Casting Emission Reduction Program

Prepared by:
TECHNIKON LLC
5301 Price Avenue ▼ McClellan, CA, 95652 ▼ (916) 929-8001
www.technikonllc.com

US Army Contract DAAE 30-02-C-1095
FY 2002 Tasks

Real Time Emission Measurement

Test #1409-240

Originally Published
31 July 2003
This document has been revised for public distribution.

United States Environmental Protection Agency

CISA

AMERICAN FOUNDRY SOCIETY, INC.

UNITED STATES COUNCIL FOR AUTOMOTIVE RESEARCH

USCAR

DAIMLERCHRYSLER Ford Motor Company General Motors

THIS PAGE INTENTIONALLY LEFT BLANK

Real Time Emission Measurement

1409-240

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

VP Measurement Technologies: *//Original Signed//* _____
Clifford Glowacki, CIH — Date

VP Operations: *//Original Signed//* _____
George Crandell — Date

President: *//Original Signed//* _____
William Walden — Date

THIS PAGE INTENTIONALLY LEFT BLANK

TABLE OF CONTENTS

Executive Summary 1
1.0 Introduction 3
1.1 Background 3
1.2 CERP Objectives 3
2.0 Research Objectives and Methodology 5
2.1 Research Objectives 5
2.0 Experimental Methodology 5
3.0 Results and Discussion 6

LIST OF TABLES

Table 1 Method 25A Results 6
Table 2 Method 25A Results Adjusted for Mol.Wt. and Percent Carbon 7
Table 3 Relative Response Factors 8
Table 4 Corrected Relative Response Factors 9
Table 5 Test Results with Different Relative Response Factors Applied 10

APPENDICES

Appendix A Method 25A FID Charts 11
Appendix B Glossary 19

THIS PAGE INTENTIONALLY LEFT BLANK

Executive Summary

US EPA Method 25A, Total Gaseous Organic Concentration, is commonly specified for testing to determine the Volatile Organic Compound (VOC) concentration being emitted by a facility. In this test, source emissions are pumped through a flame ionization detector (FID) that has been standardized (calibrated). The objective of this work was to begin the development of an empirical database relating the molecular structure of a volatile organic compound (VOC) with its response in a flame ionization detector. The empirical data may itself be used to correct the FID response, however, it would be most beneficial if an individual compound's response could be calculated for its molecular structure. This could then be used to calculate the relative response of mixtures if the weight percentage of each compound in the mixture was known. Standard analytical techniques such as gas chromatography, gas chromatography coupled with mass spectrometry, liquid chromatography, and liquid chromatography coupled with mass spectrometry can characterize all but the most complex mixtures quickly.

For this work, a FID was set up and calibrated in accordance with Method 25A with propane in air. Propane was used because it the most common standard gas currently used during source compliance tests. A series of aliphatic and aromatic hydrocarbons standards and one (1) tertiary amine standard of known concentrations were then analyzed by the FID in replicate. Average responses were converted to relative response factors with propane assigned the value of one (1.00). The table below shows these relative response factors (RRF). Values greater than one (1.00) show the magnitude of the over estimation (positive bias) if the samples gas streams is comprised the specific compound listed. Values less than one (1.00) show a corresponding under estimation.

Compound	Response Relative to Propane
Methane	0.36
Ethane	0.71
Propane	1.05
Butane	1.41
Pentane	1.75
Hexane	2.08
Benzene	2.12
Toluene	2.39
Xylene	2.44
Ethylbenzene	2.96
Styrene	2.97
Triethylamine	1.29

Additional work must be conducted to determine the interactions in mixtures, if any, and to expand the empirical RRF database to include other compounds of interest to the metal casting industry such as phenols, alcohols, other aliphatic amines, aromatic amines, aldehydes, esters, and carboxylic acids.

THIS PAGE INTENTIONALLY BLANK.

1.0 Introduction

1.1 Background

Technikon LLC is a privately held contract research organization located in McClellan, California, a suburb of Sacramento. Technikon offers emissions research services to industrial and government clients specializing in the metal casting and mobile emissions areas. Technikon operates the Casting Emission Reduction Program (CERP). CERP is a cooperative initiative between the Department of Defense (US Army) and the United States Council for Automotive Research (USCAR). Its purpose is to evaluate alternative casting materials and processes that are designed to reduce air emissions and/or produce more efficient casting processes. Other technical partners directly supporting the project include: the American Foundry Society (AFS); the Casting Industry Suppliers Association (CISA); the US Environmental Protection Agency (US EPA); and the California Air Resources Board (CARB).

1.2 CERP Objectives

The primary objective of CERP is to evaluate the impact of new materials, equipment, and processes on airborne emissions from the production of metal castings. To accomplish this objective, the Technikon facility has been created to evaluate alternate materials and production processes designed to achieve significant airborne emission reductions, especially for organic Hazardous Air Pollutants (HAPs). HAP emissions reduction from the alternative materials, equipment and production processes is expressed as a comparison to similar emissions from a baseline or reference test. The facility has two principal testing arenas: a Pre-Production Foundry designed to measure airborne emissions from individually poured molds, and a Production Foundry designed to measure air emissions in a continuous, full-scale production process. Each of these testing arenas has been specifically designed to facilitate the collection and evaluation of airborne emissions, and associated process data. Candidate materials and/or processes are screened for emission reductions in the Pre-production Foundry and then further evaluated in the Production Foundry. The data collected during the various testing projects are evaluated to determine the impact of the alternate materials and/or processes on airborne emissions as well as on the quality and economics of casting and core manufacture. These alternate materials, equipment, and processes may need to be further adapted and defined so that they will integrate into current commercial green sand casting facilities smoothly and with minimal capital expenditure. These efforts are supported by a well-equipped analytical laboratory equipped with gas chromatographic and gas chromatographic/mass spectrometer systems that are used for method validation and method development efforts.

