



Casting Emission Reduction Program

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US Army Contract DAAE 30-02-C-1095

FY 2003 Tasks

Draft of Real Time Emission Measurement

Technikon # 1410-240

August 2004

(revised for public distribution)



UNITED STATES COUNCIL FOR AUTOMOTIVE RESEARCH

DAIMLERCHRYSLER *Ford Motor Company* General Motors

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Technikon # 1410-240

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

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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 continue 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 were 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.

In this continuation of the effort initiated under the FY 2002 tasks, subtask 2.4, 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 certified gas standards comprised of several different chemical families were analyzed by the FID in replicate. Average responses were converted to relative response factors with propane assigned the value of one (1.00). The response factors were also adjusted to a hexane basis as a convenience for readers who may be dealing with the recently published Iron and Steel Foundry MACT. Table 1 shows all of the relative response factors (RRF) that have been determined. Results contained in last years report are in *bold italics*. Values greater than one (1.00) show the magnitude of the over estimation (positive bias) if the sampled gas stream is comprised of the specific compound listed. Values less than one (1.00) show a corresponding under estimation.

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, naphthalenes, and carboxylic acids and additional alcohols, aromatic amines, aldehydes and esters.

Table 1 Compound Relative Response Factors

Compound	Relative Response Factor	
	(C3 = 1.00)	(C6 = 1.00)
Methane	0.34	0.17
Ethane	0.68	0.34
Ethylene	0.66	0.33
Acetylene	0.66	0.33
Propane	1.00	0.50
Propylene	0.97	0.49
Butane	1.35	0.68
1,3-Butadiene	1.30	0.65
Pentane	1.67	0.84
Hexane	1.99	1.00
Cyclohexane	1.95	0.98
Benzene	2.03	1.02
Toluene	2.28	1.15
Xylene	2.33	1.17
Ethylbenzene	2.83	1.42
Styrene	2.84	1.43
Trimethylbenzene	2.74	1.38
Triethylamine	1.23	0.62
Pyridine	1.44	0.73
Aniline	1.12	0.56
N,N-Dimethylaniline	1.10	0.55
Acetone	0.69	0.35
Methylethylketone	1.00	0.50
Methylisobutylketone	1.68	0.84
Diethylether	0.99	0.50
1,4-Dioxane	0.67	0.34
Methanol	0.24	0.12
Ethanol	0.45	0.23
Isopropanol	0.74	0.37
Methylacetate	0.54	0.27
Ethylacetate	0.84	0.42

Results contained in last years report are in **bold italics**.

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 with gas chromatographic and gas chromatographic/mass spectrometer systems that are used for method validation and method development efforts.

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2.0 Research Objectives and Methodology

2.1 RESEARCH OBJECTIVES

The objectives of this Phase 2 research were two fold:

1. Continue 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. Continue the evaluation of the relationship(s) between the relative response factor results and each compound's molecular characteristics such as molecular weight, weight percentage carbon, carbon number, and molecular structure.

2.0 EXPERIMENTAL METHODOLOGY

EPA Protocol 1 gas standards consisting of several chemical families 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 air.

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. 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.

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3.0 Results and Discussion

Table 2 shows the individual run results for each of the compounds evaluated including those compounds (*in bold italics*) previously reported under FY 2002 subtask 2.4. The known concentration of each test gas, the average results, standard deviation, and percent relative standard deviation are also shown. The repeatability of the results is within the Method 25A requirements of 5% RSD.

Table 2 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
<i>Methane</i>	<i>190.00</i>	<i>68.57</i>	<i>68.61</i>	<i>68.57</i>	<i>68.58</i>	<i>0.02</i>	<i>0.04</i>
<i>Ethane</i>	<i>190.00</i>	<i>134.64</i>	<i>134.59</i>	<i>134.58</i>	<i>134.60</i>	<i>0.03</i>	<i>0.03</i>
Ethylene	199.00	130.87	130.93	130.88	130.89	0.03	0.02
Acetylene	203.50	134.80	134.97	134.85	134.87	0.09	0.06
<i>Propane</i>	<i>190.00</i>	<i>198.90</i>	<i>199.01</i>	<i>199.12</i>	<i>199.01</i>	<i>0.11</i>	<i>0.06</i>
Propylene	200.50	193.46	193.45	193.60	193.50	0.09	0.04
<i>Butane</i>	<i>190.00</i>	<i>268.92</i>	<i>268.82</i>	<i>268.69</i>	<i>268.81</i>	<i>0.12</i>	<i>0.04</i>
1,3-Butadiene	202.00	262.31	261.89	262.25	262.15	0.23	0.09
<i>Pentane</i>	<i>189.70</i>	<i>331.31</i>	<i>331.32</i>	<i>331.24</i>	<i>331.29</i>	<i>0.04</i>	<i>0.01</i>
<i>Hexane</i>	<i>190.00</i>	<i>395.78</i>	<i>395.81</i>	<i>395.56</i>	<i>395.72</i>	<i>0.14</i>	<i>0.04</i>
Cyclohexane	200.00	388.98	389.58	389.85	389.47	0.45	0.11
<i>Benzene</i>	<i>190.30</i>	<i>404.55</i>	<i>404.09</i>	<i>404.46</i>	<i>404.37</i>	<i>0.24</i>	<i>0.06</i>
<i>Toluene</i>	<i>10.00</i>	<i>23.90</i>	<i>23.91</i>	<i>23.89</i>	<i>23.90</i>	<i>0.01</i>	<i>0.06</i>
<i>Xylene</i>	<i>9.60</i>	<i>23.39</i>	<i>23.41</i>	<i>23.43</i>	<i>23.41</i>	<i>0.02</i>	<i>0.10</i>
<i>Ethylbenzene</i>	<i>9.00</i>	<i>26.67</i>	<i>26.66</i>	<i>26.61</i>	<i>26.65</i>	<i>0.03</i>	<i>0.11</i>
<i>Styrene</i>	<i>9.00</i>	<i>26.67</i>	<i>26.75</i>	<i>26.80</i>	<i>26.74</i>	<i>0.07</i>	<i>0.24</i>
Trimethylbenzene	10.00	27.39	27.37	27.41	27.39	0.02	0.07
<i>Triethylamine</i>	<i>8.10</i>	<i>10.07</i>	<i>10.54</i>	<i>10.64</i>	<i>10.42</i>	<i>0.31</i>	<i>2.96</i>
Pyridine	99.50	143.64	143.63	143.64	143.64	0.00	0.00
Aniline	9.90	11.08	11.14	11.06	11.09	0.04	0.38
N,N-Dimethylaniline	10.10	10.94	11.17	11.20	11.10	0.14	1.29
Acetone	197.00	135.29	135.49	135.51	135.43	0.12	0.09
Methylethylketone	199.90	200.33	200.49	200.75	200.53	0.21	0.11
Methylisobutylketone	20.00	33.57	33.53	33.55	33.55	0.02	0.06
Diethylether	199.70	197.18	197.32	197.33	197.28	0.09	0.04
1,4-Dioxane	199.40	133.98	133.80	133.86	133.88	0.09	0.07
Methanol	210.70	49.56	50.08	50.18	49.94	0.34	0.67
Ethanol	210.30	94.92	95.37	95.46	95.25	0.29	0.30
Isopropanol	210.30	155.04	155.09	155.20	155.11	0.08	0.05
Methylacetate	201.20	108.18	108.38	108.36	108.30	0.11	0.10
Ethylacetate	200.30	168.10	168.36	168.29	168.25	0.14	0.08

Results contained in last years report are in *bold italics*.

