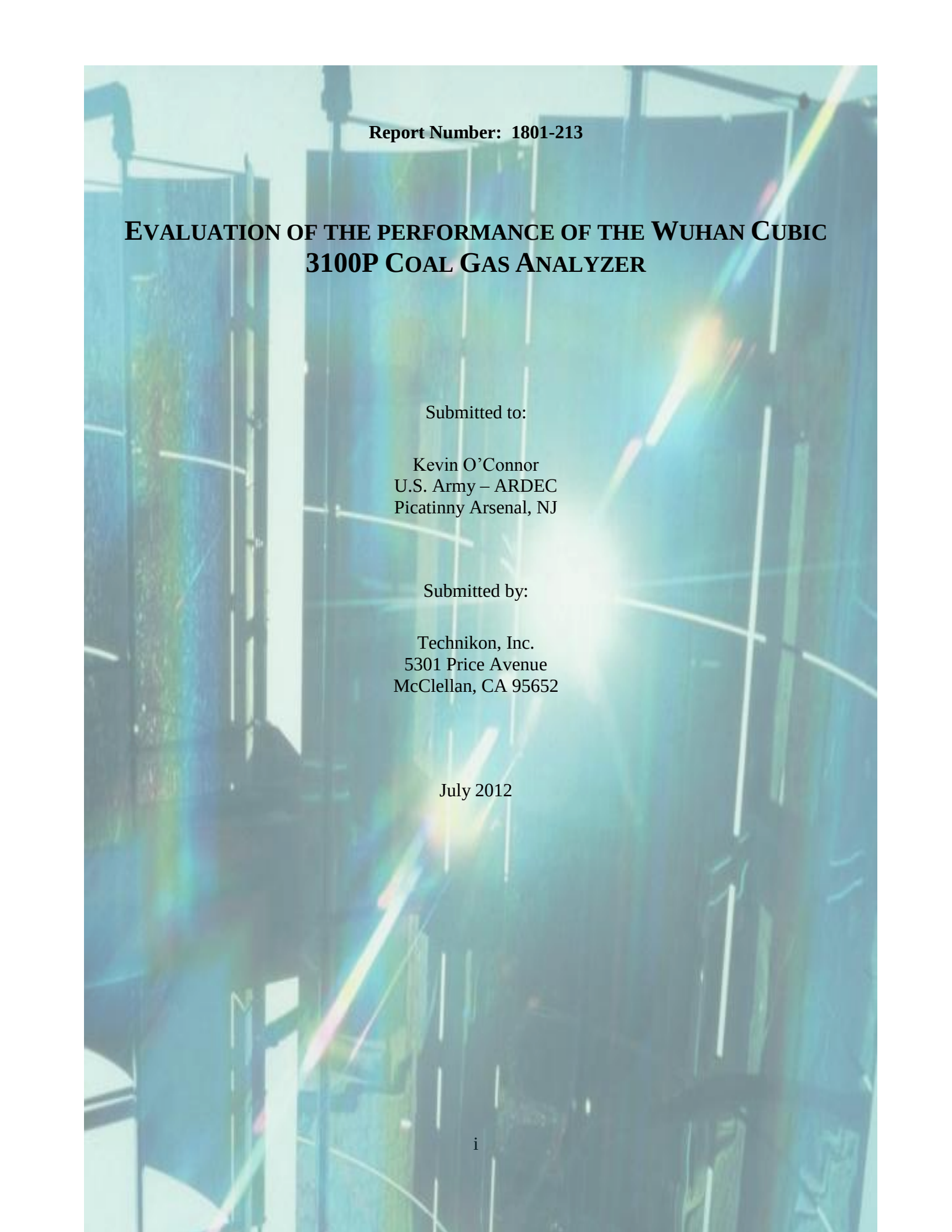




Report Number: 1801-213

EVALUATION OF THE PERFORMANCE OF THE WUHAN CUBIC 3100P COAL GAS ANALYZER

Submitted to:

Kevin O'Connor
U.S. Army – ARDEC
Picatinny Arsenal, NJ

Submitted by:

Technikon, Inc.
5301 Price Avenue
McClellan, CA 95652

July 2012

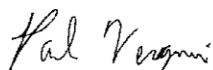
Report Documentation Page				Form Approved OMB No. 0704-0188	
Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.					
1. REPORT DATE 01 JUL 2012		2. REPORT TYPE N/A		3. DATES COVERED -	
4. TITLE AND SUBTITLE Evaluation of the Performance of the Wuhan Cubic 3100P Coal Gas Analyzer				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) U.S. Army-ARDEC Picatinny Arsenal, New Jersey				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release, distribution unlimited					
13. SUPPLEMENTARY NOTES The original document contains color images.					
14. ABSTRACT					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT UU	18. NUMBER OF PAGES 24	19a. NAME OF RESPONSIBLE PERSON
a. REPORT unclassified	b. ABSTRACT unclassified	c. THIS PAGE unclassified			

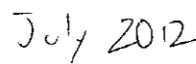
EVALUATION OF THE PERFORMANCE OF THE WUHAN CUBIC 3100P COAL GAS ANALYZER

Technikon Report # 1801-213

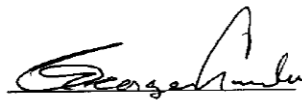
This report has been reviewed for completeness and accuracy and approved for release by the following:

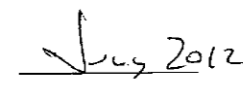
Chemical Engineer


Paul Vergnani


Date

Vice President


George Crandell


Date

CONTENTS

1.0	Introduction.....	1
2.0	Equipment Description	2
2.1	Diablo Analytical 3000 Real-Time Gas Analyzer	2
2.2	Wuhan Cubic Optoelectronic Model 3100P Coal Gas Analyzer	3
2.3	NOVA Model 7904C-RM Furnace Atmosphere Gas Analyzer	5
2.4	EnviroNics 4000/4040 Gas Mixing and Dilution Systems	5
2.5	Additional Equipment	6
3.0	Testing Procedure	6
3.1	Diablo Method Development and Validation	7
3.2	Analyzer Performance Using Simulated Syngas	11
4.0	Conclusions.....	18
5.0	Recommendations.....	19
6.0	Works Cited	19