THIS PAGE INTENTIONALLY LEFT BLANK

2.0 Research Objectives and Methodology

2.1 Research Objectives

The objectives of this Phase 1 research were three fold:

1. Begin the development of an empirical database of flame ionization detector relative response factors that can be used to correct US EPA Method 25A (TGOC) data from results based on propane to a basis that more accurately represents the chemical composition of the emission samples.
2. Compare recent TGOC propane basis results from core mixing and pouring/cooling/shakeout tests with results adjusted for the determined relative response factors that best represent the chemical composition of the emissions.
3. Conduct a preliminary evaluation of the relationship(s) between the relative response factor results and each compounds molecular characteristics such as molecular weight, weight percentage carbon, and carbon number.

2.0 Experimental Methodology

EPA Protocol 1 gas standards of consisting of each of several aliphatic hydrocarbons and several aromatic hydrocarbons were purchased for this work. Concentrations of the compounds in the standards ranged from approximately ten (10) parts per million by volume (ppmv) to two hundred (200) ppmv. The balance of the gas in each standard was nitrogen. An existing aliphatic amine standard was also analyzed to begin the evaluation of the FID response effect of atoms other that carbon and hydrogen.

The flame ionization detector was calibrated in accordance with US EPA Method 25A with Protocol 1 standards containing approximately 10, 100, 300, and 1000 ppmv propane in air. The gas containing each test compound was sampled several times by the FID. Each sampling run consisted of calibration verification with the 100-ppmv propane in air or 10-ppmv propane in air. The test gas was then introduced into the FID until the response remained stable for at least three minutes. "Zero" air was then introduced into the FID until the response returned to zero. This procedure was repeated at least three (3) times or until three successive runs were recorded with a percent relative standard deviation of less 5.0% as required for a Method 25A system calibration check,

3.0 Results and Discussion

Table 1 shows the individual run results for each of the compounds evaluated. Also shown are the known concentration of the test gas, the average results, standard deviation, and percent relative standard deviation. The repeatability of the results is within the Method 25A requirements of 5% RSD. The results also show that more variability in the triethylamine results than in the aliphatic and aromatic hydrocarbon results. This is probably due to the very polar nature of the tertiary amine.

Table 1 Method 25A Results

Compound	Known Conc. (ppmv)	Run 1 Test Results (ppmv)	Run 2 Test Results (ppmv)	Run 3 Test Results (ppmv)	Ave Test Results (ppmv)	Standard Deviation	% RSD
Methane	190.00	68.61	68.61	68.61	68.58	0.02	0.04
Ethane	190.00	134.64	134.59	134.58	134.60	0.03	0.03
Propane	190.00	198.90	199.01	199.12	199.01	0.11	0.06
Butane	190.00	268.92	268.82	268.69	268.81	0.12	0.04
Pentane	189.70	331.31	331.32	331.24	331.29	0.04	0.01
Hexane	190.00	395.78	395.81	395.56	395.72	0.14	0.04
Benzene	190.30	404.55	404.09	404.46	404.37	0.24	0.06
Toluene	10.00	23.90	23.91	23.89	23.90	0.01	0.06
Xylene	9.60	23.39	23.41	23.43	23.41	0.02	0.10
Ethylbenzene	9.00	26.67	26.66	26.61	26.65	0.03	0.11
Styrene	9.00	26.67	26.75	26.80	26.74	0.07	0.24
Triethylamine	8.10	10.07	10.54	10.64	10.42	0.31	2.96

Table 2 shows the results of adjusting the average test results with each compounds molecular weight and percent carbon content. Both of these adjustments produced factors that are concentration dependent. To be useable in real world testing, the relationship between molecular structure and FID response cannot be concentration dependent since concentration can/will vary with process variability.

Table 2 Method 25A Results Adjusted for Mol.Wt. and Percent Carbon

Compound	Molecular Weight	Percent Carbon	Ave Test Results (ppmv)	Ave Test Results Adjusted for Mol. Wt.	Ave Test Results Adjusted for % Carbon
Methane	16	75.0	68.58	4.29	91.44
Ethane	30	80.0	134.60	4.49	168.26
Propane	44	81.8	199.01	4.52	243.23
Butane	58	82.8	268.81	4.63	324.81
Pentane	72	83.3	331.29	4.60	397.55
Hexane	86	83.7	395.72	4.60	472.66
Benzene	78	92.3	404.37	5.18	438.06
Toluene	92	91.3	23.90	0.26	26.18
Xylene	106	90.6	23.41	0.22	25.85
Ethylbenzene	106	90.6	26.65	0.25	29.42
Styrene	104	92.3	26.74	0.26	28.97
Triethylamine	101	71.3	10.42	0.10	14.61

Table 3 shows the FID response for each compound relative to the propane in air calibration standard. The table also shows these relative response factors (RRF) for each compound adjusted for the compound molecular weight, percentage carbon, and carbon number. All three relationships show similar trends with the adjustment for carbon number providing the best factors for the aliphatic hydrocarbons (methane through hexane). The RRF for the aromatic hydrocarbons shows an apparent trend of reduced response from benzene through xylene. This may be due to the addition of one methyl group to the benzene to yield toluene and a second methyl group to yield xylene. The trend is reversed with ethylbenzene and styrene. This reversal may be due to the ethyl group and ethylene groups on the two compounds, respectively. Finally, the triethylamine response is much lower than would be expected of a molecule containing six (6) carbon atoms. This might be due to the strong electro negative nature of amines.

Table 3 Relative Response Factors

Compound	Number of Carbon Atoms	Molecular Weight (Mol. Wt.)	Percent Carbon	Relative Response Factor (C3 = 1.00)	Adjusted for Mol. Wt.	Adjusted for % Carbon	Adjusted for Carbon Number
Methane	1	16	75.0	0.36	2.26	0.48	1.08
Ethane	2	30	80.0	0.71	2.36	0.89	1.06
Propane	3	44	81.8	1.05	2.38	1.28	1.05
Butane	4	58	82.8	1.41	2.44	1.71	1.06
Pentane	5	72	83.3	1.75	2.43	2.10	1.05
Hexane	6	86	83.7	2.08	2.42	2.49	1.04
Benzene	6	78	92.3	2.12	2.72	2.30	1.06
Toluene	7	92	91.3	2.39	2.60	2.62	1.02
Xylene	8	106	90.6	2.44	2.30	2.69	0.91
Ethylben-zene	8	106	90.6	2.96	2.79	3.27	1.11
Styrene	8	104	92.3	2.97	2.86	3.22	1.11
Triethyl-amine	6	101	71.3	1.29	1.27	1.80	0.64

The relative response factor of the propane in nitrogen test gas (1.05) shown in Table 3 was unexpected. This suggests that a possible positive bias exists if calibration gases are prepared in nitrogen instead of air and are used for compliance testing. Table 4 shows the RRF of each compound corrected for the apparent positive bias caused by the nitrogen balance in the test gases and then adjusted for carbon number. The same conclusions can be drawn from this table as were drawn from Table 3. The clustering of the aliphatic hydrocarbon RRF around 1.00 is what would be theoretically expected.