Table 3 shows the number of carbon atoms, molecular weight, percentage carbon and FID response for each compound relative to the propane in air calibration standard. Compounds from the FY 2002 subtask 2.4 are shown in ***bold italics***. The table also shows these relative response factors (RRF) for each compound adjusted for the compound's carbon number and relative to the Iron and Steel Foundry MACT required calibrant, hexane (C6). FID plots for each compound may be found in Appendix A.

Table 3 Relative Response Factors

Compound	Number of Carbon Atoms	Molecular Weight	Percent Carbon	Relative Response Factor (C3 = 1.00)	Corrected for Carbon Number	Relative Response Factor (C6 = 1.00)
<i>Methane</i>	<i>1</i>	<i>16.04</i>	<i>74.8</i>	<i>0.36</i>	<i>1.03</i>	<i>0.17</i>
<i>Ethane</i>	<i>2</i>	<i>30.07</i>	<i>79.8</i>	<i>0.71</i>	<i>2.03</i>	<i>0.34</i>
Ethylene	2	28.05	85.6	0.66	1.97	0.33
Acetylene	2	26.02	92.2	0.66	1.99	0.33
<i>Propane</i>	<i>3</i>	<i>44.10</i>	<i>81.6</i>	<i>1.05</i>	<i>3.00</i>	<i>0.50</i>
Propylene	3	42.08	85.6	0.97	2.90	0.49
<i>Butane</i>	<i>4</i>	<i>58.12</i>	<i>82.6</i>	<i>1.41</i>	<i>4.05</i>	<i>0.68</i>
1,3-Butadiene	4	54.09	88.7	1.30	3.89	0.65
<i>Pentane</i>	<i>5</i>	<i>72.15</i>	<i>83.2</i>	<i>1.75</i>	<i>5.00</i>	<i>0.84</i>
<i>Hexane</i>	<i>6</i>	<i>86.18</i>	<i>83.5</i>	<i>2.08</i>	<i>5.97</i>	<i>1.00</i>
Cyclohexane	6	84.16	85.6	1.95	5.84	0.98
<i>Benzene</i>	<i>6</i>	<i>78.11</i>	<i>92.2</i>	<i>2.12</i>	<i>6.09</i>	<i>1.02</i>
<i>Toluene</i>	<i>7</i>	<i>92.14</i>	<i>91.2</i>	<i>2.39</i>	<i>6.85</i>	<i>1.15</i>
<i>Xylene</i>	<i>8</i>	<i>106.17</i>	<i>90.4</i>	<i>2.44</i>	<i>6.98</i>	<i>1.17</i>
<i>Ethylbenzene</i>	<i>8</i>	<i>106.17</i>	<i>90.4</i>	<i>2.96</i>	<i>8.48</i>	<i>1.42</i>
<i>Styrene</i>	<i>8</i>	<i>104.15</i>	<i>92.2</i>	<i>2.97</i>	<i>8.51</i>	<i>1.43</i>
Trimethylbenzene	9	120.20	89.9	2.74	8.22	1.38
<i>Triethylamine</i>	<i>6</i>	<i>101.19</i>	<i>71.2</i>	<i>1.29</i>	<i>3.68</i>	<i>0.62</i>
Pyridine	5	79.10	75.9	1.44	4.33	0.73
Aniline	6	93.13	77.3	1.12	3.36	0.56
N,N-Dimethylaniline	8	121.18	79.2	1.10	3.30	0.55
Acetone	3	58.08	62.0	0.69	2.06	0.35
Methylethylketone	4	72.11	66.6	1.00	3.01	0.50
Methylisobutylketone	6	100.16	71.9	1.68	5.03	0.84
Diethylether	4	74.12	64.8	0.99	2.96	0.50
1,4-Dioxane	4	88.10	54.5	0.67	2.01	0.34
Methanol	1	32.04	37.5	0.24	0.71	0.12
Ethanol	2	46.07	52.1	0.45	1.36	0.23
Isopropanol	3	60.10	59.9	0.74	2.21	0.37
Methylacetate	3	74.08	48.6	0.54	1.61	0.27
Ethylacetate	4	88.11	54.5	0.84	2.52	0.42

Results contained in last years report are in ***bold italics***.

A review of the data in Table 3 by chemical family suggests the following:

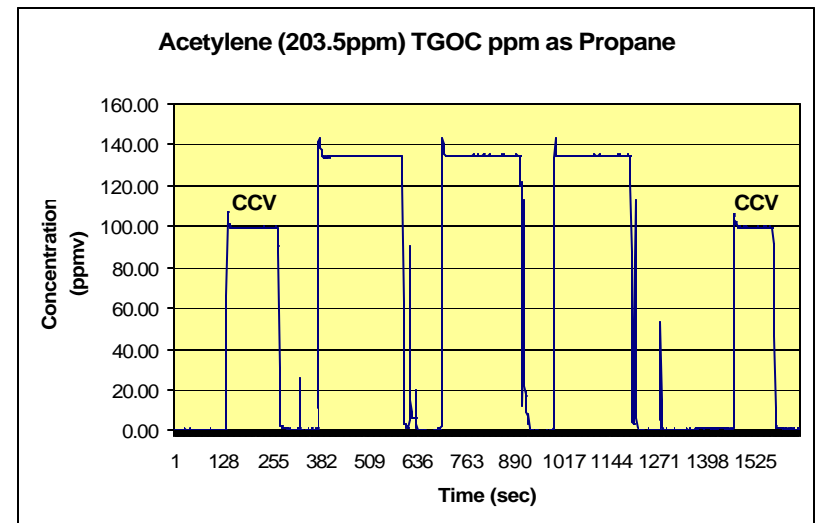
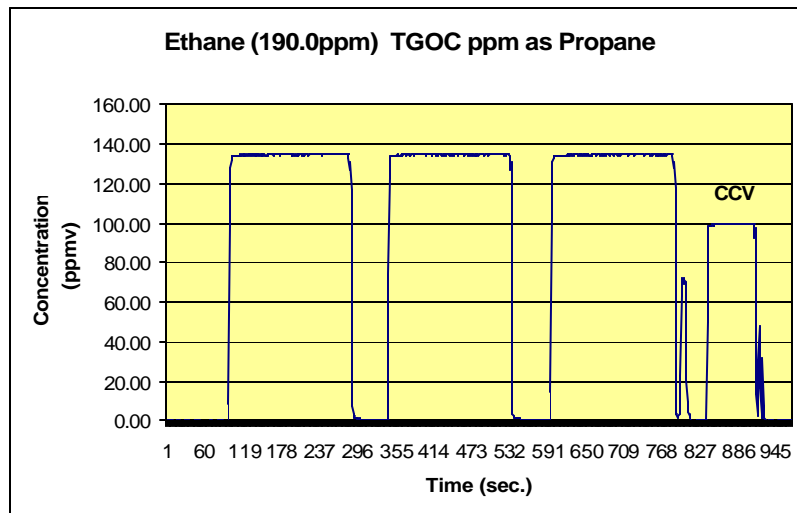
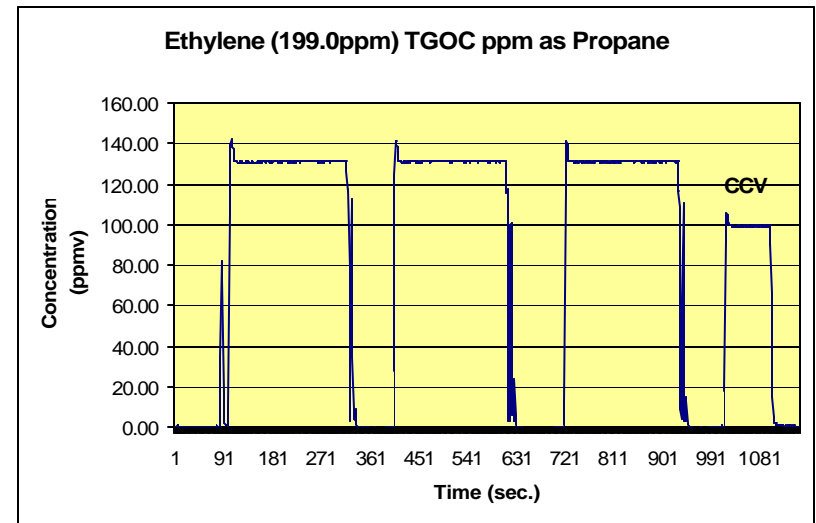
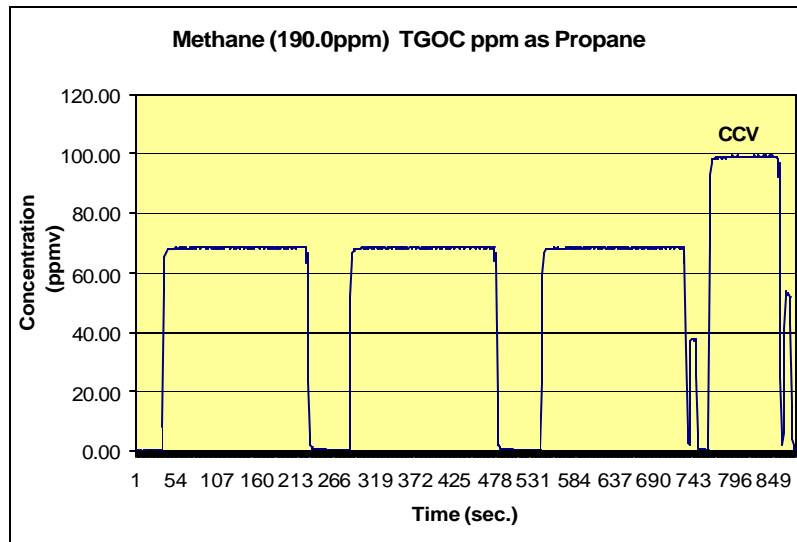
1. For the aliphatic hydrocarbons, relative response factors are based on number of carbon atoms in the molecule. The addition of olefinic or acetylenic (double or triple) bonds or the change from a normal structure to a cyclic structure seems to have little effect. Additional work would have to be conducted to determine if the slight decrease in response observed is "real" or the result of test variability.
2. The aromatic hydrocarbon results are much more difficult to interpret. The determined response factors should be confirmed through the analysis of additional standard gases before any conclusions are drawn.
3. The same must be said for the amines. Additional gas samples must be analyzed to determine if the data are accurate or the result of concentration instability due to the polar nature of these compounds.
4. The data for the ketones, compounds with a carbonyl oxygen, show a consistent response loss equivalent to one (1) carbon atom.
5. The limited ether and alcohol results suggest that a singly bound oxygen will reduce the response of the carbon atom that it is bound to by approximately 0.5 units. Additional ethers and alcohols need to be studied to confirm these observations.
6. The response of the two esters appears to be an additive combination of the effect of a carbonyl oxygen and a singly bonded oxygen in that the response of both esters was reduced by about 1.5 carbon atoms.

