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Characterization of Emissions and Occupational Exposure Associated with Five Cover Gas Technologies for Magnesium Die Casting

Office of Air and Radiation
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Characterization of Emissions and Occupational Exposure Associated with Five Cover Gas Technologies for Magnesium Die Casting

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Executive Summary

This measurement study was conducted to evaluate the greenhouse gas (GHG) emissions and occupational exposure associated with five cover gas technologies used in a cold chambered die casting operation. Sulfur hexafluoride (SF_6) is widely used for the protection of molten magnesium, but with the goal of eliminating the use of SF_6 in this application by 2010, the magnesium industry and U.S. Environmental Protection Agency (EPA) have been evaluating the use of alternative gases. This study expands upon previous research by evaluating additional alternative cover gases and including an occupational exposure component.[1] This study examined the use of AM-Cover™ using HFC-134a (supplied by Advanced Magnesium Technologies), MTG-Shield™ using Novec™ 612 (supplied by Matheson Tri-Gas, Taiyo Nippon Sanso, and 3M™), sulfur dioxide (SO_2) (gas blender supplied by Polycontrols Inc.), and frozen carbon dioxide (CO_2) and SF_6 (both provided by Lunt Manufacturing) on a single cold chambered magnesium die casting machine located at a Lunt Manufacturing facility in Hampshire, Illinois. Each cover gas mixture was evaluated under identical process and machine operating parameters. With the exception of frozen CO_2, each cover gas was injected into and extracted from the crucible headspace under similar parameters to characterize emissions and byproducts as the cover gases interact with the melt surface and undergo thermo-degradation. The results reported were from measurements taken inside the crucible headspace and from worker exposure/ambient air sampling points. Table ES-1 summarizes some of the details and results from the crucible head space component of the study. Measurements were conducted using multiple cover gas mixtures, and in the case of frozen CO_2, a different injection location and physical phase of chemical. The cover gas destruction rates listed in Table ES-1 have been corrected for crucible dilution effects.[2] Table ES-2 summarizes the results from continuous monitoring of ambient air at two worker stations associated with the die casting machine.

MTG-Shield™ using Novec™ 612 with CO_2 Carrier Gas

The primary destruction byproducts measured while running MTG-Shield™ using Novec™ 612 with CO_2 as a cover gas were CO, COF_2, C_3F_8, C_2F_6, CHF_3 and HF (see Table 2-1 for a listing of chemical formulas and compound names). The C_2F_6 concentrations ranged from below detectable limits (BDL) to 13 parts per million by volume (ppmv) and the COF_2 concentrations ranged from BDL to 36 ppmv, depending on injected concentration and stability of the crucible headspace. HF concentrations were detected at levels of 7 to 450 ppmv for the range of mixtures evaluated. Higher feed gas concentrations resulted in higher concentrations of HF. Additional compounds detected included CH_4, C_2H_4, and CH_2O. CH_4 was detected above

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[1] Characterization of Cover Gas Emissions from U.S. Magnesium Industry Die Casting Operation, March 2004.

[2] The term destruction is utilized throughout the remainder of this report to represent the thermo-degradation and disassociation of the cover gas agent resulting in byproduct formation and melt protection.

ambient concentrations and C_2H_4 and CH_2O spiked during ingot loading. Low levels of N_2O (< 5 ppmv) and NO_2 (0.4 to 5 ppmv) were detected during casting and tended to increase during ingot loading periods.

AM-Cover™ using HFC-134a with CDA Carrier Gas

The primary destruction products measured while running AM-Cover™ with HFC-134a with a compressed dry air (CDA) carrier gas were CO, HF, and COF_2. HF concentrations were measured from 448 to 1,199 ppmv with higher values correlating to higher concentrations of HFC-134a in the feed gas. Concentrations of COF_2 ranged from 16 to 59 ppmv. The time series concentration plots for these and other compounds are presented in Appendix A. They illustrate that additional destruction products, such as CH_2O and C_2H_4, are formed with the addition of ambient air during the ingot loads. Some compounds, such as CH_2O, NO, N_2O and NO_2 also had background levels inside the headspace that sharply increased during ingot loading.

Table ES-1. Cover Gas Average Concentrations and Observed Destruction

Cover Gas Mixture Components	Date	Time	Cover Gas Mixture Flow [a] (lpm)	Cover Gas Delivery Conc. [a] (ppmv)	Cover Gas Measured Conc. (ppmv)	Cover Gas Destruction[b]
Novec™ 612/CO_2	8/22/06	0910-1005	~36	800	198.8	74%
Novec™ 612/CO_2	8/22/06	1008-1135	~36	600	142.5	76%
Novec™ 612/CO_2	8/22/06	1138-1301	~36	400	55.4	86%
Novec™ 612/CO_2	8/22/06	1347-1425	~36	300	3.2	99%
Novec™ 612/CO_2	8/23/06	0906-0958	~36	200[c]	75.8	61%
Novec™ 612/CO_2	8/23/06	1108-1248	~36	200[d]	64.2	67%
Novec™ 612/CO_2	8/23/06	1252-1556	~36	150	30.8	79%
HFC-134a/CDA	8/24/06	1510-1736	~40	4,200	1,198.3	71%
HFC-134a/CDA	8/25/06	0810-1215	~40	3,600	810.7	77%
SF_6/CDA	8/24/06	0939-1311	~35	3,000	1,966.1	32%
SF_6/CDA	8/24/06	1806-1902	~35	3,000	1,932.2	34%
SO_2/CDA	8/28/06	1105-1130	~39	10,000	6,086.6	37%
SO_2/CDA	8/28/06	1133-1218	~39	8,500	5,521.3	33%
SO_2/CDA	8/28/06	1222-1348	~39	7,000	4,652.5	32%
SO_2/CDA	8/28/06	1351-1500	~39	6,000	4,157.3	29%
SO_2/CDA	8/28/06	1504-1552	~39	5,000	3,401.3	30%
SO_2/CDA	8/29/06	0845-1001	~39	5,000	3,042.0	37%
SO_2/CDA	8/29/06	1005-1155	~39	4,000	2,518.2	35%
Frozen CO_2	8/29/06	1651-1829	Liquid CO_2 at 100 psi[e]	1,000,000	957,390.1	4%

[a] As provided by Lunt Manufacturing, AMT, Polycontrols, and Matheson Tri-Gas/TNSC
[b] Dilution corrected values from Table 5-1
[c] Data collected prior to a dross
[d] Data collected after a dross
[e] Liquid CO_2 dewar at 100 psi

The detection of CH_2O and C_2H_4 was sporadic, with a few measurable spikes occurring during ingot loading. Detection of SF_6 was also observed at low concentrations and is a residual from previously used SF_6 cover gas.

SF_6 with CDA Carrier Gas

The primary destruction byproducts measured while using SF_6 with CDA as a cover gas were HF and SO_2. HF concentrations ranged from 1 to 49 ppmv for the first and second tests, respectively. N_2O and NO_2 levels were also vastly different between the two test periods. CH_2O levels were somewhat consistent between tests with the second test slightly less than the first. Low levels of C_2H_2 were also observed during the first test. CH_4 was observed at an average of approximately 3 ppmv during both tests, slightly above the ~2 ppmv normally seen in ambient air.

The primary difference between the 2 test episodes is the time the SF_6 had been purging the crucible head space prior to sampling. The SF_6 mixture had been flowing for approximately

17 hours before the first test, whereas the second test had started immediately after a cover gas changeover to SF_6. The longer purge period prior to testing had a pronounced effect on the emissions, as the HF, N_2O, NO_2 and CO concentrations were all significantly lower. These compounds also follow a pattern of concentration increases during ingot loadings. The temperature instability of the crucible headspace gas (due to dilution with cold ambient air during ingot loadings) and/or the displacement of cover gas by excess ambient air may have played a role in this effect.

SO_2 with CDA Carrier Gas

There were few destruction byproducts that could be attributed to SO_2. Most of the observed compounds were either a carry-over effect of residual chemicals from the previous cover gas used in the crucible (e.g., SF_6 and HF), ambient air components (H_2O, CO_2, CH_4), destruction byproducts formed from ambient air dilution during ingot loading (CH_2O and C_2H_4) or nitrogen oxides formed from the CDA carrier gas. H_2SO_4 was not measured at concentrations above its minimum detection limit (0.051 ppmv) within the crucible headspace.

Frozen CO_2

The final cover gas tested was frozen CO_2. As the gas cooled through expansion, it froze, forming solid phase CO_2 which was gravity fed into the crucible. The obvious difference between the frozen CO_2 and all the other cover gases was the method of injection. Compressed CO_2 was delivered to the nozzle at a pressure of 100 psi from a liquid CO_2 dewar. Due to the inconsistencies associated with delivery and crucible headspace pressures, effects of dilution also differed. However, the quadrupole mass spectrometer (QMS) also monitored N_2 concentrations during the CO_2 cover gas testing to enable a calculation of dilution (described in Section 4-6). The delivery/formation of the frozen CO_2 was controlled and optimized by regulating the injection into the crucible with a solenoid valve.

CO_2 had very few decomposition by-products, with the exception of CO. A very small amount of C_2H_4 was consistently present throughout the testing. SO_2, HF and SF_6 were observed during the testing, but were present as a carry-over effect of residual chemicals from previous cover gases used in the crucible. The presence of low concentrations of nitrogen oxides was most likely due to thermal decomposition of ambient air entering the crucible through leaks and ingot loading.

Observed Percent Destruction for Cover Gases

Table ES-1 lists the destruction estimates for all cover gases examined. The destruction estimates, which are corrected for dilution effects (i.e., the effects of air ingression into the crucible headspace), are calculated as the percent difference between the delivery concentration and the measured concentration in the crucible headspace. Average destruction estimates for Novec™ 612, HFC-134a, and SO_2 were on the order of 77%, 74%, and 33%, respectively. Frozen CO_2 had the lowest observed destruction at 4%. In comparison, destruction estimates for SF_6 were on the order of 33% for this study.

The destruction rates estimated for SF_6 in this study were significantly higher than what was estimated during previous research (on the order of 10%). This is likely due to the much lower feed gas SF_6 concentrations utilized in this study, and reduced levels of dilution resulting in destruction having a larger share of the reduction in measured concentration.

Occupational Exposure Monitoring

Since each cover gas used in this study can result in emissions that may be harmful to exposed workers, monitoring of the ambient air near worker breathing zones was performed. A second FTIR was used to monitor the breathing air at two locations based on their probability for worker activity. This component of the study was especially relevant to SO_2 due to its stringent occupational exposure limits. For Novec™ 612, HFC-134a, and SF_6-based cover gases, the monitored zone was at the end of the casting process where the part was robotically dropped to an area where the worker inspects the part and places it on a pallet for transfer to the finishing process. This station was occupied by a worker about 50% of the time and was approximately 18 feet from the crucible. For SO_2 and frozen CO_2 cover gases, the area above the crucible was monitored near the ingot loading door. Although the worker activity is lighter at this location, the potential for elevated exposure concentrations is the highest due to direct contact with escaping crucible gases. Table ES-2 lists the monitoring results for the primary compounds of concern that were observed along with their established permissible exposure limit (PEL) and short term exposure limit (STEL). SF_6 was consistently present throughout the monitoring due to its usage at the other casting operations occurring throughout the facility. With the exception of a single measurement when SO_2 was being tested, continuous monitoring of these worker areas found concentrations of the primary compounds of concern that were either BDL or well below PEL and STEL values.[3]

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[3] All applicable safety precautions (e.g., operational procedures) should be followed when using SO_2.

Table ES-2. Observed Compounds from Occupational Exposure Ambient Air Monitoring

Cover Gas	Date	Zone**		Novec™612 (ppmv)	HFC-134a (ppmv)	SF_6 (ppmv)	SO_2 (ppmv)	HF (ppmv)	CO (ppmv)	COF_2 (ppmv)	CH_2O (ppmv)
Permissible Exposure Limit (PEL)				150	1,000	1,000	2	3	50	2	0.75
Short-term Exposure Limit (STEL)				n/a	n/a	n/a	5	6	400	5	2
MTG-Shield™	**8/22**	**1**	**Max**	BDL	n/a	0.08	n/a	BDL	11.60	BDL	BDL
			Average	BDL	n/a	0.06	n/a	BDL	7.07	BDL	BDL
MTG-Shield™	**8/23**	**1**	**Max**	BDL	n/a	0.19	n/a	BDL	14.45	BDL	BDL
			Average	BDL	n/a	0.06	n/a	BDL	6.80	BDL	BDL
AM-Cover™	**8/24**	**1**	**Max**	n/a	0.050	0.16	n/a	BDL	15.33	BDL	BDL
			Average	n/a	0.020	0.10	n/a	BDL	5.28	BDL	BDL
AM-Cover™	**8/25**	**1**	**Max**	n/a	0.078	0.29	n/a	BDL	6.48	BDL	BDL
			Average	n/a	0.038	0.18	n/a	BDL	2.75	BDL	BDL
SF_6	**8/24**	**1**	**Max**	n/a	n/a	0.28	BDL	BDL	9.48	BDL	BDL
			Average	n/a	n/a	0.18	BDL	BDL	2.75	BDL	BDL
SO_2	**8/28**	**2**	**Max**	n/a	n/a	0.23	1.60*	BDL	7.22	BDL	BDL
			Average	n/a	n/a	0.19	0.14	BDL	1.21	BDL	BDL
SO_2	**8/29**	**2**	**Max**	n/a	n/a	0.07	BDL	BDL	11.49	BDL	BDL
			Average	n/a	n/a	0.03	BDL	BDL	7.06	BDL	BDL
Frozen CO_2	**8/29**	**2**	**Max**	n/a	n/a	0.23	n/a	BDL	11.46	BDL	BDL
			Average	n/a	n/a	0.16	n/a	BDL	4.55	BDL	BDL

BDL = below detectable limits
n/a = not applicable
*Occurred during an instance when the ingot loading door was open for a prolonged period due to an ingot loading malfunction.
**Zone 1 was located at the process end where the part is robotically dropped to the worker.
Zone 2 was located near the ingot loading area of the crucible.

Potential Climate Impact

A key factor in evaluating alternative cover gas compounds was their composite global warming potentials (GWPs) as compared to SF_6. Global warming potentials are based on the heat-absorbing ability and decay rate of each gas relative to that of carbon dioxide. The GWP provides a construct for converting emissions of various gases into a common measure, denominated in carbon dioxide equivalents. For each cover gas compound and its applicable destruction byproducts (e.g., C_3F_8, C_2F_6), a composite global warming impact estimate was developed using the IPCC second assessment report GWP values.[4] The overall GWP-weighted gas emission rate for each cover gas regime was estimated using the measured average concentrations of each gas, their molecular weights and the delivery cover gas flow rates. This resulted in a normalized CO_2 emission equivalent for each alternative cover gas that could be directly compared to the CO_2 emission equivalent of SF_6.

Based on this approach, results indicate that the MTG-Shield™ using Novec™ 612, AM-Cover™ using HFC-134a, and frozen CO_2 have a GHG emission impact that is at least 98% lower than SF_6. The SO_2 cover gas has an associated GHG emission impact that is 99% lower than SF_6.

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[4] IPCC, Climate Change 2001: The Scientific Basis. Intergovernmental Panel on Climate Change, 2001, Cambridge University Press. Cambridge, U.K.

1.0 Introduction

This report presents and interprets the results of a series of cover gas emissions measurements on a single cold chambered magnesium die casting machine. Measurements were conducted by URS Corporation (URS) at a Lunt Manufacturing facility located in Hampshire, Illinois between the 22nd and 29th of August, 2006. Measurements were made in a continuous and real-time fashion with an extractive-type Fourier Transform Infrared (FTIR) spectroscopic system, an extractive Quadrapole Mass Spectrometer (QMS), and an extractive-type oxygen (O_2) continuous emission monitor (CEM).

The focus of the study was to assess destruction byproducts and emissions for five different cover gases on a die casting machine operating under identical operational parameters. Cover gases are used to prevent surface oxidation and burning of the molten metal during processing. The five cover gases evaluated in this study were: 1) MTG-Shield™ using Novec™ 612 (supplied by Matheson Tri-Gas, Taiyo Nippon Sanso, and 3M™), 2) AM-Cover™ using HFC-134a (supplied by Advanced Magnesium Technologies), 3) SO_2 (gas mixer supplied by Polycontrols Technologies, Inc.), and 4) frozen CO_2 and 5) SF_6 (supplied by Lunt Manufacturing). Objectives for this study were:

- To characterize the greenhouse gas emissions (GHG) from various cover gas regimes used for magnesium melt protection during die-casting operations. Emissions measurements by FTIR were employed to identify the gaseous fluorides, acids and perfluorocarbons (PFCs) that may result from cover gas decomposition.
- To identify any detectable occupational exposure emissions associated with the use of each cover gas. Worker exposure areas were monitored for known and suspected compounds and reaction by-products using a long path FTIR.
- To determine the extent of destruction for each cover gas. As a control measure, each cover gas was injected into the confines of a single process crucible during identical casting operations.
- To determine the amount of dilution from ambient air into the crucible during normal operation. Direct measurement (of O_2 by CEM) and analysis of nitrogen (by QMS) during the Novec™ 612 studies provided an accurate determination of head space dilution, to be applied to all other cover gases (of nearly equal injection flow rates), except CO_2 (of unknown injection flow rate).
- To determine the GHG emissions from the cover gas technologies and overall reduction in GHG emissions attributable to the use of MTG-Shield™ using Novec™ 612, AM-Cover™ using HFC-134a, SO_2 and CO_2 as compared to SF_6.

The measurement schedule, sampling locations, and test conditions are summarized in Table 1-1. The die casting process parameters are summarized in Table 1-2. The measurements were conducted under these conditions during identical casting activity for all cover gases employed. An HPM 400 die-casting machine (#1), fabricating an automotive lock body housing, was chosen for the testing. Figure 1-1 depicts the die casting crucible that was tested at the Lunt Manufacturing facility.

Testing was carried out using independent cover gas flow controls through the existing gas distribution apparatus affixed to the crucible cover. The MTG-Shield™ cover gas was generated via a dedicated supply cabinet in which cylinders of liquid Novec™-612 are heated to supply a constant concentration gas stream to a gas mixing panel using a gas blending cabinet built and operated by Matheson Tri-Gas/TNSC. The AM-Cover™ cover gas was generated using a gas blender provided by Lunt Manufacturing. The SO_2 cover gas was generated using a gas blending cabinet built and operated by Polycontrols. SF_6 was supplied using the existing centralized gas distribution system at the facility. There were five cover gas injection points evenly spaced in a ring around the top of the crucible. Each injection point was modified by Lunt Manufacturing engineers by installing a 45 degree nozzle that directed the flow of cover gas onto the melt surface. There was also a sixth cover gas injection point at the top of the ingot loading hatch. The directional nozzle modification to the existing cover gas delivery system resulted in improved melt protection effectiveness for four of the cover gases examined. Frozen CO_2 was delivered through a system where it was gravity fed to the melt surface using a single injection point near the center of the crucible lid.

Table 1-1. Test Schedule for FTIR Sampling at the Lunt Facility

Date	Time	Cover Gas Mixture Components	Cover Gas Mixture Flow[a] (lpm)	Cover Gas Delivery Conc. [a] (ppmv)	Ingot Type
8/22/06	0740	**Dross**			
8/22/06	0910-1005	Novec™-612/CO_2	~36	800	AZ91D
8/22/06	1008-1135	Novec™-612/CO_2	~36	600	AZ91D
8/22/06	1138-1301	Novec™-612/CO_2	~36	400	AZ91D
8/22/06	1347-1425	Novec™-612/CO_2	~36	300	AZ91D
8/23/06	0906-0958	Novec™-612/CO_2	~36	200	AZ91D
8/23/06	1000-1100	**Dross**			
8/23/06	1108-1248	Novec™-612/CO_2	~36	200	AZ91D
8/23/06	1252-1556	Novec™-612/CO_2	~36	150	AZ91D
8/24/06	0939-1311	SF_6/CDA	~35	3,000	AZ91D
8/24/06	1312	**Dross**			
8/24/06	1510-1736	HFC 134a/CDA	~40	4,200	AZ91D
8/24/06	1806-1902	SF_6/CDA	~35	3,000	AZ91D
8/25/06	0730	**Dross**			
8/25/06	0810-1215	HFC 134a/CDA	~40	3,600	AZ91D
8/28/06	1015	**Dross**			
8/28/06	1105-1130	SO_2/CDA	~39	10,000	AZ91D
8/28/06	1133-1218	SO_2/CDA	~39	8,500	AZ91D
8/28/06	1222-1348	SO_2/CDA	~39	7,000	AZ91D
8/28/06	1351-1500	SO_2/CDA	~39	6,000	AZ91D
8/28/06	1504-1552	SO_2/CDA	~39	5,000	AZ91D
8/29/06	0845-1001	SO_2/CDA	~39	5,000	AZ91D
8/29/06	1005-1155	SO_2/CDA	~39	4,000	AZ91D
8/29/06	1651-1829	Frozen CO_2	Liquid CO_2 at 100 psi	1,000,000	AZ91D

[a] As provided by Lunt Manufacturing, AMT, Polycontrols, and Matheson Tri-Gas/TNSC.

Table 1-2. Magnesium Die Casting Machine Parameters

Parameter	**Machine #1**[a]
Facility	Lunt Manufacturing: Hampshire, IL
Furnace Temperature (^oF)	1,260
Ingot Weight (lbs)	23
Furnace Capacity (lbs)	600
Alloy Type	AZ91D
Mg Casting Rate (seconds/part)	33
Mg Pump Type	Cold Chambered Gas Displacement
Mg Shot Weight (lbs)	0.8
Metal Throughput (lbs/hr)	85.6
Product	Automotive Lock Body Housing
Molten surface area (sq ft)	12.6
Ingot Loading	Automatic Feed

[a] As provided by Lunt Manufacturing

Figure 1-1. Die Casting Machine Crucible at Lunt Manufacturing

2.0 Principles of FTIR Monitoring

Almost every chemical compound absorbs infrared (IR) light to some degree in a particular region of the mid-infrared spectrum. These absorption properties can be used to identify and quantify chemical compounds in a complex mixture of gases. As stated by Beer's Law, the magnitude of a compound's IR absorbance is directly proportional to the product of its concentration in the mixture and the sample cell optical path length. This product is otherwise known as the compound's *optical depth*. The extractive FTIR instruments used by URS are able to achieve parts-per-billion (ppb) detection levels because the optical path length within the measurement cell is magnified many times by reflecting the IR beam between a series of mirrors before it reaches the detector. The mirrors provide a fixed optical path length best suited to the gas mixture being sampled. In this case, optical path lengths of 20.1 meters (for worker exposure monitoring) and 5.1 meters (for crucible head space monitoring) were utilized.

2.1 The Spectrum Analysis Method

An infrared spectrum analysis is performed by matching the features of an observed spectrum to those of reference gases of known concentration. If more than one feature is present in the same region, then a linear combination of references is used to match the compound feature. The standards are scaled to match the observed band intensities in the sample. This scaling also matches the unknown concentrations. An infrared spectrum can be collected and analyzed in approximately one second, but spectra are normally averaged over one- to five-minute integration periods to produce adequate signal-to-noise limits and ppb detection levels.

The scaled references are added together to produce a composite that represents the best match with the sample. A classical least squares mathematical function is used to match the standards' absorption profiles with those of the observed spectrum in specified spectral analysis regions. The compounds of interest together with compounds expected to cause spectral interference are included in the analysis region.

2.2 Creating the Spectrum Analysis Method

The spectrum analysis methods used for the tests at the Lunt Manufacturing facility were developed by URS scientists by selecting the spectral regions and sub-regions that are least affected by primary IR absorbers (H_2O and CO_2, in this case) while also producing the best detection limit possible for the target compounds. Target compounds are initially determined prior to sampling and are based on previous tests and the cover gas composition. However, many destruction byproduct gases were found during data analysis requiring many iterations of data processing and interpretation. Typically, an analysis method is iteratively refined by using it to analyze a representative set of infrared spectra while varying the method. The optimum method is indicated when both the 95% confidence levels and the bias on the individual compounds are minimized. Table 2-1 lists the range of references included in the analysis method used by the FTIR systems for the tests. Each reference is described in terms of its optical depth (i.e., concentration times cell path length (ppmv-meters) range.

After setting up the FTIR instruments on-site, signal-to-noise ratio (SNR) assessments were performed. This was determined by measuring the noise equivalent absorbance (NEA) of each FTIR system while sampling nitrogen. The NEA is derived by ratioing two consecutive single beam spectra to produce a “zero” spectrum, then measuring the peak-to-peak absorbance at a frequency region of interest. This represents the noise level of the instruments under field conditions. By determining the concentration level for each contaminant that scales down its analyzed spectral features to the NEA (representing a SNR of 1 or better), the compound’s SNR-limited minimum detection limit (MDL) can be estimated.

Due to the complexity of the sample matrices, the detection limits reported in Section 4 for each compound were calculated using one of two different methods. The first method was used when spectroscopic interferences *were* taken into account for those contaminants that have overlapping absorption features and an increase in their noise based MDLs was expected. To determine this MDL, an actual data set of spectra where the target analyte was not observed (via spectral validation by a URS spectroscopist), but all other process gases were present, was used. Within this data set, any positive concentration observed for the target analyte would be a mathematical anomaly created by interferences. Three times the standard deviation of the data set is an approximation of the method limited MDL that contains over 99% of all expected data points within the noise scatter. This method is preferred to the theoretical “noise based” detection limit since it accounts for the effects of interferences. The calculation is a more conservative and practical calculation and therefore was used wherever possible. The second method was conducted when the analyte of interest was always present in the sample stream or there were insufficient data points for the previously mentioned method.

A theoretical noise-based detection limit was determined by comparing the peak-to peak noise value calculated from the NEA spectrum to the absorbance intensities and optical depth of the lowest concentration reference used in the analytical method. The equation below shows the calculation for theoretical noise-based detection limits. Note that this MDL is multiplied by two as a conservative estimate (to include at least 95% of all noise scatter). For all MDL calculations, a peak-to-peak noise of 1 x 10^{-3} absorbance units was used.

$$\frac{\text{Peak - to - Peak Noise}}{\text{2 x MDL x Path Length}} = \frac{\text{Reference Absorbance}}{\text{Reference Pathlength} \times \text{Reference Concentration}}$$

Table 2-1. Analysis Method Parameters for Major Contaminants and Spectroscopic Interferants

Chemical Formula	**Compound**	**SF_6 (ppmv-meters)**	**HFC-134a (ppmv-meters)**	**Novec™ 612 (ppmv-meters)**	**SO_2 (ppmv-meters)**	**CO_2 (ppmv-meters)**
H_2O	Water	2.89-22.3*	2.89-22.3*	2.89-22.3*	2.89-22.3*	2.89-22.3*
CO_2	Carbon Dioxide	70-2,110	2.06-33.45*	137-510*	70-2,110	137-510*
SF_6	Sulfur Hexafluoride	58-92,701	56-280	56-280	56-280	56-280
$C_2H_2F_4$	HFC-134a	n/a	9,700-27,575	n/a	n/a	n/a
$C_3F_7C(O)C_2F_5$	Novec™ 612	n/a	n/a	99-991	n/a	n/a
SO_2	Sulfur Dioxide	518-10,415	n/a	n/a	518-35,770	518-35,770
CO	Carbon Monoxide	26-20,358	1,500-11,200	784-20,358	26-3,863	784-20,358
HF	Hydrofluoric Acid	1-2,000	1-2,000	1-2,000	1-2,000	1-2,000
COF_2	Carbonyl Fluoride	50-5,000	50-5,000	50-5,000	n/a	50-5,000
C_2H_2	Acetylene	111-5,550	111-5,550	111-5,550	n/a	111-5,550
C_2H_4	Ethylene	86-2,576	86-2,576	86-2,576	86-2,576	86-2,576
C_2F_6	Hexafluoroethane	448-1,119	448-1,119	448-1,119	n/a	n/a
CF_4	Carbon Tetrafluoride	5.6-1,120	5.6-1,120	5.6-1,120	n/a	n/a
CHF_3	Trifluoromethane	112-560	112-560	112-560	n/a	n/a
CH_3F	Methyl Fluoride	177-1,182	177-1,182	177-1,182	n/a	n/a
CH_4	Methane	87-21,119	87-21,119	87-21,119	87-21,119	87-21,119
OF_2	Oxygen Difluoride	1,750-14,000	1,750-14,000	1,750-14,000	n/a	n/a
CH_2O	Formaldehyde	92-1,838	92-1,838	92-1,838	92-1,838	92-1,838
CH_2O_2	Formic Acid	76	76	76	76	76
NO	Nitric Oxide	53-2,043	53-2,043	53-2,043	53-2,043	53-2,043
N_2O	Nitrous Oxide	102-1,019	102-1,019	102-1,019	102-1,019	102-1,019
NO_2	Nitrogen Dioxide	34-1,544	34-1,543	34-1,543	34-1,543	34-1,543
H_2SO_4	Sulfuric Acid	n/a	n/a	n/a	164	n/a
SO_3	Sulfur Trioxide	n/a	n/a	n/a	1400	n/a

*Expresses in %-meters since high concentration references were required.