LIST OF FIGURES

Figure 1: Diablo 3000 RTGA	2
Figure 2: Bypass Sampling Schematic for the Diablo 3000 RTGA	3
Figure 3: Wuhan Cubic Optoelectronic Model 3100P Coal Gas Analyzer	4
Figure 4: Sample Conditioning System	4
Figure 5: NOVA Model 7904C-RM Analyzer	5
Figure 6: Environics Gas Mixing and Dilution Systems	6
Figure 7: 2-Step Gas Mixing Schematic	13

LIST OF TABLES

Table 1: Analytical Specifications for Model 3100P Analyzer	3
Table 2: Analytical Specifications for NOVA Model 7904C-RM Analyzer	5
Table 3: Primary and Secondary Mass Spectral Peaks of Pertinent Compounds	7
Table 4: LQL Determination Test Matrix	8
Table 5: Diablo RTGA Calibration Range	11
Table 6: Valve Positions for Step 1	14
Table 7: Step-1 Compositions for the 4 Test Simulated Syngas Mixtures	14
Table 8: Valve Positions for Step-2	15
Table 9: Simulated Syngas Compositions	15
Table 10: Results Summary for Test Mix 1	16
Table 11: Results Summary for Test Mix 2	17
Table 12: Results Summary for Test Mix 3	17
Table 13: Results Summary for Test Mix 4	18

LIST OF ABREVEATIONS AND ACRONYMS

ARDEC	Armament Research, Development and Engineering Center
CH ₄	Methane
C _n H _m	Higher hydrocarbons
CO	Carbon Monoxide
CO ₂	Carbon Dioxide
DoD	Department of Defense
ECD	Electrochemical Detector
H ₂	Hydrogen
LQL	Lower Quantitation Limit
mL/min	Milliliters per minute
MS	Mass Spectroscopy
NDIR	Non-Dispersive Infrared
NIST	National Institute of Standards and Technology
O ₂	Oxygen
RETC	Renewable Energy Testing Center
RTGA	Real Time Gas Analyzer
TCD	Thermal Conductivity Detector

1.0 Introduction

The Renewable Energy Testing Center (RETC) is a uniquely equipped testing facility that is focused on the evaluation and testing of renewable energy technologies. The facility is capable of fabricating, operating, and testing the performance of technologies using a number of analytical techniques. The facility is operated by Technikon under contract with the U.S. Army ARDEC. Technikon brings its wealth of technical and management experience to support and evaluate the prospective technologies.

Many renewable energy technologies are based on gasifying a solid waste material of some sort. The waste could be from agricultural sources, such as nut shells, rice hulls, or wood chips. It may also be from municipal waste streams, which include paper, plastic, food scraps, and a number of other materials. In any case, the goal is to gasify the carbonaceous material in the waste, creating hydrogen (H_2), carbon monoxide (CO), carbon dioxide (CO_2), and methane (CH_4). The ability to monitor these gases continuously in real time is important to properly evaluate the performance of the equipment. Additionally the ability to monitor oxygen (O_2) concentration is an important piece of process safety information, because the upper and lower flammability limits for hydrogen gas are 4% and 74.2% respectively (Weast, Robert C. ed, 1982).

Technikon has used a Diablo Analytical 5000A Real-Time Gas Analyzer (RTGA) to perform these analyses to date. This analyzer is basically a laboratory grade mass spectrometer (MS) modified with a heated continuous bypass sampling system. In theory the system is capable of continuous measurement of produced syngas to low percent concentration levels. In practice, the unit lacks the robustness necessary to perform these analyses in a process environment. This is due to the original design of the MS as a piece of laboratory equipment. It was designed to operate in a climate controlled environment with little mechanical vibration or electro-magnetic interference. Because of these limitations, the unit has been operated as grab-sample analyzer, with discrete bag samples being taken at numerous points during operation. This is very valuable data, but may not capture performance variations or important process dynamics.

To allow the capture of real-time data from gasifier operation, Technikon purchased a Wuhan Cubic Optoelectronic Model 3100P portable coal gas analyzer. This analyzer uses multiple measurement techniques to detect CH_4 , CO, CO_2 , H_2 , O_2 , and higher hydrocarbons (C_nH_m). It uses Non-Dispersive Infrared (NDIR) to measure CH_4 , C_nH_m , CO, and CO_2 . It uses an Electrochemical Detector (ECD) to measure O_2 , and a Thermal Conductivity Detector (TCD) to measure H_2 . Because the TCD is not selective for hydrogen, the analyzer uses a software algorithm to correct the TCD reading for the other gases detected by NDIR and ECD.

The purpose of this testing has been to evaluate the performance of the 3100P analyzer on simulated and real samples, to validate the performance of the software algorithm, and to establish that there are no matrix interferences inherent in the syngas that would result in inaccurate data. This testing also evaluated the performance of a NOVA Analytical Systems model 7904C-RM furnace atmosphere gas analyzer. This analyzer is owned by Sierra Energy, one of the partners testing a gasifier at the RETC. The system is similar in operation to the model 3100P, but lacks the ability to measure C_nH_m and O_2 . The equipment and methods used for this testing are described below.

2.0 Equipment Description

To evaluate the performance of the analyzers they will be compared to the Diablo RTGA, using simulated syngas samples, as well as real operating samples. These tests will measure the precision, accuracy, and response time of the different analyzers. The following sections describe the equipment and supplies that will be used to perform the testing tasks.

2.1 Diablo Analytical 3000 Real-Time Gas Analyzer

The Diablo 3000 RTGA is based on the Agilent model 5973N quadrupole mass selective detector. This MS is a widely used piece of analytical equipment that has a strong performance record in a number analytical laboratories. Due to the well established performance history of this equipment, it will be the benchmark for comparing the performance of the other analyzers. The Diablo system adds a heated bypass sampling loop to the inlet of the MS, which facilitates analyzing a continuous sample stream at 40 milliliters per minute (mL/min). The system uses a custom software package to provide continuous monitoring of the sample composition. Figure 1 is a picture of the analyzer and Figure 2 is a schematic of the sampling inlet.



