	2.16E-08	COEN Canada Inc; Model 795 R; Rated Capacity: 316 MMBTU/hr
	Treater	99.960	0	6.25E-10	4.38E-06	4.11E-08	Eclipse Combustion Canada; Rated Capacity 6.25 MMBTU/hr
Location 5 Cold Heavy Oil Production	Tank Heater	99.734	0	2.74E-10	1.96E-06[1]	9.80E-08	CLM Tank & Equipment Ltd: Rated Capacity :0.5 MM BTU
	Screw Pump Engine	99.894	0	2.67E-10	5.50E-05	9.89E-08	Ford 300 Engine
Location 6 Sour Processing Plant	Steam Boiler	99.818	0	8.29E-10	2.28E-06	2.96E-08	Toronto Iron Works; Rated Steam:31750 kg/hr; Rated Capacity:29.2 E3 m3/day
Location 7 Conventional Oil Production	Treater	99.977	0	4.02E-10	3.90E-05	5.98E-08	Superior Propane; Serial # 9801665; Duty 1.4 MMBTU
	Reciprocating Engine	99.891	0	3.57E-10	4.70E-05	5.95E-08	Cameron CFA34 - 432KW; 1800 RPM; Model 12SGTB

[1] Sample line freezing problems were experienced and result was most probably affected.

Table 5: Average and standard deviation for combustion efficiency and acrolein and arsenic emission factors for equipment subcategories sampled.

Equipment Subcategory	Sources Sampled	Combustion Efficiency		Acrolein Emission Factor		Arsenic Emission Factor	
		Average	STDEV	Average	STDEV	Average	STDEV
		%	%	kg/GJ (fuel)	kg/GJ (fuel)	kg/GJ (fuel)	kg/GJ (fuel)
Compressor	5	98.85%	0.018 %	1.82E-05	4.07E-05	3.16E-11	2.74E-11
Reboiler	3	99.98%	0.00037 %	0.0	0.0	1.50E-11	1.05E-11
Treater	2	99.97%	0.00012 %	0.0	0.0	2.62E-11	2.02E-11
Boiler/Generator	2	99.91%	0.0012 %	0.0	0.0	2.81E-11	2.33E-11
Tank Heater	1	99.73%	NA	0.0	NA	8.69E-13	NA
All Sources	13	99.51%	0.012 %	6.99E-06	2.52E-05	2.40E-11	2.10E-11

Table 6: Arsenic concentrations measured in the flue gas and calculated for combustion air and fuel gas for the 13 sources sampled.

	Location 1		Location 2		Location 3		Location 4		Location 5		Location 6	Location 7		Ave All Sources	ST DEV
	Process Heater	Recip Engine	Process Heater	Recip Engine	Process Heater	Recip Engine	Steam Gen	Treater	Tank Heater	Pump Engine	Steam Boiler	Treater	Recip Engine		
Flue Gas, $\mu g/m^3$	10.6	40.3	4.2	3.5	5.6	2.6	17.4	9.0	1.5	42.5	6.6	47.6	57.4	19.2	20.1
Combustion Air, $\mu g/m^3$	9.7	37.8	4.0	3.2	5.1	2.4	15.8	8.6	1.5	41.7	6.2	46.1	55.7	18.3	19.5
Fuel Gas, $\mu g/m^3$	129.9	646.1	101.6	34.9	66.4	33.2	190.7	182.5	72.7	2077.1	100.1	1521.0	1945.8	546.3	767.6

[1] Sample line freezing most likely affected the results for this source.

[2] Removal of Location 5 Tank Heater and Pump Engine, and Location 7 Treater and Recip Compressor results in significantly reduced concentrations for :

- Dry Flue Gas: Average = 11.1 $\mu g/m^3$; STDEV = 11.9 $\mu g/m^3$
- Combustion Air: Average = 10.3 $\mu g/m^3$; STDEV = 11.1 $\mu g/m^3$
- Fuel Gas: = Average 165.1 $\mu g/m^3$; STDEV = 189.0 $\mu g/m^3$.

4.2 OTHER SUBSTANCES

Numerous other organic and metallic substances were identified and quantified. For each case, the emission factor was determined.

4.2.1 OTHER ORGANIC SUBSTANCES

A total of 184 of organic and inert substances were identified during the analytical work and, in general, were source specific in terms of the number identified. Many were common to all sources and a few were noted in only one or two sources.

Table 7 summarized the frequency of occurrence for those substances with a ratio measured to LDL emission factor greater than 1000. Although methane only occurred at concentrations greater than 1000 times LDL with a frequency slightly greater than 50% (7 of 13 sources), it was present at lower concentrations in all sources.

No attempt was made to explain the reason for a compounds presence at a specific source type. Measured and LDL emission factors and the ratio for all substances for each source sampled are tabulated in **Table 43** of Appendix A.