Table 4 Corrected Relative Response Factors

Compound	Number of Carbon Atoms	Relative Response Factor (C3 = 1.00)	Adjusted for Carbon Number	RRF Corrected for Apparent N_2 Bias	Adjusted for Carbon Number
Methane	1	0.36	1.08	0.34	1.03
Ethane	2	0.71	1.06	0.68	1.01
Propane	3	1.05	1.05	1.00	1.00
Butane	4	1.41	1.06	1.35	1.01
Pentane	5	1.75	1.05	1.67	1.00
Hexane	6	2.08	1.04	1.99	0.99
Benzene	6	2.12	1.06	2.03	1.01
Toluene	7	2.39	1.02	2.28	0.98
Xylene	8	2.44	0.91	2.33	0.87
Ethylbenzene	8	2.96	1.11	2.83	1.06
Styrene	8	2.97	1.11	2.84	1.06
Triethylamine	6	1.29	0.64	1.23	0.61

Table 5 shows the effect of different RRFs applied to the Method 25A results from several tests conducted at CERP. Results from the CERP tests have been based on propane calibration because propane has been the predominant calibrant used by the foundry industry for this method. The proposed MACT standard requires the use of hexane as a calibration standard. As seen in the TGOC as hexane column below, this change of calibrant will reduce the apparent VOC (TGOC) emissions from a facility approximately two (2) fold. Calibration of the FID with the ethylbenzene, a compound that is more similar in molecular structure to the predominant foundry emissions than hexane, would reduce the measured VOCs even more.

Table 5 Test Results with Different Relative Response Factors Applied

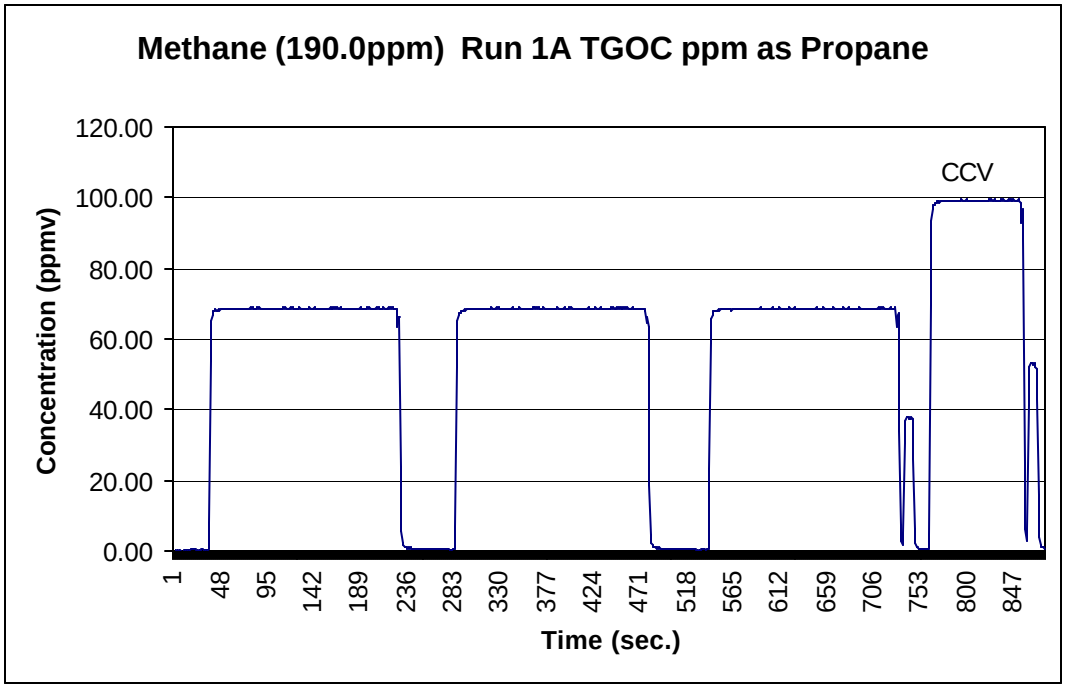
Test Type	TGOC as Propane	TGOC as Hexane	TGOC As Ethylbenzene
Phenolic Urethane Mixing	4147	1991	1401
Phenolic Urethane Mixing	2861	1374	966
Phenolic Urethane Mixing	693	333	234
PU No-Bake Pouring/cooling	93	44	31
PU Pouring/cooling/shakeout	59	28	20
PU Pouring/cooling/shakeout	35	17	12