Figure 1: Diablo 3000 RTGA

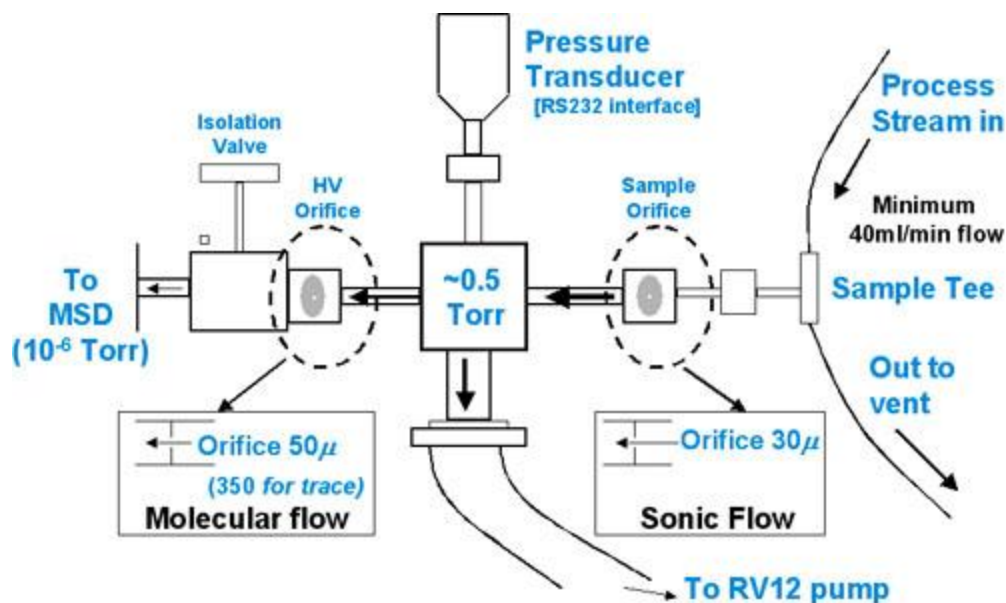


Figure 2: Bypass Sampling Schematic for the Diablo 3000 RTGA

2.2 Wuhan Cubic Optoelectronic Model 3100P Coal Gas Analyzer

The Model 3100P Coal Gas Analyzer is a continuous gas analyzer that uses a combination of NDIR, ECD, and TCD analytical techniques to determine the composition of the major components found in a typical syngas stream. Table 1 summarizes the analytical specifications for the analyzer.

Table 1: Analytical Specifications for Model 3100P Analyzer

Species	Method	Range (%)	Resolution (%)	Precision (%)
CO	NDIR	0-80	0.01	≤ 2
CO ₂	NDIR	0-50	0.01	≤ 2
CH ₄	NDIR	0-15	0.01	≤ 2
C _n H _m	NDIR	0-10	0.01	≤ 2
H ₂	TCD	0-45	0.01	≤ 3
O ₂	ECD	0-25	0.01	≤ 3

The unit has a built in sampling pump that will draw sample at around 1000 mL/min. To prevent contaminating the analyzer, gas samples need to be free of particulate, tars, and moisture. Figure 3 is a picture of the analyzer, and Figure 4 is a picture of the sample conditioning system.



Figure 3: Wuhan Cubic Optoelectronic Model 3100P Coal Gas Analyzer



Figure 4: Sample Conditioning System

2.3 NOVA Model 7904C-RM Furnace Atmosphere Gas Analyzer

The NOVA Model 7904C-RM operates in similar fashion to the Model 3100P analyzer. However it does not have the capability to quantify C_nH_m or O_2 . The unit has a built in sample pump that samples at 1000 mL/min. Figure 5 is a picture of the unit, and Table 2 is a list of the analytical specifications.



Figure 5: NOVA Model 7904C-RM Analyzer

Table 2: Analytical Specifications for NOVA Model 7904C-RM Analyzer

Species	Method	Range (%)	Resolution (%)	Precision (%)
CO	NDIR	0-60	0.1	± 1
CO ₂	NDIR	0-30	0.1	± 1
CH ₄	NDIR	0-20	0.1	± 1
H ₂	TCD	0-50	0.1	± 1

2.4 Environics 4000/4040 Gas Mixing and Dilution Systems

The Environics Gas Mixing and Dilution systems was used to generate the calibration gases for the instruments, as well as the simulated syngas test mixtures. Each module is capable of mixing four gases with an concentration accuracy of $\pm 1.0\%$ of the set point. In order to create a wide concentration range of samples for calibration and testing, the two modules were connected together, allowing the mixing of samples with up to seven components. Figure 6 is of the two modules.



Figure 6: Environics Gas Mixing and Dilution Systems

2.5 Additional Equipment

To formulate the required calibration and testing mixes, the following Ultra-High Purity gases with suitable high pressure regulators were required.

- Argon
- Carbon Dioxide
- Carbon Monoxide
- Hydrogen
- Methane
- Nitrogen
- Oxygen
- Propane (C_nH_m compound)

Clean 1-liter and 25-liter Tedlar sampling bags were required for sampling and calibration of the equipment.

3.0 Testing Procedure

The testing regimen to evaluate the analyzer is broken into three tasks. The first is method development and validation of the Diablo RTGA as the benchmark, the second is evaluating analyzer performance using known concentration simulated syngas samples, and the third is evaluating the performance on a real syngas process stream. These tasks are explained in detail in the following section. These tasks assume the equipment has been installed as directed by the manufacturer, and have been tested for proper operation. The equipment was also calibrated

using the manufacturers recommended procedures. Refer to the operating manuals for detailed procedures.

Warning! The following procedures involve the handling of flammable and poisonous gases. Do not mix oxygen with other flammable gases such as methane or hydrogen at concentrations over 1% by volume. Make sure vent lines from analyzers are connected to proper exhaust manifolds to prevent the accumulation of flammable or poisonous gases. As a precaution all operations should be conducted with an ambient gas sensor capable of detecting CO, H₂, and hydrocarbon lower explosive limit!