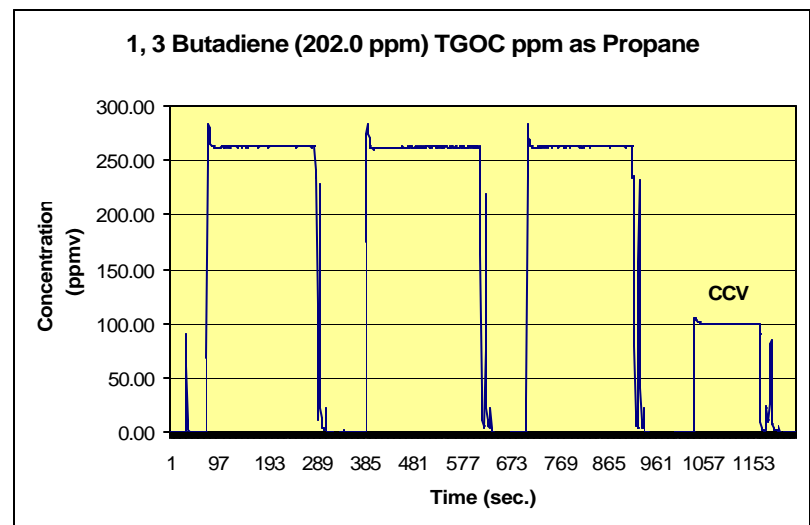
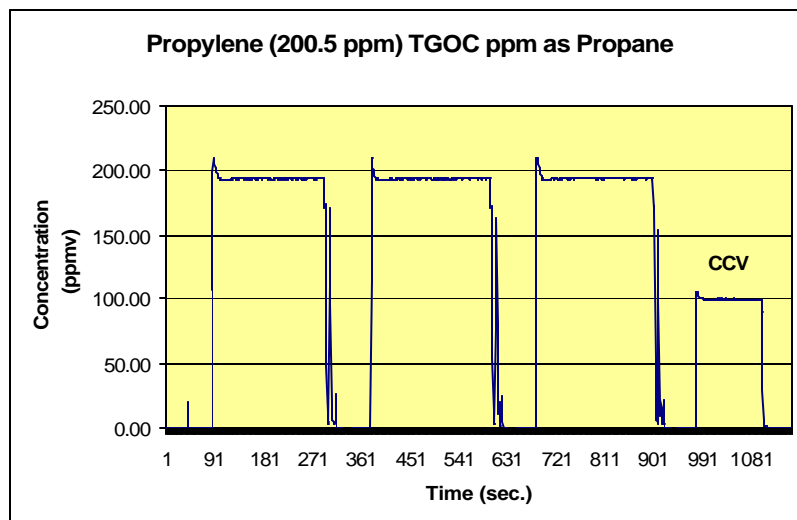
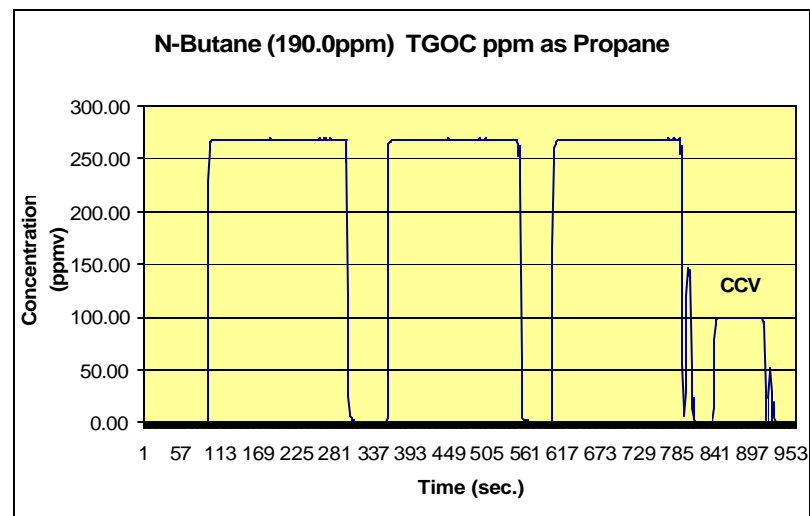
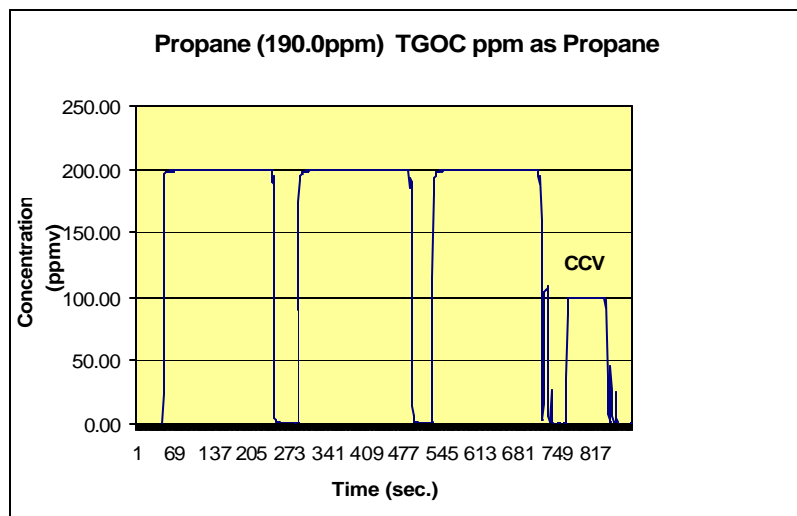
Future work should include verification of the aromatic hydrocarbon and amine results reported herein, confirmation that composite response factors for mixtures can be calculated from the empirically determined response factor and the concentration of each compound in a mixture, and beginning to develop the calculations for hydrocarbons that will enable the prediction of FID response from molecular structure.