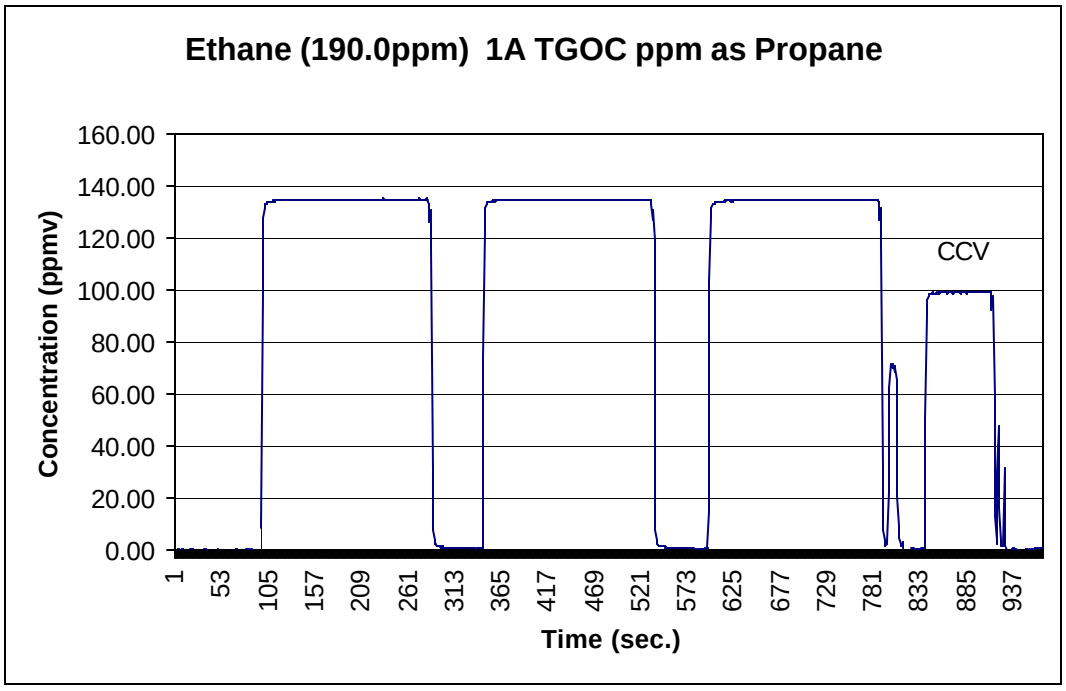
Appendix A shows the TGOC (THC) charts for each of the test runs. The accompanying continuous calibration verification (CCV) response is labeled on each chart.

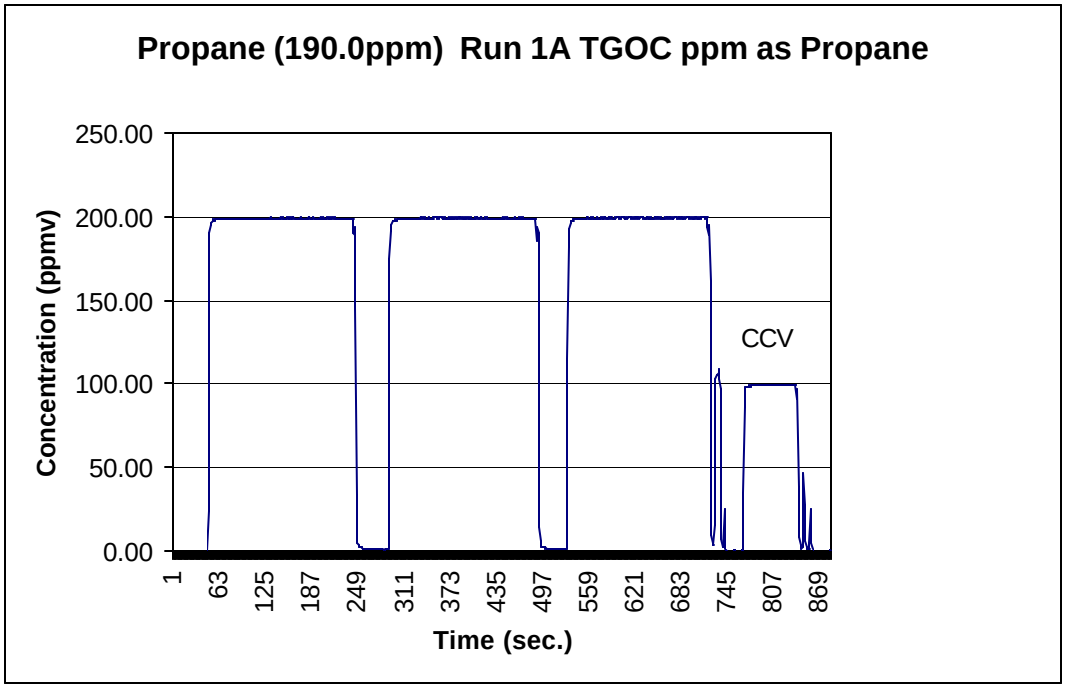
Future evaluation of the effect of molecular structure on FID response should include an expanded list of test compounds comprised of those of most interest to the metal casting industry such as phenols, aliphatic and aromatic amines, esters, alcohols, and carboxylic acids. A study of the effect of nitrogen instead of air as the calibration standard balance gas, should also be conducted.