Table 7: Frequency of occurrence for compounds where the measured to LDL emission factor ratio is greater than 1000.

Component	CAS Number	Frequency in 13 Sources	Maximum Value of the Ratio	Emission Factor LDL, kg/(GJ fuel)
Methane	74-82-8	7	133,580	5.82E-06
2-Methylpentane	107-83-5	2	94,197	6.35E-08
Pentane	109-66-0	2	70,230	5.32E-08
Nonane	111-84-2	1	57,772	9.46E-08
3-Methylpentane	96-14-0	2	47,099	6.35E-08
Heptane	142-82-5	1	36,230	7.39E-08
Hexane	110-54-3	2	28,984	6.35E-08
Cyclopentane	287-92-3	1	24,525	5.17E-08
Decane	124-18-5	1	21,795	1.05E-07
Methylcyclopentane	96-37-7	1	16,749	6.21E-08
Undecane	1120-21-4	1	10,898	1.15E-07
Octane	111-65-9	1	7,539	8.42E-08
Methylcyclohexane	108-87-2	1	6,103	4.42E-04
Isopentane	78-78-4	1	5,464	5.32E-08
Cyclobutane, isopropyl-	872-56-0	1	4,372	2.41E-06
Cyclopentane, 1,3-dimethyl-	2453-00-1	1	3,129	2.41E-06
Cyclohexane, 1,3-dimethyl-, cis-	638-04-0	1	2,641	2.76E-06
Methane, nitro-	75-52-5	1	2,248	4.51E-08
Butane	106-97-8	1	2,013	5.82E-06
Cyclopentane, ethyl-	1640-89-7	1	1,769	2.41E-06

Table 7: Frequency of occurrence for compounds where the measured to LDL emission factor ratio is greater than 1000.

Component	CAS Number	Frequency in 13 Sources	Maximum Value of the Ratio	Emission Factor LDL, kg/(GJ fuel)
Phthalic anhydride	85-44-9	1	1,723	1.09E-07
Cyclopentane, 1,2,4-trimethyl-	2815-58-9	1	1,651	2.76E-06
Dodecane	112-40-3	2	1,597	1.26E-07
Cyclopentane, 1,1-dimethyl-	1638-26-2	1	1,380	2.41E-06
Camphor	76-22-2	1	1,182	3.74E-06
Benzene, 1,3,5-trimethyl-	108-67-8	1	1,171	2.96E-06
Cyclohexane, 1,2-dimethyl-, trans-	6876-23-9	1	1,103	2.76E-06

Notes: The LDL Emission factor is calculated based on the following conditions: Estimated Dry Flue Gas Flow rate: 21.84 ± 13.84 m^3/h and High Heating Value: 37.51 ± 1.85 GJ/ (m^3fuel)

4.2.2 OTHER METAL SUBSTANCES

Metallic substances were identified and quantified for each source based on a specific suite of 36 substances. Thus, emission factors for all inorganic substances are presented for all sources. The detailed results are presented in Appendix A. All metallic substance emission factors were determined to be very small and within one or two orders of magnitude of the lower detection limit. In addition, it is noted that the metallic substances are reported as if they were pure metal substances but in most cases these emissions would be tied up as one or more salts of the noted substance.

4.3 COMBUSTION EFFICIENCY

Combustion efficiency was considered to be an important indicator of performance and was determined in various ways for each source sampled. Combustion efficiency not only indicated the fuel efficiency but may be an indicator of poor substance destruction or the potential formation of unwanted substances in the flue gas emissions.

The calculation methods for the three combustion efficiencies are:

$$CE_{TOC} = \frac{(C_{inlet,nonCO2}) - (C_{outlet,nonCO2})}{(C_{inlet,nonCO2})} \, x100\% \qquad \text{(Equation 4.1)}$$

Where:

CE_{TOC} is the total organic carbon based combustion efficiency
$C_{inlet,nonCO2}$ is the TOC in the inlet fuel gas excluding carbon dioxide
$C_{outlet,nonCO2}$ is the TOC in the outlet flue gas excluding carbon dioxide

This method was used to make sure that all compounds identified in the fuel and flue gases were accounted for in the combustion efficiency calculation.

$$CE_{CH4} = \frac{(CH4_{inlet}) - (CH4_{outlet})}{(CH4_{inlet})} x100\% \qquad \text{(Equation 4.2)}$$

Where:

CE_{CH4}	is the total methane based combustion efficiency
$CH4_{inlet}$	is the methane in the inlet fuel gas
$CH4_{outlet}$	is the methane in the outlet flue gas

This method considered methane to be a basic indicator of combustion efficiency.

$$CE_{THC} = \frac{(C_{inlet,non\ CO2}) - (THC_{outlet})}{(C_{inlet,non\ CO2})} x100\% \qquad \text{(Equation 4.3)}$$

Where:

CE_{THC}	is the total hydrocarbon based combustion efficiency
$C_{inlet,nonCO2}$	is the inlet gas without carbon dioxide
THC_{outlet}	is the outlet total hydrocarbon

This method approximates the traditional use of a THC combustion analyzer to determine combustion efficiency.