In some instances compounds absorb infrared light in regions that were interfered by higher concentration compound absorbances, providing large differences in MDL from one data set to another. An example would be CF_4. The MDL for CF_4 in the HFC-134a data set was 3.8 ppmv but only 0.013 ppb in the SF_6 data set. CF_4 was difficult to detect in a sample stream containing high HFC-134a concentrations since its strongest absorbance peak is in a region that HFC-134a absorbs infrared in. Therefore, an alternative region was chosen where the absorbance intensity of CF_4 was much weaker, thus increasing its detection limit. In the SF_6 data set the strongest CF_4 absorbance peak was in a relatively clean region, resulting in the lower MDL.

2.3 Reference Generation

Since the use of HFC-134a and Novec™ 612 within the magnesium industry is relatively new, FTIR references were required to be generated for both gases. Additionally, high concentration CO_2 references were required since concentrations greater than 85% CO_2 were observed when used as a carrier gas for Novec™ 612, and during the frozen CO_2 injections. The Novec™ 612 references were obtained from a previous study[5]. These references were generated from certified gas standards, made gravimetrically on NIST certified scales, from pure Novec™ 612. The standard was certified at ± 2 percent at 201 ppmv Novec™ 612 by HP Gas Products located in Baytown, Texas. The standard was diluted at 5 different levels with gaseous nitrogen and FTIR reference samples were measured via the following procedure:

1. Evacuate and fill the FTIR sample cell with nitrogen 5 times
2. Evacuate the cell using a roughing vacuum pump
3. Add ultra high purity (UHP) nitrogen to a cell pressure of 400-650 torr
4. Add Novec™ 612 gas standard while recording pressure differential
5. Fill cell to 750 torr with N_2
6. Measure gas reference

With this approach the pressure was monitored at each reference step with a calibrated Baratron pressure sensor made by MKS. By knowing the amount of standard added as a function of pressure, the concentration was calculated by the following equation.

$$\text{Reference Concentration} = \frac{\text{Pressure of the Standard Added}}{\text{Total Pressure}} \times \text{Bottle Concentration}$$

HFC-134a references were also made in similar fashion. Each gas reference sample was saved and used to generate calibration curves that were then applied to the Novec™ 612 and HFC-134a data. For CO_2, additional gas standards at high concentrations were generated from a gas cylinder containing 62.92% CO_2 during the previous study[3]. Using this CO_2 gas concentration in a longer path length cell (20.1m as opposed to 5.11m), references were generated such that the CO_2 calibration curve had an effective upper limit of 100% CO_2. Figure 2-1 is a schematic of the configuration used for generating these references.

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[5] Characterization of Cover Gas Emissions From US Magnesium Die Casting Operations. March 2004

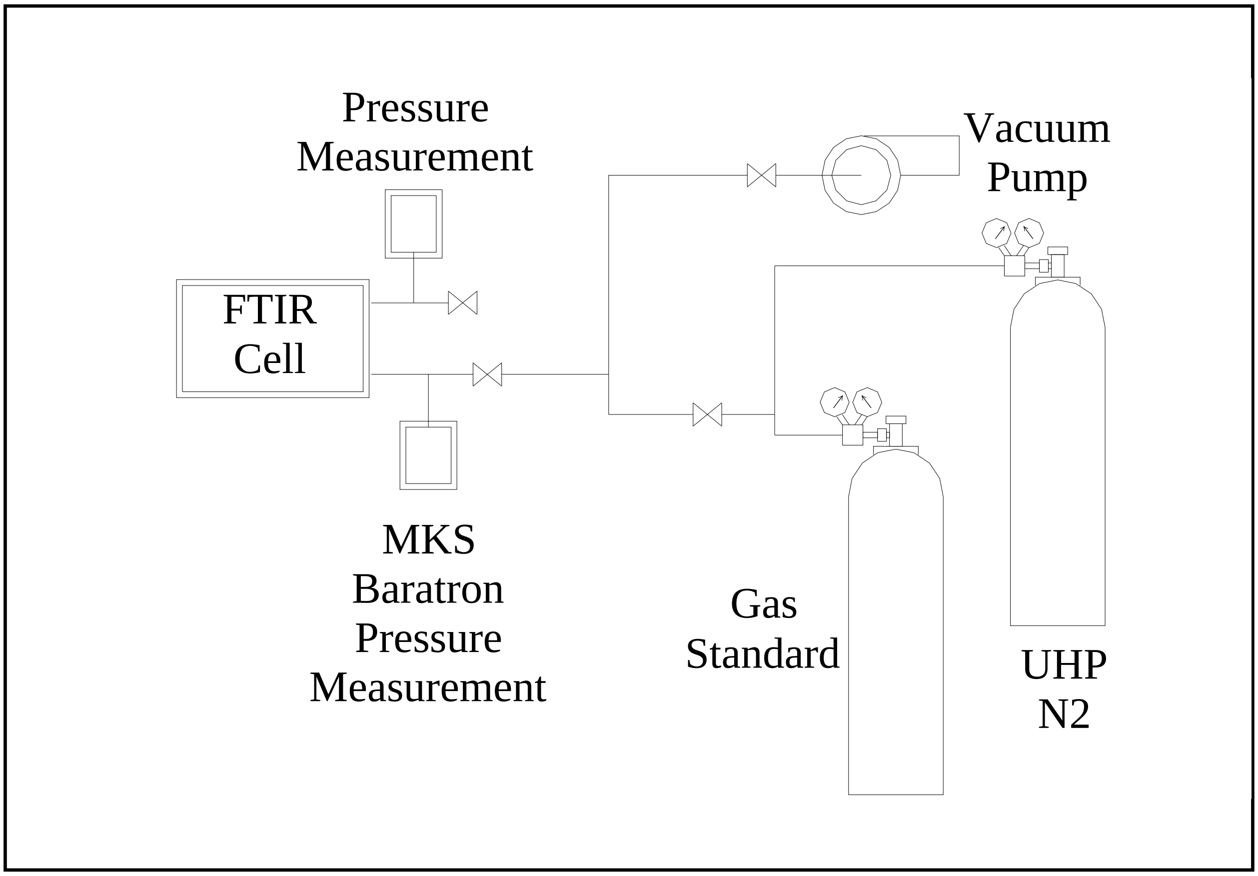

Figure 2-1. Reference Generation Hardware Configuration

3.0 The Extractive FTIR and Other Sampling Systems

Two extractive-type FTIR systems were used for measurements conducted at Lunt Manufacturing. MKS (On-Line) FTIR spectrometers and sample cells were used. The crucible head space monitoring system included two monel sample probes (3/8” OD), a heated PFA-grade Teflon extraction line, the On-Line FTIR spectrometer interfaced to a heated, nickel-coated sample cell, a venturi sample pump, and an exhaust tube. Given this configuration, real-time monitoring consisted of pulling a continuous gas stream, in equal portions from each sample probe, through the sampling system into the heated FTIR sample cell. Sample flow was maintained at approximately 3.2 liters per minute (lpm) by a venturi pump connected to the outlet of the FTIR cell. A schematic is shown in Figure 3-1. The worker exposure/ambient air monitoring system consisted of a length of unheated ¼” PFA grade Teflon extraction line, the MKS On-Line FTIR spectrometer, a heated (35°C), long path length (20.1 m), nickel-coated sample cell, a venturi sample pump, and an exhaust line. The sample gas was pulled from the worker breathing zone at approximately 3 lpm through the extraction line and into the sample cell.

Inside each FTIR cell, a set of optically matched gold-plated mirrors reflects an infrared beam through the sample gas multiple times. As the beam passes through the sample, the molecules in the sample absorb some of its energy. After exiting the cell, the infrared beam is directed to a liquid-nitrogen cooled mercury/cadmium/telluride (MCT) detector, a photoconductive device that produces an electrical voltage proportional to the amount of infrared light that strikes it. The strength of the absorption at particular frequencies is a measure of the compound’s concentration. The total distance traveled by the infrared beam inside the cell is the cell path length, and is an important variable used in determining sample concentrations. For this project, cell path lengths were fixed at 20.1 m for the worker exposure system and 5.1 m for the crucible head space system.

The crucible FTIR sample cell and extraction lines were maintained at a temperature of 150°C (to prevent any condensation losses and preclude the formation of HF mists). The worker exposure/ambient air monitoring extractive line was at room temperature and the cell was maintained at 35°C. For both FTIR systems, cell pressures were continuously recorded during measurement periods using a pressure sensor calibrated over the 0-900 torr range. Instrumental resolutions were set to 0.5 cm^{-1} and signal averaging was performed over 3- and 5-minute periods for the crucible spectrometer and ambient spectrometer, respectively.

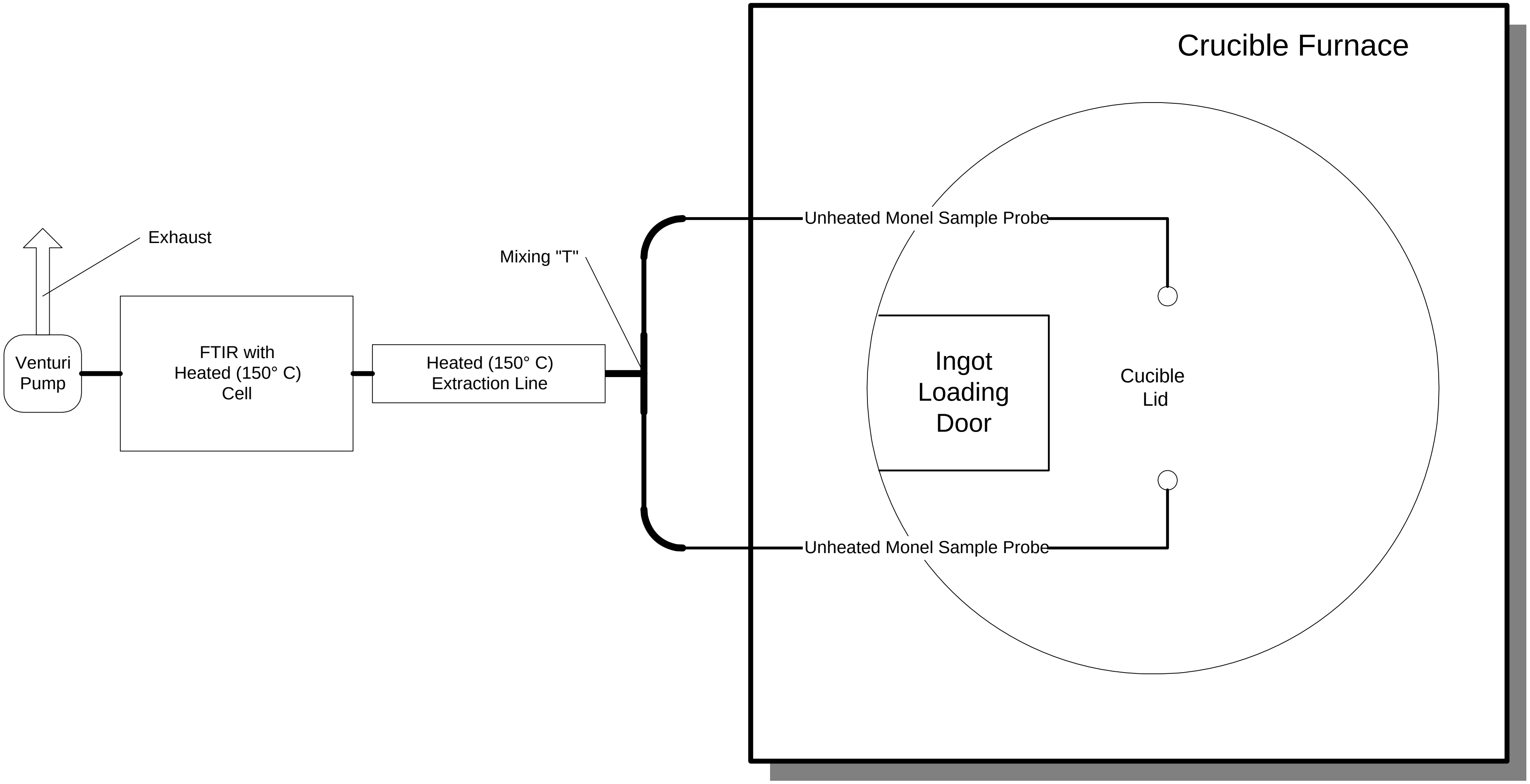

Figure 3-1. Sampling System Schematic

A single die-casting crucible was tested for all cover gases and is illustrated in Figure 3-2 along with the sample extraction locations on the crucible lid. These two sample points were used simultaneously for each set of tests. The probe lengths and connecting tubing were identical in length and fed into a "T" where both gas streams mixed. The sample ports were existing openings in the crucible lid normally used for thermocouples, pump assemblies, etc., and allowed enough room for the sample probes to be placed through the lid without altering its design. Simultaneously sampling from two points allowed for a more representative sample of the headspace area (as compared to sampling from one point at a time). Ideally, a larger manifold and more sample points would be used, but this was not feasible due to the excessive crucible lid modifications required.

The two sampling points were equally spaced on each side of the ingot feed door. Samples at both points were simultaneously extracted through monel tubes inserted into the headspace. The locations had no bearing on the cover gas distribution regime and, when combined, provided representative gas mixture from the headspace of the crucible. Also of note is that the sampling regime, in terms of elevation above the melt surface, was consistent between the two sample extraction locations. The magnesium ingots were automatically fed to the crucible as needed, approximately every 15 minutes, so the loading door would open then immediately close after an ingot was dropped. The door would remain open for less than 10 seconds during this process.

In order to measure the potential occupational exposure concerns associated with the use of these cover gases, the second FTIR was set up to sample from the two primary worker stations at this die casting machine. The first location (Zone 1) is near the part drop point for the robotic arm. At this stage in the die casting process the part is briefly examined by the worker and placed in a container for transport to the next stage in the production process. A sample line was run from the FTIR to a steel support beam adjacent to the drop table where the worker generally stands. The sample point was located 18 feet from the edge of the crucible and 63 inches above the floor (to simulate a typical respiration height). Samples were taken on a continuous basis from this point during testing of AM-Cover™, MTG-Shield™, and SF_6. The second location (Zone 2) was 30 inches away and 12 inches above the ingot loading hatch on the crucible lid.

Ventilation around the casting machine (and throughout the whole facility) was substantial. The machine is approximately 60 feet from a large overhead door opened to the outside; there were multiple industrial floor fans in the area, and there is a sub-floor fresh air supply vent located 30 feet from the machine that was directing a continuous flow of fresh air towards the machine. Additionally, the entire facility has high-volume exhaust fans in the ceiling that contribute to the area around the machine (and the whole facility) having a very high air exchange rate.

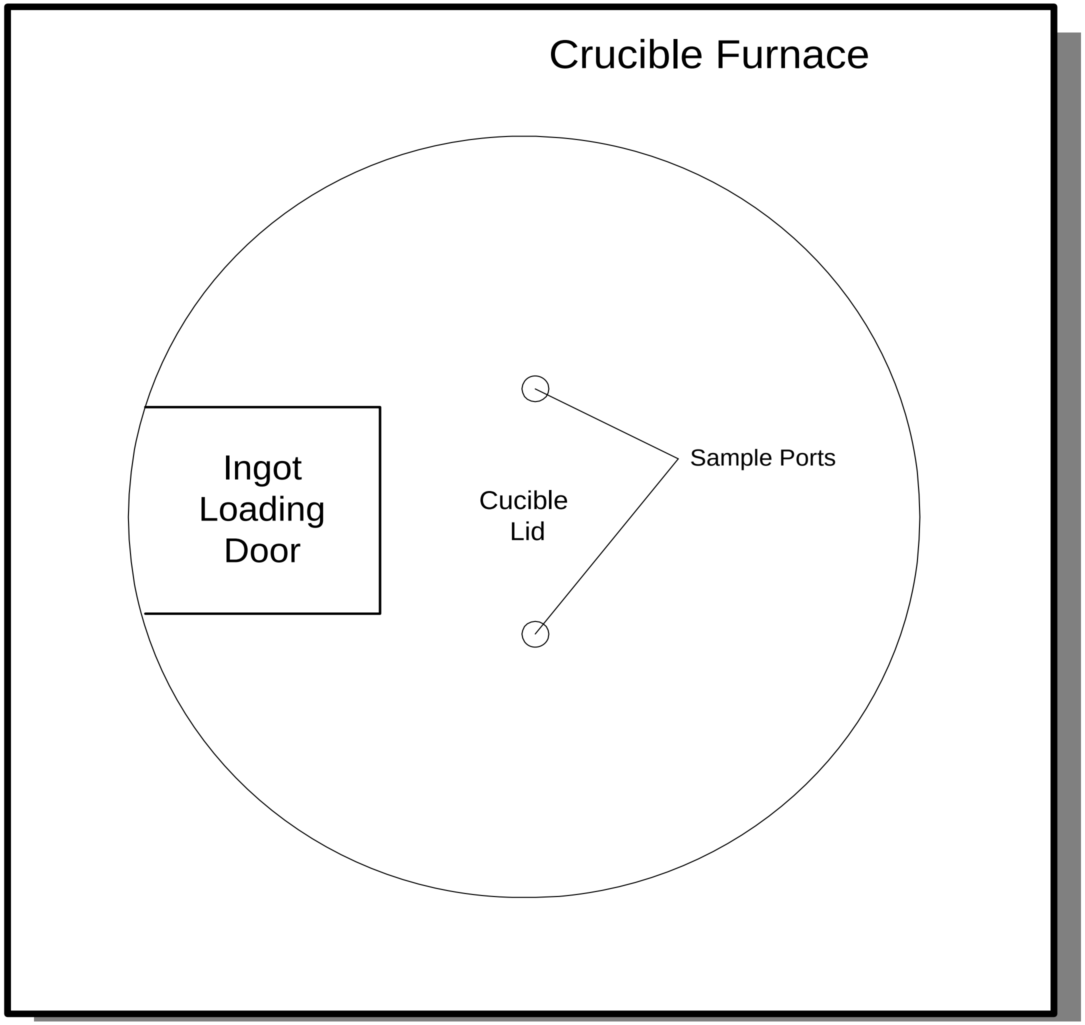

Figure 3-2. Sample Locations for the Tested Crucible

3.1 Hydrogen/Oxygen Analyzer

Figure 3-3. Nova 340WP Oxygen and Hydrogen Analyzer

A Nova Model 340WP portable analyzer was used over a 2-hour period during a MTG-Shield™ using MTG-Shield™ cover gas test for the continuous measurement of oxygen concentrations. The instrument is shown in Figure 3-3. This instrument uses an electrochemical sensor to measure oxygen over a range of 0 to ambient levels (20.9%). A chemical reaction occurs when the sensor is exposed to oxygen, resulting in a millivolt output proportional to the oxygen concentration in the sample gas. This small voltage was used to display the measured oxygen concentration on the instrument's front panel meter as well as fed to a portable strip chart. A slipstream was taken from the inlet to the FTIR sampling the crucible headspace and fed into the O_2 analyzer. A continuous reading was recorded onto a strip chart. Since the sampling system was a closed system and the Novec™ 612 was diluted with CO_2, the O_2 present was assumed to be due to mostly ambient air, but presumably a fraction was formed/destroyed during reactions between the cover gas mixture and the melt surface, thereby biasing the dilution results. This behavior warranted the need for quadrapole mass spectrometry (QMS) to monitor an inert gas, in this case N_2, in order to accurately gauge ambient air dilution effects.

3.2 Quadrapole Mass Spectrometer (QMS)

Quadrapole mass spectrometers (QMS) are often used for residual gas analysis in various industrial applications. It was incorporated in this study to determine the overall combined dilution or ambient air entering the crucible, from leaks and ingot loading. Traditionally, mass spectrometers have been used as research instruments for analysis under vacuum applications. The recent advancements of the technology coupled with the development of atmospheric samplers and closed ion sources, has enabled atmospheric sampling via QMS. The “high pressure” QMS, otherwise know as residual gas analyzers (RGAs) are smaller, more robust, and much more portable than their laboratory predecessors. The RGA used for this testing was a Leybold Inficon Transpector Closed Ion Source 2 and is shown in Figure 3-4. The Leybold RGA utilizes a differentially pumped atmosphere-to-analyzer chamber sample interface.

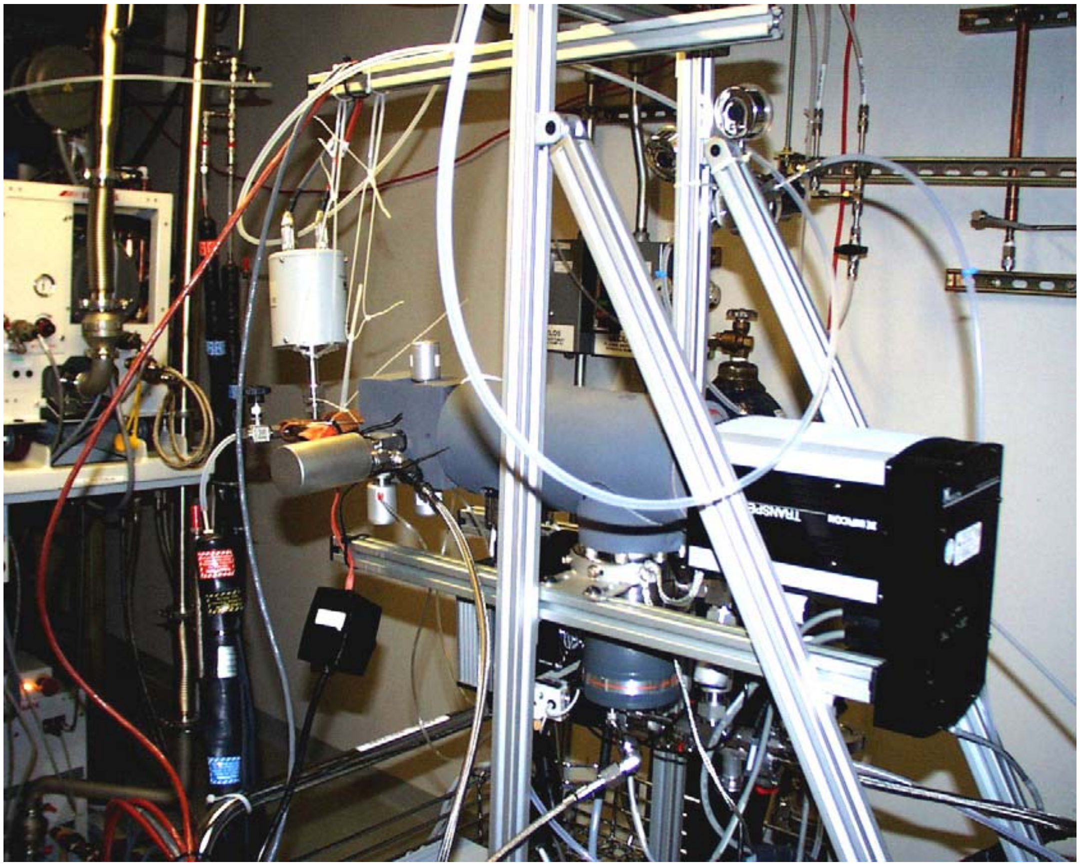

Figure 3-4. The QMS used to Monitor N_2 Inside the Crucible for Dilution Calculation

This allows sample gas, at or near atmospheric pressure, to “leak into” the QMS ionizer region under controlled rates via precision orifices. All the sample components can then be simultaneously ionized and mass selected for quantitative analysis. However, the analyzer’s response factors, over all the mass units, are highly dependent on the ionizer’s chamber pressure, energy, etc., so a careful calibration must be performed on-site and under a consistent sampling configuration. This is presented in Section 4.6.

3.3 FTIR Calibrations and System Checks

A series of on-site calibration and system checks was performed on each FTIR and sampling system prior to testing to ensure data of known quality. These checks consisted of the following:

3.3.1 Cell Leak Checks

This test checks the integrity of each cell by pulling a vacuum on it and then monitoring the leak rate. The acceptance criteria for this test is a leak rate < 2 torr/minute. The evacuated pressure on each FTIR sample cell did not change over a 1-minute period.

3.3.2 Infrared Detector Linearity Checks

For best results, it must be assured that the infrared detector yields a linear response throughout a reasonable absorbance range at all the frequencies in a set of test spectra. A software linearizer is used to continuously adjust the MCT detector preamp signal in order to achieve the desired response. To optimize the linearizer, background spectra are acquired with and without a polyethylene film in the IR beam. Comparison of the strongly absorbing polyethylene bands in the low, mid and high frequency regions against a clean background enables the processor to appropriately set the linearizer terms (offset, linear, quad, cubic and delay). This procedure was run prior to the start of testing, and subsequent spectra were visually checked on a periodic basis to confirm that linearity was maintained.

3.3.3 Noise Equivalent Absorbance (NEA) or Signal-to-Noise Ratio (SNR) Tests

This provides a measure of the system noise, that is the sensitivity of the instrument for the specified spectral resolution (0.5 cm^{-1}, in this case) and number of scans (256, or two minutes of signal averaging, in most cases). An NEA test was run upon set-up. The results for both systems, which were used to assess the field detection limits, were as follows:

20.1m Path Length System 2010
Range = 1000-1100cm^{-1}, RMS Noise=0.22 milliAU
Range = 2450-2550cm^{-1}, RMS Noise=0.25 milliAU
Range = 4200-4300cm^{-1}, RMS Noise=0.72 milliAU

5.11m Path Length System 2030
Range = 1000-1100cm^{-1}, RMS Noise=0.15 milliAU
Range = 2450-2550cm^{-1}, RMS Noise=0.16 milliAU
Range = 4200-4300cm^{-1}, RMS Noise=0.76 milliAU

3.3.4 Path Length

The sample cell used for these tests was geometrically fixed at 20.1 meters for the FTIR system used for the occupational exposure sampling, and 5.1 meters for the FTIR system used for sampling the headspace of the crucible.

3.3.5 Spectrometer Frequency and Resolution Checks

A real-time check of frequency position and resolution was performed prior to and directly after each round of testing by monitoring a specific water absorption line (present in ambient air). The position of this line must not deviate more than ± 0.005 cm^{-1} from the reference value over the course of each test. Likewise, the line width (directly related to instrument resolution) of this line must not deviate more than ± 0.05 cm^{-1} from the reference value over the course of each test.