3.1 Diablo Method Development and Validation

Because the Diablo utilizes mass spectroscopy for analysis, it is a good technology to compare the other analyzers to. However it does have limitations. It identifies compounds based on their molecular weight. This is problematic when two compounds share the same molecular weight, as CO and N₂ do. Due to molecular fragmentation, most molecules also have a secondary response at a different weight. Table 3 shows the primary and secondary mass spectral peaks for the compounds of interest (National Institute of Standards and Technology, 2011).

Table 3: Primary and Secondary Mass Spectral Peaks of Pertinent Compounds

	N ₂	O ₂	CO	CH ₄	C ₃ H ₈	CO ₂	H ₂
Primary	28	32	28	16	29	44	2
Secondary (in Descending Order of Strength)	14	16	12	15	28	28	1
			16	14	27	16	
				13	44	12	
				12	43	45	
				17	39	22	
					41		
					26		
					15		
					42		
					38		
					40		
					37		
					14		

In order to analyze for all of the compounds of interest, a new data analysis algorithm using secondary peak responses was developed and tested. Due to the lower response of the secondary peaks, the lower limit of quantitation (LQL) will be adversely affected. The following matrix establishes the tests that will determine LQL of the method. All gas mixtures use argon as the balance gas.

Table 4: LQL Determination Test Matrix

Hydrogen at mass 2									
		Mass Abundance							
Date	4/3/2012	4/4/2012	4/5/2012	4/6/2012	4/9/2012	4/10/2012	4/11/2012		
Concentration (%)	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5	Trial 6	Trial 7	Average	Std. Dev
0	0	0	0	0	0	0	0	0	0
1	0	590.2667	572.459	565.1148	536.7869	535.377	2402.426	743.2044	761.0771
2	29713.44262	29294.95	29194.23	28728	27838.16	27819.8	27758.43	28621	815.1139
3	42432.2623	42096.52	41833.7	40947.41	39606.82	39877.77	39749.25	40934.82	1203.23
4	55038.81967	54625.05	54334.95	53334.69	51892.33	52063.74	51785.57	53296.45	1393.728
5	67757.2459	67306.36	66624.26	65776.13	63798.16	63924.85	63738.49	65560.79	1739.382
Oxygen at mass 32									
		Mass Abundance							
Date	4/3/2012	4/4/2012	4/5/2012	4/6/2012	4/9/2012	4/10/2012	4/11/2012		
Concentration (%)	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5	Trial 6	Trial 7	Average	Std. Dev
0	4046.83871	3437.355	3759.516	4010	3709.129	3782.129	3663.516	3772.641	208.2246
1	35048.13115	35118.3	34735.48	34733.77	33963.02	34519.48	33603.02	34531.6	559.6361
2	68763.80328	68321.31	67809.05	67524.72	66268.72	66009.84	65036.46	67104.84	1358.952
3	101593.8361	100887.1	99904.39	99439.08	97854.43	97207.61	95942.69	98975.59	2048.08
4	133934.1639	133317.8	131906.5	131298.9	129044.5	127983.1	126919.3	130629.2	2692.819
5	166430.4262	165457.8	163836.9	162597.8	159766	159133.4	157469.4	162098.8	3390.747
Propane at mass 29									
		Mass Abundance							
Date	4/3/2012	4/4/2012	4/5/2012	4/6/2012	4/9/2012	4/10/2012	4/11/2012		
Concentration (%)	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5	Trial 6	Trial 7	Average	Std. Dev
0	22.64516129	21.35484	22.54839	29.70968	32.77419	14.6129	21.32258	23.56682	5.979119
1	52806.95082	53883.93	52489.05	52140.72	51293.25	51676.46	50762.62	52150.43	1035.715
2	104744.7869	105706.1	103788.5	102741.4	102003.3	101140.6	99929.18	102864.8	2033.416
3	154584.1311	153249.6	152936.9	151886.7	149472.5	147191.6	147808.5	151018.6	2871.254
4	203104.5246	201554.9	200360.9	199133.4	195845.2	193225.4	193542.3	198109.5	3932.31
5	266329.1803	264341	262594.1	262052.7	256003.1	253680.3	254081	259868.8	5174.827
Propane at mass 14									
		Mass Abundance							
Date	4/3/2012	4/4/2012	4/5/2012	4/6/2012	4/9/2012	4/10/2012	4/11/2012		
Concentration (%)	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5	Trial 6	Trial 7	Average	Std. Dev
0	672.3225806	549.7097	634.0645	663.871	598.7742	632.6452	606.0323	622.4885	41.95839
1	2219.967213	2076.738	2108.377	2080.246	2083.082	1961.967	2030.049	2080.061	78.36142
2	3506.213115	3337.164	3419.492	3359.197	3234.164	3225.721	3270.426	3336.054	102.7251
3	4779.819672	4754.18	4650.902	4555.377	4518.098	4533.475	4455.902	4606.822	124.0032
4	6035.262295	6050.508	5904.443	5856.492	5712.377	5781.066	5663.361	5857.644	150.3602
5	7698.213115	7666.934	7685.541	7490.131	7281.164	7336.689	7210.902	7481.368	207.1175