These different combustion efficiencies were calculated and the results are included with the detailed organic substance results tables for each source in Appendix A. The methods used to calculate combustion efficiency do not show any large differences for any of the sources. Even for Location 1, where the combustion efficiency was only 95.65%, the difference between the three methods was very small.

5 RELEVANT PUBLISHED EMISSION FACTORS

Published emission factors for acrolein and arsenic were identified through a literature search of US EPA and European jurisdictions. The only results identified were those reported by the US EPA and published in WebFIRE.

For acrolein, emission factors are published for two categories of natural gas-fired internal combustion sources: Rich Burn 4-cycle Engines and Boilers. The emission factor determined for the compressor at Location 1 is between the two values shown in **Table 8** for Internal Combustion Engines.

Table 8: Literature values of published emission factors of acrolein.

	Internal Combustion Engines: 4-cycle Rich Burn - Natural Gas[1]	**External Combustion Engines: Boilers < 100 MM Btu/hr Natural Gas[2]**
Emission Factor, kg/GJ (fuel)	1.13E-3 – 2.65 E-6	1.13E-03

[1] US EPA 2000b.
[2] US EPA 2000a.

For arsenic, the only emission factor identified was for combustion boilers used in the power generation sector and the details are presented in **Table 9**. The average arsenic emission factor determined for the sampled sources was 4.16E-06 kg/GJ and this value is 1 order of magnitude less than the published value reported for external combustion boilers.

Table 9: Literature value of published emission factor for arsenic.

	Electric Generation[1]/External Combustion Boilers[2, 3]
Emission Factor, kg/GJ (fuel)	8.60E-05

[1] Tangentially Fired Units and Boilers = 0 - 100 Million Btu/hr except Tangential
[2] 10-100 and >100 Million Btu/hr
[3] US EPA 1998.

Alberta ambient air quality objectives for arsenic were published in 2005 as noted in **Table 10**. In addition, ambient air concentrations of arsenic were reported for the Edmonton Central AQM station. The observed concentrations were well below the AAAQO values. Ambien air concentrations reported by others for remote, rural and urban areas are noted in **Table 10**. These values appear to be comparable to the values reported for Edmonton Central. As noted in **Table 11**, theoretical values calculated for combustion air at the seven locations sampled appear to be significantly higher that AAAQO or observed values in Alberta.

In addition, research results for organic arsenic in a number of natural gas samples from wells in several unspecified gas fields in USA are included in **Table 10**. As noted in **Table 11**, theoretical values calculated for fuel gas at the seven locations sampled appear to be in line with concentrations observed in natural gas samples at locations in USA.

Table 10: Arsenic concentrations reported in selected literature for ambient air and natural gas.

	µg/m^3	**µg/m^3**
Alberta Ambient Air Quality Objective[1]	1-hour Average	Annual Average
	0.1	0.01
Edmonton Central AQM Station[1]	Range for period of 1993-2003	
	Low	High
	0.03E-03	4.48E-03
	Average	1.02E-3
Ambient Air[2]	Low	High
Rural area	1.00E-03	1.00E-02
Non-contaminated urban areas	3.00E-03	3.00E-02
Ambient Air[3]		
Remote areas	0.007E-03	1.9E-03
Rural area	1E-03	28E-03
Urban areas	2E-03	2320E-03
Natural Gas[4]	Range	
Numerous US field samples of natural gas	10	63000

[1] Alberta Environment 2005.
[2] WHO 2000.
[3] Schroeder et al (1987) in UK Environment Agency 2008.
[4] Irgolic et al 1991.

Table 11: Comparison of theoretical values calculated for arsenic in combustion air and fuel gas with values reported in selected literature.

	µg/m^3	**µg/m^3**
Alberta Ambient Air Quality Objective[1]	1-hour Average	Annual Average
	0.1	0.01
Edmonton Central AQM Station[1] (Range for period of 1993-2003)	Low	High
	0.03E-03	4.48E-03
Combustion Air (Table 6) (Theoretical)		
Range	1.5	55.82
Average	18.3	
Natural Gas[2]	Range	

Table 11: Comparison of theoretical values calculated for arsenic in combustion air and fuel gas with values reported in selected literature.

	$\mu g/m^3$	**$\mu g/m^3$**
Numerous US field samples of natural gas; Range	10	63000
Fuel Gas (Table 6) (Theoretical) Range	33.2	2077.1
Fuel Gas (Table 6) (Theoretical) Average	546.3	

[1] Alberta Environment 2005.