3.3.6 Spectral Background

A spectral background is essentially a “blank spectrum” in that it does not contain any of the target compounds present in the sample. It was created by purging the cell with ultra-high-purity (UHP) nitrogen while collecting a spectrum. This spectrum was then used by the analytical software to ratio against each sample spectrum to produce an absorbance spectrum for quantitative analysis. A new spectral background was generated each day prior to the beginning of testing.

3.3.7 Sample Cell Exchange Rate

Given sampling flow rates on the order of 3 liters/min through either cell during the testing, a complete sample exchange takes place every 12 seconds for the 5.1 meter cell, and 32 seconds for the 20.1 meter cell. Since spectral signal averaging was conducted over 3- and 5-minute intervals (for the headspace and worker zone respectively), each collected spectrum represented an integrated average over multiple sample cell exchanges.

3.3.8 FTIR Measurement Error

As with all analytical devices, extractive FTIR measurements are known to have a given error associated with them. Steps were taken throughout the measurement process to minimize sampling error. Sampling error is dependant on many factors including spectral interferences contained in the sample stream, instrumental noise of the FTIR systems, infrared detector nonlinearities, and optical depth of references that were applied. Errors were minimized by applying a series of references at various optical depths to account for any nonlinearities or dynamic concentration swings in the sample matrix. Spectra were also manually inspected for qualitative and quantitative validation. As a result of these efforts, the measurements taken in this study have a level of uncertainty that was significantly lower than ±30 %.

4.0 Test Results

This section presents all the cover gas test data and is broken into sections according to cover gas type as they were chronologically tested: MTG-Shield™ using Novec™ 612, AM-Cover™ using HFC-134a, SF_6, SO_2, and frozen CO_2. Additionally, the QMS calibration/dilution data and occupational exposure testing are included in sections 4.6 and 4.7, respectively. Table 1-1 of Section 1.0 shows the test schedule, cover gas injection flow rates and concentrations used during testing. Data collected during sampling downtime (i.e., probe taken out while switching cover gases) or abnormal operation (drossing) were excluded from the data tables, plots and calculations of this report. For compounds not observed above their respective MDLs a "BDL" (Below Detection Limit) was reported. There were some data sets that would bracket the MDL, i.e. had values above and below the detection limits. To calculate average values over these data sets, a value of half the MDL was used in place of the BDL values. Normally a range for average values is reported using zero for the low range and the detection limit for the high range. However, the following data tables are simplified by using the "average value" (half the MDL) of the detection limit to calculate concentration averages. When calculating the standard deviation for data sets containing concentrations above and below the MDLs, the raw data was used in place of the BDL so as not to bias the deviation. Since the standard deviations were calculated with the ingot loading times included (known dilution from ambient air when the loading door was opened), they were skewed high and representative of a non-stable system. Detection limits were calculated as three times the standard deviation while the analytes were not present in the sample streams (see Section 2 for a detailed explanation). When an analyte was present, a method based detection limit was determined by using the noise-based equation defined in Section 2.2.

On several instances immediately after connecting the extraction line to the sample probes, low concentrations of hydrochloric acid (HCl) were detected that would slowly decay throughout each testing period. This behavior was independent of cover gas process activity (for no chlorine was employed in any gas mixtures) and therefore is attributed to chlorine being stripped from the Teflon core in the extraction line, or possible contamination from another source.

The data in this section are summarized in Tables 4-1 through 4-12. Appendix A presents plots detailing data trends and process activities, such as ingot loading, for all the compounds that were observed above detection limits. BDL data entries were plotted as zero on the charts in Appendix A. The data summaries in Tables 4-1 through 4-12 represent normal crucible operation specific to this machine (HWP 400 die casting Machine 1) fabricating a specific part (automotive lock body housing). The periods when the ingot door was open for ingot loading were included in the results presented data tables.[6] Comparisons of this data to other die-casting machines would not be entirely appropriate, since the operational parameters would most likely be different (thereby affecting the average dilution). However, all the data in this study was collected on a single crucible/die-casting machine, fabricating the same part, providing a direct comparison of the five different cover gas technologies.

4.1 MTG-Shield™ using Novec™ 612 with CO_2 Carrier Gas

A series of tests was run that sequentially lowered the injected concentrations of Novec™ 612 in the MTG-Shield™ cover gas mixture to optimize its performance. The MTG-Shield™ cover gas was used over a two-day period at six different levels for a step-wise approach to optimization beginning with the highest level (800 ppmv) on the morning August 22nd and ending with the lowest level (150 ppmv) on the afternoon of August 23rd. Table 4-1 presents the data summary for the *observed* compounds at each level tested during normal casting conditions. Appendix A contains the respective time series plots for the observed compounds. Additional compounds were monitored but not observed above their MDLs. Table 4-2 presents the MDLs for all the compounds monitored during the MTG-Shield™ testing. Testing during day 1 indicates that the Novec™ 612 destruction increases as its inlet concentration level decreases. So, as the inlet concentration decreases, the destruction rate approaches 100% - the optimal condition for melt protection. During day 2 this trend was repeatable, with the absolute destruction rates slightly lower.

In addition to CO_2 and unreacted Novec™ 612, destruction byproducts of CO, COF_2, HF, CH_4, C_2F_6, CHF_3, and C_3F_8 were observed. HF concentrations were detected at levels of 7 to 450 ppmv for the range of mixtures evaluated.[7] Higher feed gas concentrations resulted in higher concentrations of HF. Formaldehyde, C_2H_4, N_2O and NO_2 were also observed, and were believed to be present mostly as a function of ambient air dilution. For CH_2O and C_2H_4, this was supported by the observation of slight concentration increases during ingot loading, then sharp decays to baseline levels or BDL immediately after ingot drops. This effect was less pronounced for N_2O and NO_2. An interesting trend also occurred with CO as the Novec™ 612 was sequentially decreased. Average CO concentrations were very stable (just over 800 ppmv) during the 800, 600, and 400 ppmv Novec™ 612 cover gas tests.

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[6] The crucible headspace was not purged with the new cover gas prior to measurements so the initial readings for each cover gas include a small protection overlap with the previous one used. The impact of this is likely to be negligible in terms of overall cover gas performance from a GHG emission perspective.

[7] The addition of dry air to the cover gas mixture to minimize unwanted byproducts (and reduce GHG emissions) was not feasible given the short duration of this study. A more accurately optimized system would likely include a dry air component.

Table 4-1. Data Summary for MTG-Shield™ using Novec-612™ with CO_2 Carrier Gas

	H_2O (%)	CO_2 (%)	Novec™-612 (ppmv)	CO (ppmv)	COF_2 (ppmv)	HF (ppmv)	CH_4 (ppmv)	C_2F_6 (ppmv)	C_2H_4 (ppmv)	CH_2O (ppmv)	CHF_3 (ppmv)	N_2O (ppmv)	NO_2 (ppmv)	C_3F_8 (ppmv)
Min (800ppmv)	0.2	62.8	143.1	461.5	28.5	132.7	2.0	6.7	BDL	BDL	4.1	2.8	0.4	6.3
Max (800ppmv)	0.3	96.9	212.7	1,005.6	35.9	450.3	5.1	12.7	BDL	0.4	7.4	4.7	1.7	21.2
Average (800ppmv)	0.2	92.3	198.8	868.2	32.3	381.2	3.8	9.8	BDL	0.2	6.6	3.5	0.9	13.5
Stdev	0.1	8.2	16.1	123.8	2.3	79.2	1.0	2.1	n/a	0.1	0.8	0.5	0.4	5.2
Min (600ppmv)	0.2	88.5	129.3	714.4	13.2	290.3	1.3	5.6	BDL	BDL	4.7	2.4	0.4	2.8
Max (600ppmv)	0.3	97.7	147.6	995.7	19.0	336.1	5.5	10.3	BDL	0.5	6.0	3.6	1.7	14.1
Average (600ppmv)	0.3	93.7	142.5	828.4	16.3	313.3	4.1	7.6	BDL	0.2	5.3	3.1	0.9	7.6
Stdev	0.0	2.8	4.4	64.5	1.3	13.9	1.0	1.3	n/a	0.1	0.3	0.3	0.4	3.4
Min (400ppmv)	0.2	34.5	31.9	100.8	BDL	82.7	1.5	BDL	BDL	BDL	0.4	2.2	0.7	BDL
Max (400ppmv)	1.5	96.9	77.3	1,286.1	6.5	180.0	19.4	4.8	3.8	3.1	4.3	6.3	5.3	3.0
Average (400ppmv)	0.4	86.3	55.4	838.9	2.9	110.9	5.1	1.9	0.6	0.5	2.4	3.2	1.6	0.7
Stdev	0.4	16.1	9.2	287.7	1.7	21.7	4.8	1.1	1.2	0.8	0.8	1.0	1.3	1.6
Min (300ppmv)	0.2	49.1	2.2	451.3	BDL	6.9	3.1	BDL	BDL	BDL	0.1	1.1	1.0	BDL
Max (300ppmv)	1.3	95.3	3.7	5,031.0	BDL	23.6	10.6	BDL	BDL	1.0	0.4	3.0	3.8	BDL
Average (300ppmv)	0.5	81.6	3.2	1,871.0	BDL	11.9	5.6	BDL	BDL	0.4	0.3	2.2	1.9	BDL
Stdev	0.4	17.5	0.5	1,361.1	n/a	5.3	2.5	n/a	n/a	0.2	0.1	0.6	1.0	n/a
Novec™612 Testing on 8/23/07														
Pre Dross Min (200ppmv)	0.2	63.4	65.5	438.9	3.5	146.0	BDL	1.6	BDL	BDL	2.5	2.1	BDL	BDL
Pre Dross Max (200ppmv)	0.9	98.0	96.9	1,287.1	8.9	244.8	67.3	5.8	19.9	10.3	4.8	4.8	2.1	7.9
Pre Dross Avg. (200ppmv)	0.4	89.0	75.8	764.7	6.3	170.0	8.9	3.6	2.3	1.4	3.6	2.9	0.5	3.3
Stdev	0.2	10.2	7.8	211.2	1.3	23.6	17.4	1.5	5.3	2.9	0.7	0.7	0.5	3.5
Post Dross Min (200ppmv)	0.2	68.4	59.8	852.5	2.0	24.9	1.4	0.7	BDL	BDL	1.9	2.0	1.4	BDL
Post Dross Max (200ppmv)	0.9	96.9	81.8	1,983.2	6.1	160.0	7.6	1.8	BDL	0.4	3.3	4.1	5.0	BDL
Post Dross Avg. (200ppmv)	0.3	92.1	64.2	1,421.0	4.9	120.8	4.8	1.2	BDL	0.2	2.6	2.8	2.3	BDL
Stdev	0.1	5.3	3.8	227.4	0.8	28.0	1.3	0.3	n/a	0.1	0.3	0.5	0.8	n/a
Min (150ppmv)	0.2	61.7	24.7	677.2	BDL	46.3	2.4	0.1	BDL	BDL	0.8	1.6	BDL	BDL
Max (150ppmv)	1.1	98.7	40.3	2,028.2	1.1	117.0	12.6	0.9	2.5	2.4	2.3	3.4	3.0	BDL
Average (150ppmv)	0.3	91.7	30.8	1,270.8	0.4	61.3	4.9	0.6	0.4	0.3	1.5	2.3	1.0	BDL
Stdev	0.1	6.4	2.5	267.2	0.5	13.0	1.9	0.1	0.5	0.4	0.2	0.4	0.6	n/a

BDL = below detectable limit; n/a = not applicable

Table 4-2. MDL Summary for all Monitored Compounds During MTG-Shield™ Tests

Compound	**Minimum Detection Limit (ppmv)**
H_2O	n/a
CO_2	n/a
Novec™-612	n/a
CO	n/a
COF_2	n/a
HF	n/a
CH_4	0.023*
C_2F_6	0.104
C_2H_2	4.08
C_2H_4	0.379
CF_4	3.803
CH_2O_2	0.256
CH_2O	0.312
CH_3F	1.333
CHF_3	0.022*
N_2O	n/a
NO_2	0.149
NO	0.689
OF_2	19.292
SF_6	0.069
C_3F_8	1.08

n/a= not applicable since compound was consistently present throughout the testing

*Noise based MDL

However, upon decreasing to 300 ppmv, a large increase in CO was observed. Referring to the CO plot in Appendix A, a large CO spike followed by subsequent decay is observed which is due to reaction of CO_2 with the fresh Mg melt surface created by ingot loading. This may be an indicating factor that the optimal cover gas concentration is near 300 ppmv for Novec™ 612. A similar effect was observed after the dross performed during the 200 ppmv Novec™ 612 testing. Although a burn upon a clean melt surface should be expected, the CO concentrations did not decrease throughout the post-dross 200 ppmv and 150 ppmv cover gas injections. Water vapor was also observed throughout the entire test periods, mostly from ambient air dilution. There were also absorbance features for two unknown compounds observed sporadically during testing. One of these features was most likely due to a C-F or HC=CH functional group.

4.2 AM-Cover™ using HFC-134a with CDA Carrier Gas

Two concentrations of HFC-134a mixed with compressed dry air (CDA) were injected (4,200 and 3,600 ppmv) during August 24th and 25th, 2006. The HFC-134a cover gas standard was diluted with facility CDA and mixed with a gas blender provided by Lunt Manufacturing and operated by Advanced Magnesium Technologies (AMT). Each cover gas mixture's HFC-134a concentration was verified by FTIR prior to injection into the crucible. To accomplish this, the outlet of the gas blender was connected directly to the heated extraction line leading to the FTIR. The gas blending parameters were adjusted until the desired HFC-134a concentration was achieved. The gas mixture was then delivered into the crucible. Table 4-3 presents the data summary for the *observed* compounds at each level tested during normal casting conditions. Additional compounds were monitored but not observed above their respective MDLs. Table 4-4 presents the MDLs for all the compounds monitored during the HFC-134a testing. In addition to the compounds listed in Table 4-4, there was an unknown absorbance profile observed in the HFC-134a spectra. Searches of URS reference libraries did not provide a positive match; however, based on the absorbance frequencies and band shapes it is believed to be due to a compound terminating with a double bonded hydrocarbon functional group ($–CH=CH_2$). Time series plots for the observed compounds are displayed in Appendix A.

Table 4-3. Data Summary for AM-Cover™ using HFC-134a with CDA Carrier Gas

	H_2O (%)	CO_2 (%)	CO (ppmv)	HFC 134a (ppmv)	HF (ppmv)	COF_2 (ppmv)	CH_4 (ppmv)	C_2H_4 (ppmv)	CH_2O (ppmv)	SF_6 (ppmv)	N_2O (ppmv)	NO_2 (ppmv)	NO (ppmv)	SiF_4 (ppmv)
AM-Cover Testing on 8/24/06														
Min (4,200 ppmv)	0.5	0.1	339.9	671.6	448.0	15.7	BDL	BDL	BDL	0.3	2.2	5.2	BDL	0.9
Max (4,200 ppmv)	0.9	0.3	905.4	1,957.8	1,199.4	55.1	2.5	BDL	0.9	1.7	35.0	77.7	20.4	4.5
Average (4,200 ppmv)	0.6	0.3	628.0	1,198.3	914.9	38.7	0.6	BDL	0.2	0.8	15.8	52.0	9.1	2.6
Stdev	0.1	0.1	150.4	437.7	206.9	10.5	0.5	n/a	0.2	0.3	10.2	25.2	7.5	1.0
AM-Cover Testing on 8/25/06														
Min (3,600 ppmv)	0.5	0.2	311.9	475.7	669.8	16.1	BDL	BDL	BDL	0.2	4.7	22.7	0.8	0.3
Max (3,600 ppmv)	1.1	0.3	713.0	1,512.3	929.5	59.1	2.7	BDL	0.6	0.8	38.7	84.5	28.0	1.4
Average (3,600 ppmv)	0.6	0.3	452.2	810.7	785.2	37.3	0.5	BDL	0.1	0.3	19.9	66.6	18.5	0.6
Stdev	0.1	0.0	106.3	276.1	58.9	11.8	0.5	n/a	0.1	0.1	7.1	12.1	8.3	0.3

BDL = below detectable limit
n/a = not applicable

Table 4-4. MDL Summary for All Monitored Compounds During AM-Cover™ Tests

Compound	Minimum Detection Limit (ppmv)
H_2O	n/a
CO_2	n/a
CO	n/a
HFC-134a	n/a
HF	n/a
COF_2	n/a
CH_4	0.374
C_2H_2	0.163
C_2H_4	0.213
CF_4	3.80
CH_2O_2	11.99
CH_2O	0.162
C_2F_6	0.566
CH_3F	0.916
CHF_3	0.278
SF_6	n/a
OF_2	0.676
N_2O	n/a
NO_2	n/a
NO	1.99
SiF_4	n/a

n/a = not applicable since compound was consistently present throughout the testing

The amount of HFC-134a destruction during each test was 71% and 77% for the 4,200 ppmv and 3,600 ppmv cover gas concentrations, respectively. It was evident from the HFC-134a plots in Appendix A that the HFC-134a crucible concentrations decayed throughout the first two hours of each test. Since there was no indication of magnesium burns during testing, the injection of lower (optimized) HFC-134a cover gas concentrations may be acceptable and might also provide slightly higher destruction rates and reduced emissions.

Gradual concentration decays were observed for CO and COF_2. An inverse effect to these decays was observed for HF and the nitrogen oxides (N_2O, NO, and NO_2). This is easily explained for HF, since the greater HFC-134a destruction in the cover gas produces a larger concentration of the by-products. Over the first 2-hours of each test the NO_2 concentration continually increased before settling at approximately 70 ppmv. However, the N_2O and NO concentrations continually increased throughout each test. Although it was an interesting dynamic, no plausible explanation could be inferred from the current data.

In addition to unreacted HFC-134a and the nitrogen oxides formed from the CDA carrier gas, destruction by-products (HF, COF_2, and CO) were also observed during each test. HF concentrations were measured from 448 to 1,199 ppmv with higher values correlating to higher concentrations of HFC-134a in the feed gas. Low concentrations of C_2H_4 and CH_2O were also sporadically observed, usually coincident with ingot loading. Detection of SF_6 was also observed at low concentrations and is a residual from previously used SF_6 cover gas. SiF_4 was continuously observed and is believed to have formed as a result of contamination inside the crucible, perhaps from fiberglass insulation. Water and CO_2 were observed and were likely present in the CDA carrier gas and any ambient air that entered the crucible through leaks.

4.3 SF_6 with CDA Carrier Gas

Sulfur hexafluoride is the most commonly used cover gas in the magnesium die casting industry, and exclusively used at Lunt Manufacturing. The SF_6 cover gas was only monitored at a single injection concentration (~3,000 ppmv) corresponding to the current levels used by Lunt Manufacturing. The testing was completed on the 24th of August 2006 over two independent periods. These periods were separated by five hours, the time when testing of the 4,200 ppmv HFC-134a cover gas occurred. A summary of all the *observed* compounds is presented in Table 4-5. Additional compounds were monitored, but not observed above their respective MDLs. Table 4-6 presents the MDLs for all compounds monitored during the SF_6 testing. Time series plots for the observed compounds are displayed in Appendix A. The destruction of SF_6 during testing was measured at approximately 33%. This is much lower than the other cover gases with the exception of SO_2 and frozen CO_2 (note that SF_6 carries more available free fluorine per molecule than does HFC-134a, and has less possible destruction-to-byproduct pathways than does Novec™ 612).

One observation of note was that the nitrogen oxides and HF were observed at much higher concentrations upon initial change over to SF_6 from the HFC-134a. The limited data set does show indication of decay and it is assumed that the concentrations would have continued to the levels observed prior to the HFC-134a tests. The differences are believed to be an effect of instability inside the crucible from temperature effects and/or the extended time it takes to completely displace the previously used cover gas. Another factor in this effect may involve the reaction dynamics between the molten magnesium and the SF_6/CDA mixture.

Table 4-5. Data Summary for SF_6 with CDA Carrier Gas

	H_2O (%)	**CO_2 (%)**	**CO (ppmv)**	**SF_6 (ppmv)**	**HF (ppmv)**	**CH_4 (ppmv)**	**C_2H_2 (ppmv)**	**CH_2O (ppmv)**	**N_2O (ppmv)**	**NO_2 (ppmv)**	**NO (ppmv)**	**SO_2 (ppmv)**
SF_6 Testing on 8/24/06 (first run)												
Min (3,000 ppmv)	0.9	0.0	5.0	641.8	0.7	BDL	BDL	BDL	0.9	3.5	BDL	2.3
Max (3,000 ppmv)	2.1	0.1	183.2	2,187.1	8.2	32.2	2.8	7.0	4.1	8.1	BDL	56.4
Average (3,000 ppmv)	1.2	0.0	23.0	1,966.1	3.5	3.1	0.4	0.7	2.4	6.0	BDL	35.9
Stdev	0.2	0.0	33.7	325.9	1.8	4.9	0.8	0.9	0.5	1.0	n/a	11.9
SF_6 Testing on 8/24/06 (second run)												
Min (3,000 ppmv)	1.0	0.0	3.5	1,760.6	27.1	0.9	BDL	BDL	17.6	33.5	2.1	23.2
Max (3,000 ppmv)	1.2	0.1	46.8	2,032.4	49.1	5.5	BDL	1.0	32.2	47.1	15.9	51.9
Average (3,000 ppmv)	1.1	0.0	11.1	1,932.2	34.0	3.0	BDL	0.3	23.1	38.2	7.4	36.6
Stdev	0.1	0.0	13.7	97.8	6.7	1.5	n/a	0.3	3.7	4.2	3.7	9.1

BDL = below detectable limit
n/a = not applicable

Table 4-6. MDL Summary for All Monitored Compounds During SF_6 Tests

Compound	Minimum Detection Limit (ppmv)
H_2O	n/a
CO_2	n/a
CO	n/a
SF_6	n/a
HF	n/a
COF_2	1.02
CH_4	0.230
C_2H_2	0.039*
C_2H_4	41.00
CF_4	0.013
CH_2O_2	0.280
CH_2O	0.204*
C_2F_6	0.290
CH_3F	0.303
CHF_3	0.129
NO	1.27
OF_2	0.934
N_2O	n/a
NO_2	0.107
NO	1.27
SO_2	1.71

n/a = not Applicable since compound was consistently present throughout the testing.
*Noise based MDL

Although there is no conclusive evidence, the theory is that with a clean melt surface, created from a dross or during an ingot drop, the probability to form HF is maximized from greater amounts of liberated fluorine (as the SF_6 is destroyed via reaction with the melt surface). As the protective MgO/MgF layer forms atop the melt surface, it acts as a barrier separating the melt surface from the SF_6/CDA cover gas, thereby minimizing the destruction of SF_6 and subsequent formation of HF.

SF_6 destruction to form HF and SO_2 was also observed throughout the tests. The SO_2 concentrations were rather variable ranging from 2-56 ppmv during the tests. Sharp decreases were observed during ingot loading, presumably from dilution. HF concentrations, on average, were 4 and 34 ppmv for the first and second tests, respectively. The recovery of the SO_2 back to the pre-ingot loading concentration trended behind the recovery time of the other gases. As previously mentioned nitrogen oxides (N_2O and NO_2) were observed throughout the test and are likely resultant from the destruction of the CDA carrier gas. Formaldehyde and acetylene were also detected during the tests. This was the only cover gas where acetylene (C_2H_2) was observed. Ambient air components (CH_4, CO_2, H_2O and CO) were observed throughout the tests. With the exception of CO, all the averaged ambient air compounds were near or slightly above normal concentrations. CO had transient spikes on the order of 47-183 ppmv presumably from short-lived burns inside the crucible.

4.4 SO_2 with CDA Carrier Gas

Sulfur dioxide mixtures were injected at six different concentrations over a two-day period beginning on the 28th of August and concluding on the 29th of August, 2006. The gas mixer was built and operated by Polycontrols. The existing CDA supply was passed through a desiccant-type dryer to remove excess moisture prior to blending with SO_2. An initial SO_2 concentration of 1% was injected followed by successively lower concentration injections to a minimum concentration of 0.4% SO_2. Two sampling tests at 0.5% SO_2 were conducted approximately 16 hours apart. A summary of all the *observed* compounds is presented in Table 4-7. The MDLs for all the compounds monitored during the SO_2 tests are listed in Table 4-8 and time series plots of concentration data are displayed in Appendix A.

There were few destruction byproducts that could be attributed to SO_2. Most of the observed compounds were either a carry-over effect of residual chemicals from the previous cover gas used in the crucible (e.g., SF_6 and HF), ambient air components (H_2O, CO_2, CH_4), destruction byproducts formed from ambient air dilution during ingot loading (CH_2O and C_2H_4) or nitrogen oxides formed from the CDA carrier gas. Slightly elevated levels of observed CO, with respect to ambient levels, were also observed. H_2SO_4 was not measured at concentrations above its minimum detection limit (0.051 ppmv) within the crucible headspace.

Five different SO_2 concentrations (1%, 0.85%, 0.7%, 0.6% and 0.5%) were injected during the first day of SO_2 testing followed by two concentrations on the second day (0.5% and 0.4%). As the SO_2 concentration was lowered, the relative rate of destruction also decreased. A repeat of the 0.5% SO_2 test was done at the beginning of the 2nd day of SO_2 testing and the destruction rates were similar, 30% during day 1 and 37% during day 2. However, the overall SO_2 destruction throughout the entire testing only varied marginally (29% - 37%). This small variance is indicative of an equilibrium effect between the SO_2/CDA cover gas mixture and the liquid melt as compared to the other mixtures, which appeared to rely more on total mass coverage of the melt surface. In other words, the carrier gas (CDA) most likely plays a more prominent role in melt coverage than do the diluents for the fluorinated cover gases, which rely more on the amount of available F^- mass to produce MgF coverage. The least amount of SO_2 destruction (29%) was observed during the 0.6% SO_2 concentration and the largest amount destroyed was 37% during the 1% and 0.5% SO_2 cover gas concentrations.