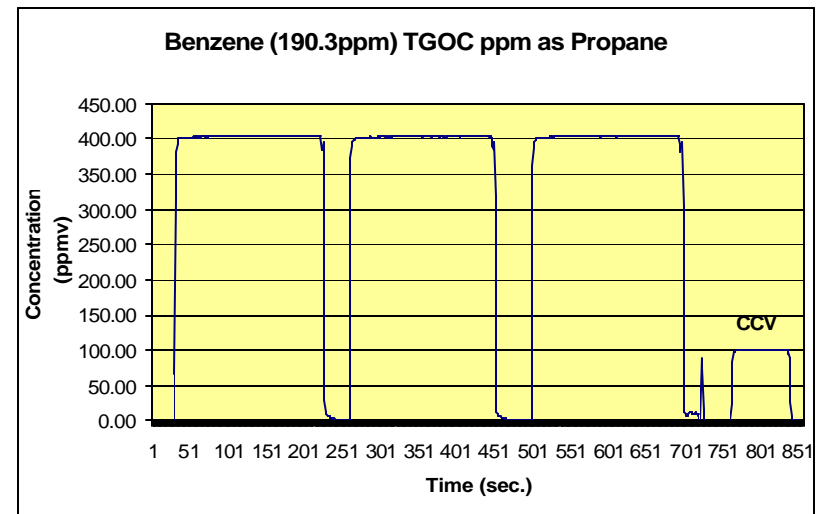
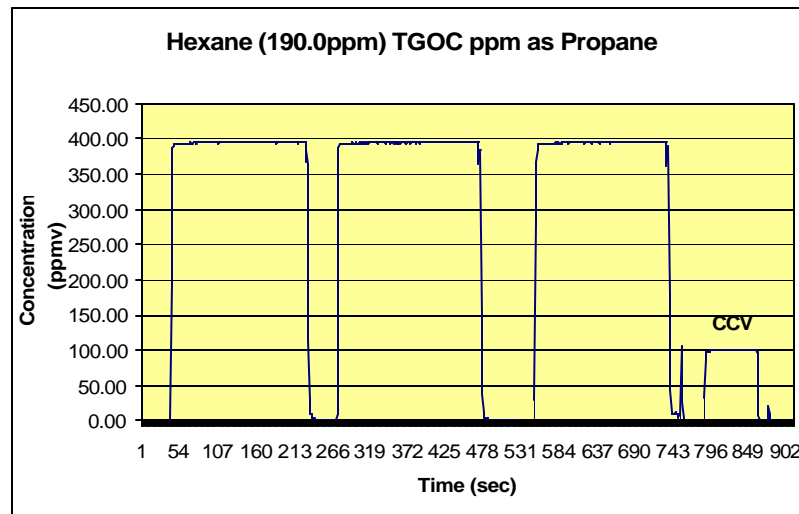
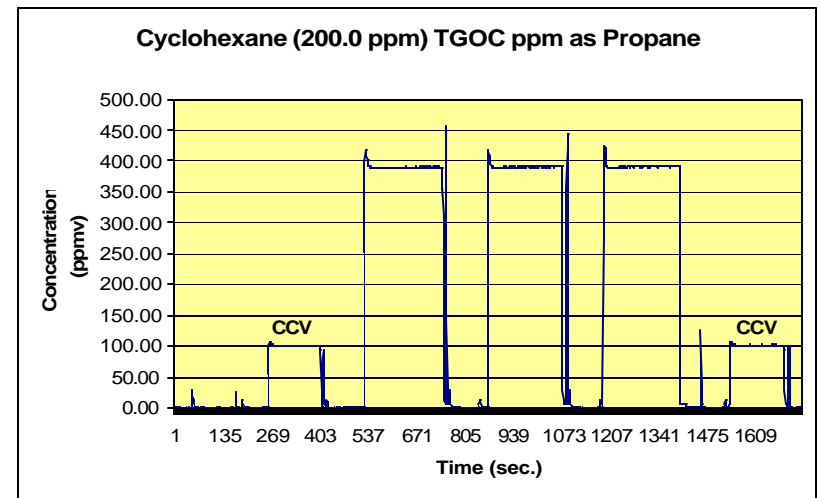
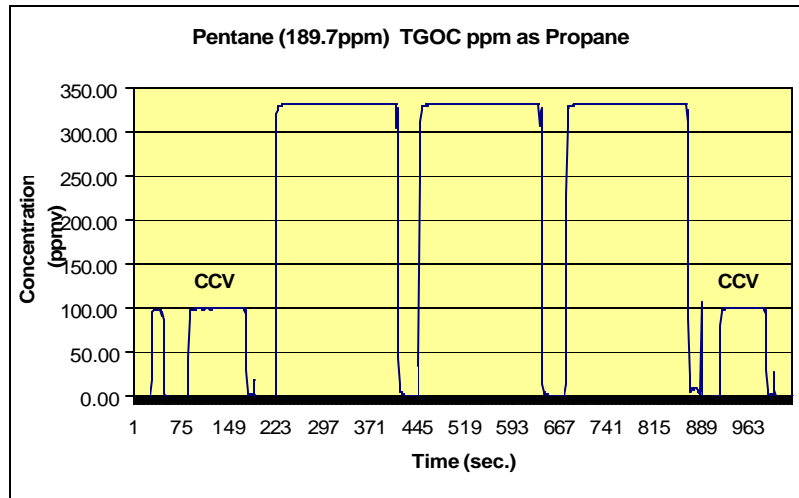
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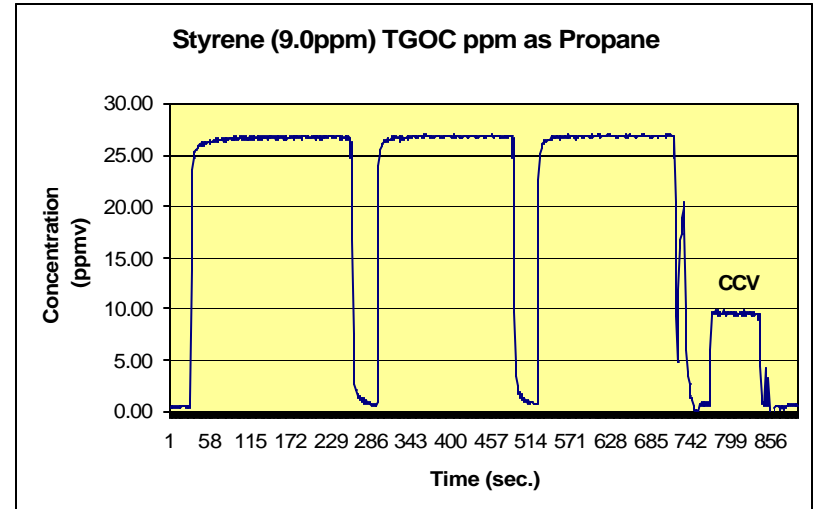
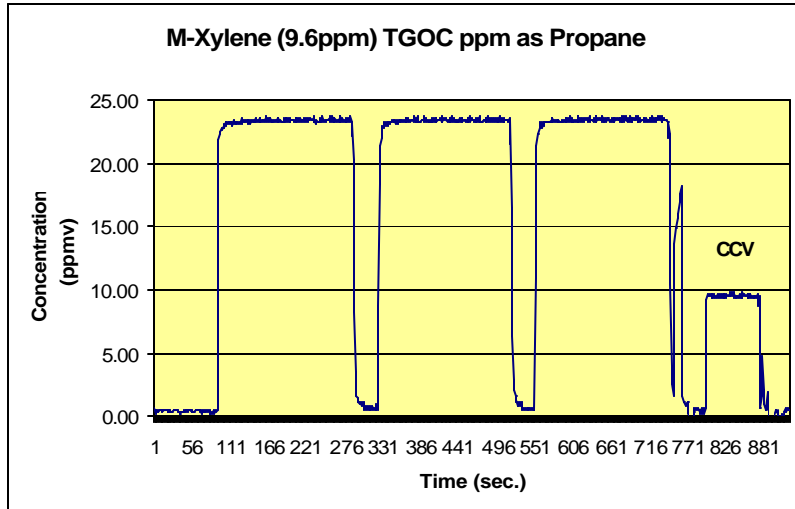
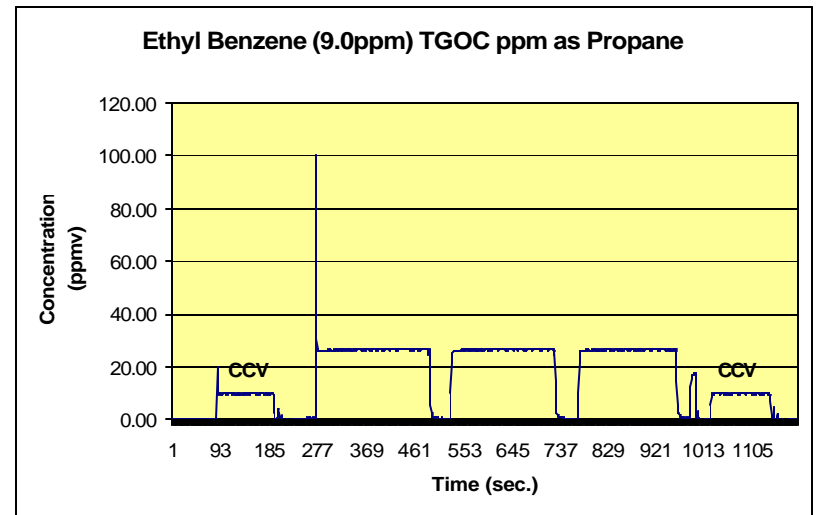
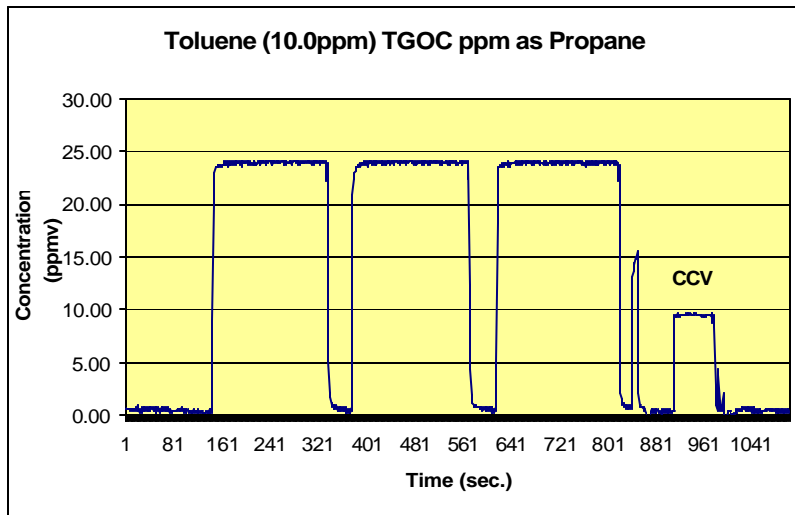
APPENDIX A METHOD 25A FID CHARTS