Propane at mass 15									
		Mass Abundance							
Date	4/3/2012	4/4/2012	4/5/2012	4/6/2012	4/9/2012	4/10/2012	4/11/2012		
Concentration (%)	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5	Trial 6	Trial 7	Average	Std. Dev
0	111.2258065	146.4839	69.45161	128.5806	72.77419	92.16129	103.0968	103.3963	28.1909
1	4650.868852	5016.738	4821.623	4672.934	4725.344	4669.361	4698.279	4750.735	130.2733
2	9116.327869	9068.82	9163.754	9023.508	8765.197	8642.328	8733.77	8930.529	210.4729
3	13848.47541	13834.79	13437.43	13143.33	12903	13026.85	12856.31	13292.88	420.1147
4	18012.72131	18065.84	17704.26	17330.75	17005.16	17047.08	16864.82	17432.95	495.8832
5	23460.98361	23397.64	23084.46	22691.8	22201.97	22258.1	22032.52	22732.5	590.9198
Propane at mass 28									
		Mass Abundance							
Date	4/3/2012	4/4/2012	4/5/2012	4/6/2012	4/9/2012	4/10/2012	4/11/2012		
Concentration (%)	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5	Trial 6	Trial 7	Average	Std. Dev
0	7605.83871	6110.548	6891.613	7369.129	6826.484	6991.065	6647.677	6920.336	485.8092
1	45624.91803	43860.85	44342.95	43767.34	43035.67	42295.48	42534.3	43637.36	1147.063
2	80557.37705	78843.8	79297.7	78074.75	76145.31	75728.79	75835.93	77783.38	1910.271
3	114625.1803	114284.5	112715.4	110608.7	108846.3	109434.8	107855.3	111195.7	2699.831
4	147672.1311	147700.5	145656.7	142863.7	140505.2	141026.6	139618.6	143577.6	3420.915
5	190723.1475	190048.5	187875.7	185987.1	182152.4	182007.6	180177.8	185567.5	4194.209
Propane at mass 44									
		Mass Abundance							
Date	4/3/2012	4/4/2012	4/5/2012	4/6/2012	4/9/2012	4/10/2012	4/11/2012		
Concentration (%)	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5	Trial 6	Trial 7	Average	Std. Dev
0	353.9032258	318.1613	281.8065	314.6452	252.8387	269.9032	239.1613	290.0599	40.66241
1	13830.09836	13970.62	13664.87	13552.34	13326.33	13456.75	13132.84	13561.98	288.7688
2	27027.14754	27360.66	26658.36	26478.03	26364.2	26072.13	25674.89	26519.34	566.2571
3	39824.78689	39286.95	39354.1	39117.11	38451.02	37871.48	37958.03	38837.64	750.315
4	52288.39344	51521.97	51311.08	51137.84	50435.41	49521.05	49691.67	50843.92	1007.92
5	68511.34426	67922.75	67614.56	67201.31	65968.26	65209.57	65291.54	66817.05	1323.41
Carbon Dioxide at mass 44									
		Mass Abundance							
Date	4/3/2012	4/4/2012	4/5/2012	4/6/2012	4/9/2012	4/10/2012	4/11/2012		
Concentration (%)	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5	Trial 6	Trial 7	Average	Std. Dev
0	353.9032258	318.1613	281.8065	314.6452	252.8387	269.9032	239.1613	290.0599	40.66241
1	45437.2459	45098.89	44792.66	44358.82	43491.28	43696	43005.25	44268.59	900.5594
2	91539.14754	90626.89	90886.03	89105.7	87678.43	86907.28	86255.21	88999.81	2094.525
3	136207.7377	135544.7	134797.6	132896.8	130799.9	130180.7	128949.9	132768.2	2852.574
4	180881.8361	179670	178584.1	176246.6	173511.3	172446.4	171064.7	176057.9	3812.162
5	225133.1148	224100.7	222359.1	220054	215967.5	214485	212220.9	219188.6	5021.89

Carbon Dioxide at mass 28									
		Mass Abundance							
Date	4/3/2012	4/4/2012	4/5/2012	4/6/2012	4/9/2012	4/10/2012	4/11/2012		
Concentration (%)	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5	Trial 6	Trial 7	Average	Std. Dev
0	7605.83871	6110.548	6891.613	7369.129	6826.484	6991.065	6647.677	6920.336	485.8092
1	12135.22951	12018.8	11898.97	11955.34	11919.31	11730.31	11489.02	11878.14	211.0454
2	17770.22951	17672	17562.36	17492.72	17329.31	17202.89	16824.18	17407.67	321.7193
3	23198.16393	23231.34	23089.57	22848	22774.3	22462.16	22222.56	22832.3	381.1562
4	28633.96721	28761.7	28448.79	28178.23	27764.46	27654.95	27409.57	28121.67	521.9842
5	34075.67213	34076.46	33820.72	33402.75	33052.85	32828.85	32568.92	33403.75	609.4346
Methane at mass 15									
		Mass Abundance							
Date	4/3/2012	4/4/2012	4/5/2012	4/6/2012	4/9/2012	4/10/2012	4/11/2012		
Concentration (%)	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5	Trial 6	Trial 7	Average	Std. Dev
0	111.2258065	146.4839	69.45161	128.5806	72.77419	92.16129	103.0968	103.3963	28.1909
1	42655.08197	42233.97	41897.7	41388.72	40638.16	40642.49	40167.48	41374.8	929.8256
2	85473.83607	85336.26	84418.1	83401.44	81804.07	81513.7	81244.72	83313.16	1815.856
3	127619.8033	126962.1	125845.9	124379.4	122022.7	121274	121303.5	124201	2700.544
4	168937.9672	168015.7	166798.7	164687.7	161804.6	160454.3	160508.9	164458.3	3580.624
5	209107.9344	207995.8	206128.3	203612.3	200345.2	198679.1	198921.4	203541.4	4334.491
Methane at mass 14									
		Mass Abundance							
Date	4/3/2012	4/4/2012	4/5/2012	4/6/2012	4/9/2012	4/10/2012	4/11/2012		
Concentration (%)	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5	Trial 6	Trial 7	Average	Std. Dev
0	672.3225806	549.7097	634.0645	663.871	598.7742	632.6452	606.0323	622.4885	41.95839
1	8652.47541	8480.623	8491.721	8283.115	8191.393	8212	8102.984	8344.902	199.2266
2	16673.81967	16589.31	16440.41	16241.59	15953.52	15830.8	15777.11	16215.22	367.3919
3	24550.95082	24456.79	24269.38	23987.28	23513.84	23401.18	23291.8	23924.46	523.0463
4	32496.39344	32186.23	31937.44	31500.72	30972.46	30751.74	30630.95	31496.56	735.802
5	40104.2623	39712.66	39438.3	38934.56	38240.92	37934.3	37944.26	38901.32	883.3657
Nitrogen at mass 14									
		Mass Abundance							
Date	4/3/2012	4/4/2012	4/5/2012	4/6/2012	4/9/2012	4/10/2012	4/11/2012		
Concentration (%)	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5	Trial 6	Trial 7	Average	Std. Dev
0	672.3225806	549.7097	634.0645	663.871	598.7742	632.6452	606.0323	622.4885	41.95839
1	4101.819672	3997.246	3968.328	3996.529	3918.426	3860.787	3817.279	3951.488	95.16444
2	7692.704918	7623.984	7538.295	7499.098	7364.033	7309.066	7268.951	7470.876	161.433
3	11167.2623	11164.39	11082.46	10950.25	10788.3	10691.92	10650.57	10927.88	219.734
4	14788.80328	14740.39	14560.41	14474.02	14252.2	14013.08	13943.64	14396.08	336.1434
5	18334.81967	18139.28	18128.13	17952.66	17509.9	17394.33	17317.77	17825.27	410.0647