Table 4-7. Data Summary for SO_2 with CDA Carrier Gas

	H_2O (%)	CO_2 (ppmv)	CO (ppmv)	CH_4 (ppmv)	SO_2 (ppmv)	N_2O (ppmv)	NO_2 (ppmv)	NO (ppmv)	CH_2O (ppmv)	C_2H_4 (ppmv)	SF_6 (ppmv)	HF (ppmv)
SO_2 Testing on 8/28/06												
Min (1%)	0.3	409.5	1.8	1.0	5,280.7	2.9	1.1	0.8	BDL	BDL	0.1	3.6
Max (1%)	0.6	492.5	17.1	6.5	6,617.5	3.9	2.2	2.5	0.3	1.7	0.2	8.9
Average (1%)	0.4	435.2	6.0	2.7	6,086.6	3.4	1.5	1.5	0.2	0.4	0.1	6.8
Stdev (1%)	0.1	28.6	6.3	1.9	390.2	0.4	0.4	0.7	0.7	1.9	0.0	2.1
Min (0.85%)	0.2	398.4	1.0	1.2	4,277.8	2.6	0.9	0.5	BDL	BDL	0.0	6.5
Max (0.85%)	0.7	484.7	7.2	3.2	5,933.5	3.4	1.8	1.5	BDL	0.3	0.1	12.9
Average (0.85%)	0.3	421.6	2.0	1.9	5,521.3	2.8	1.3	1.0	BDL	0.1	0.1	8.7
Stdev (0.85%)	0.1	25.4	2.1	0.6	463.9	0.2	0.3	0.3	n/a	0.1	0.0	2.0
Min (0.70%)	0.2	401.0	0.9	1.3	3,555.4	2.3	0.8	0.6	BDL	BDL	0.0	3.9
Max (0.70%)	0.6	547.4	16.4	5.4	5,041.9	3.6	2.1	1.5	BDL	0.4	0.1	11.5
Average (0.70%)	0.3	424.9	3.0	2.3	4,652.5	2.9	1.3	1.1	BDL	0.1	0.0	6.1
Stdev (0.70%)	0.1	40.2	4.0	1.0	370.6	0.3	0.3	0.3	n/a	0.1	0.0	2.2
Min (0.60%)	0.2	394.7	0.8	1.5	3,563.8	2.3	0.4	0.5	BDL	BDL	0.0	3.2
Max (0.60%)	0.4	448.2	17.3	4.0	4,380.7	3.3	1.3	1.4	1.1	1.4	0.1	7.4
Average (0.60%)	0.2	406.5	2.4	2.2	4,157.3	3.0	1.1	1.0	0.2	0.1	0.0	4.1
Stdev (0.60%)	0.1	12.5	3.6	0.5	256.2	0.3	0.2	0.2	0.3	0.3	0.0	1.0
Min (0.50%)	0.1	392.1	0.9	1.5	2,788.3	2.4	0.4	0.4	BDL	BDL	0.0	2.3
Max (0.50%)	0.4	438.9	7.3	3.3	3,689.3	3.4	1.1	1.1	0.4	0.7	0.1	6.1
Average (0.50%)	0.2	406.3	2.3	2.1	3,401.3	2.9	0.9	0.8	0.2	0.1	0.0	3.6
Stdev (0.50%)	0.1	15.4	1.9	0.6	311.2	0.2	0.2	0.2	0.2	0.2	0.0	1.2
SO_2 Testing on 8/29/06												
Min (0.50%)	0.3	428.1	1.4	1.0	1,980.9	1.6	0.8	BDL	BDL	BDL	0.0	0.1
Max (0.50%)	0.8	494.4	33.1	8.8	3,284.3	2.4	1.5	BDL	0.9	3.5	0.1	0.3
Average (0.50%)	0.4	442.5	5.0	2.3	3,042.0	1.9	1.2	BDL	0.3	0.3	0.1	0.2
Stdev (0.50%)	0.1	15.5	7.3	1.8	300.2	0.2	0.2	0.0	0.2	0.7	0.0	0.0
Min (0.40%)	0.3	410.0	1.1	1.0	1,890.8	1.4	0.5	BDL	BDL	BDL	0.0	0.1
Max (0.40%)	0.7	479.9	22.3	5.2	2,717.7	2.0	1.3	BDL	0.5	1.1	0.1	0.3
Average (0.40%)	0.4	432.1	3.7	2.0	2,518.2	1.6	1.0	BDL	0.3	0.2	0.0	0.2
Stdev (0.40%)	0.1	14.3	4.1	1.1	196.5	0.1	0.2	n/a	0.2	0.3	0.0	0.1

BDL = below detectable limit; n/a = not applicable

Table 4-8. MDL Summary for All Monitored Compounds During SO_2 Tests

Compound	Minimum Detection Limit (ppmv)
H_2O	n/a
CO_2	n/a
CO	n/a
CH_4	n/a
SO_2	n/a
HF	n/a
SF_6	n/a
N_2O	n/a
NO_2	n/a
NO	0.335
CH_2O	0.213
C_2H_4	0.075
H_2SO_4	0.051
SO_3	9.81

n/a = not applicable since compound was consistently present throughout the testing.

Another interesting trend was observed in the HF data between both 0.5% SO_2 tests. Measured HF concentrations ranged from 0.1 ppmv to 13 ppmv over both tests. The HF concentrations during the second test were much lower (95% less) than what was observed during the 0.5% SO_2 test on the first day, presumably due to continuing displacement of free fluorine off the melt surface and complete purging of residual SF_6 cover gas out of the crucible environment.

4.5 Frozen CO_2

The final cover gas tested was frozen CO_2. Testing began at 1651 on the 29th of August and ended at 1828 of the same day. The frozen CO_2 was formed by expansion of compressed liquid/gaseous CO_2. As the gas cooled through expansion, it froze, forming solid phase CO_2 which was gravity fed into the crucible. The obvious difference between the frozen CO_2 and all the other cover gases is the method of injection and its chemical state. Compressed CO_2 was delivered to the nozzle at a pressure of 100 pounds per square inch (psi) from a liquid CO_2 dewar. The delivery/formation of the frozen CO_2 was controlled and optimized by regulating the injection into the crucible with a solenoid valve.

The amount of CO_2 destruction was minimal averaging 4% over the entire sample period. This was the lowest destruction of all the cover gases. As a result, CO_2 had very few decomposition by-products, with the main one being CO. A small amount of C_2H_4 was consistently present throughout the testing. Sulfur dioxide, HF and SF_6 were observed during the testing, but were likely present as a carry-over effect of residual chemicals from previous cover gases used in the crucible. The presence of nitrogen oxides was most likely due to thermal decomposition of ambient air entering the crucible through leaks and intrusion during ingot loading. Table 4-9 lists the *observed* compounds during the frozen CO_2 cover gas testing. Table 4-10 presents all the compounds monitored along with the MDLs for those that were not observed. Time series plots for each observed compound during the frozen CO_2 cover gas test are presented in Appendix A.

Table 4-9. Data Summary for Frozen CO_2

	H_2O (%)	CO_2 (%)	CO (ppmv)	SO_2 (ppmv)	HF (ppmv)	CH_4 (ppmv)	C_2H_4 (ppmv)	N_2O (ppmv)	NO_2 (ppmv)	NO (ppmv)	SF_6 (ppmv)
Min (100%)	0.1	52.7	181.9	9.2	BDL	BDL	0.6	BDL	BDL	BDL	0.1
Max (100%)	0.6	100.0	883.9	37.4	0.2	2.6	1.3	3.4	0.9	1.7	0.4
Average (100%)	0.2	95.7	401.8	22.5	0.0	0.8	0.8	0.5	0.1	0.6	0.2
Stdev	0.1	11.5	202.0	5.9	0.0	0.7	0.2	0.9	0.2	0.6	0.1

BDL = below detectable limit

n/a = not applicable

Table 4-10. MDL Summary for All Monitored Compounds During Frozen CO_2 Testing

Compound	Minimum Detection Limit (ppmv)
H_2O	n/a
CO_2	n/a
CO	n/a
SO_2	n/a
HF	n/a
CH_4	n/a
C_2H_2	0.287
C_2H_4	n/a
CH_2O_2	0.253
CH_2O	0.193
COF_2	0.069
N_2O	0.466
NO_2	0.117
NO	1.03
SF_6	n/a

n/a = not applicable since compound was consistently present throughout the testing.

4.6 Determination of Dilution

As discussed at the end of Section 3.1 and throughout 3.2, quadrapole mass spectrometry (QMS) was used to monitor N_2 inside the crucible for a determination of dilution (via ambient air). With the exception of MTG-Shield™ using Novec™ 612 and frozen CO_2, all the cover gases used CDA as their carrier gas. Since ambient air is the only source of dilution into the crucible, it was impossible to determine dilution from all the cover gases where CDA was used. Furthermore, since frozen CO_2 was gravity fed to the crucible as a solid it was unique and not representative for all the other cover gases. Therefore, dilution was determined from the MTG-Shield™ cover gas tests and applied to all the other cover gas tests, except frozen CO_2. Since the sampling system was a closed system and the Novec™ 612 cover gas was diluted only with CO_2, any N_2 present was from the intrusion of ambient air into the crucible headspace. A slip-stream of the extracted sample gas was delivered to the QMS and monitored for N_2. The QMS response was calibrated for nitrogen over a concentration 0%-50% range using the Polycontrols gas blender. This calibration was then fit to a linear regression (y = ax + b) and applied to the sample data using Equation 4-1. Figure 4-1 displays the QMS calibration curve.

$$y = 10.65e\text{-}9x + 2.86e\text{-}9 \qquad \text{Equation 4-1}$$

Where:

y = N_2 response as read by the QMS and
x = % N_2

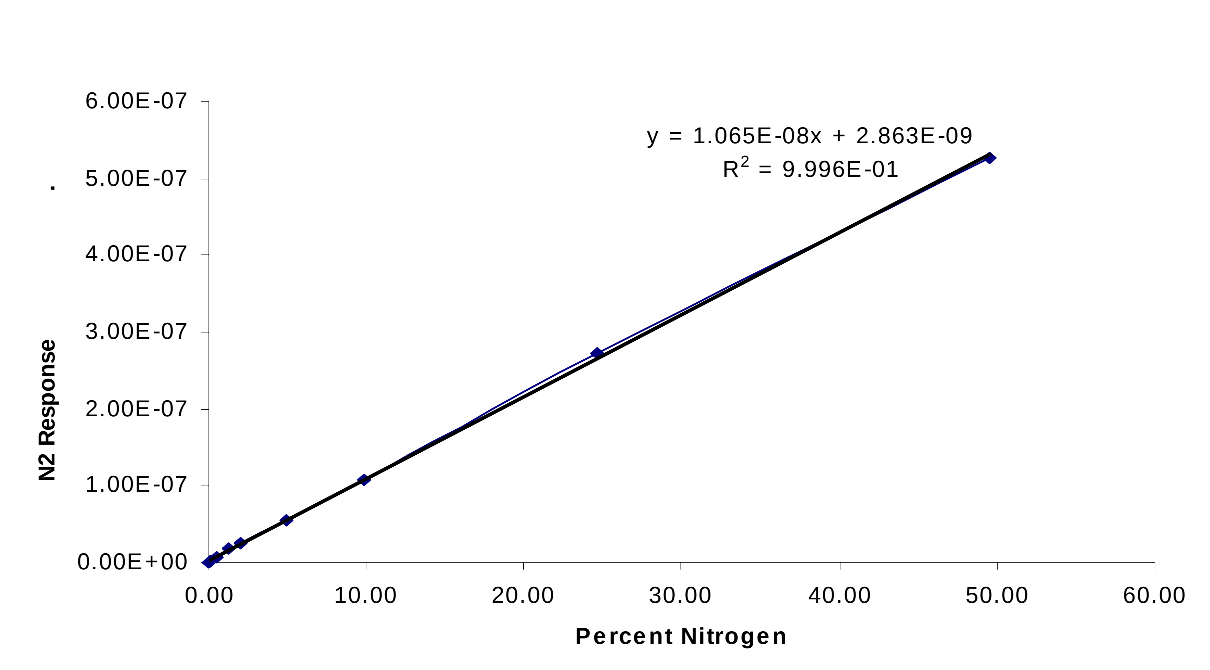

Figure 4-1. QMS Response Curve for 0-50% Nitrogen

The a and b coefficients in the calibration equation (Equation 4-1) are on the order of 10^{-9} because they represent the QMS detector response, which was an electron multiplier that produced electrical signals in the nanoamp (10^{-9} amperes) range. Nitrogen was monitored for the entire MTG-Shield testing performed on the 23rd of August and the raw data is plotted in Figure 4-2. The average QMS N_2 response was then applied to Equation 4-1 giving the % N_2 observed in the crucible. Since ambient air is 78% N_2 the dilution was calculated from Equation 4-2.

% Dilution = % N_2 / 0.78 (as calculated from Equation 4-1) Equation 4-2

Applying equations 4-1 and 4-2 to the QMS data set gave an average dilution of 3.0% during the MTG-Shield™ testing. For the purposes of this study dilution is considered to be the amount of ambient air intrusion resulting in a proportional decrease in head-space cover gas concentration relative to the feed gas concentration. This dilution set included data when the ingot door was open for loading and is therefore only applicable to this particular die-casting machine fabricating this particular part. The dilution was also calculated with the ingot loading periods omitted. Surprisingly, at 2.7% dilution, there is little difference between the two, thus indicating that the majority of the 3.0% dilution is from leaks in the crucible lid allowing for ambient air ingression into the headspace. Oxygen was also monitored continuously over a two-hour period during the MTG-Shield™ testing as described in Section 3.1. The periods where the ingot door was opened were omitted and the average O_2 concentration inside the crucible was calculated at 4.5%. This was slightly greater than the 2.7% observed using the QMS monitoring of N_2 when the ingot loading periods were omitted. The QMS and O_2 analyzers were not running simultaneously which may be a cause for the slight discrepancy. It should be noted that it is virtually impossible to measure the actual crucible dilution with complete accuracy due to limitations of the operational setting. Dilution during the frozen CO_2 testing was estimated to be 0.4% using the N_2 tracer method – this is likely due to the high volume of CO_2 being injected into the crucible.

Estimated dilution rates of 3% - 4.5% are significantly lower than what was estimated during previous research in 2003. Dilution in the 2003 study was estimated to be on the order of 20% - 25% using intermittent measurements of O_2 as the only dilution indicator.[8] The significant reduction in dilution is likely due to the following factors:

- The crucible in this study was significantly "tighter" due to the addition of insulation batting that sealed all openings for potential ambient air intrusion;
- The rate of ingot loading (about every 15 minutes) was 1/5th that of the previous study resulting in significantly less ambient air intrusion during this process; and
- The use of continuous measurements of N_2 as a dilution indicator provided a more accurate (and lower) estimate than the previous approach.

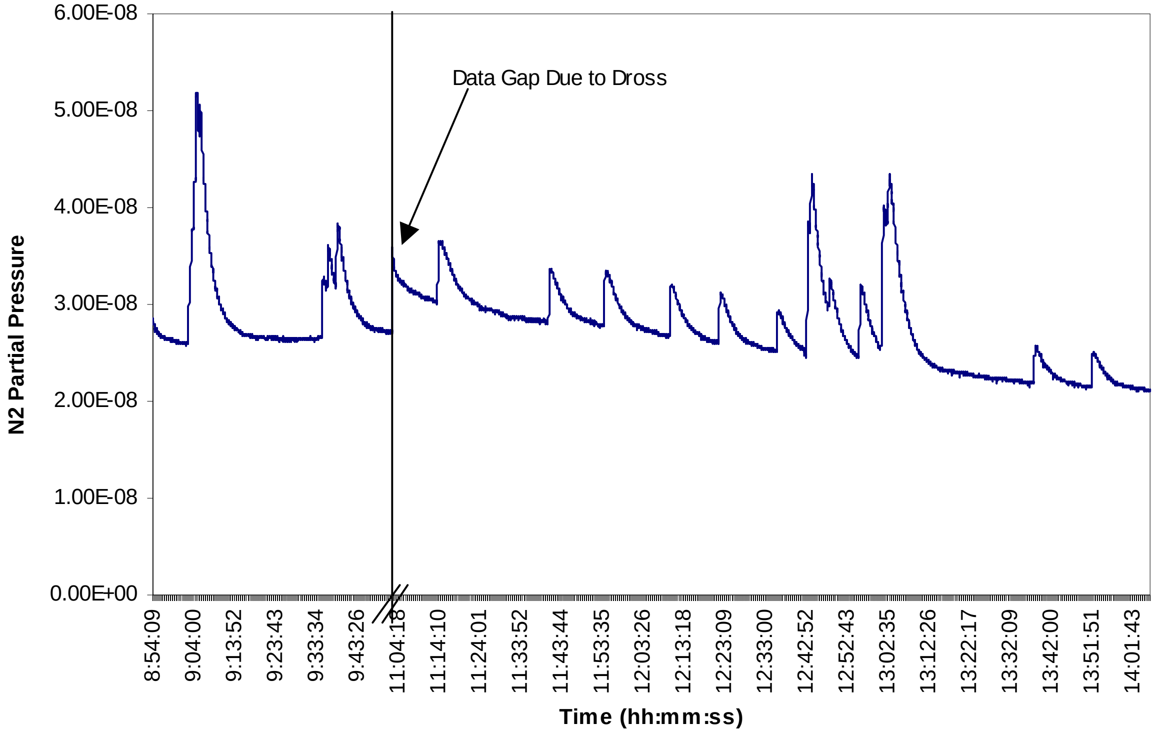

Figure 4-2. QMS Response to N_2 During MTG-Shield™ Sampling

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[8] Characterization of Cover Gas Emissions from U.S. Magnesium Industry Die Casting Operation, March 2004. Dilution in the 2004 report is defined as the expected head-space concentration relative to the feed gas after dilution (75 - 80%). This is the inverse of the definition presented above so direct comparison would be 20 - 25%.

4.7 Occupational Exposure Monitoring

Each of the cover gases evaluated in this study can produce emissions that may be of concern from an occupational exposure standpoint. For this reason, a second FTIR was used to monitor ambient air for any potential occupational exposure hazards associated with the usage of each cover gas. For example, formaldehyde (CH_2O), carbonyl fluoride (COF_2), SO_2 and HF have very low Occupational Safety and Health Administration (OSHA) 8-hour time-weighted average permissible exposure limits (PELs) of 0.75, 2, 2, and 3 ppmv, respectively.[9] Occupational exposure details, including short term exposure limits (STELs) and symptoms of chronic exposure for the primary compounds and byproducts of concern during monitoring are provided in Table 4-11. As an additional point of interest, in prior measurement trials involving Novec™ 612, the presence of perfluoroisobutylene (PFIB) as a possible byproduct of cover gas degradation was noted; however, monitoring for this compound was not possible due to the absence of an available spectral FTIR reference.[10]

Two worker breathing zones were monitored during the testing. The first zone was monitored during the use of the MTG-Shield™, AM-Cover™, and SF_6 cover gases. This zone was located at the end of the process where the part was robotically dropped to a worker who inspects and files it. This is the area where the worker operating the machine spent the bulk of his time. The 2nd zone was at the crucible lid near the ingot door and was monitored during the SO_2 and frozen CO_2 cover gases. This zone represents a worst-case location in that it is near the most probable location for direct exposure to cover gas emissions. This is especially relevant to the use of SO_2 and the likelihood for there to be direct exposure to cover gas during crucible maintenance operations such as drossing.

It should be noted that this study should be considered only as a screening of potential risks from an occupational perspective. A true industrial hygiene occupational exposure study would involve personal air-packs worn by workers during normal operations. However, this study does provide highly accurate information resulting from continuous monitoring of ambient air at the primary worker stations.

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[9] OSHA Permissible Exposure Limits (PELs). <http://www.osha.gov>

[10] Mibrath, D., "Development of 3M™ Novec™ 612 Magnesium Protection Fluid as a Substitute for SF_6 Over Molten Magnesium," International Conference on SF_6 and the Environment: Emission Reduction Technologies, November 21-22, 2002, San Diego, CA.

Table 4-11. Cover Gas Compound Occupational Exposure Details

Compound	PEL	STEL	Acute Exposure	Chronic Exposure
SF_6 – Sulfur Hexafluoride[11]	1,000	NA	Nausea, vomiting, difficulty breathing, dizziness, fatigue, emotional disturbances, tingling sensation, suffocation, convulsions, coma	No information available.
HFC-134a – 1,1,1,2 Tetrafluoroethane[12]	1,000	NA	Rapid evaporation of the liquid may cause frostbite. The substance may cause effects on the central nervous system and cardiovascular system, resulting in cardiac disorders.	No information available.
Novec™ 612[13]	150	NA	Contact with the eyes during product use is not expected to result in significant irritation. Contact with the skin or ingestion during product use is not expected to result in significant irritation or health effects. May present an inhalation hazard if thermal decomposition occurs. The primary thermal decomposition byproducts of concern include CO, HF, CO_2, and perfluoroisobutylene (PFIB).	No information available.
CO – Carbon Monoxide[14]	50	400	Acute exposure to carbon monoxide may include headache, flushing, nausea, vertigo, weakness, irritability, unconsciousness, and in persons with pre-existing heart disease and atherosclerosis, chest pain and leg pain.	Repeated bouts of carbon monoxide poisoning may cause anorexia, headache, lassitude, dizziness, and ataxia.
HF - Hydrofluoric Acid[15]	3.0	6.0	The substance is corrosive to the eyes, the skin and the respiratory tract. Inhalation of this gas or vapor may cause lung oedema. The substance may cause hypocalcemia. Exposure above the OEL may result in death.	The substance may cause fluorosis.
SO_2 – Sulfur Dioxide[16]	2.0	5.0	Respiratory tract irritation, rhinorrhea, choking, and coughing.	Permanent pulmonary impairment, which is caused by repeated episodes of bronchoconstriction.
COF_2 - Carbonyl Fluoride[17]	2.0	5.0	Irritation to eyes, skin, mucous membrane, respiratory system; eye, skin burns; lacrimation (discharge of tears); cough, pulmonary edema, dyspnea (breathing difficulty), frostbite.	Gastrointestinal pain, muscle fibrosis, skeletal fluorosis.
CH_2O – Formaldehyde[18]	0.75	2.0	Irritation eyes, nose, throat, respiratory system; lacrimation (discharge of tears); cough; wheezing.	Potential occupational carcinogen.

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[11] Matheson Tri Gas. Material Safety Data Sheet: Sulfur Hexafluoride. 2003.
[12] ICSC: NENG 1281 International Chemical Safety Cards (WHO/IPCS/ILO), CDC/NIOSH: HFC 134a, 1998.
[13] 3M Material Safety Data Sheet, 3M™ Novec™ 612 Magnesium Protection Fluid, 2007.
[14] Tennessee OSHA. Instruction CPL 2.501 – Local Emphasis Program – Carbon Monoxide, 1999.
[15] ICSC: NENG 0283 International Chemical Safety Cards (WHO/IPCS/ILO), CDC/NIOSH: HF, 2000.
[16] CDC/NIOSH 1988 OSHA PEL Project Documentation: Sulfur Dioxide, 1998.
[17] NIOSH Publication No. 2005-151. NIOSH Pocket Guide to Chemical Hazards: Carbonyl Fluoride. 2005.
[18] NIOSH Publication No. 2005-151. NIOSH Pocket Guide to Chemical Hazards: Formaldehyde. 2005.

4.7.1 Observed Compounds During Occupational Exposure Monitoring

With the exception of one instance during the use of SO_2, monitoring at both sampling zones did not detect concentrations of any cover gas compound or byproduct that would be of concern from an occupational exposure perspective. The primary compounds of concern were either monitored at levels that were well below their respective PELs, or were below detectable limits of the FTIR. Table 4-12 lists the all the primary compounds of concern monitored during the testing.

SF_6 was continuously observed throughout the testing regardless of the cover gas being used for melt protection. A continuous background level of SF_6 was expected since it is used as a cover gas in all crucibles throughout the facility. Carbon monoxide was also continuously observed well above ambient levels regardless of location or cover gas. This was most likely due to combustion during the short-lived burns that occurred as each shot of molten magnesium is cast and/or possible CO formation as a byproduct during small burns within the crucibles. All the observed compounds were below the OSHA 8-hour PEL. The one incidence that indicated the potential for an occupational exposure concern occurred during the use of SO_2. A maximum recorded reading of 1.6 ppmv was observed which is approaching the OSHA 8-hour PEL of 2 ppmv. This brief occurrence was observed approximately 30 inches from, and 12 inches above the ingot door during a period when it was open for a prolonged period of time due to an ingot loading malfunction. This measurement identifies a health concern to the worker that would occur while performing maintenance on the crucible lid or performing a dross. It is certain that personal protective equipment (PPE) in the form of a respirator would be required for workers performing crucible maintenance on a machine running dilute SO_2 as a cover gas.

While these tests do not represent a rigorous industrial hygiene analysis, the results illustrate that given the ventilation present at this facility, the crucible head space gases are sufficiently diluted to an extent that harmful concentrations were not found in ambient air close to the primary worker breathing zones. The potential for occupational exposure at the ground level of the facility is also reduced due to the convection currents carrying escaping cover gas upward towards the ceiling and the high-volume exhaust fans.

Table 4-12. Monitored Compounds from Occupational Exposure Ambient Monitoring

Cover Gas	**Date**	**Zone****		**Novec™612 (ppmv)**	**HFC-134a (ppmv)**	**SF_6 (ppmv)**	**SO_2 (ppmv)**	**HF (ppmv)**	**CO (ppmv)**	**COF_2 (ppmv)**	**CH_2O (ppmv)**
Permissible Exposure Limit (PEL)				150	1000	1000	2	3	50	2	0.75
Short-term Exposure Limit (STEL)				n/a	n/a	n/a	5	6	400	5	2
MTG-Shield™	**8/22**	**1**	**Max**	BDL	n/a	0.08	n/a	BDL	11.60	BDL	BDL
			Average	BDL	n/a	0.06	n/a	BDL	7.07	BDL	BDL
MTG-Shield™	**8/23**	**1**	**Max**	BDL	n/a	0.19	n/a	BDL	14.45	BDL	BDL
			Average	BDL	n/a	0.06	n/a	BDL	6.80	BDL	BDL
AM-Cover™	**8/24**	**1**	**Max**	n/a	0.050	0.16	n/a	BDL	15.33	BDL	BDL
			Average	n/a	0.020	0.10	n/a	BDL	5.28	BDL	BDL
AM-Cover™	**8/25**	**1**	**Max**	n/a	0.078	0.29	n/a	BDL	6.48	BDL	BDL
			Average	n/a	0.038	0.18	n/a	BDL	2.75	BDL	BDL
SF_6	**8/24**	**1**	**Max**	n/a	n/a	0.28	BDL	BDL	9.48	BDL	BDL
			Average	n/a	n/a	0.18	BDL	BDL	2.75	BDL	BDL
SO_2	**8/28**	**2**	**Max**	n/a	n/a	0.23	1.6*	BDL	7.22	BDL	BDL
			Average	n/a	n/a	0.19	0.14	BDL	1.21	BDL	BDL
SO_2	**8/29**	**2**	**Max**	n/a	n/a	0.07	BDL	BDL	11.49	BDL	BDL
			Average	n/a	n/a	0.03	BDL	BDL	7.06	BDL	BDL
Frozen CO_2	**8/29**	**2**	**Max**	n/a	n/a	0.23	n/a	BDL	11.46	BDL	BDL
			Average	n/a	n/a	0.16	n/a	BDL	4.55	BDL	BDL

BDL = below detectable limit
n/a = not applicable
*Occurred during an instance when the ingot loading door was open for a prolonged period of time due to a loading malfunction.
**Zone 1 was located at the process end where the part is robotically dropped to the worker. Zone 2 was located near the ingot loading area of the crucible.

5.0 Conclusions

5.1 Cover Gas Test Observations

The cover gas test results were described in detail in Section 4 and will be summarized in this section. Each cover gas was sampled, in an identical fashion, from the crucible head space of Lunt Manufacturing's HPM 400 die-casting machine (#1) fabricating an automotive lock body housing. Furthermore, all the cover gases except frozen CO_2 were delivered to the crucible head space in a similar manner. This testing setup allowed for a direct comparison of five different magnesium melt cover gases as they relate to greenhouse gas emissions and occupational exposure.

One observation which occurred multiple times throughout the testing was the inconsistencies between measurements using the same cover gas performed on different days. This was most prominent in the HF, Novec™ 612 and nitrogen oxide concentrations during the MTG-Shield™ and SF_6 tests. The most likely cause was instability in the crucible brought on by a cover gas change. It is evident from constant gradual decays observed in the cover gas concentrations upon initial injection, as well as the length of time required to effectively purge the carry-over gases from previous cover gases, that there was a significant time period associated with purging the crucible and reaching equilibrium in the head-space.