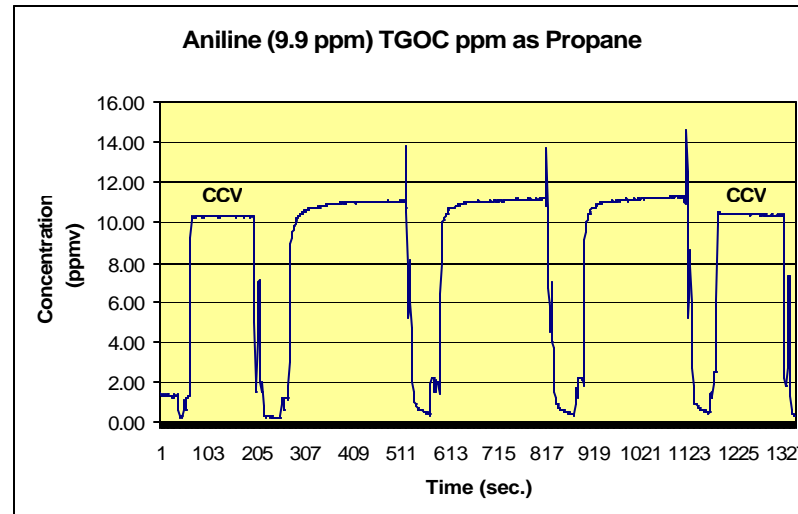
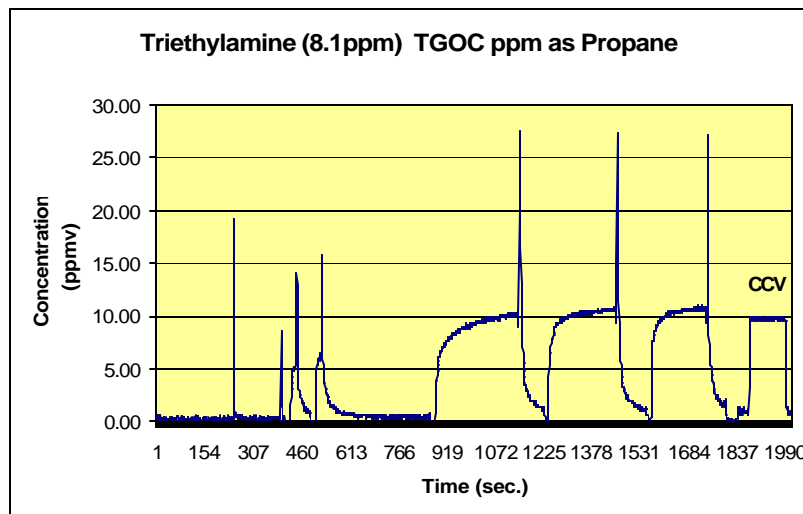
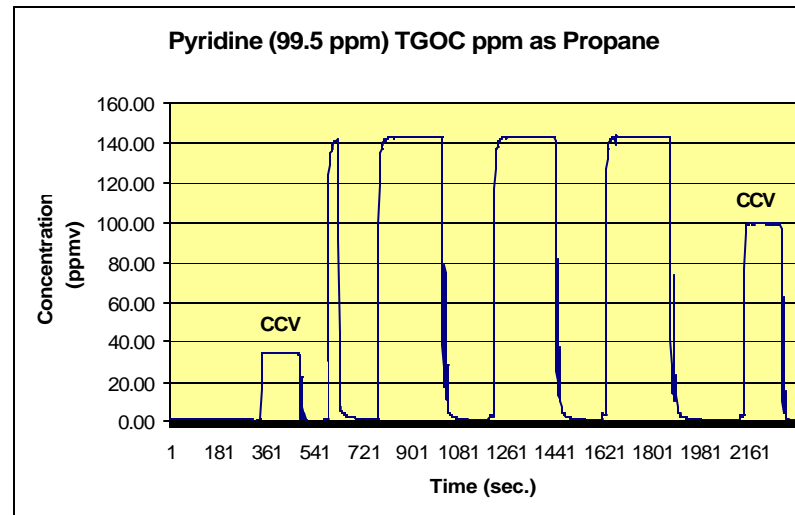
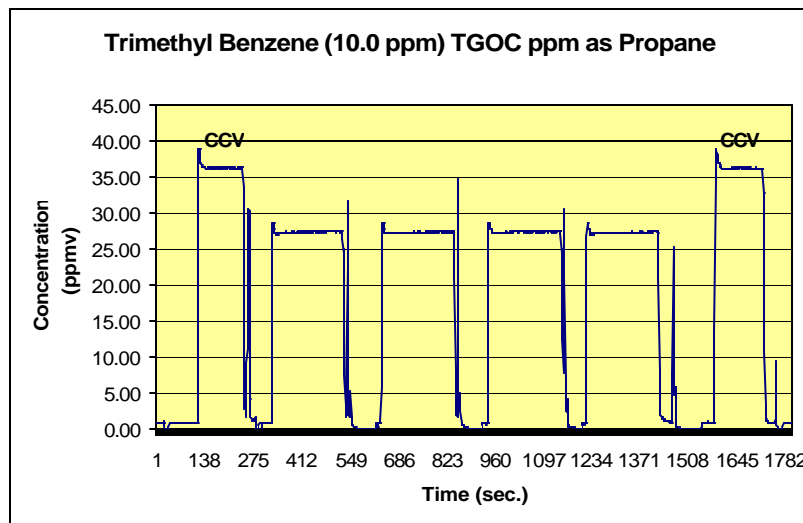
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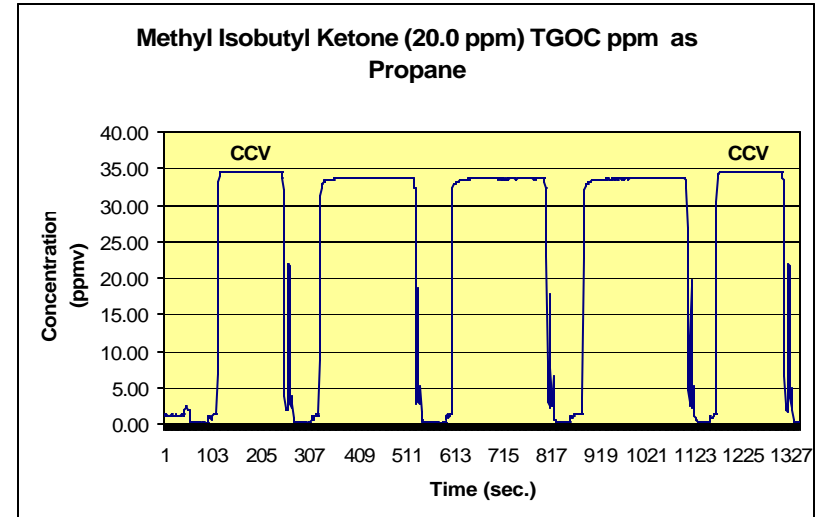
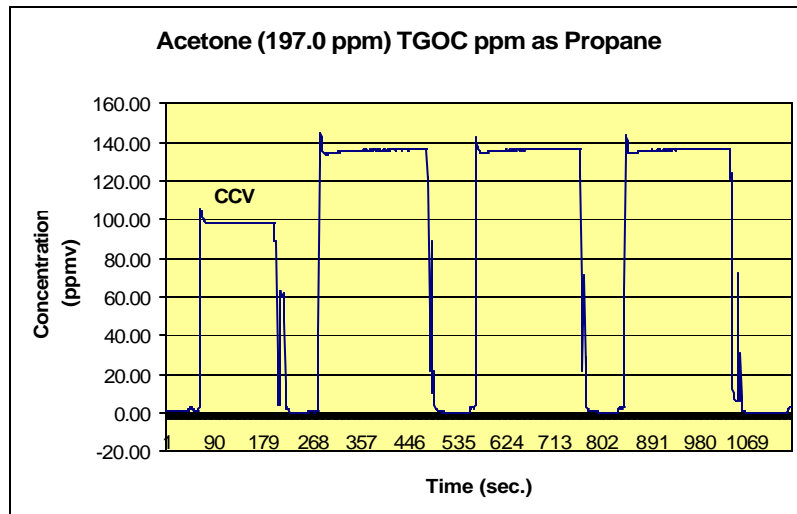
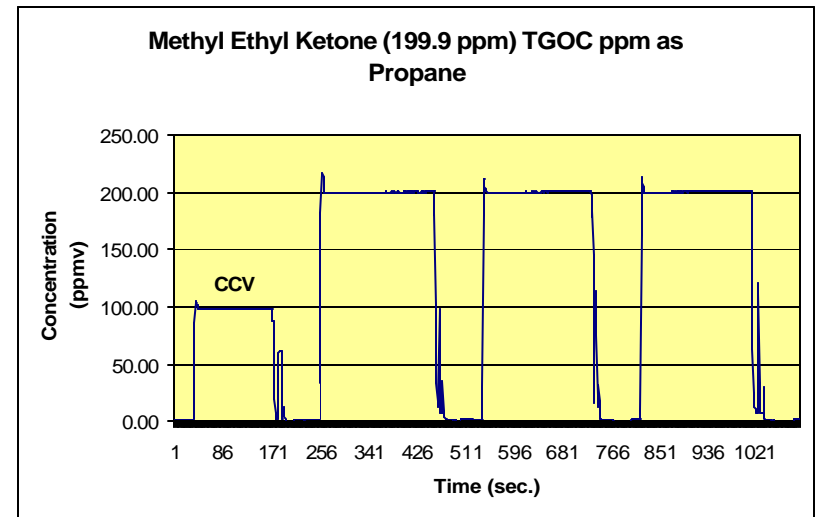
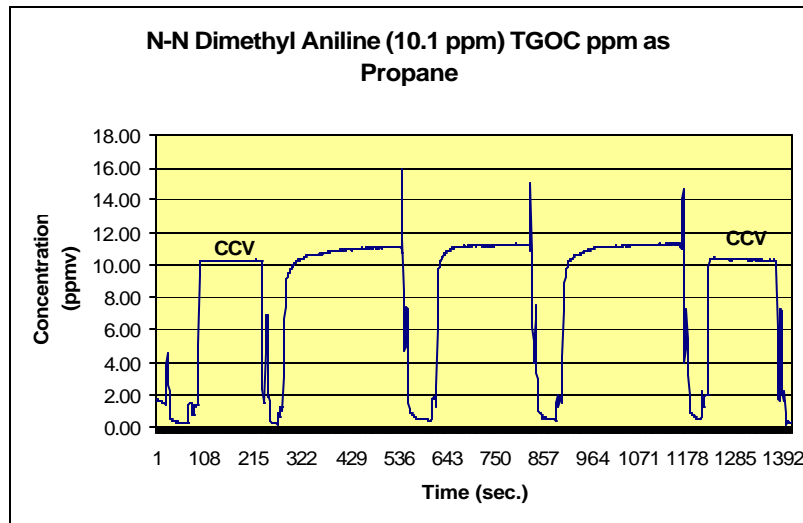