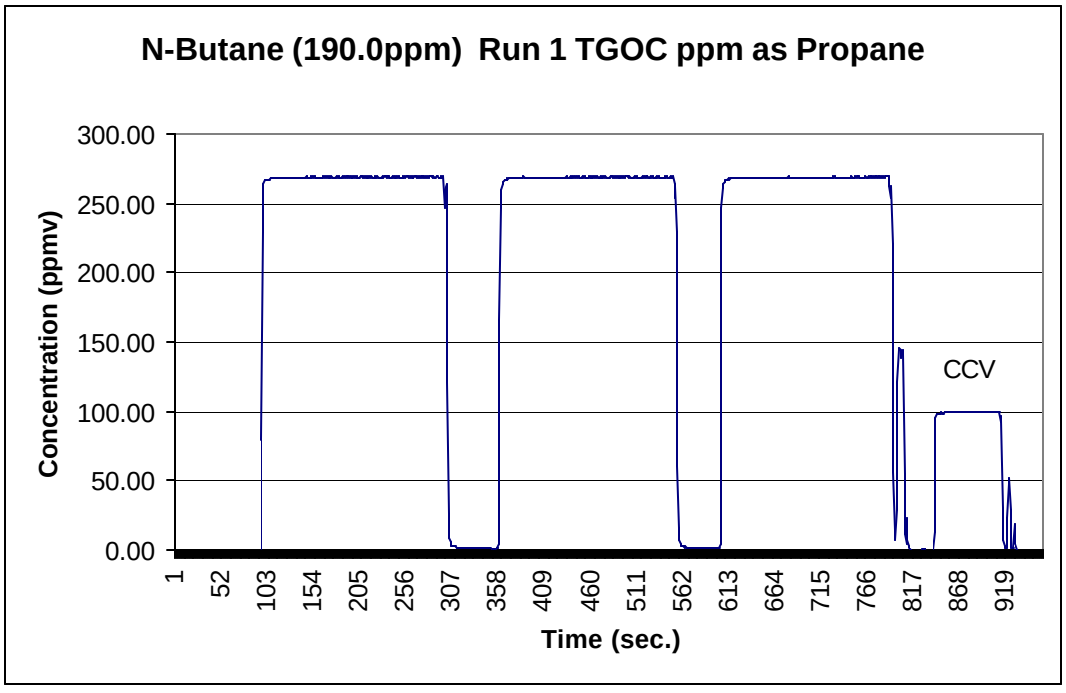
APPENDIX A METHOD 25A FID CHARTS

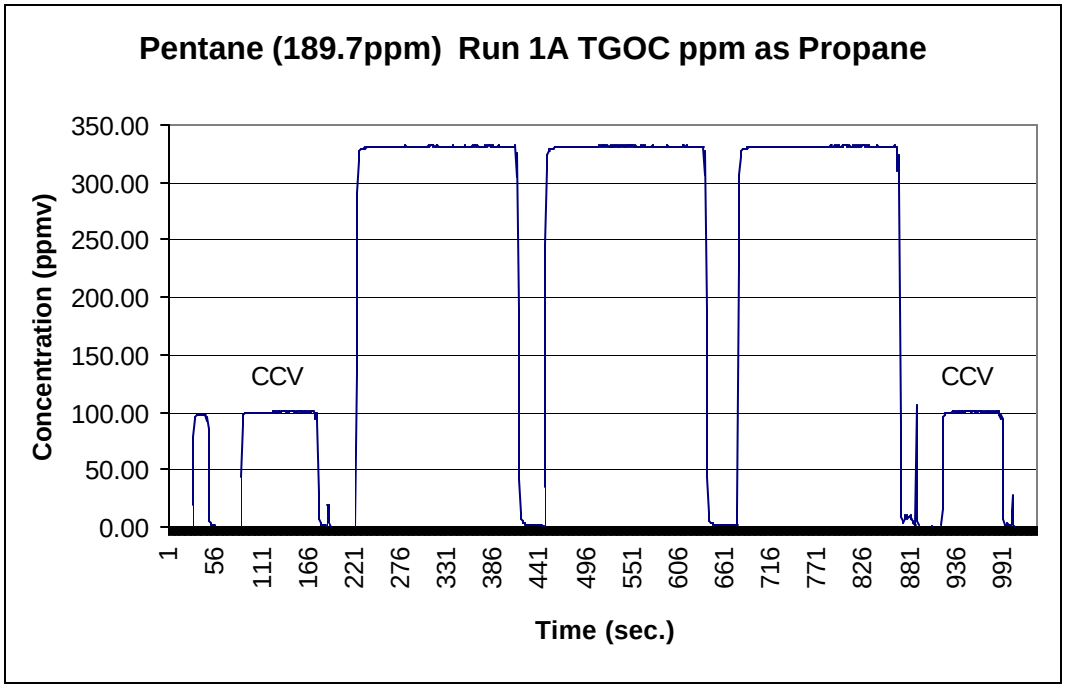
THIS PAGE INTENTIONALLY LEFT BLANK

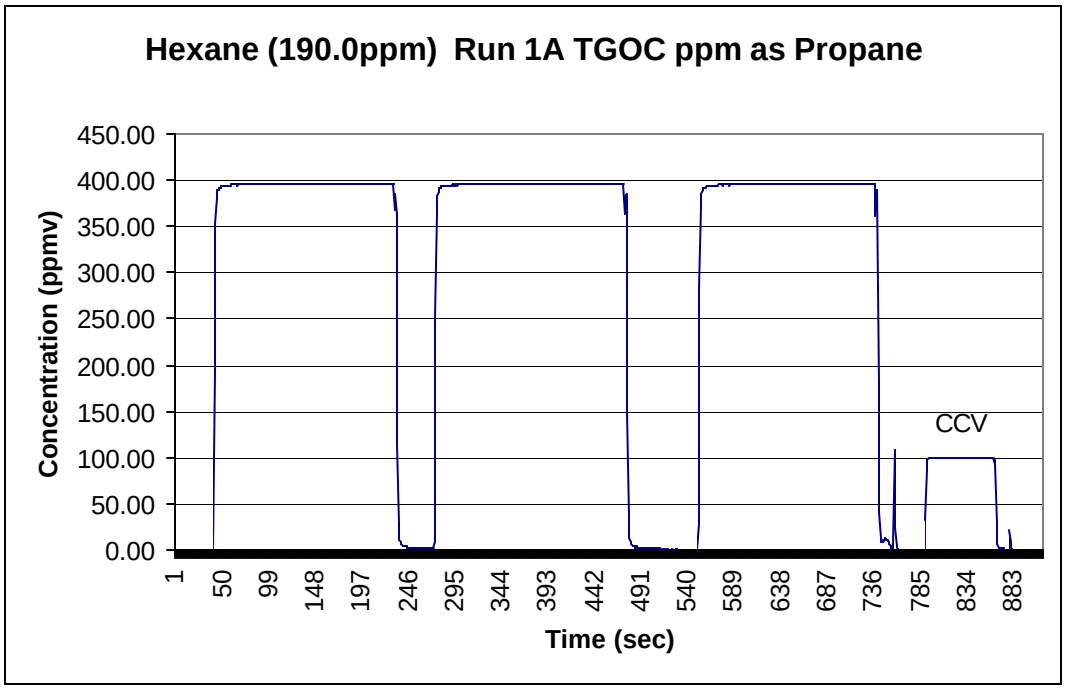

Methane (190.0ppm) Run 1A TGOC ppm as Propane
Concentration (ppmv)
120.00
100.00
80.00
60.00
40.00
20.00
0.00
CCV
1
48
95
142
189
236
283
330
377
424
471
518
565
612
659
706
753
800
847
Time (sec.)