5.1.1 MTG-Shield™ using Novec™ 612 with CO_2 Carrier Gas

The primary destruction by-products detected when using MTG-Shield™ using Novec™ 612 gas were; CO, COF_2, HF, C_2F_6, CHF_3 and C_3F_8. Measurements were conducted while successively lowering concentrations of Novec™ 612 cover gas beginning at 800 ppmv and ending at 150 ppmv. The first day of testing started with the Novec™ 612 cover gas injected at a concentration of 800 ppmv and lowered to 600, 400 and 300 ppmv. As the Novec™ 612 concentration decreased, COF_2, HF, C_2F_6, CHF_3 and C_3F_8 concentrations also decreased in succession although not by the same percentages as the cover gas. The low Novec™ 612, HF and other by-products observed at the end of the first day of sampling (COF_2 and C_2F_6 were BDL and Novec™ 612 and HF averaged less than 5 and 12 ppmv respectively) did not continue the downward trend during the 2nd day even though lower cover gas concentrations (200 and 150 ppmv) were used. The 300 ppmv Novec™ 612 cover gas concentration used during the 1st day of testing resulted in lower HF, Novec™ 612 and other by-products than either the 200 or 150 ppmv Novec™ 612 cover gas concentrations tested during the 2nd day. It is believed that the length of Novec™ 612 usage during the first day of testing provided a more stable crucible operation toward the end of the 6-hour testing episode than the testing conducted on day 2.

5.1.2 AM-Cover™ using HFC-134a with CDA Carrier Gas

The primary destruction by-products detected when using AM-Cover™ using HFC-134a cover gas were CO, COF_2, and HF. Measurements were conducted using two HFC-134a cover gas concentrations (4,200 and 3,600 ppmv). This 14.8% decrease in cover gas concentration had very little effect on COF_2 reduction (4%) but did reduce the HFC-134a, HF, and CO concentrations in the crucible by 32%, 14% and 28%, respectively. Concentrations of these compounds steadily decayed throughout the tests indicating that upon a cover gas change there was a significant period required to effectively purge out the crucible headspace. Additional byproducts such as CH_2O, NO, N_2O and NO_2 and C_2H_4 were formed, or slightly increased, with the addition of ambient air during the ingot loads. The non-process gases, SF_6 and SiF_4 were also observed throughout testing. The SF_6 presence was a residual from its use prior to AM-Cover™.

5.1.3 SF_6 with CDA Carrier Gas

A 3,000 ppmv SF_6/CDA cover gas mixture was monitored over two independent time periods. The primary compounds detected when using SF_6 are: HF and SO_2. For both cold chamber measurements, average HF concentrations were on the order of 4 to 34 ppmv. Low levels of NO, N_2O and NO_2 were detected, ranging from 1 to 47 ppmv. CH_2O and C_2H_2 were observed sporadically throughout testing near their respective FTIR detection limits. This was the only cover gas where C_2H_2 was observed. Ambient air components (CH_4, CO_2, H_2O and CO) were observed throughout the testing. With the exception of CO, all the averaged ambient air compounds were near or slightly above their atmospheric concentrations. CO had transient spikes on the order of 47 - 183 ppmv, presumably from short-lived burns inside the crucible.

5.1.4 SO_2 with CDA Carrier Gas

Sulfur dioxide cover gas was monitored over a 2-day period at six different concentrations. The SO_2 cover gas concentrations ranged from a high of 1% to a low of 0.4 %. There were no destruction by-products which could be solely attributed to SO_2. The remainder of the observed compounds are either a function of residual gases from the previous cover gas used in the crucible (SF_6 and HF), ambient air components (H_2O, CO_2, CH_4), by-products formed from ambient air dilution during ingot loading (CH_2O and C_2H_4) or nitrogen oxides formed from the CDA carrier gas and/or ambient air dilution from ingot loading. Ambient concentrations of SO_2 were below occupational exposure limits or not detectible during the study (See Section 4.7 for more details).[19]

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[19] All applicable safety precautions (e.g., operational procedures) should be followed when using SO_2.

5.1.5 Frozen CO_2

Frozen CO_2 was the final cover gas tested. The frozen CO_2 was gravity fed to the crucible as a solid and sublimed once inside. As with SO_2, CO_2 had very few decomposition by-products with the main one being CO. A very small amount of C_2H_4 was consistently present throughout the testing. SO_2, HF and SF_6 were observed during the testing but were carry-over gases from previous cover gases used in the crucible. The presence of nitrogen oxides is most likely due to thermal decomposition of ambient air entering the crucible through leaks and ingot loading. The amount of CO_2 destroyed during the testing averaged 3%. This was by far the lowest amount destroyed of all the cover gases tested. Since the injection flow rates were not accurately monitored and the CO_2 dewar was not weighed before and after the tests, the absolute amount of CO_2 used was unknown.

5.2 Cover Gas Destruction

One of the main objectives with this cover gas study was to determine the level of destruction. Destruction estimates were calculated as:

$$\text{Percent Destruction} = \frac{\text{Delivery Concentration} - \text{Dilution Corrected Measured Concentration}}{\text{Delivery Concentration}}$$

Table 5-1 provides a summary of all the tests and calculated destruction rates. The measured concentration value in the above equation was corrected for dilution due to leaks and ingot loading as calculated by the QMS.[20]

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[20] See section 4.6 for further explanation of dilution determination

Table 5-1. Percent Destruction for Cover Gas Testing

Cover Gas Mixture Components	Table	Date	Time	Cover Gas Mixture Flow [a] (lpm)	Cover Gas Delivery Conc. [a] (ppmv)	Cover Gas Measured Conc. (ppmv)	Dilution Factor	Cover Gas Destruction
Novec™ 612/CO_2	4-1	8/22/06	0910-1005	~36	800	198.8	0.03	74%
Novec™ 612/CO_2	4-1	8/22/06	1008-1135	~36	600	142.5	0.03	76%
Novec™ 612/CO_2	4-1	8/22/06	1138-1301	~36	400	55.4	0.03	86%
Novec™ 612/CO_2	4-1	8/22/06	1347-1425	~36	300	3.2	0.03	99%
Novec™ 612/CO_2	4-1	8/23/06	0906-0958	~36	200*	75.8	0.03	61%
Novec™ 612/CO_2	4-1	8/23/06	1108-1248	~36	200**	64.2	0.03	67%
Novec™ 612/CO_2	4-1	8/23/06	1252-1556	~36	150	30.8	0.03	79%
HFC-134a/CDA	4-3	8/24/06	1510-1736	~40	4,200	1,198.3	0.03	71%
HFC-134a/CDA	4-3	8/25/06	0810-1215	~40	3,600	810.7	0.03	77%
SF_6/CDA	4-5	8/24/06	0939-1311	~35	3,000	1,966.1	0.03	32%
SF_6/CDA	4-5	8/24/06	1806-1902	~35	3,000	1,932.2	0.03	34%
SO_2/CDA	4-7	8/28/06	1105-1130	~39	10,000	6,086.6	0.03	37%
SO_2/CDA	4-7	8/28/06	1133-1218	~39	8,500	5,521.3	0.03	33%
SO_2/CDA	4-7	8/28/06	1222-1348	~39	7,000	4,652.5	0.03	32%
SO_2/CDA	4-7	8/28/06	1351-1500	~39	6,000	4,157.3	0.03	29%
SO_2/CDA	4-7	8/28/06	1504-1552	~39	5,000	3,401.3	0.03	30%
SO_2/CDA	4-7	8/29/06	0845-1001	~39	5,000	3,042.0	0.03	37%
SO_2/CDA	4-7	8/29/06	1005-1155	~39	4,000	2,518.2	0.03	35%
Frozen CO_2	4-9	8/29/06	1651-1829	Dewar at 100 psi	1,000,000	957,390.1	0.00	4%

[a] As provided by Lunt Manufacturing, AMT, Polycontrols, and Matheson Tri-Gas/TNSC.

*Data collected before a dross.

**Data collected after a dross.

The percent destruction of Novec™ 612 increased as the cover gas concentration was successively lowered and exhibited the highest destruction rate of all the cover gases tested, ranging from 61% - 99%. A concentration between 150 and 400 ppmv appears to be optimal once the crucible has been sufficiently purged with the Novec™ 612 cover gas. Destruction of HFC-134a also increased as the concentration of the cover gas was lowered. HFC-134a was not optimized to the extent that Novec™ 612 was, so only limited conclusions can be drawn when comparing the two. It is believed that the destruction would have increased had lower HFC-134a cover gas concentrations been tested. As it was, the HFC-134a displayed the 2nd highest destruction (71% - 77%). SF_6 was tested on two occasions at the same concentration and was consistent with respect to amount destroyed. However, at approximately 33% it was much less than the cover gas destruction rates for Novec™ 612 and HFC-134a (>61% or greater). The SO_2 cover gas destruction was not significantly dependant on injected concentration (to the extent tested). Like SF_6, the percent destroyed was relatively low, at 29% - 37%. Finally, CO_2 displayed the lowest destruction at only 4%.

The destruction rates estimated for SF_6 in this study were significantly higher than what was estimated during the 2003 study. This is likely due to the much lower feed gas concentrations utilized in this study – 3,000 ppmv compared to 5,000 and 19,000. Also, the reduced level of dilution in this study results in the destruction of the cover gas having a larger share of the reduction in measured concentration.

5.3 Global Climate Change Potential Discussion

One of the benefits of using AM-Cover™, MTG-Shield™, SO_2 or CO_2 as cover gases for magnesium melt protection is their contribution to global climate change is significantly lower when compared to SF_6. This is evident when comparing their estimated global warming potentials (GWPs). Table 5-2 presents GWPs of several compounds detected during this study.

Table 5-2. Comparison of 100-Year GWP Estimates from the Intergovernmental Panel on Climate Change (IPCC) Second (1996) Assessment Report

Gas	IPCC GWP
Methane	21
Nitrous Oxide	310
HFC-134a	1,300
Perfluoromethane (CF_4)	6,500
Perfluoroethane (C_2F_6)	9,200
Perfluoropropane (C_3F_8)	7,000
Sulfur Hexafluoride (SF_6)	23,900

IPCC (1996), Climate Change 1995: The Scientific of Climate Change. Intergovernmental Panel on Climate Change, Cambridge University Press. Cambridge, U.K.

The crucible headspace contains a large variety of compounds, but only those with corresponding GWP values were used in estimating the overall GWP impact of switching to alternate cover gases. This calculation consisted of multiplying the average concentrations (parts per million by volume) for each of the component cover gases and applicable destruction products, with their respective GWP factors (obtained from the Second Assessment Report of the Intergovernmental Panel on Climate Change) to obtain a GWP-weighted value. The summation of all the GWP-weighted values for a particular cover gas resulted in the normalized CO_2 equivalent which was compared to the CO_2 equivalent corresponding to SF_6.[21]

Table 5-3 shows that when comparing the normalized CO_2 equivalent, or composite GWP, the alternate cover gases have a much lower impact. An obvious source for this reduction can be found in a direct comparison of cover gas GWPs shown in Table 5-2. Novec™ 612's GWP has not been supplied by the IPCC, but is likely to be extremely low (i.e., Novec™ 612 is a fluorinated ketone, which is assumed to have a GWP on the order of 1).[22] In addition to having lower GWPs, the alternate fluorinated cover gas compounds have much higher destructions (on the order of 61-99%) as compared to SF_6 (on the order of 33%). While the use of HFC-134a and Novec™ 612 does produce destruction byproducts with GWPs, their impact is minimal due to the very low concentrations generated. Although the SO_2 and CO_2 cover gases degrade as much or less than SF_6, they both have much lower GWPs than SF_6. Compared to using SF_6, switching to AM-Cover™ or MTG-Shield™ produces a reduction in overall global warming impact of at least 97%.[23] Changing the cover gas from SF_6 to dilute SO_2 reduces the global warming impact even more (>99.9%) but introduces a more complex operational scenario due to toxicity concerns. Switching to frozen CO_2 provides a reduction in global warming impact of 98% relative to SF_6.

The above comparison does not include the specific flow rates for each cover gas. In order to provide a more comprehensive analysis of composite GWP, an additional comparison was conducted. Using the ideal gas law, the molecular weights of each gas and the delivery flow rate of the cover gas was used to estimate the composite emission rate in grams per hour (g/hr). This equation can be described as follows:

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[21] Residual SF_6 concentrations were excluded from the overall GWP calculations for the alternative gases.
[22] D'Anna B, Sellevag S.R., Wirtz K., and Nielsen C.J. Photolysis Study of Perfluoro-2-methyl-3-pentanone Under Natural Sunlight Conditions Environ Sci and Tech 2005 39(22) 8708-8711
[23] Please refer to Section 5.4 for a discussion regarding the uncertainty associated with this methodology.

$$Emission\ Rate\left(\frac{grams}{hour}\right) = ppm \times MW \times lpm \times \frac{60\ \text{min}}{hour} \div \left(38.6\ liters/mole \times 10^{6}\right)$$

ppm = measured average concentration in parts per million
MW = molecular weight in grams per mole
lpm = gas flow in liters per minute

These values were summed to provide a composite GWP value that was weighted by the cover gas flow rate. The average flow weighted GWP values were then compared against the corresponding values for SF_6. Based on this approach, all of the cover gas alternatives were observed to reduce GHG emissions by at least 98% relative to SF_6.[24] Details of the flow-weighted GHG emission impacts are presented in Table 5-4.

5.4 Uncertainty Discussion

The results of this measurement study should not be interpreted to represent an absolute analysis of GHG emissions associated with HFC-134a, Novec™ 612, SO_2, CO_2 and SF_6 cover gas usage. While this study does present a relatively accurate measurement analysis and approximate comparison of GHG emissions, there are several areas of uncertainty inherent with this methodology. These areas of uncertainty include FTIR and QMS error, error associated with blending gases, dilution correction, and analytical and operational variation of the die-casting machine evaluated.

Measurements taken by the FTIR and QMS are subject to variability inherent with highly complex analytical equipment. While all prudent steps were taken during the measurement study to minimize this contributor to uncertainty (see Sections 3.3 and 4.6), a small degree of error is unavoidable.

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[24] It should be noted that fully optimized cover gas systems will result in slightly better performance than the average values reported here.

Table 5-3. Normalized GWP Comparison of Measured Emissions from Inside the Crucible Headspace

Table	Cover Gas Mixture Components[a]	Cover Gas Delivery Conc. (ppm)	GWP Weighted Cover Gas[b]	GWP Weighted CO_2	GWP Weighted CH_4	GWP Weighted N_2O	GWP Weighted C_2F_6	GWP Weighted C_3F_8	Normalized CO_2 Equivalent	Average by Cover Gas	Chg . from SF_6
4-1	Novec™ 612/CO_2	800	199	951,127	80	1,098	89,864	94,430	1,136,798	980,997[c]	**98%**
4-1	Novec™ 612/CO_2	600	143	964,973	85	951	69,697	53,260	1,089,109		
4-1	Novec™ 612/CO_2	400	55	889,151	106	991	17,221	4,940	912,465		
4-1	Novec™ 612/CO_2	300	3	841,046	118	688	0	0	841,855		
4-1	Novec™ 612/CO_2	200	76	916,790	188	896	33,380	23,368	974,697		
4-1	Novec™ 612/CO_2	200	64	949,285	101	868	10,947	0	961,265		
4-1	Novec™ 612/CO_2	150	31	944,754	102	714	5,191	0	950,792		
4-3	HFC-134a/CDA	4,200	1,557,833	2,781	12	4,896	0	0	1,583,642	1,327,242[d]	**97%**
4-3	HFC-134a/CDA	3,600	1,053,924	2,520	11	6,180	0	0	1,070,841		
4-5	SF_6/CDA	3,000	46,989,729	468	66	751	0	0	46,991,015	46,589,491[e]	
4-5	SF_6/CDA	3,000	46,180,244	486	65	7,173	0	0	46,187,968		
4-7	SO_2/CDA	10,000	0	435	57	1,039	0	0	1,532	1,288[f]	**99.9%**
4-7	SO_2/CDA	8,500	0	422	40	871	0	0	1,333		
4-7	SO_2/CDA	7,000	0	425	47	886	0	0	1,359		
4-7	SO_2/CDA	6,000	0	407	46	929	0	0	1,381		
4-7	SO_2/CDA	5,000	0	406	45	894	0	0	1,345		
4-7	SO_2/CDA	5,000	0	443	47	597	0	0	1,087		
4-7	SO_2/CDA	4,000	0	432	43	508	0	0	983		
4-9	Frozen CO_2	1,000,000	0	957,390	17	169	0	0	957,576	957,576[g]	**98%**

[a] As provided by Lunt Manufacturing, AMT, Polycontrols, and Matheson Tri-Gas/TNSC.

[b] GWP weighting based on dilution corrected concentration for the primary cover gas constituent (e.g., Novec™ 612, HFC-134a, SF_6)

[c] Average composite GWP for Novec™ 612/CO_2 tests (Table 4-1)

[d] Average composite GWP for HFC-134a/CDA tests (Table 4-3)

[e] SF_6 composite GWP baseline estimate for comparison with other tests (Table 4-5)

[f] Average composite GWP for SO_2 test (Table 4-7)

[g] Average composite GWP for CO_2 test (Table 4-9)

Table 5-4. GWP (Weighted by Cover Gas Flow) Comparison of Measured Emissions from Inside the Crucible Head Space

Table	Cover Gas Mixture Components[a]	Cover Gas Delivery Conc. (ppm)	GWP Weighted Cover Gas[b] (g/hr)	GWP Weighted CO_2 (g/hr)	GWP Weighted CH_4 (g/hr)	GWP Weighted N_2O (g/hr)	GWP Weighted C_2F_6 (g/hr)	GWP Weighted C_3F_8 (g/hr)	Normalized CO_2 GWP Equivalent (g/hr)	Average by Cover Gas (g/hr)	Chg. from SF_6
4-1	Novec™ 612/CO_2	800	4	2,342	0	3	694	994	4,037	2,790[c]	**99%**
4-1	Novec™ 612/CO_2	600	3	2,377	0	2	538	560	3,480		
4-1	Novec™ 612/CO_2	400	1	2,190	0	2	133	52	2,378		
4-1	Novec™ 612/CO_2	300	0	2,071	0	2	0	0	2,073		
4-1	Novec™ 612/CO_2	200	1	2,258	0	2	258	246	2,765		
4-1	Novec™ 612/CO_2	200	1	2,338	0	2	85	0	2,426		
4-1	Novec™ 612/CO_2	150	1	2,327	0	2	40	0	2,369		
4-3	HFC-134a/CDA	4,200	9,882	8	0	13	0	0	9,903	8,306[d]	**98%**
4-3	HFC-134a/CDA	3,600	6,686	7	0	17	0	0	6,710		
4-5	SF_6/CDA	3,000	373,336	1	0	2	0	0	373,339	370,131[e]	
4-5	SF_6/CDA	3,000	366,905	1	0	17	0	0	366,923		
4-7	SO_2/CDA	10,000	0	1	0	3	0	0	4	3[f]	**>99.9%**
4-7	SO_2/CDA	8,500	0	1	0	2	0	0	3		
4-7	SO_2/CDA	7,000	0	1	0	2	0	0	4		
4-7	SO_2/CDA	6,000	0	1	0	2	0	0	4		
4-7	SO_2/CDA	5,000	0	1	0	2	0	0	4		
4-7	SO_2/CDA	5,000	0	1	0	2	0	0	3		
4-7	SO_2/CDA	4,000	0	1	0	1	0	0	3		
4-9	Frozen CO_2	1,000,000	0	8,460	0	0	0	0	8,460	8,460[g]	**98%**

[a] As provided by Lunt Manufacturing, AMT, Polycontrols, and Matheson Tri-Gas/TNSC.

[b] GWP weighting based on dilution corrected concentration for the primary cover gas constituent (e.g., Novec™ 612, HFC-134a, SF_6)

[c] Average composite flow rate weighted GWP for Novec™ 612/CO_2 tests (Table 4-1)

[d] Average composite flow rate weighted GWP for HFC-134a/CDA tests (Table 4-3)

[e] SF_6 composite flow rate weighted GWP baseline estimate for comparison with other tests (Table 4-5)

[f] Average composite flow rate weighted GWP for SO_2 test (Table 4-7)

[g] Flow rate weighted GWP for CO_2 is based on an estimated flow rate of 0.0012 gal/second when solenoid is open.

Characterization of Emissions and Occupational Exposure Associated with Melt Protection Technologies for Magnesium Die Casting

Appendix A

October 2007

EPA 430-R-07-008

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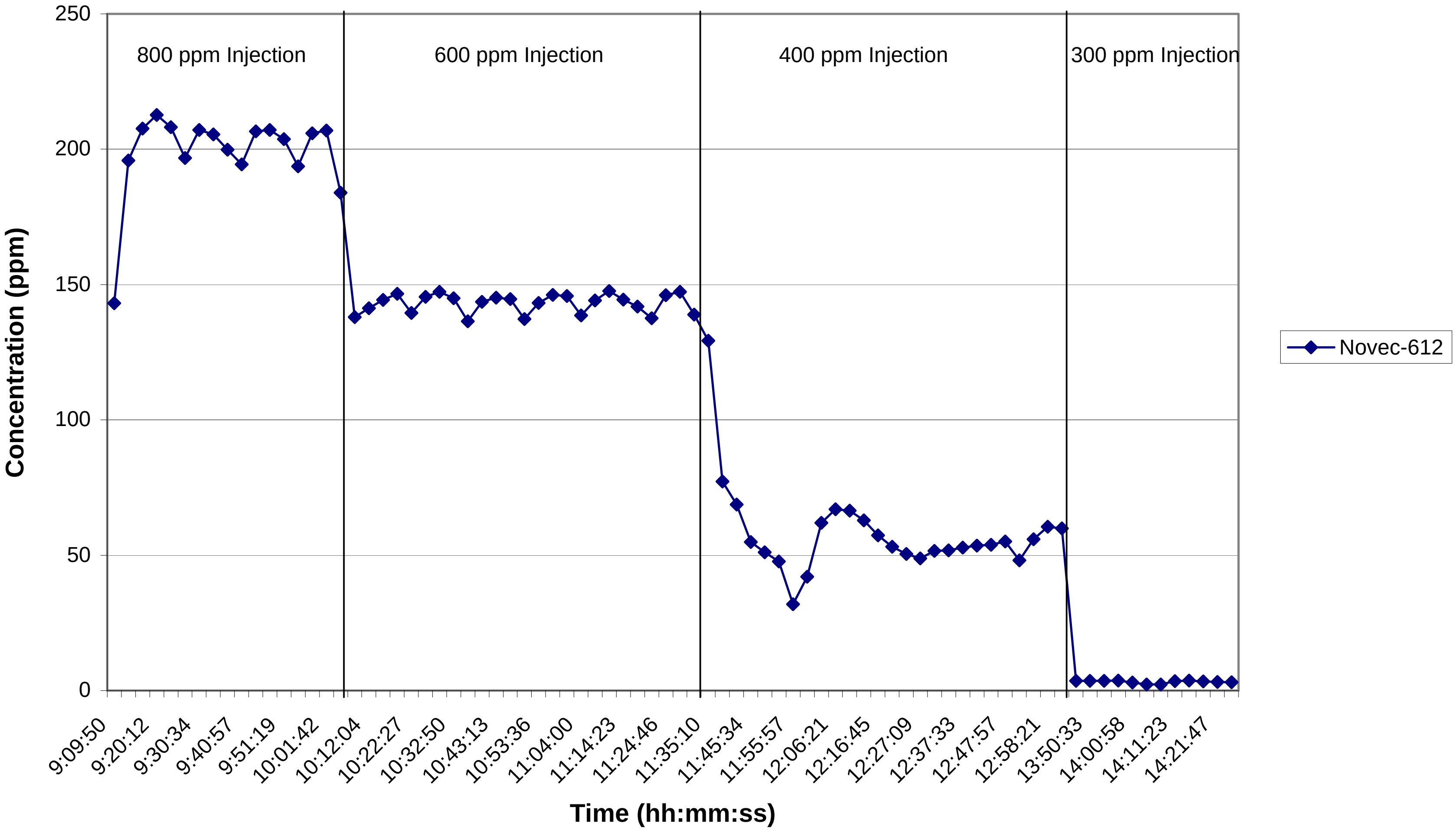
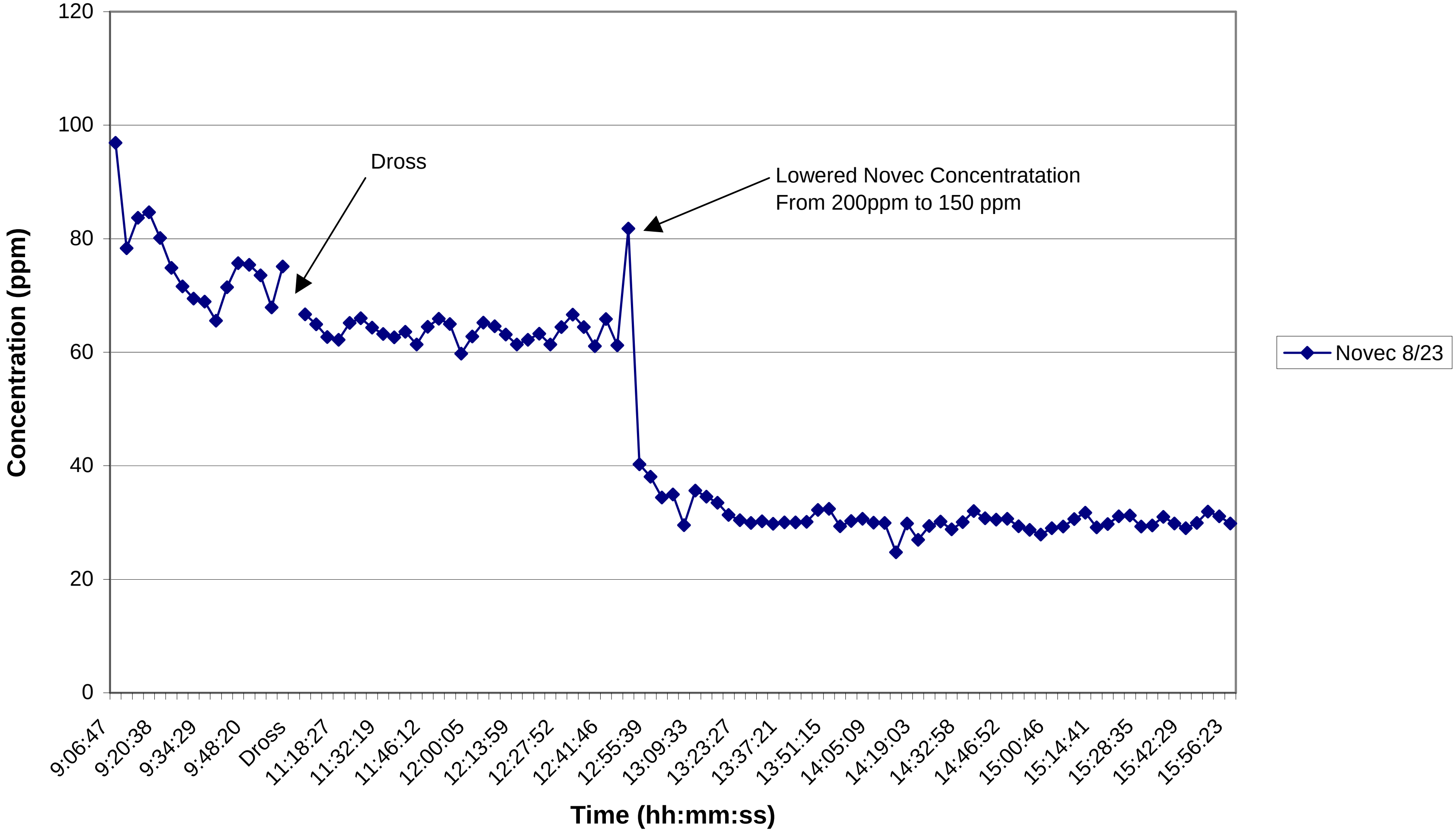
Appendix A-1