[2] Irgolic et al 1991.

6 CONCLUSIONS AND RECOMMENDATIONS

A measurement campaign was conducted that included thirteen samples from six different combustion source types at seven different locations in Alberta. The intended use of the field data collected was to determine the emission factors of acrolein and arsenic. The final outcome was to provide updated and credible emission factor values pertinent to the UOG industry considering:

1. a range of fossil fuel and waste gas combustion sources,
2. a range of waste gas and fossil fuel gas qualities, and
3. a range of geographical locations.

Acrolein was detected in one compressor engine emission which had a combustion efficiency of 96%. The emission factor was comparable to the values reported in literature. All other sources, including those of the same type with combustion efficiencies greater than 99.0%, did not exhibit any acrolein emissions.

The fact that acrolein was detected at one source with relatively low combustion efficiency, and not at any others locations, suggests a possible link between combustion efficiency and acrolein formation in the combustion process. It is recommended that this potential link by investigated with additional testing. The following test program is recommended.

- Check the combustion efficiency of the compressor engine at Location 1 and, if it is observed to be about the same (96%), repeat testing of the compressor engine without any changes to the engine.
- Tune the engine to a combustion efficiency of at least 99% and repeat the emission test.
- Consider including in the test program one or more another engines operating with an abnormally low combustion efficiency.

Arsenic was detected in all thirteen samples at levels equal to approximately two orders of magnitude above the lower detection limit. Of noteworthy significance is the fact that the arsenic emission factors developed from this study are five orders of magnitude lower than the value reported in the literature for a gas-fired combustion source.

Although arsenic was present in the flue gas associated with all combustion devices sampled, arsenic cannot be created through the combustion process. Organic and non-organic arsenic may be present in the fuel gas or in the combustion air. Therefore, the potential source of the arsenic detected in the flue gas was examined. The theoretical concentrations of arsenic in either the combustion air or in the fuel gas were calculated based on the concentrations of arsenic measured in the flue gas. The results of these calculations indicated that combustion air can be excluded as the potential source of arsenic based on the high calculated theoretical concentrations of arsenic required in the combustion air. The theoretical concentrations are considerably higher than those observed in Edmonton and higher than the AAAQO, and are not likely to be present in rural Alberta air. Conversely, fuel gas was determined to be the most likely source of arsenic as the calculated theoretical concentrations of arsenic in the fuel gas were well within the lower end of the range observed in natural gas wells located in the USA.

It is recommended that consideration be given to quantifying arsenic in Canadian natural gas fields, in plant fuel systems and sales gas delivery networks. A study of this type would provide a baseline for raw gas and address concentration changes as the gas is processed and delivered for consumption.

Emission factors of other organic and inorganic substances identified and quantified in either the fuel gas or flue gas are reported and included in Appendix A. These results were not assessed regarding their potential source, association with source type, relationship to combustion efficiency or any other potential reasons for their presence in the flue gas.

7 REFERENCES

Alberta Environment 2005. Alberta Ambient Air Quality Objectives: Arsenic, Effective May 1, 2005. http://environment.alberta.ca/01025.html

UK Environment Agency 2008. A review of the toxicity of arsenic in air, Science Report – SC020104/SR4, May 2008. http://cdn.environment-agency.gov.uk/scho0508bodr-e-e.pdf

Irgolic et al 1991. Determination of arsenic and arsenic compounds in natural gas samples. Irgolic, K. J., Llger, D., Zingaro, R. A., Spall, D. and Puri, B. K. Appl. Organometal. Chem., 5: 117–124 (1991). doi: 10.1002/aoc.590050209.

US EPA 1998. Section 1.4, Natural Gas Combustion. In: Compilation of Air Pollutant Emission Factors, Volume 1: Stationary Point and Area Sources, Fifth Edition, AP-42, Supplement D. U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards. Research Triangle Park, North Carolina.

US EPA 2000a. Section 3.1, Stationary Gas Turbines for Electricity Generation. In: Compilation of Air Pollutant Emission Factors, Volume 1: Stationary Point and Area Sources, Fifth Edition, AP-42. U.S. Environmental Protection Agency.

US EPA 2000b. Section 3.2, Natural Gas-fired Reciprocating Engines. In: Compilation of Air Pollutant Emission Factors, Volume 1: Stationary Point and Area Sources, Fifth Edition, AP-42. U.S. Environmental Protection Agency.

WHO 2000. Air Quality Guidelines for Europe: Second Edition (WHO Regional Publications, European Series, No 91) Copenhagen, Denmark, World Health Organization, Regional Office for Europe. http://www.euro.who.int/__data/assets/pdf_file/0014/123071/AQG2ndEd_6_1_Arsenic.PDF