Nitrogen at mass 28									
		Mass Abundance							
Date	4/3/2012	4/4/2012	4/5/2012	4/6/2012	4/9/2012	4/10/2012	4/11/2012		
Concentration (%)	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5	Trial 6	Trial 7	Average	Std. Dev
0	7605.83871	6110.548	6891.613	7369.129	6826.484	6991.065	6647.677	6920.336	485.8092
1	50563.54098	49262.43	48878.43	49075.15	48366.69	47591.87	47154.75	48698.98	1131.997
2	94454.29508	93856.52	92909.64	92322.36	90975.21	90024.39	89281.18	91974.8	1946.893
3	137927.3443	137590.6	136293.8	134795.5	133258.5	131713.6	131041.8	134660.2	2759.47
4	181893.2459	180630	179202.1	177685	175243.5	173619.4	172396.1	177238.5	3599.793
5	225691.2787	224021	222061.1	219926	216625.3	214940.3	213616.3	219554.5	4639.757

Carbon Monoxide at mass 28									
		Mass Abundance							
Date	4/3/2012	4/4/2012	4/5/2012	4/6/2012	4/9/2012	4/10/2012	4/11/2012		
Concentration (%)	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5	Trial 6	Trial 7	Average	Std. Dev
0	7605.83871	6110.548	6891.613	7369.129	6826.484	6991.065	6647.677	6920.336	485.8092
1	50884.19672	50709.77	50316.46	50192.52	49099.93	48538.75	48091.8	49690.49	1105.953
2	97322.22951	96702.16	96093.64	95299.93	94002.1	92958	92185.18	94937.61	1942.406
3	142709.5082	142242.6	141013	139829.5	137859.1	136308.5	135587.7	139364.3	2836.556
4	188179.9344	187294.4	185860.2	183899.3	181195.5	179703.6	178438.3	183510.2	3816.034
5	233108.9836	232161.6	229667.7	227656.4	224352.5	222104.1	220824.1	227125.1	4839.411

From the test data presented in Table 4, the LQL was determined for each compound of interest. The LQL's are entered in Table 5 as Level 1. This completes the calibration range.

Table 5: Diablo RTGA Calibration Range

Species	Zero	Level 1	Level 2	Level 3	Level 4	Level 5
CO	0	1%	15%	35%	65%	85%
CO ₂	0	1%	10%	25%	40%	55%
CH ₄	0	1%	10%	15%	20%	25%
C ₃ H ₈	0	1%	5%	7.5%	12.5%	15%
H ₂	0	2%	5%	20%	35%	50%
N ₂	0	1%	20%	40%	60%	80%
O ₂	0	1%	5%	15%	20%	25%

3.2 Analyzer Performance Using Simulated Syngas

Following validation of the LQLs using the test method above, testing began to compare the performance of the other two analyzers to the Diablo. This testing was performed using a range of simulated syngas compositions. Due to limitations with the gas mixing equipment, the method used to create these mixtures was modified, and resulted in a slightly different composition for Test Mixture 3.

A 2-part procedure was used to produce the 7 component gas mixtures required to complete the Gasboard Test Plan. The procedure is performed in steps due to the fact that the Environics Gas mixing system only has 4 inlet ports. Figure 7 shows the schematic used to perform these tests.