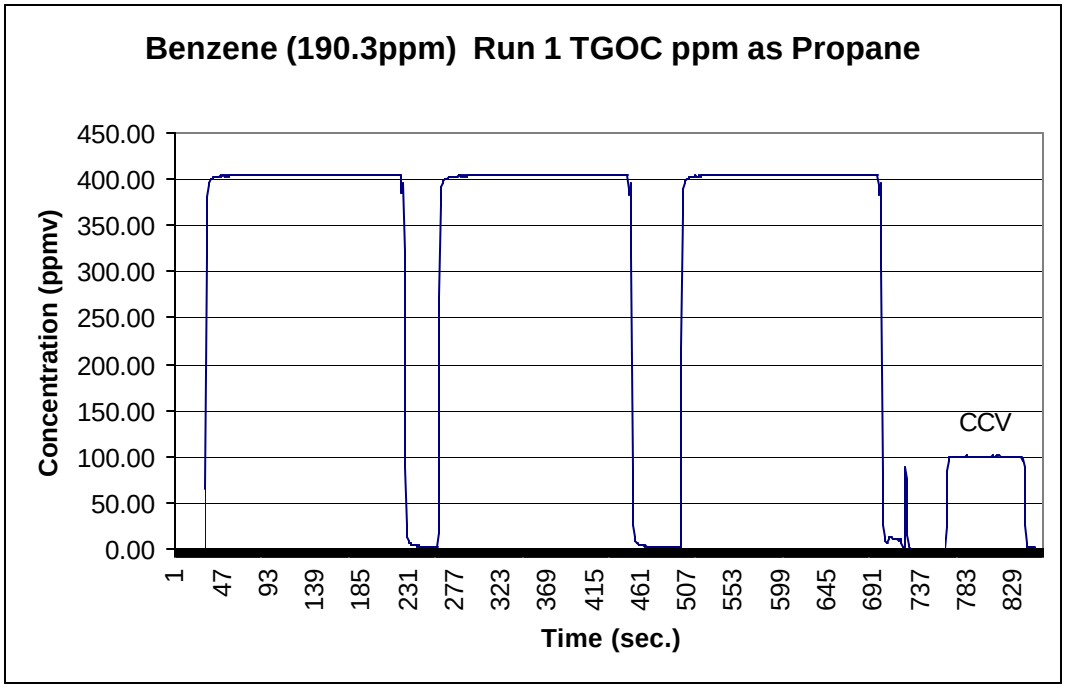

Ethane (190.0ppm) 1A TGOC ppm as Propane
Concentration (ppmv)
160.00
140.00
120.00
100.00
80.00
60.00
40.00
20.00
0.00
CCV
1
53
105
157
209
261
313
365
417
469
521
573
625
677
729
781
833
885
937
Time (sec.)

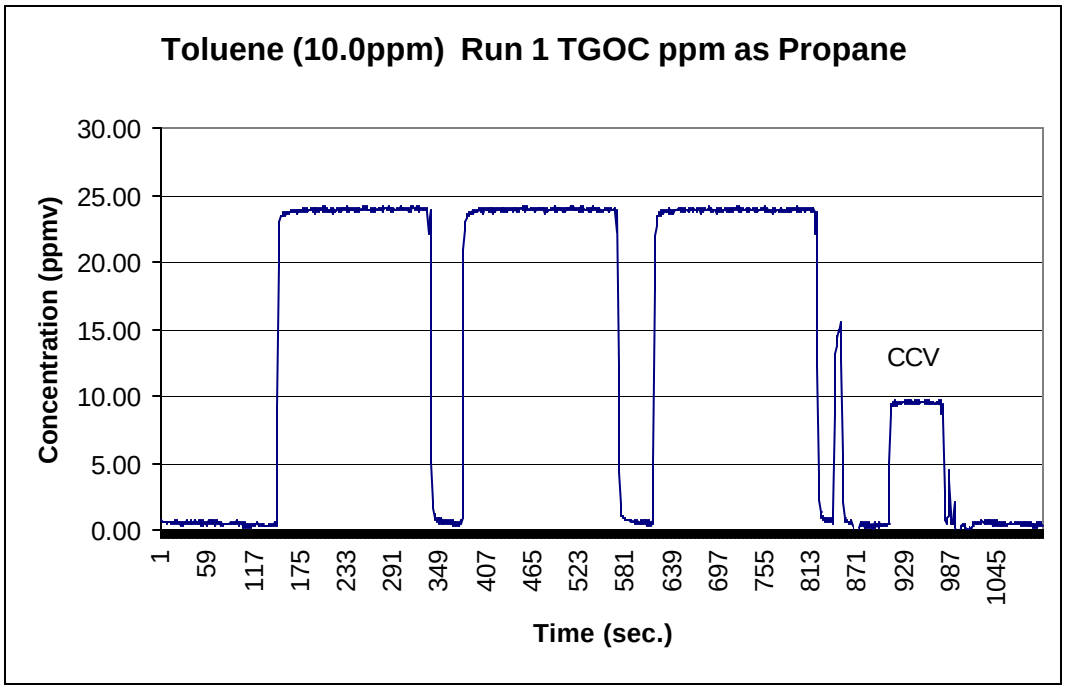

Propane (190.0ppm) Run 1A TGOC ppm as Propane
Concentration (ppmv)
250.00
200.00
150.00
100.00
50.00
0.00
CCV
1
63
125
187
249
311
373
435
497
559
621
683
745
807
869
Time (sec.)