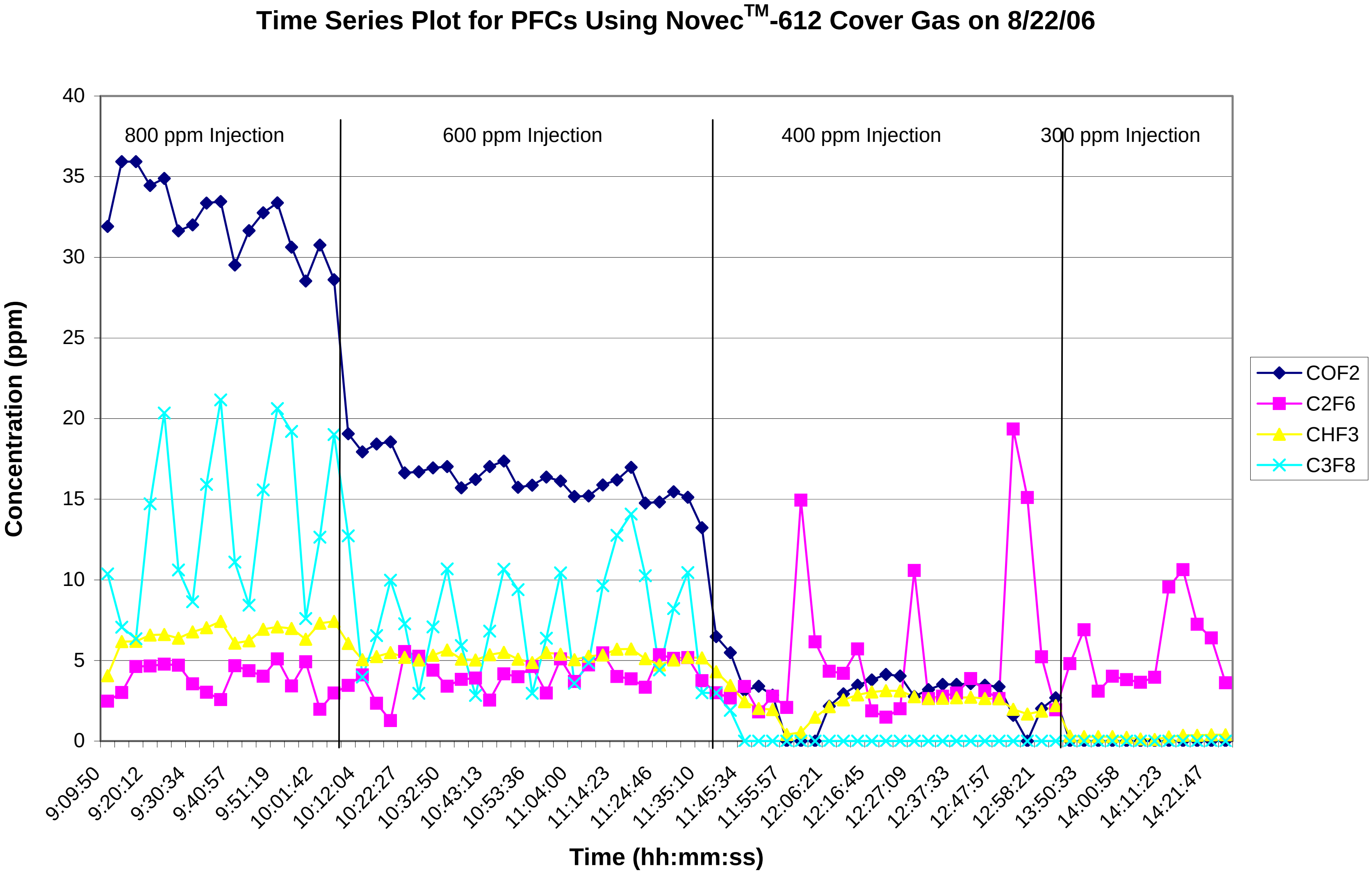
MTG-Shield™ using Novec™ 612 with CO_2 Carrier Gas Plots

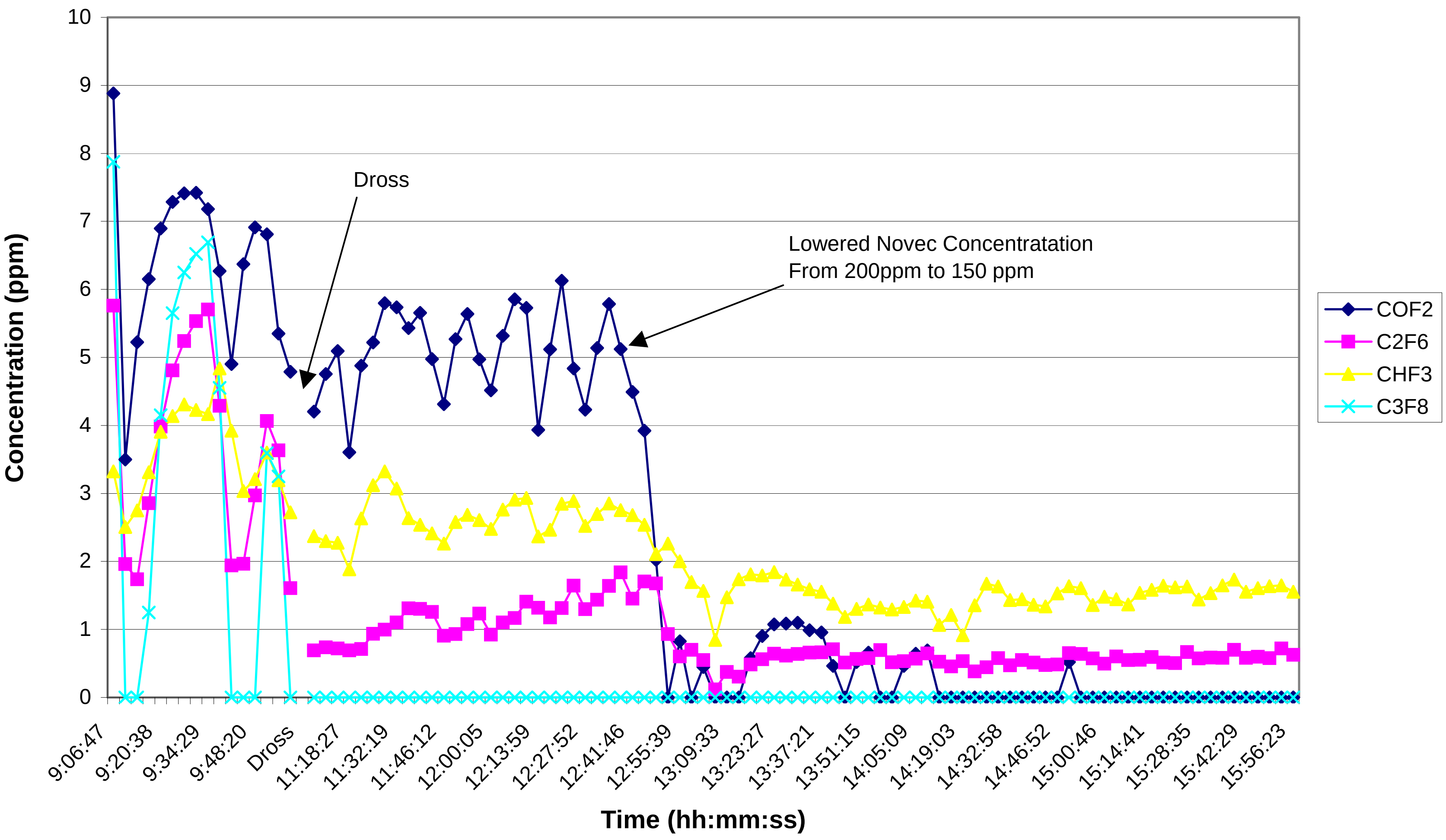
Time Series Plot for Novec^{TM}-612 on 8/22/06



Time Series Plot for Novec^{TM}-612 on 8/23/06

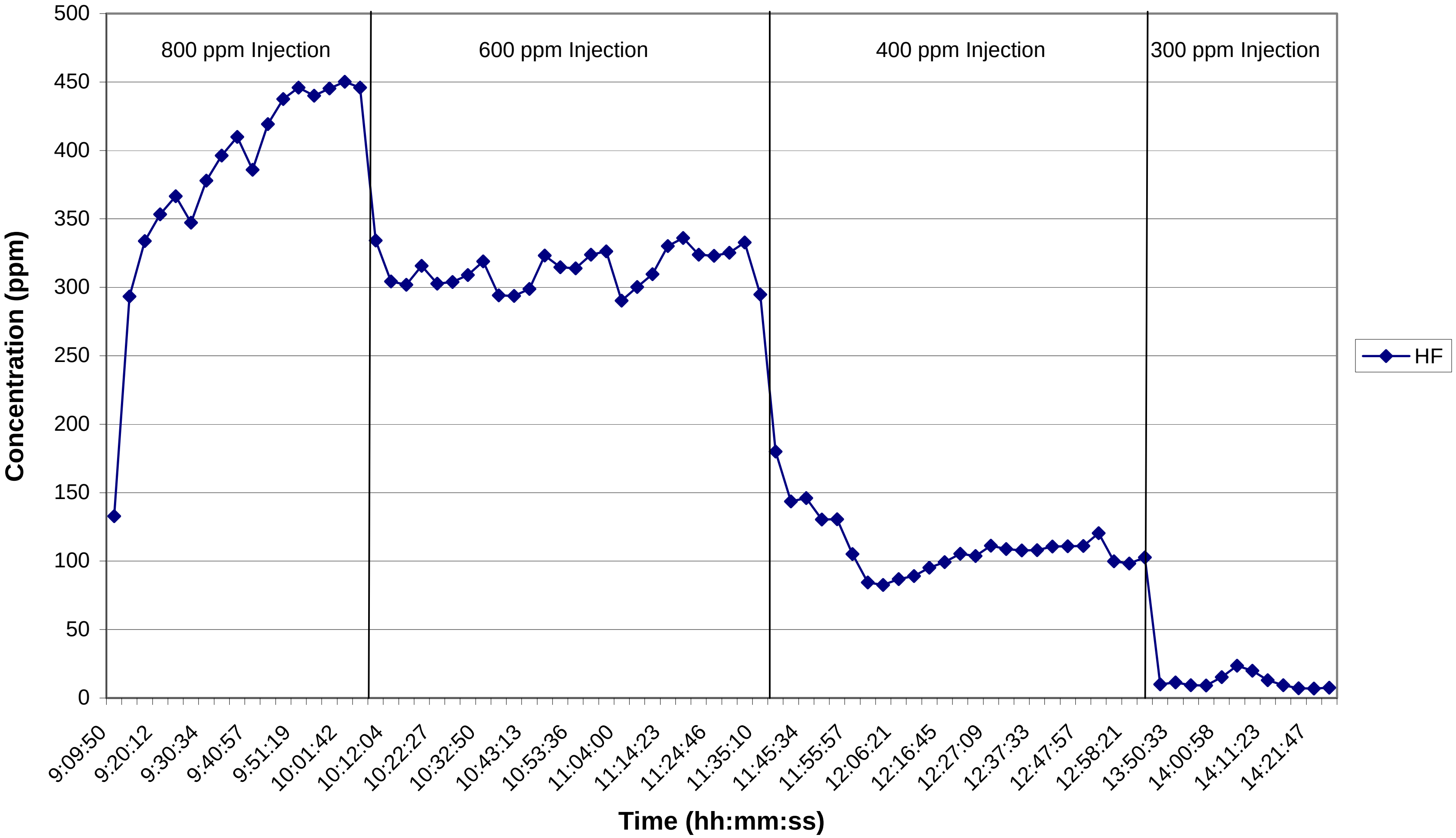



Time Series Plot for PFCs Using Novec^{TM}-612 Cover Gas on 8/22/06

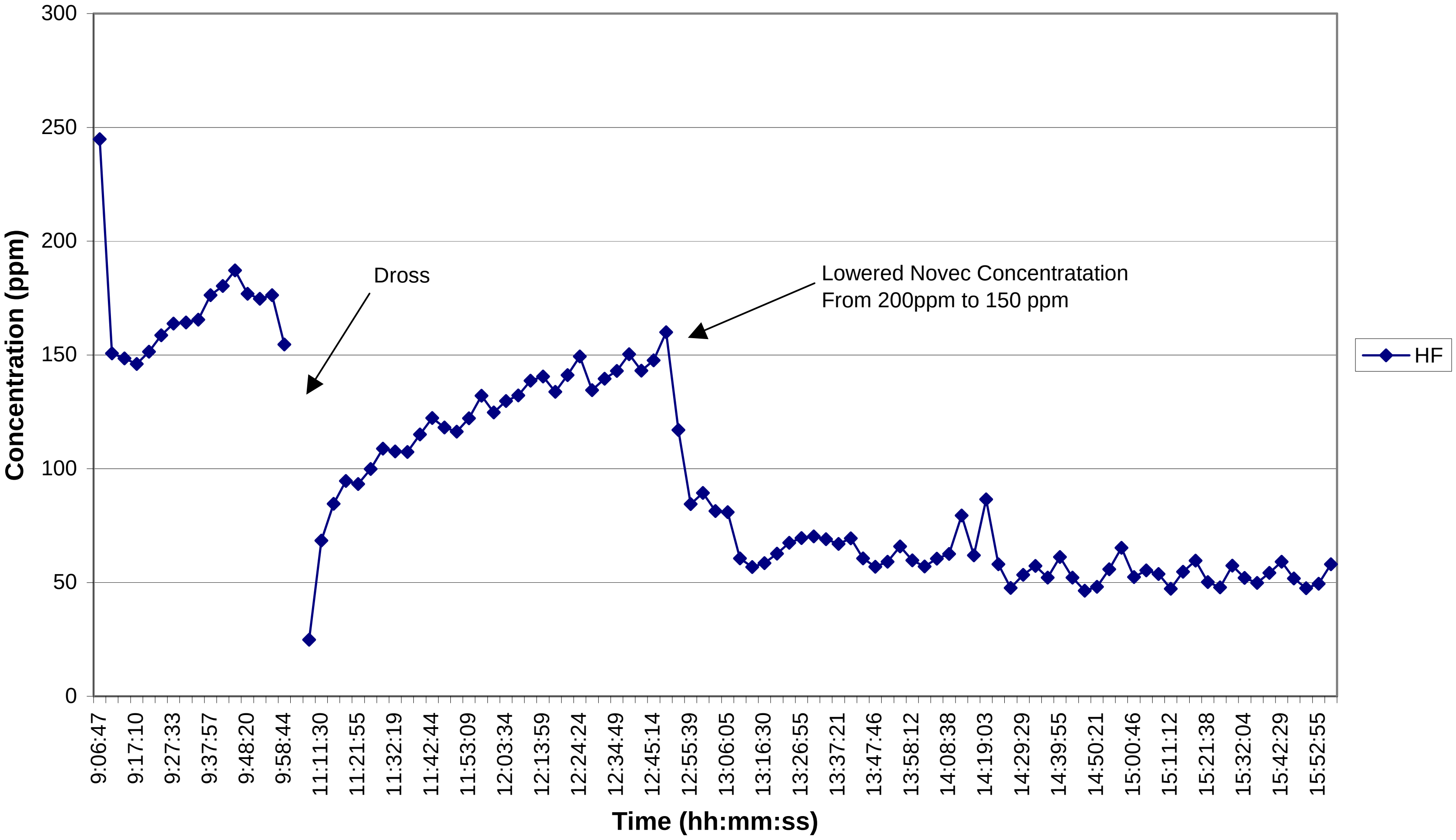


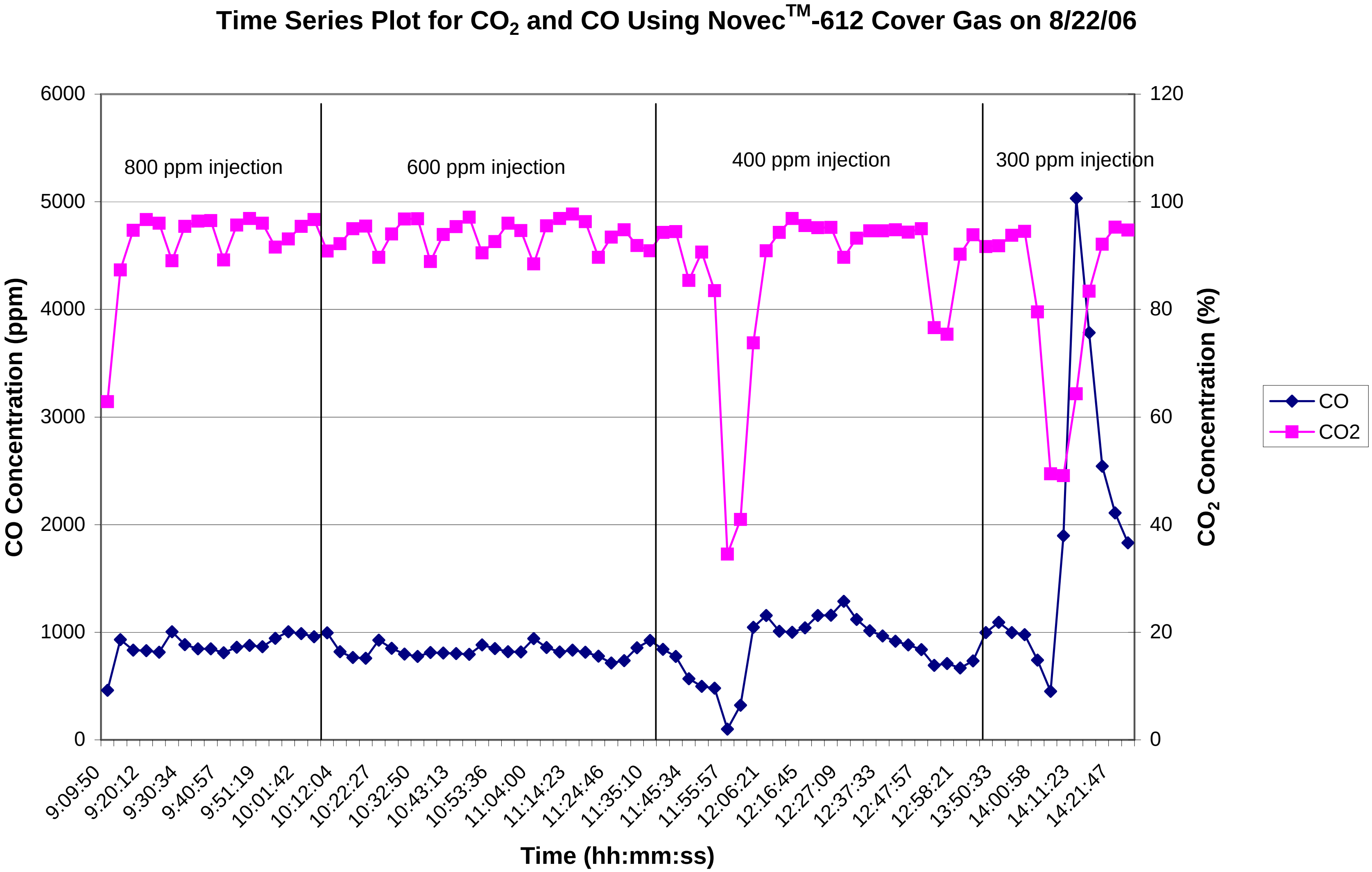
Time Series Plot for PFCs Using Novec^{TM}-612 Cover Gas on 8/23/06

Time Series Plot for HF Using Novec^{TM}-612 Cover Gas on 8/22/06



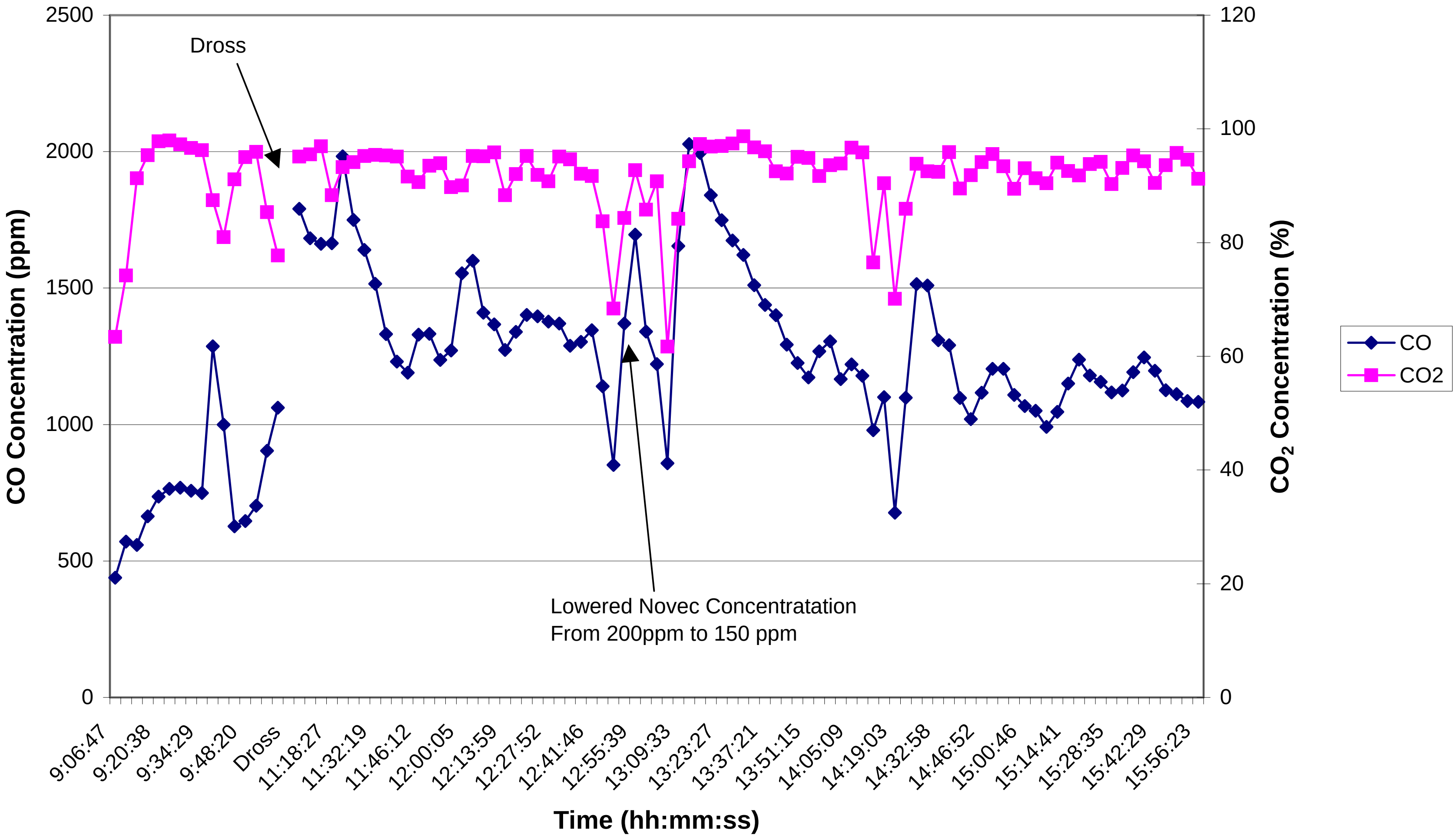
Time Series Plot for HF Using Novec^{TM}-612 Cover Gas on 8/23/06



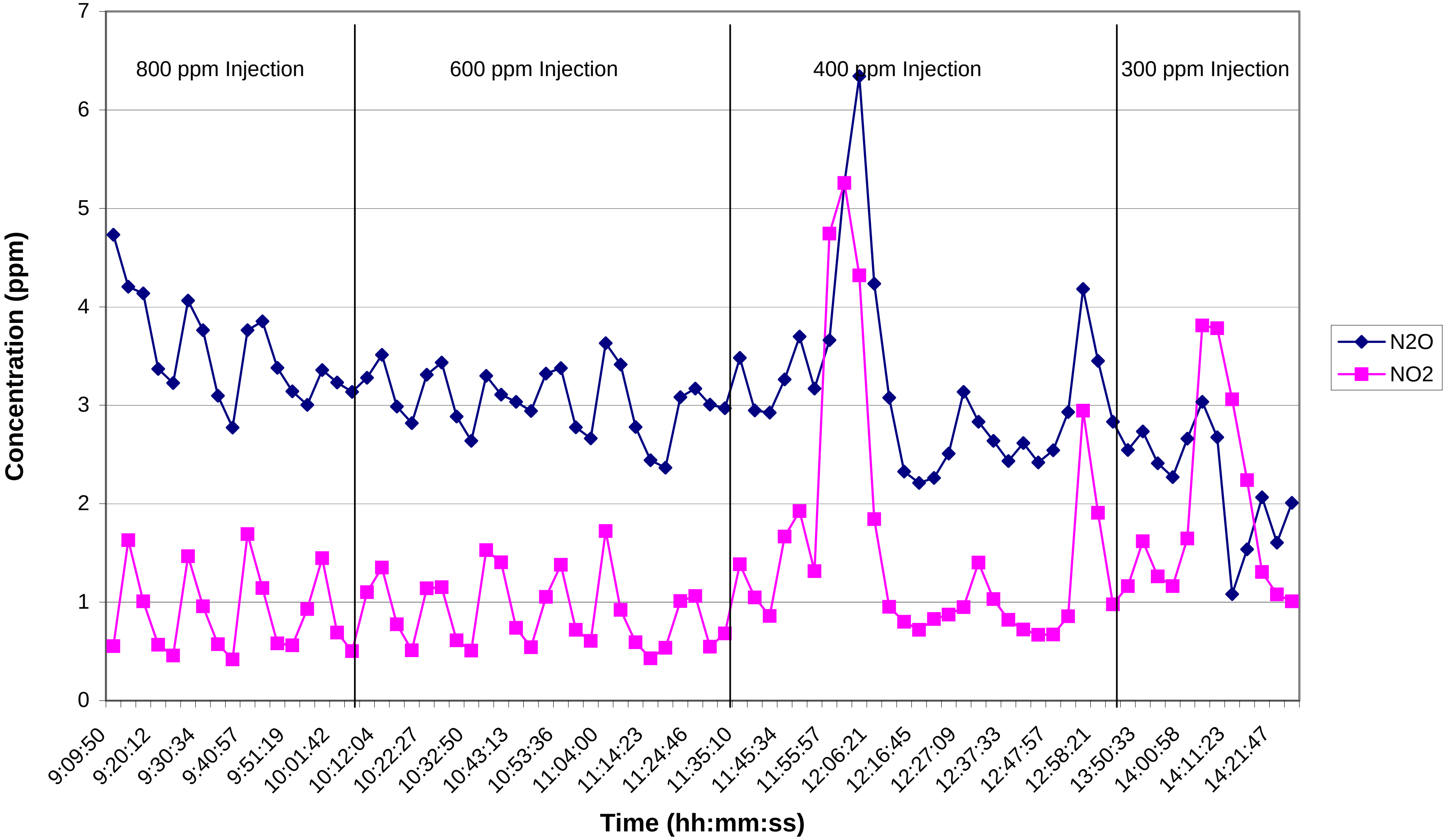


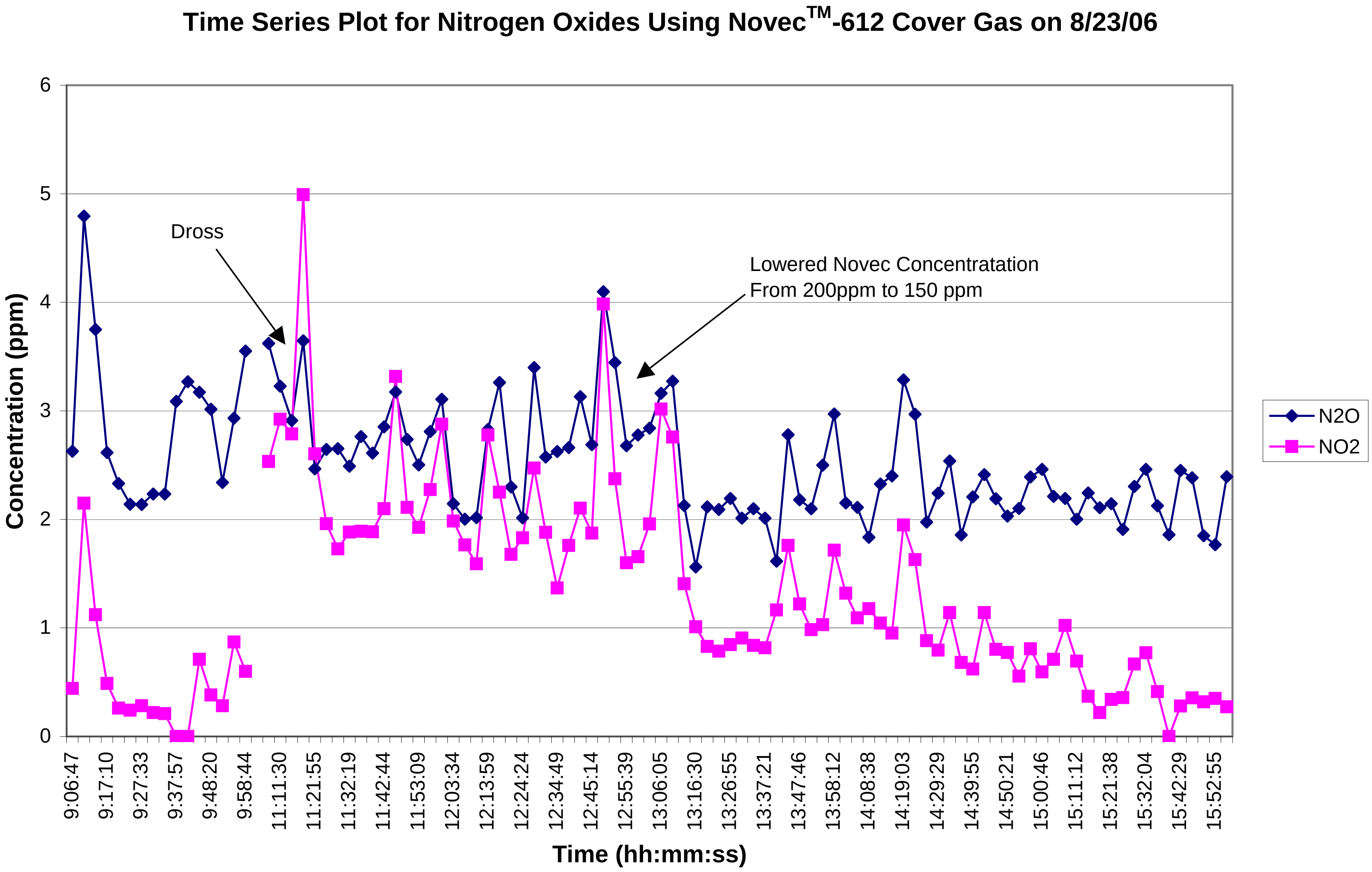
Time Series Plot for CO_2 and CO Using Novec^{TM}-612 Cover Gas on 8/22/06