Gasboard Testing- Gas Mixing System PFD

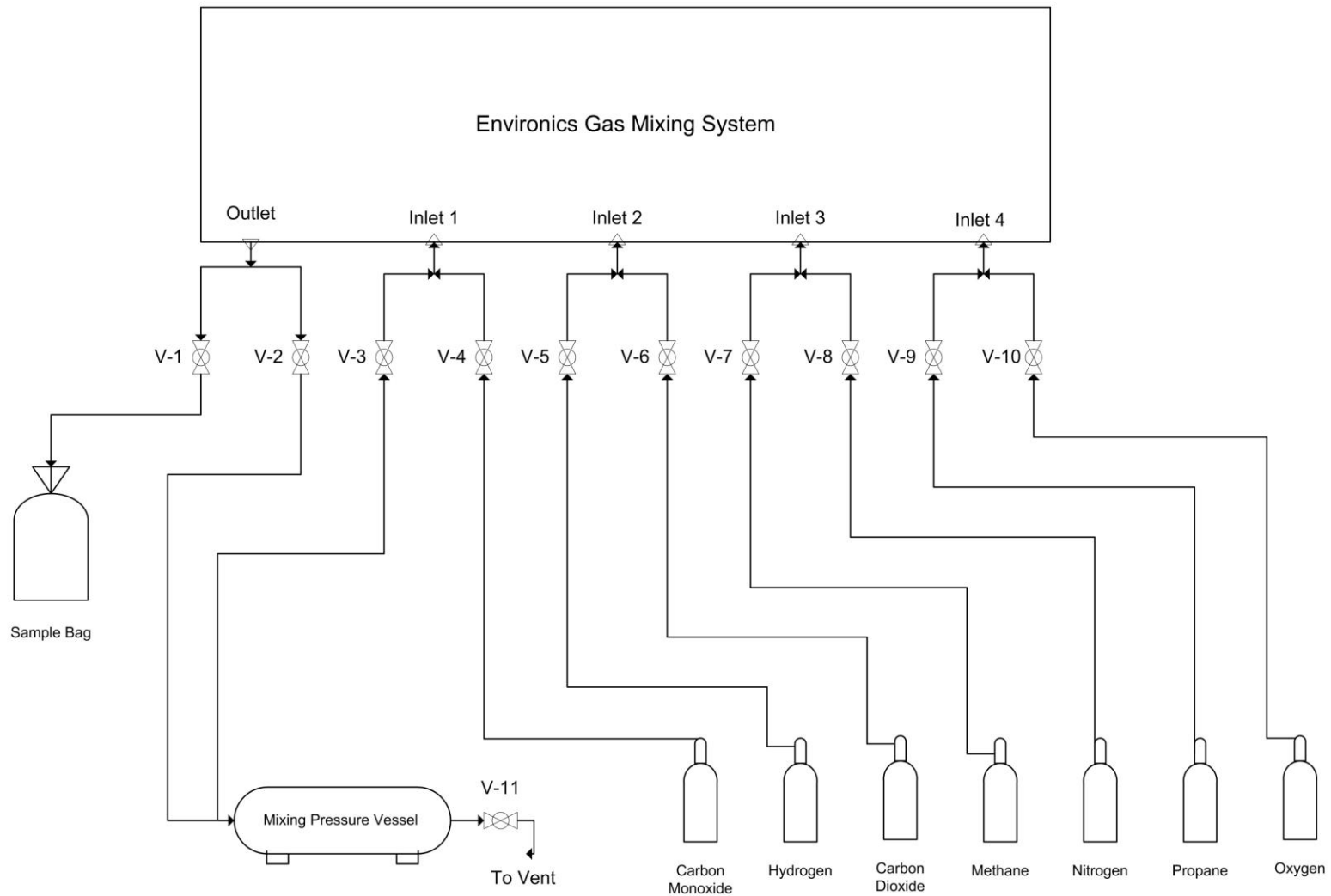


Figure 7: 2-Step Gas Mixing Schematic

The first step creates a mixture of the inert components for the overall test mixtures in Table 9. In order to do this, CO, CO₂, N₂, and O₂ are mixed through the mixing system and stored in a receiving pressure vessel. Referencing the Gas Mixing System PFD, the valves should be set to the positions shown in Table 6.

Table 6: Valve Positions for Step 1

Valve	Position
V-1	Closed
V-2	Open
V-3	Closed
V-4	Open
V-5	Closed
V-6	Open
V-7	Closed
V-8	Open
V-9	Closed
V-10	Open
V-11	Open for 5 minutes to purge, then Closed

In the Environics Software, the proper cylinders were assigned to the 4 ports. The delivery pressure for these cylinders was 50 psig. Table 7 gives the desired composition for each test mix.

Table 7: Step 1 Compositions for the 4 Test Simulated Syngas Mixtures

Species	Mix 1	Mix 2	Mix 3	Mix 4
CO	56.25%	50%	65.97%	34.29%
CO₂	25%	33.33%	27.78%	28.57%
N₂	18.75%	16.67%	3.82%	34.29%
O₂	0%	0%	2.43%	2.85%

After setting the gas compositions, the process of filling the receiver vessel started. Initially the vent valve on the receiver (V-11) is in the open position, to allow the air to be purged out of the system. After about 5 minutes of purging, V-11 is closed, and the receiver was pressurized to 40 psig. Then the program was stopped and step 2 was initiated.

Step 2 mixes the three remaining fuel components with the inert mixture prepared in Step 1. Referencing the Gas Mixing System PFD, the valve positions for this step are shown in Table 8.

Table 8: Valve Positions for Step 2

Valve	Position
V-1	Open
V-2	Closed
V-3	Open
V-4	Closed
V-5	Open
V-6	Closed
V-7	Open
V-8	Closed
V-9	Open
V-10	Closed
V-11	Closed

To configure the Environics Software, a "cylinder" was set up to represent the gas that was mixed in Step 1. The composition of the cylinder should be the same as the mixture specified in Table 7. This cylinder is connected to port 1, and set as the balance gas. The other fuel cylinders are set to the mixture compositions found in Table 9. The program is run on the Environics to fill the 25-L sample bag with the mixture for testing. Table 9 shows the component concentrations for the simulated mixtures.

Table 9: Simulated Syngas Compositions

Species	Mix 1	Mix 2	Mix 3	Mix 4
CO	45%	30%	47.5%	12%
CO₂	20%	20%	20%	10%
CH₄	5%	15%	5%	15%
C₃H₈	0%	5%	3%	10%
H₂	15%	20%	20%	40%
N₂	15%	10%	2.75%	12%
O₂	0%	0%	1.75%	1%

Once the 25-L tedlar bag was filled with the desired test composition, the sample was run on each analyzer. This eliminated any variability that could come from the gas mixing system. Each gas mix was analyzed five times on each analyzer, with each series of runs being performed on a different day. These data are used to compare the Model 3100P and the Model 7904C-RM to the Diablo RTGA, as well as generate data on how stable the instruments are over time. The results for each test mixture are presented in the following four tables.

Table 10: Results Summary for Test Mix 1

Summary Table	Test Mix 1						
		H2	CO	CO2	CH4	O2	CnHm (Propane)
Enviro-nics	Target Conc (%)	15.00	45.00	20.00	5.00	0.00	0.00
	Actual Conc (%)	14.99	44.96	19.98	4.98	0.00	0.00
	Std Dev	0.06	0.04	0.01	0.02	0.00	0.00
Diablo	Average Conc (%)	14.38	44.24	20.34	4.91	0.13	0.47
	Std Dev	0.20	0.42	0.25	0.04	0.08	0.01
	% Error from Target	4.04%	1.61%	1.77%	1.53%	NA	NA
NOVA	Average Conc (%)	14.22	46.24	19.49	5.06	NA	NA
	Std Dev	0.12	0.80	0.42	0.10	NA	NA
	% Error from Target	5%	3%	2%	2%	NA	NA
Gas Board	Average Conc (%)	13.53	43.81	19.96	5.96	0.29	-0.04
	Std Dev	0.58	0.76	0.27	0.20	0.05	0.00
	% Error from Target	9.71%	2.57%	0.10%	19.65%	NA	NA