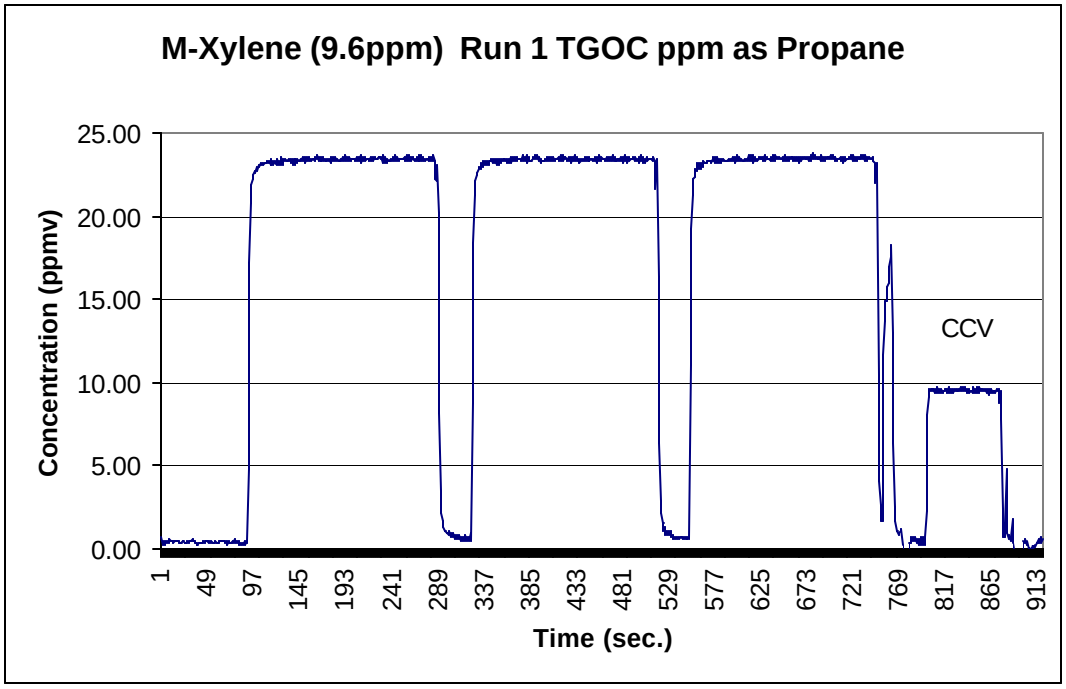

N-Butane (190.0ppm) Run 1 TGOC ppm as Propane
Concentration (ppmv)
300.00
250.00
200.00
150.00
100.00
50.00
0.00
CCV
1
52
103
154
205
256
307
358
409
460
511
562
613
664
715
766
817
868
919
Time (sec.)

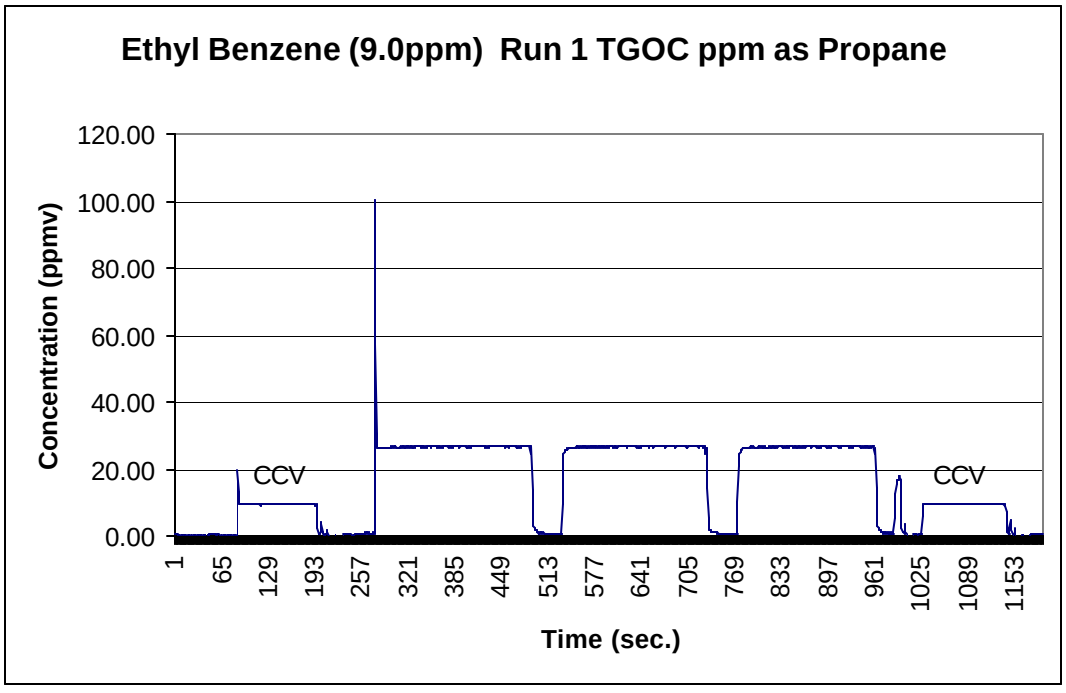

Pentane (189.7ppm) Run 1A TGOC ppm as Propane
Concentration (ppmv)
350.00
300.00
250.00
200.00
150.00
100.00
50.00
0.00
CCV
CCV
1
56
111
166
221
276
331
386
441
496
551
606
661
716
771
826
881
936
991
Time (sec.)

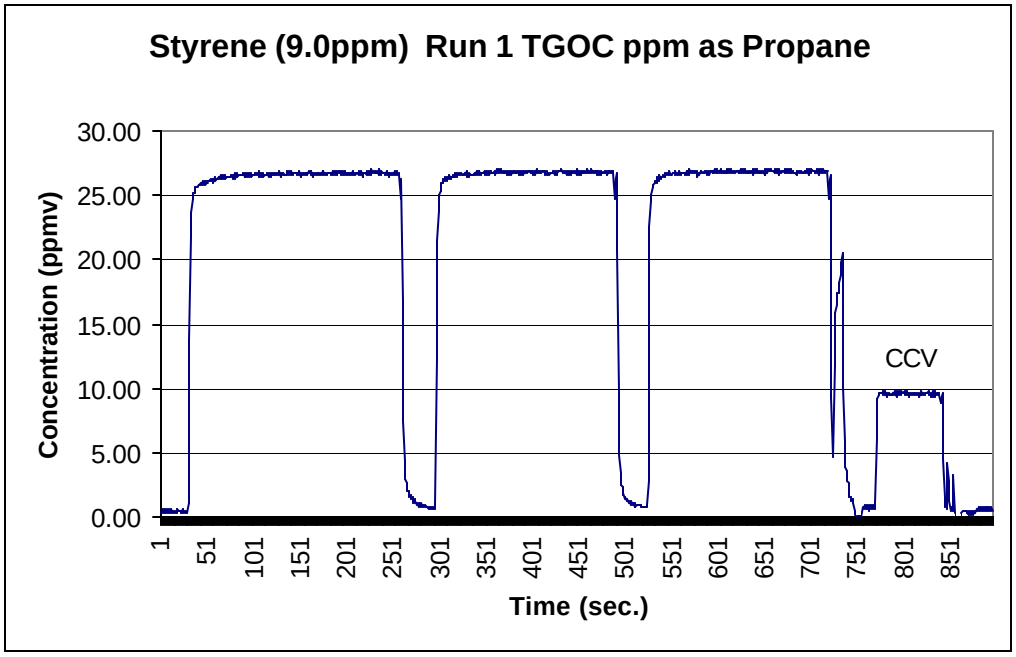

Hexane (190.0ppm) Run 1A TGOC ppm as Propane
Concentration (ppmv)
450.00
400.00
350.00
300.00
250.00
200.00
150.00
100.00
50.00
0.00
CCV
1
50
99
148
197
246
295
344
393
442
491
540
589
638
687
736
785
834
883
Time (sec)