Time Series Plot for CO_2 and CO Using Novec^{TM}-612 Cover Gas on 8/23/06



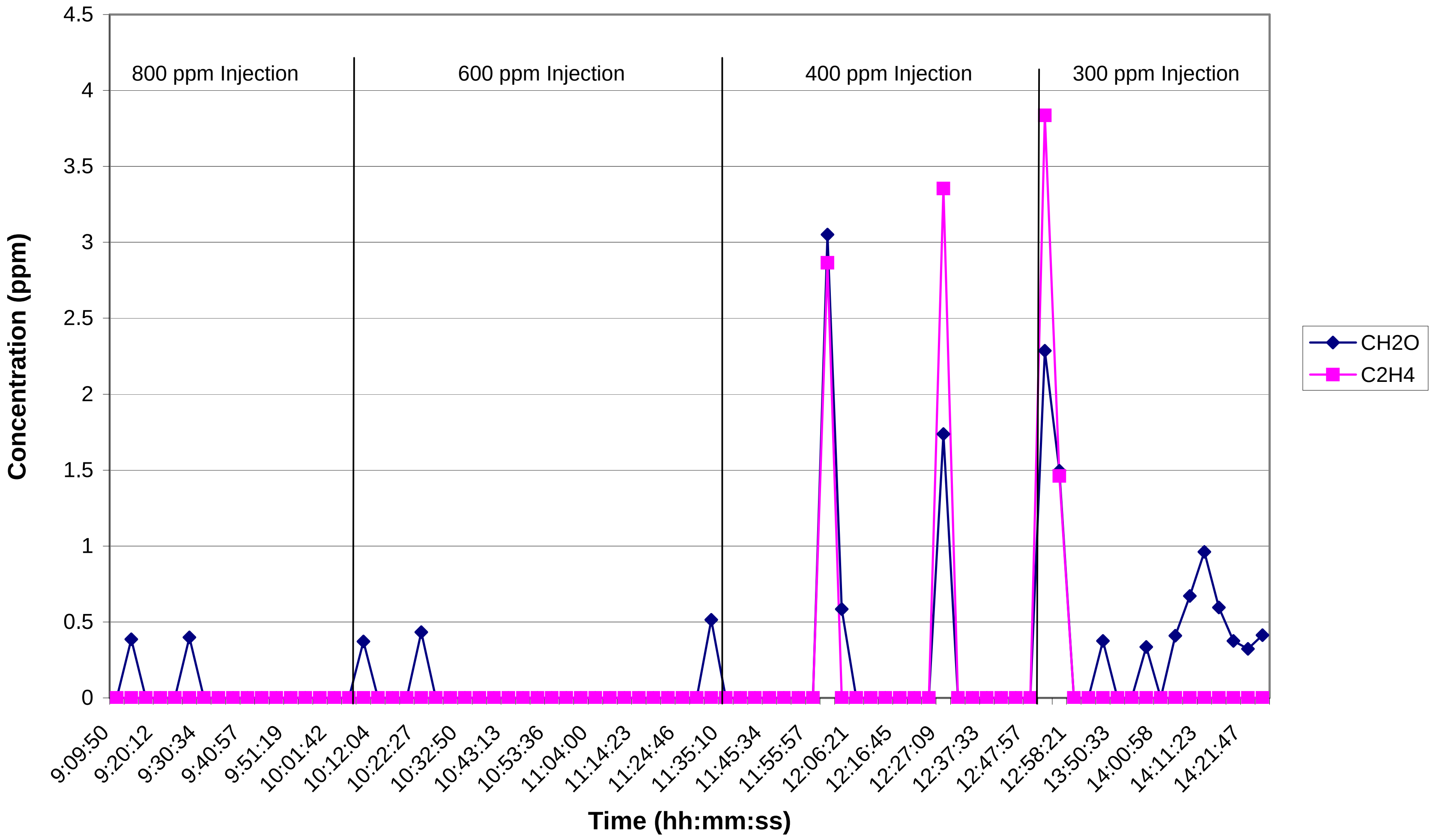
Time Series Plot for Nitrogen Oxides Using Novec^{TM}-612 Cover Gas on 8/22/06



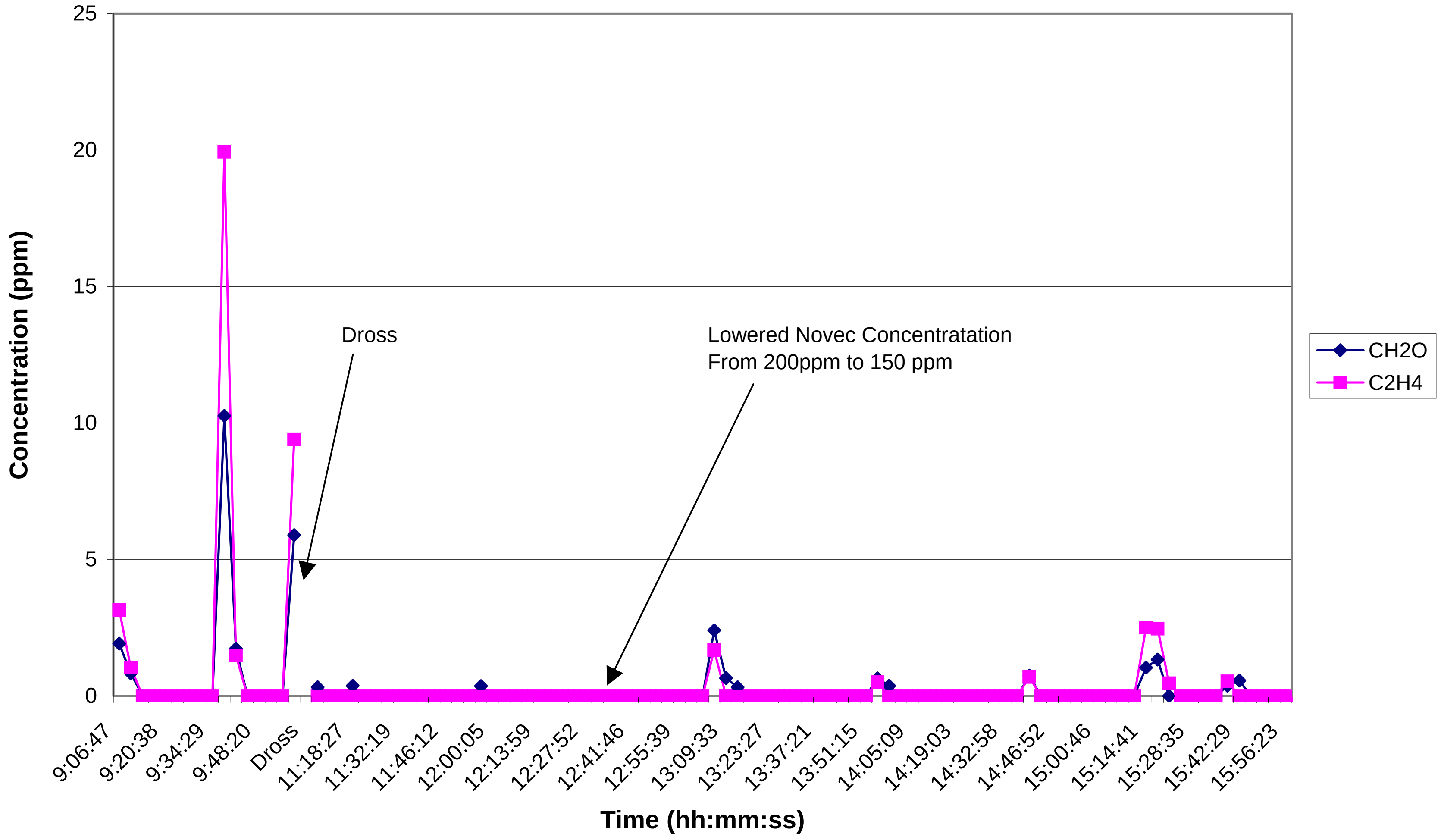


Time Series Plot for Nitrogen Oxides Using Novec^{TM}-612 Cover Gas on 8/23/06

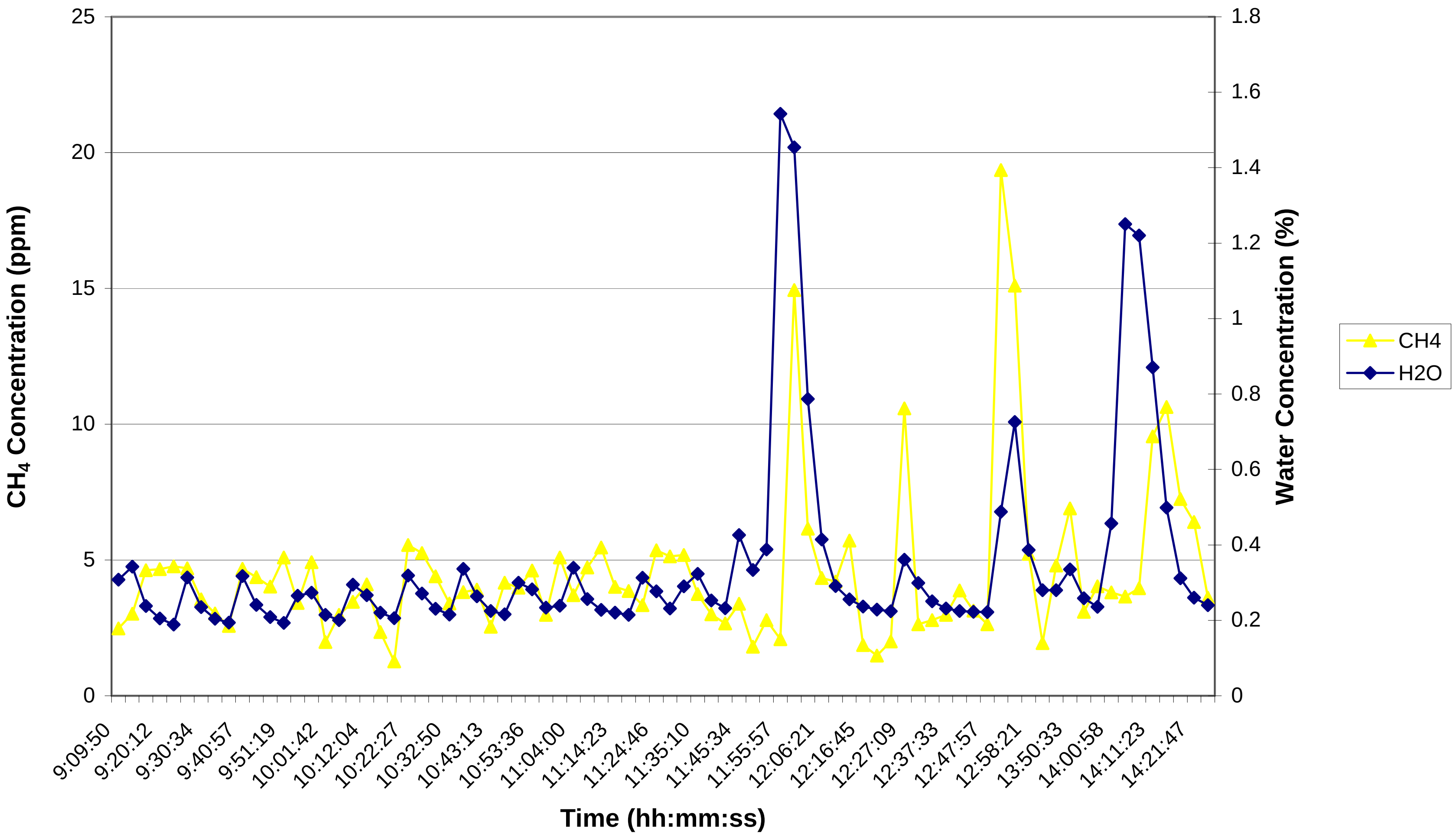
Time Series Plot for CH_2O and C_2H_4 Using Novec^{TM}-612 Cover Gas on 8/22/06



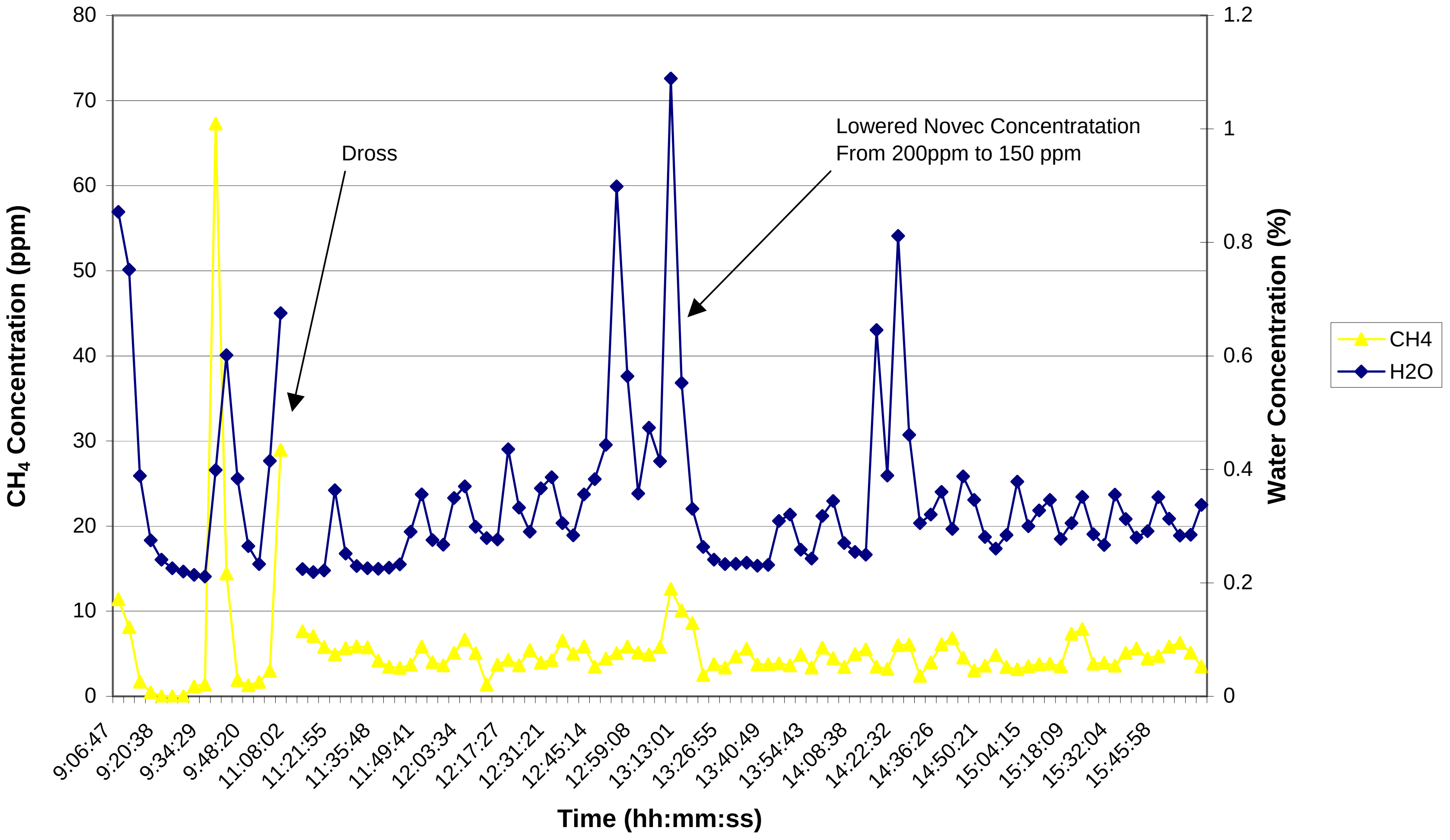
Time Series Plot for CH_2O and C_2H_4 on Using Novec^{TM}-612 Cover Gas 8/23/06



Time Series Plot for CH_4 and H_2O Using Novec^{TM}-612 Cover Gas on 8/22/06

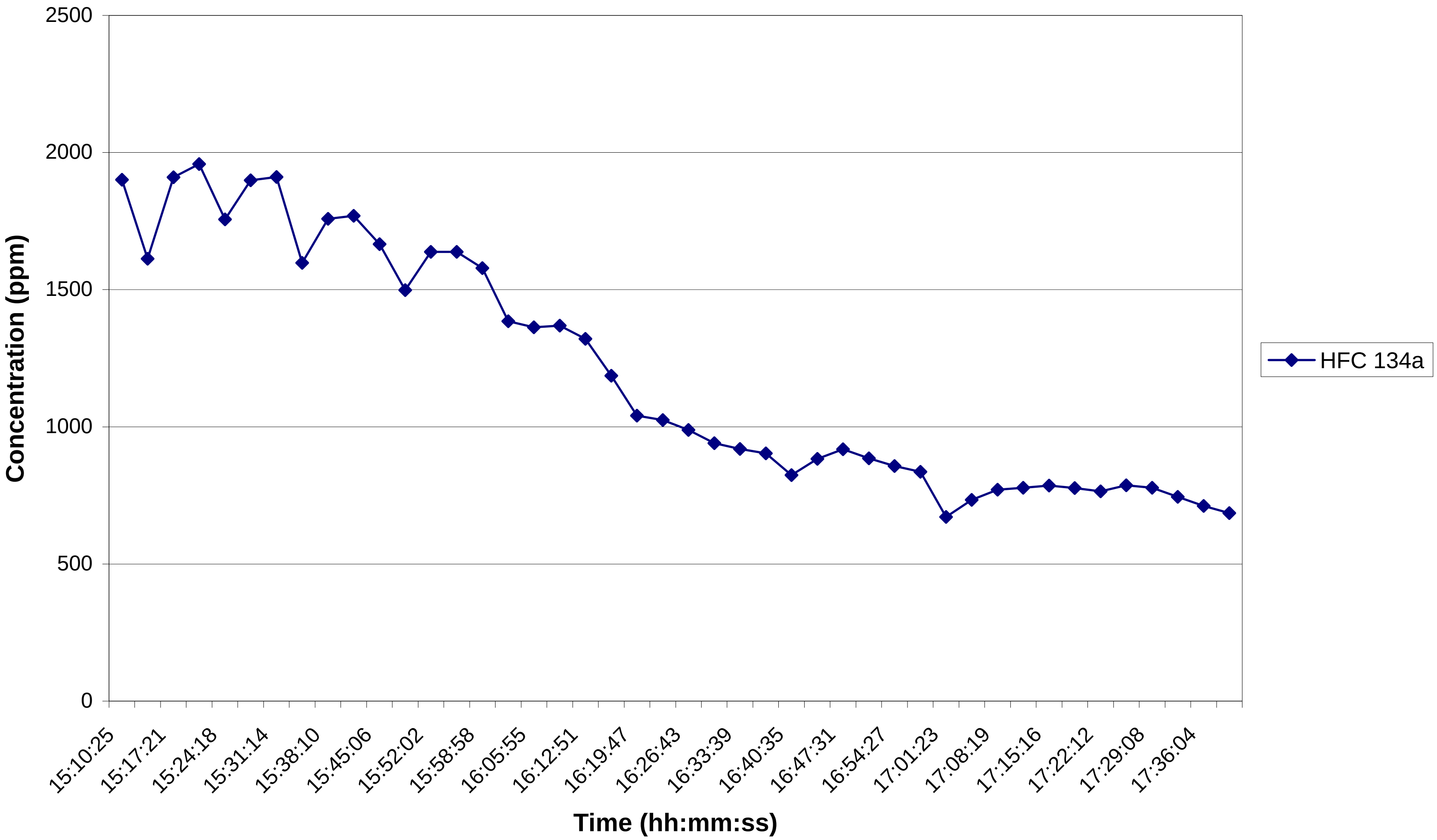


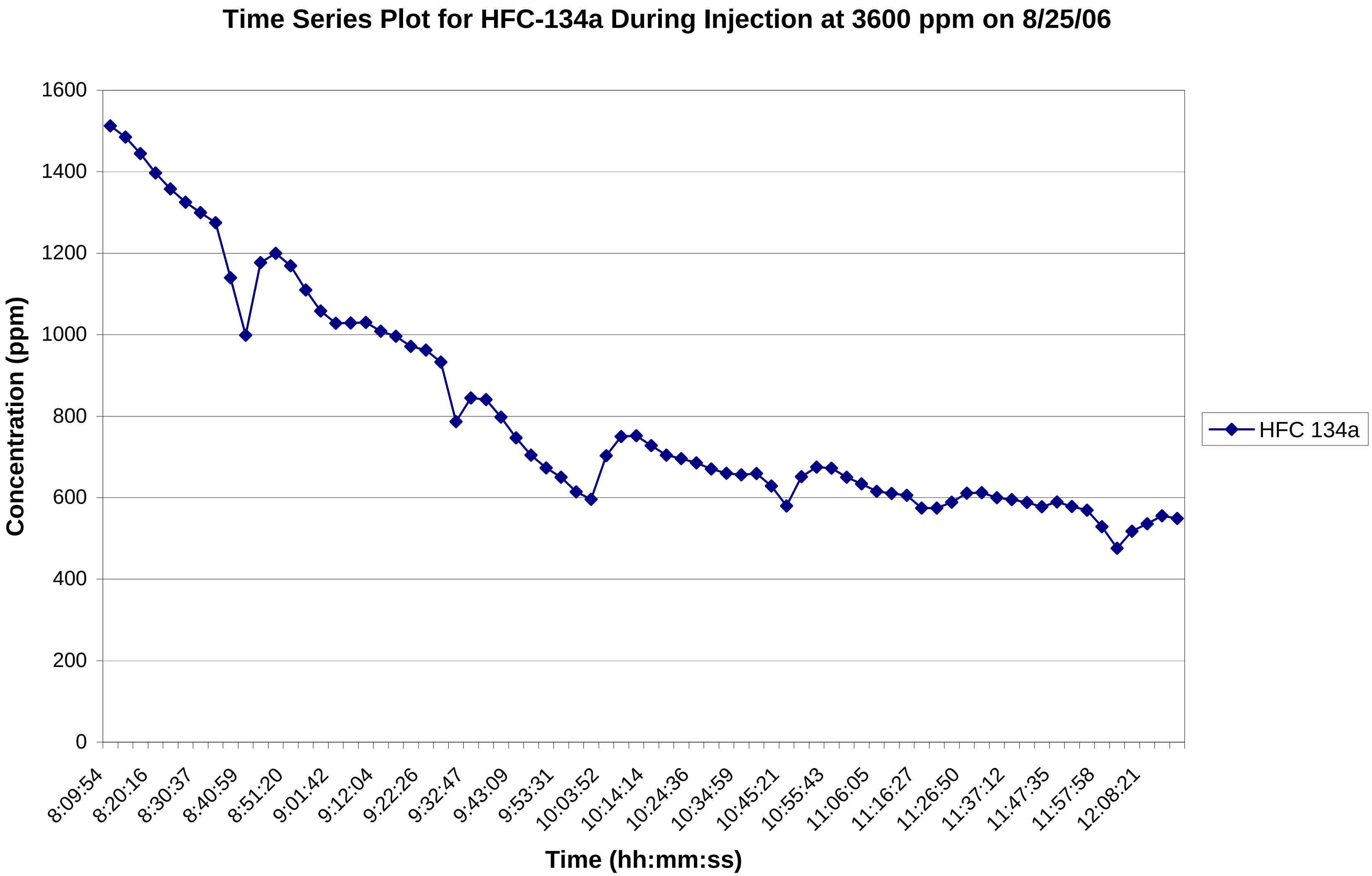
Time Series Plot for CH_4 and H_2O Using Novec^{TM}-612 Cover Gas on 8/23/06