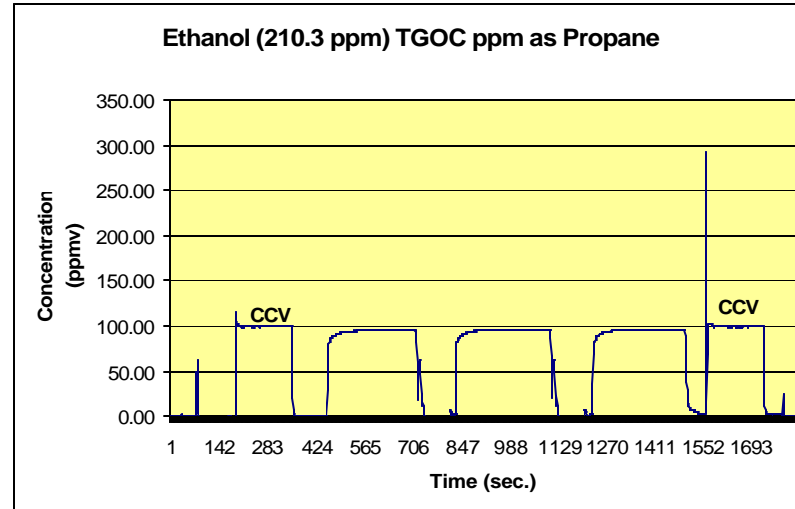
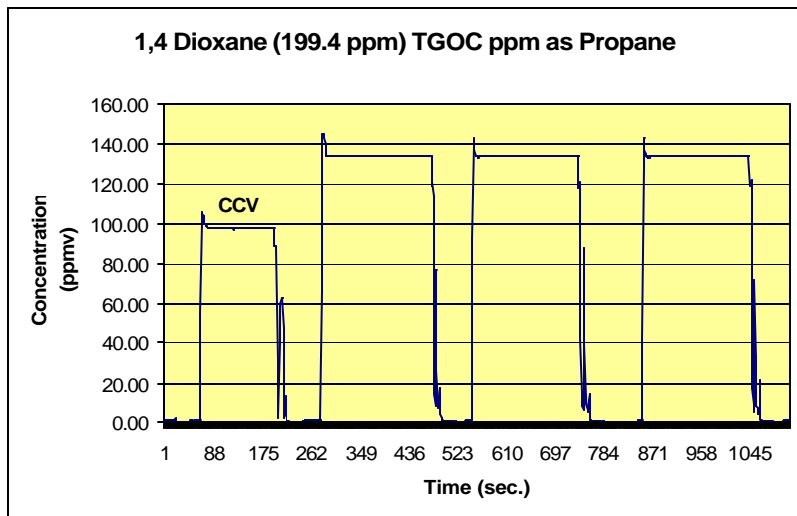
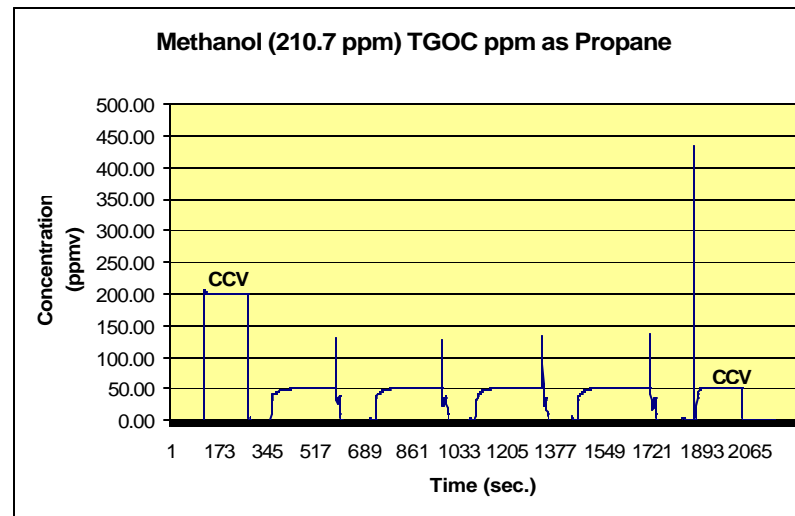
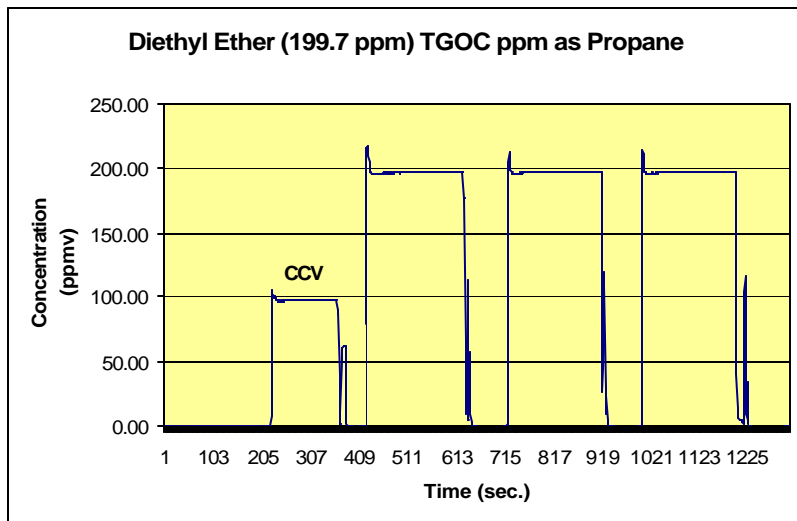