Table 11: Results Summary for Test Mix 2

Summary Table	Test Mix 2						
		H2	CO	CO2	CH4	O2	CnHm (Propane)
Environics	Target Conc (%)	20.00	30.00	20.00	15.00	0.00	5.00
	Actual Conc (%)	19.97	29.98	19.99	14.98	0.00	4.99
	Std Dev	0.03	0.02	0.01	0.01	0.00	0.00
Diablo	Average Conc (%)	19.15	31.17	20.08	15.35	0.04	5.28
	Std Dev	0.13	0.26	0.16	0.15	0.02	0.27
	% Error from Target	4.08%	3.97%	0.45%	2.46%	NA	5.81%
NOVA	Average Conc (%)	37.83	36.98	19.13	-4.46	NA	NA
	Std Dev	0.12	1.01	0.60	0.01	NA	NA
	% Error from Target	89.43%	23.32%	4.32%	129.79%	NA	NA
Gas Board	Average Conc (%)	16.34	29.52	20.11	21.30	0.17	4.60
	Std Dev	0.34	0.29	0.17	0.27	0.02	0.08
	% Error from Target	18.19%	1.55%	0.59%	42.18%	NA	7.82%

Table 12: Results Summary for Test Mix 3

Summary Table	Test Mix 3						
		H2	CO	CO2	CH4	O2	CnHm (Propane)
Environics	Target Conc (%)	20.00	47.50	20.00	5.00	1.75	3.00
	Actual Conc (%)	19.98	47.49	20.00	5.10	1.74	2.99
	Std Dev	0.03	0.03	0.02	0.01	0.00	0.02
Diablo	Average Conc (%)	19.01	47.51	20.12	5.10	1.70	3.22
	Std Dev	0.26	0.50	0.12	0.06	0.03	0.03
	% Error from Target	4.89%	0.04%	0.59%	0.00%	2.39%	7.79%
NOVA	Average Conc (%)	46.75	56.24	19.76	9.79	NA	NA
	Std Dev	0.19	0.41	0.16	2.18	NA	NA
	% Error from Target	133.93%	18.43%	1.19%	92.14%	NA	NA
Gas Board	Average Conc (%)	17.91	47.18	20.12	6.70	1.76	2.77
	Std Dev	1.04	0.91	0.10	0.13	0.03	0.06
	% Error from Target	10.35%	0.64%	0.61%	31.42%	1.06%	7.05%

Table 13: Results Summary for Test Mix 4

Summary Table	Test Mix 4						
		H2	CO	CO2	CH4	O2	CnHm (Propane)
Enviroics	Target Conc (%)	40.00	12.00	10.00	15.00	1.75	10.00
	Actual Conc (%)	39.95	12.00	10.00	14.98	0.99	9.98
	Std Dev	0.02	0.02	0.02	0.02	0.01	0.01
Diablo	Average Conc (%)	38.73	13.91	9.89	16.01	0.98	10.81
	Std Dev	0.88	0.36	0.17	0.47	0.03	1.71
	% Error from Target	3.05%	15.92%	1.12%	6.93%	0.76%	8.25%
NOVA	Average Conc (%)	-9.50	15.75	9.09	-4.47	NA	NA
	Std Dev	0.09	0.77	0.34	0.01	NA	NA
	% Error from Target	123.78%	31.23%	9.11%	129.86%	NA	NA
Gas Board	Average Conc (%)	32.69	11.29	9.94	22.14	1.07	8.86
	Std Dev	0.56	0.30	0.10	0.52	0.03	0.14
	% Error from Target	18.18%	5.93%	0.67%	47.82%	7.52%	11.28%

4.0 Conclusions

There are a number of conclusions that can be drawn from the data collected above. On the first sample that does not contain oxygen or propane, all of the instruments perform satisfactorily. The NOVA analyzer and the Gasboard 3100P perform similarly to the Diablo. The Gasboard 3100P does exhibit the highest deviation from the target values, but this deviation is under 10%.

Once propane is introduced to the test mixtures, as it is in the other 3 mixtures, the NOVA analyzer does not perform accurately. This is due to the fact that propane creates an interference in the NDIR detector. The interference results in an error in the calculations for the other concentration values.

Although the Gasboard 3100P is designed to measure C_nH_m , the presence of propane also appears to decrease the accuracy of the measured values for hydrogen and methane. This analyzer detects the higher hydrocarbons by scanning an additional infrared wavelength. However the fact that it is not specific to propane is likely decreasing the accuracy of the concentration computations for the system. It may also be possible to improve the accuracy of the analyzer by performing the calibration with a mixture containing methane and propane at known concentrations, instead of using the single point calibration recommended by the manufacturer.

The analyzer with the best performance was the Diablo RTGA with the newly developed method. The only point that this analyzer measured a value that deviated more than 10% from the target value was in for carbon monoxide in test mix 4. This was the lowest CO concentration

tested, and indicates that some additional refinement of the CO correction factors at low levels is necessary.

5.0 Recommendations

From the testing performed, the Gasboard 3100P analyzer is suitable instrument for the real-time measurement of synthesis gas composition. It does not have the same level of accuracy as the Diablo RTGA, but it is more robust than the Diablo, and therefore more useful in a process environment. To improve the accuracy of the analyzer, it is recommended that a calibration be performed with a mixture containing methane and propane if significant quantities of higher hydrocarbons are expected in the syngas. The performance of the new calibration technique should be validated with additional testing.

The NOVA analyzer is suitable for real time syngas analysis provided very low levels of higher hydrocarbons are expected. If higher hydrocarbons are present in significant quantities (over 0.5%) the analyzer is not accurate. Using this analyzer if the higher hydrocarbon content has not been validated through a different external analysis method is not recommended.

The newly developed method for the Diablo RTGA makes it suitable to analyze most syngas compositions. Some additional testing with the CO correction factors be performed at concentrations below 10% to improve the accuracy across the full range of syngas compositions is recommended.

6.0 Works Cited

National Institute of Standards and Technology. (2011). *NIST Standard Reference Database Number 69*. Retrieved January 16, 2012, from NIST Chemistry WebBook: webbook.nist.gov/chemistry

Weast, Robert C. ed. (1982). *CRC Handbook of Chemistry and Physics, 62nd Edition*. Boca Raton, FL: CRC Press Inc.