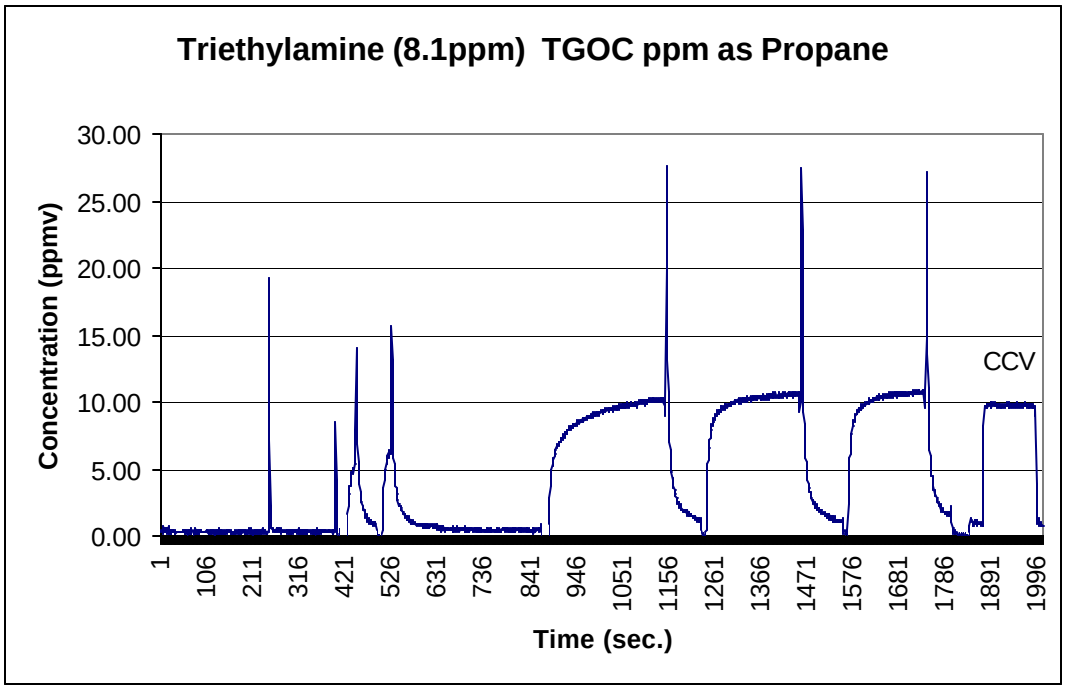

Benzene (190.3ppm) Run 1 TGOC ppm as Propane
Concentration (ppmv)
450.00
400.00
350.00
300.00
250.00
200.00
150.00
100.00
50.00
0.00
1
47
93
139
185
231
277
323
369
415
461
507
553
599
645
691
737
783
829
Time (sec.)
CCV


Toluene (10.0ppm) Run 1 TGOC ppm as Propane
Concentration (ppmv)
30.00
25.00
20.00
15.00
10.00
5.00
0.00
1
59
117
175
233
291
349
407
465
523
581
639
697
755
813
871
929
987
1045
Time (sec.)
CCV


M-Xylene (9.6ppm) Run 1 TGOC ppm as Propane
Concentration (ppmv)
25.00
20.00
15.00
10.00
5.00
0.00
CCV
1
49
97
145
193
241
289
337
385
433
481
529
577
625
673
721
769
817
865
913
Time (sec.)


Ethyl Benzene (9.0ppm) Run 1 TGOC ppm as Propane
Concentration (ppmv)
120.00
100.00
80.00
60.00
40.00
20.00
0.00
CCV
CCV
1
65
129
193
257
321
385
449
513
577
641
705
769
833
897
961
1025
1089
1153
Time (sec.)


Styrene (9.0ppm) Run 1 TGOC ppm as Propane
Concentration (ppmv)
30.00
25.00
20.00
15.00
10.00
5.00
0.00
1
51
101
151
201
251
301
351
401
451
501
551
601
651
701
751
801
851
Time (sec.)
CCV


Triethylamine (8.1ppm) TGOC ppm as Propane
Concentration (ppmv)
30.00
25.00
20.00
15.00
10.00
5.00
0.00
1
106
211
316
421
526
631
736
841
946
1051
1156
1261
1366
1471
1576
1681
1786
1891
1996
Time (sec.)
CCV

APPENDIX B GLOSSARY

THIS PAGE INTENTIONALLY LEFT BLANK

Glossary

ACFM	Actual Cubic Feet Per Minute
BO	Based on ( ).
BOS	Based on Sand.
HAP	Hazardous Air Pollutant defined by the 1990 Clean Air Act Amendment
HC as Hexane	Calculated by the summation of all area between elution of Hexane through the elution of Hexadecane. The quantity of HC is performed against a five-point calibration curve of Hexane by dividing the total area count from C6 through C16 to the area of Hexane from the initial calibration curve.
I	Invalid, Data rejected based on data validation considerations
NA	Not Applicable
ND	Non-Detect
NT	Not-Done, Lab testing was not done
POM	Polycyclic Organic Matter (POM) including Naphthalene and other compounds that contain more than one benzene ring and have a boiling point greater than or equal to 100 degrees Celsius.
PPMV	Parts Per Million by Volume
TGOC	Total Gaseous Organic Carbon
TGOC as Propane	Weighted to the detection of more volatile hydrocarbon species, beginning at C1 (methane), with results calibrated against a three-carbon alkane (propane).
VOC	Volatile Organic Compound
% RSD	Percentage Standard Deviation
RRF	Relative Response Factor
CCV	Continuous Calibration Verification