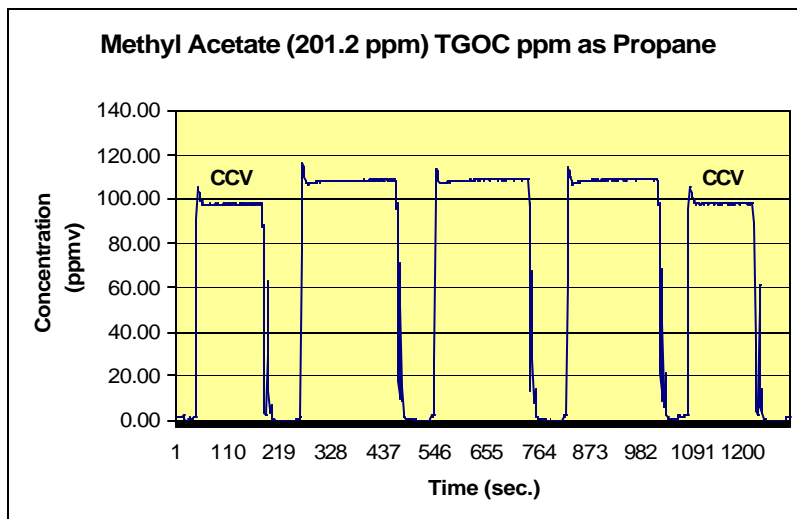
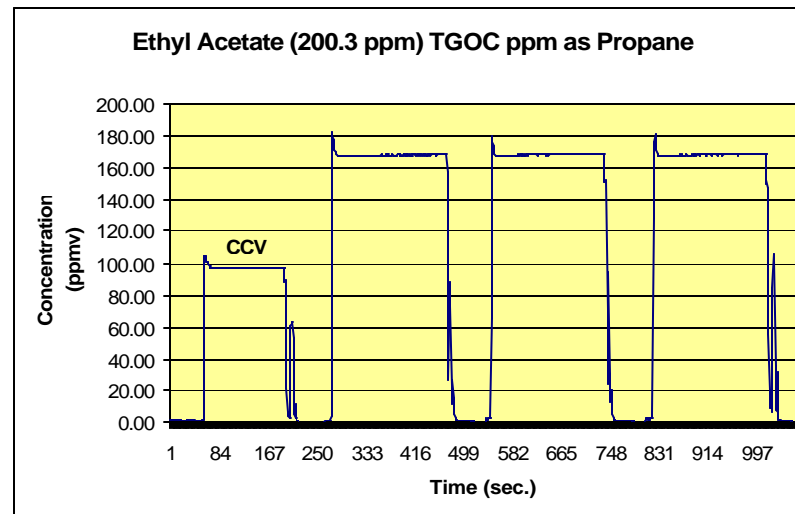
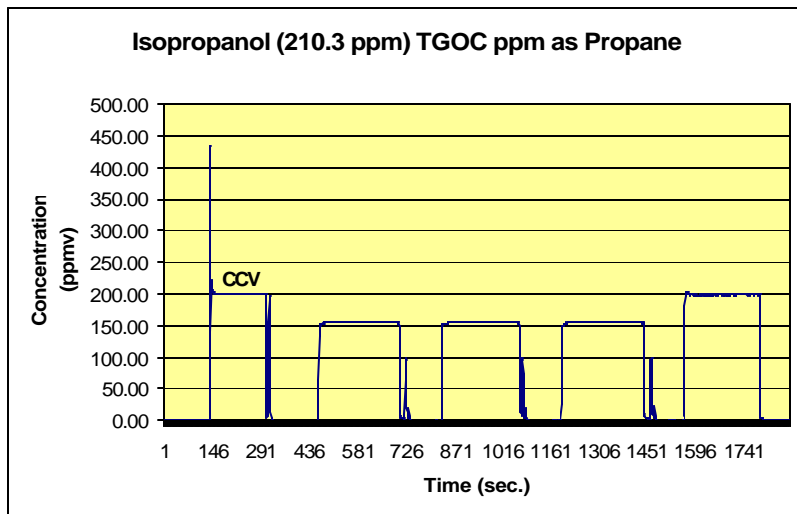












APPENDIX B GLOSSARY

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Glossary

% RSD	Percentage Standard Deviation
ACFM	Actual Cubic Feet Per Minute
BO	Based on ().
BOS	Based on Sand.
CCV	Continuous Calibration Verification
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
RRF	Relative Response Factor
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