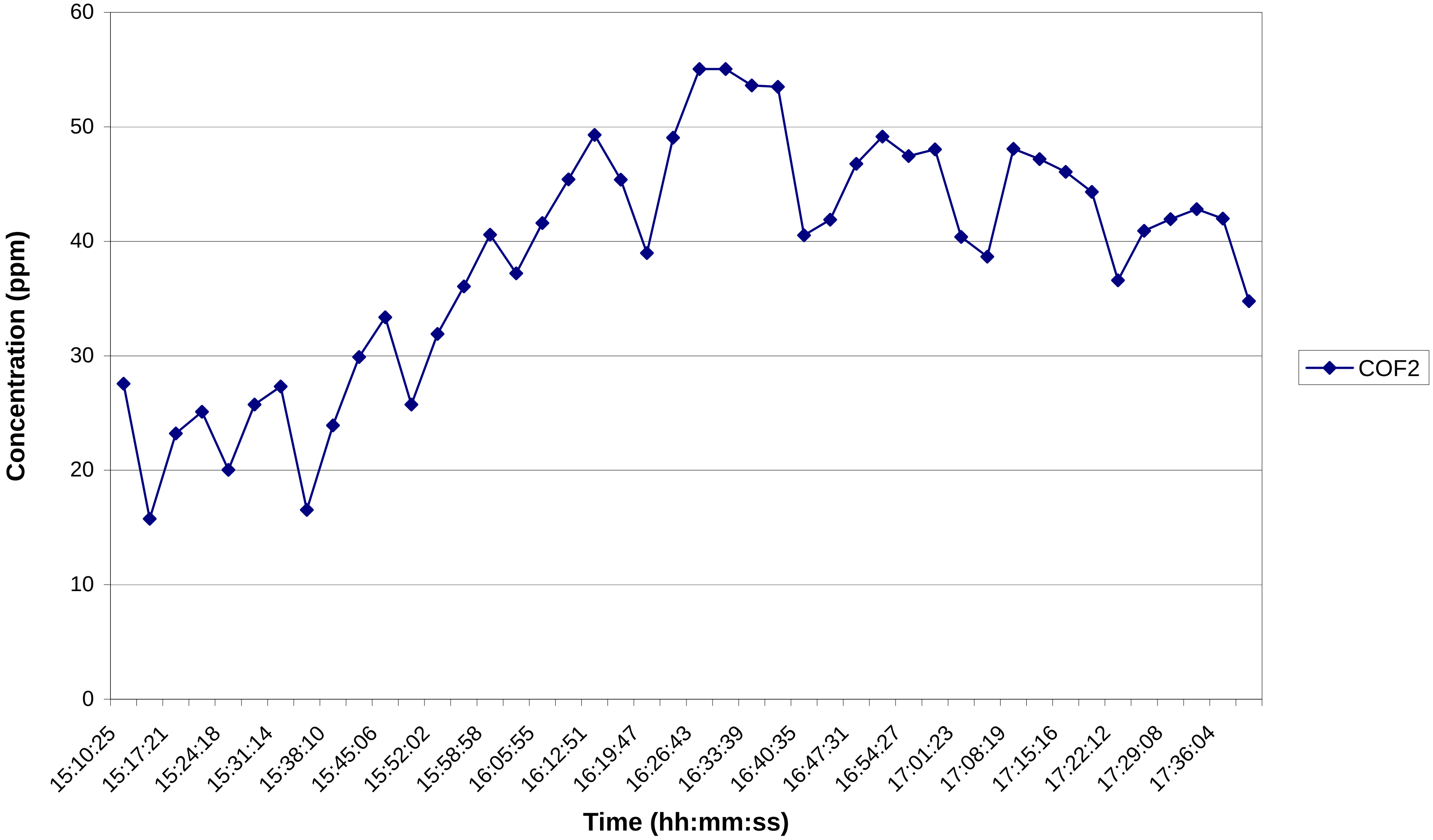
Appendix A-2
AM-Cover™ using HFC-134a with CDA Carrier Gas Plots

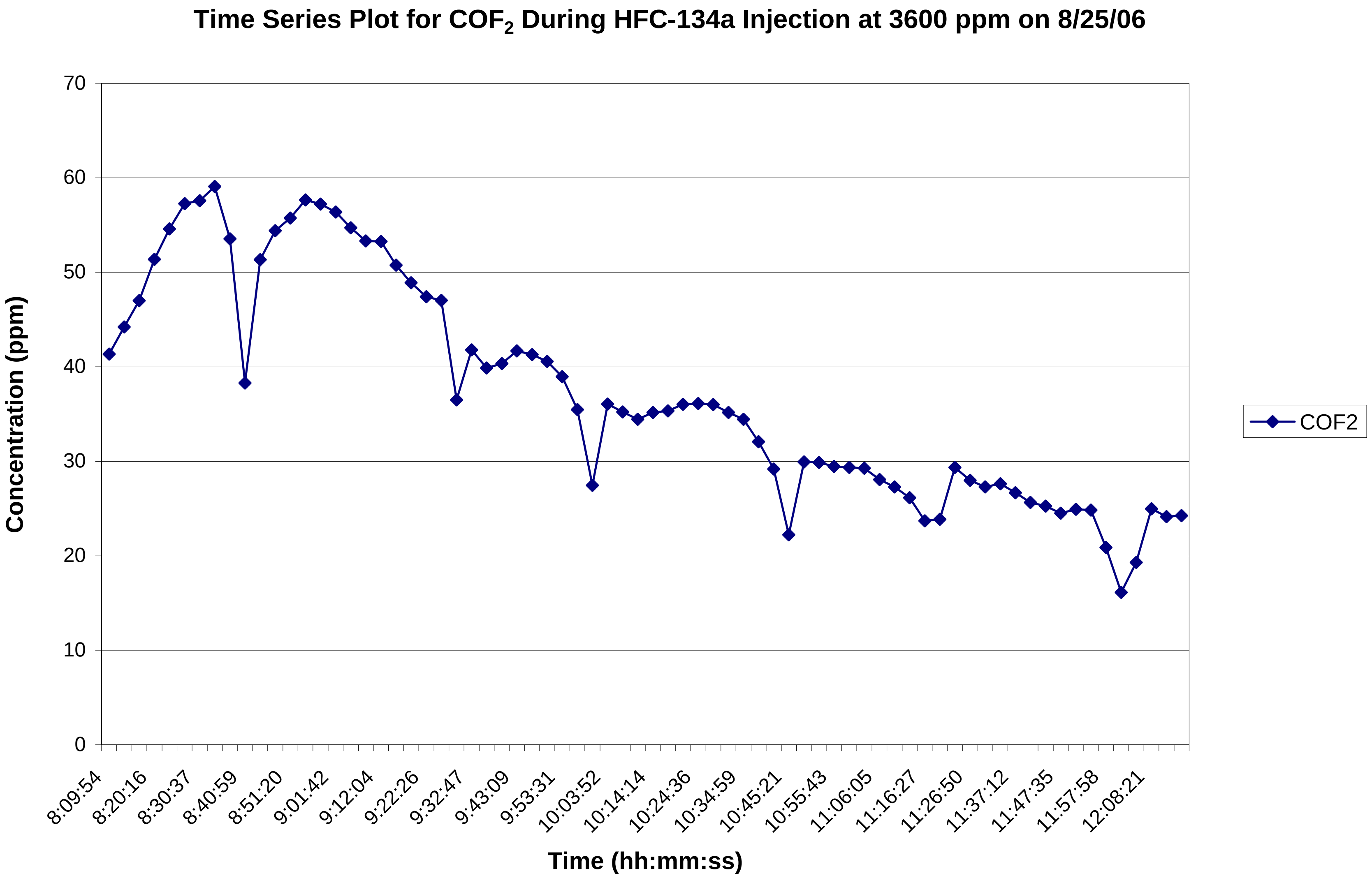
Time Series Plot for HFC-134a During Injection at 4200 ppm on 8/24/06




Time Series Plot for HFC-134a During Injection at 3600 ppm on 8/25/06
Concentration (ppm)
1600
1400
1200
1000
800
600
400
200
0
8:09:54
8:20:16
8:30:37
8:40:59
8:51:20
9:01:42
9:12:04
9:22:26
9:32:47
9:43:09
9:53:31
10:03:52
10:14:14
10:24:36
10:34:59
10:45:21
10:55:43
11:06:05
11:16:27
11:26:50
11:37:12
11:47:35
11:57:58
12:08:21
Time (hh:mm:ss)
HFC 134a

Time Series Plot for COF$_2$ During HFC-134a Injection at 4200 ppm on 8/24/06




Time Series Plot for COF_2 During HFC-134a Injection at 3600 ppm on 8/25/06
Concentration (ppm)
70
60
50
40
30
20
10
0
8:09:54
8:20:16
8:30:37
8:40:59
8:51:20
9:01:42
9:12:04
9:22:26
9:32:47
9:43:09
9:53:31
10:03:52
10:14:14
10:24:36
10:34:59
10:45:21
10:55:43
11:06:05
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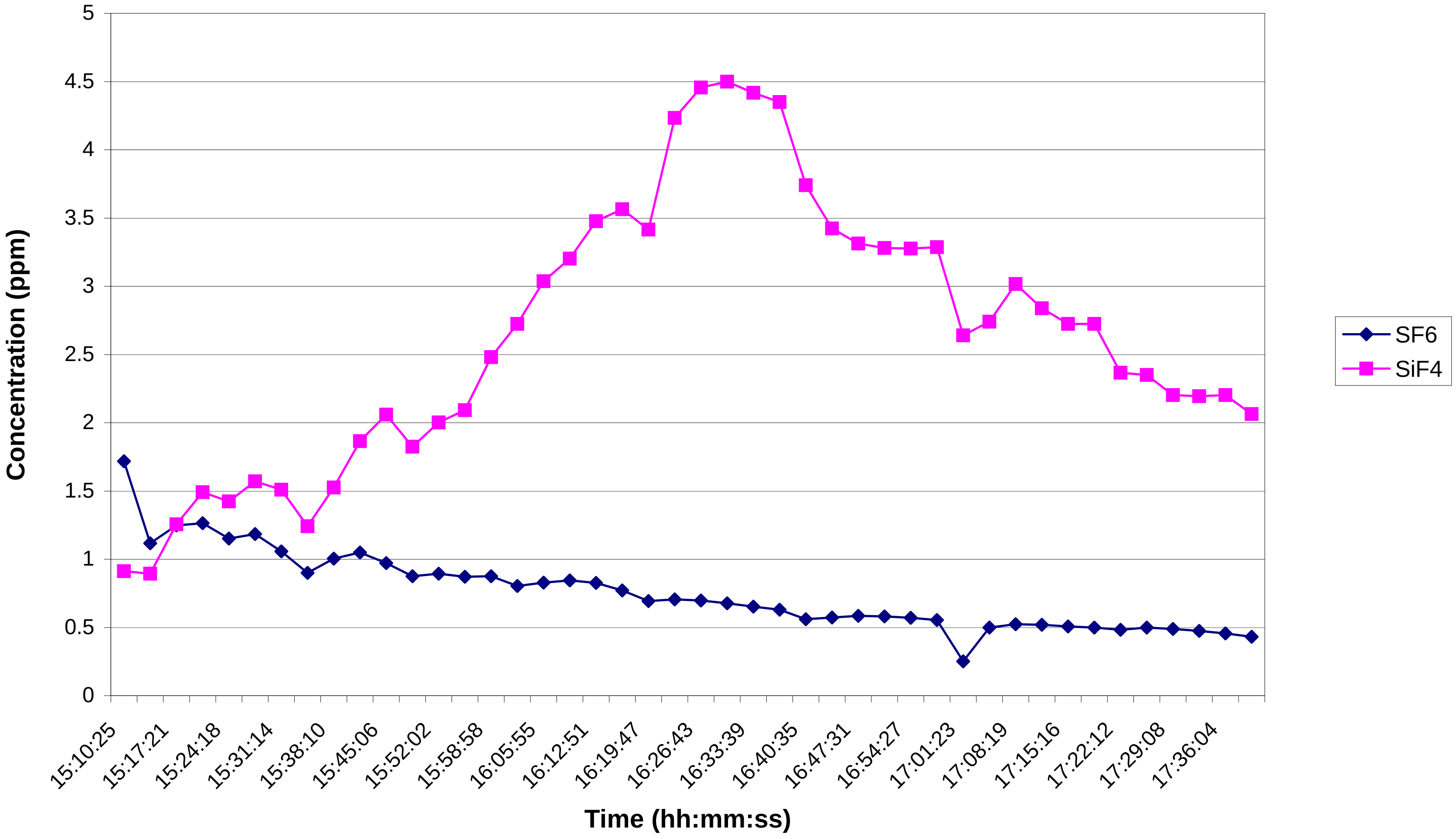
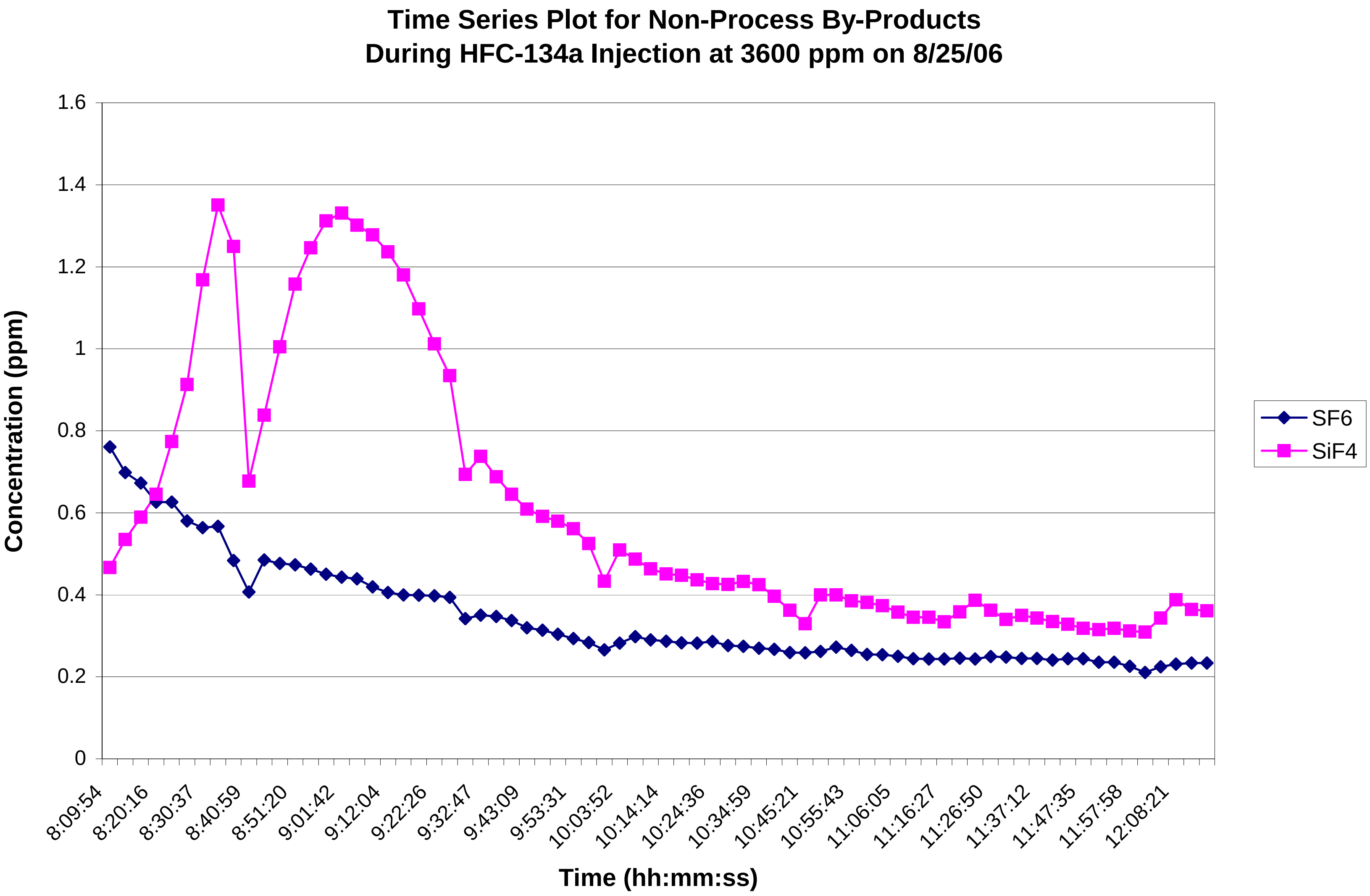
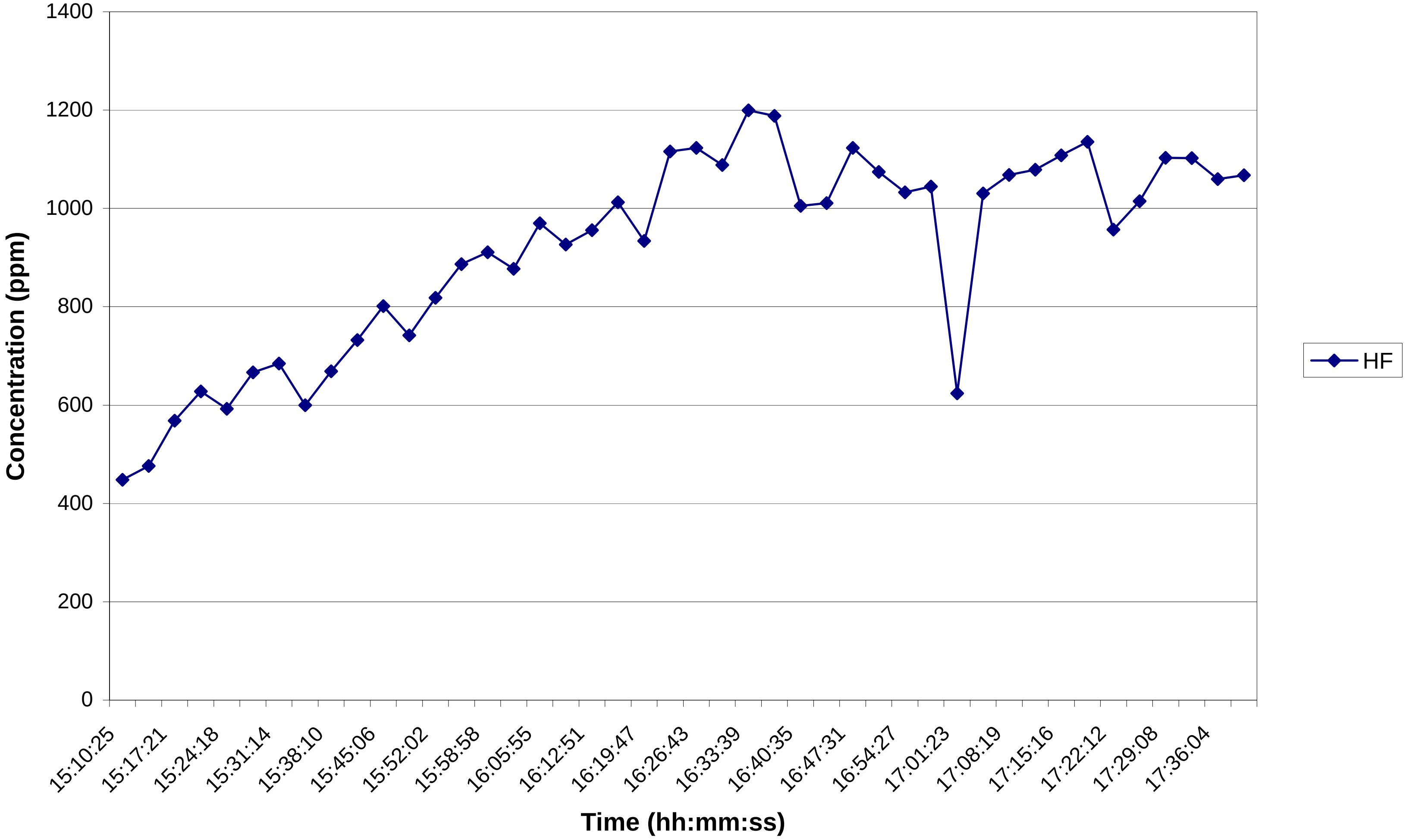
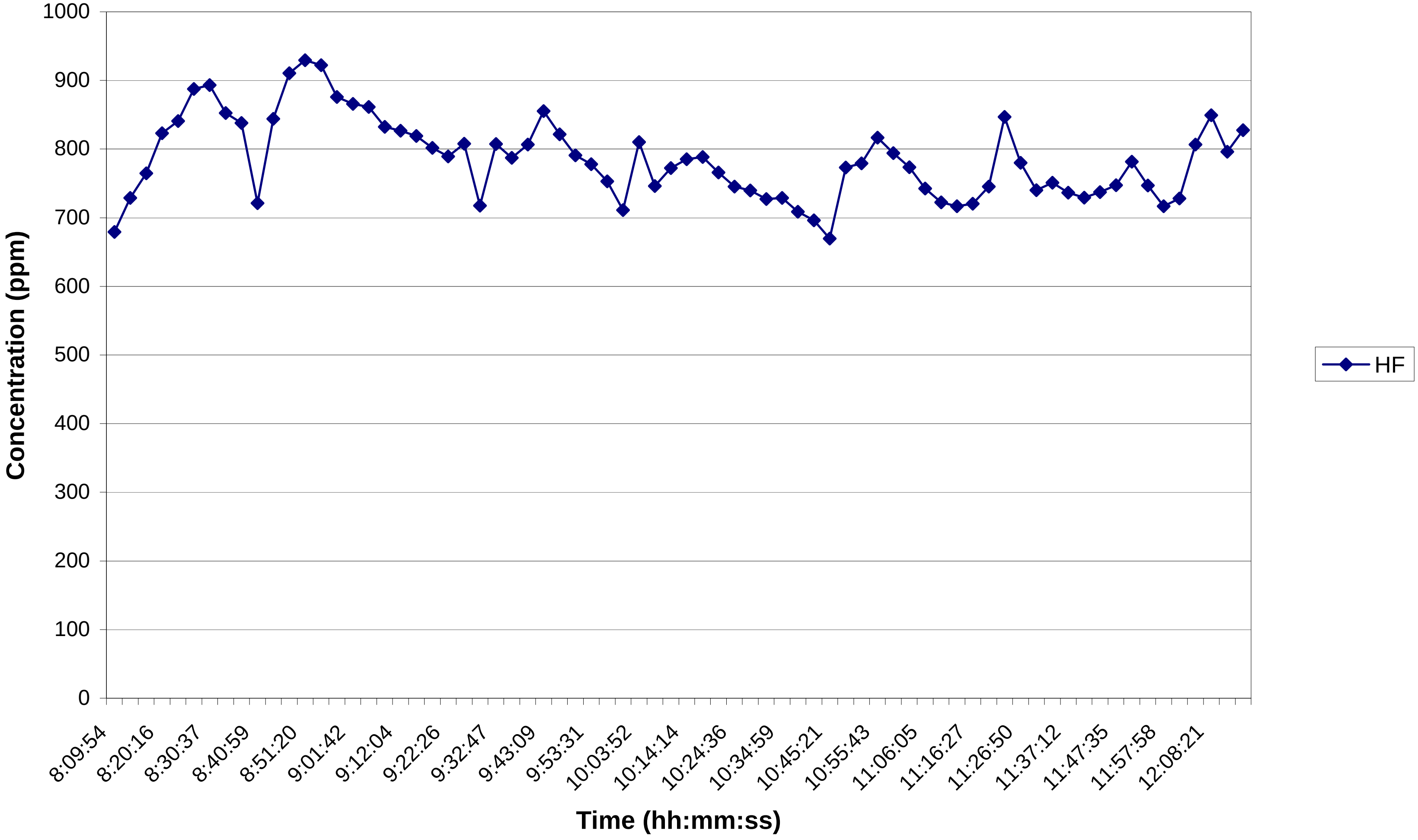
11:57:58
12:08:21
Time (hh:mm:ss)
COF2


Time Series Plot for Non-Process By-Products
During HFC-134a Injection at 4200 ppm on 8/24/06


Time Series Plot for Non-Process By-Products
During HFC-134a Injection at 3600 ppm on 8/25/06
Concentration (ppm)
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
8:09:54
8:20:16
8:30:37
8:40:59
8:51:20
9:01:42
9:12:04
9:22:26
9:32:47
9:43:09
9:53:31
10:03:52
10:14:14
10:24:36
10:34:59
10:45:21
10:55:43
11:06:05
11:16:27
11:26:50
11:37:12
11:47:35
11:57:58
12:08:21
Time (hh:mm:ss)
SF6
SiF4

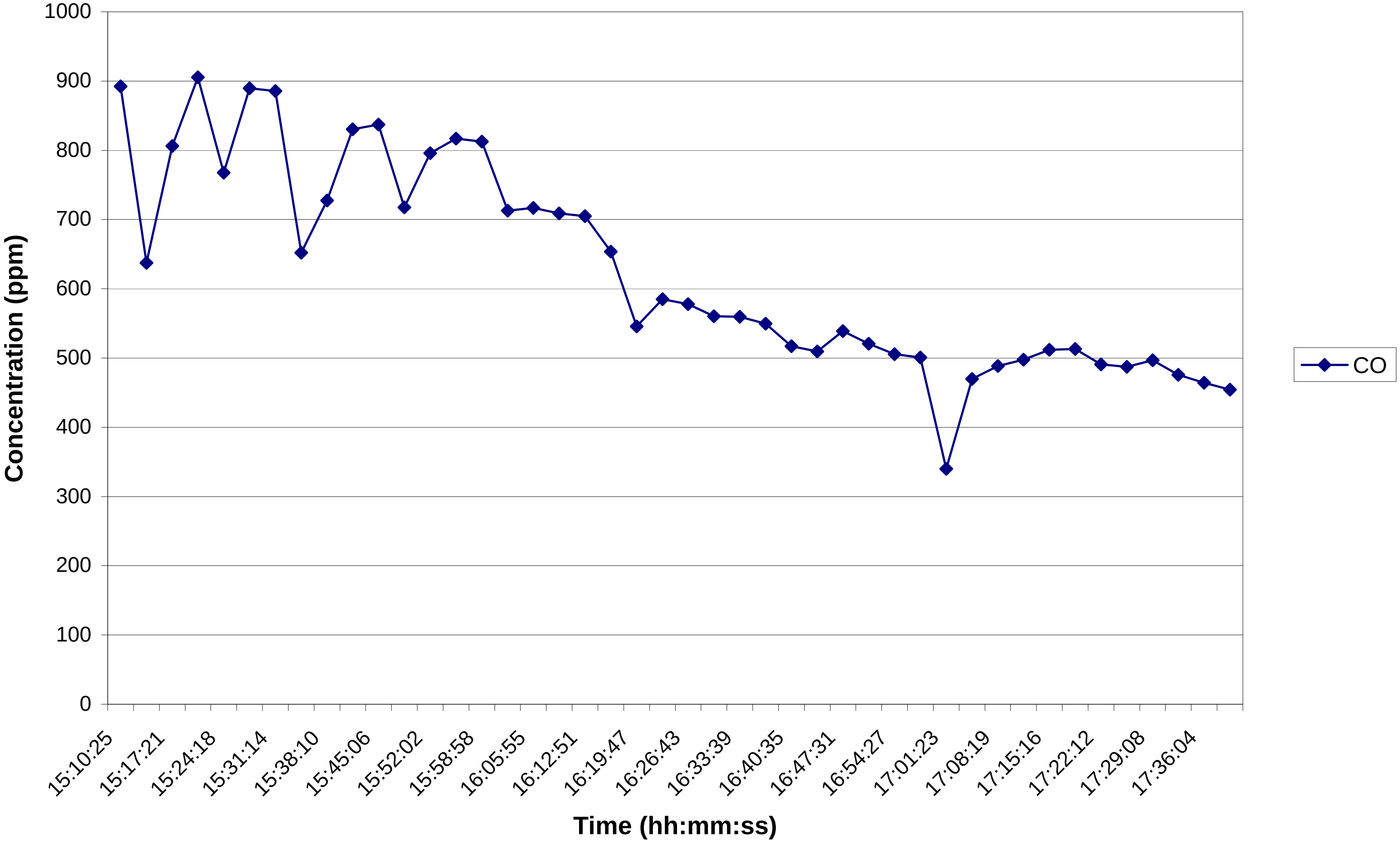
Time Series Plot for HF During HFC-134a Injection at 4200 ppm on 8/24/06

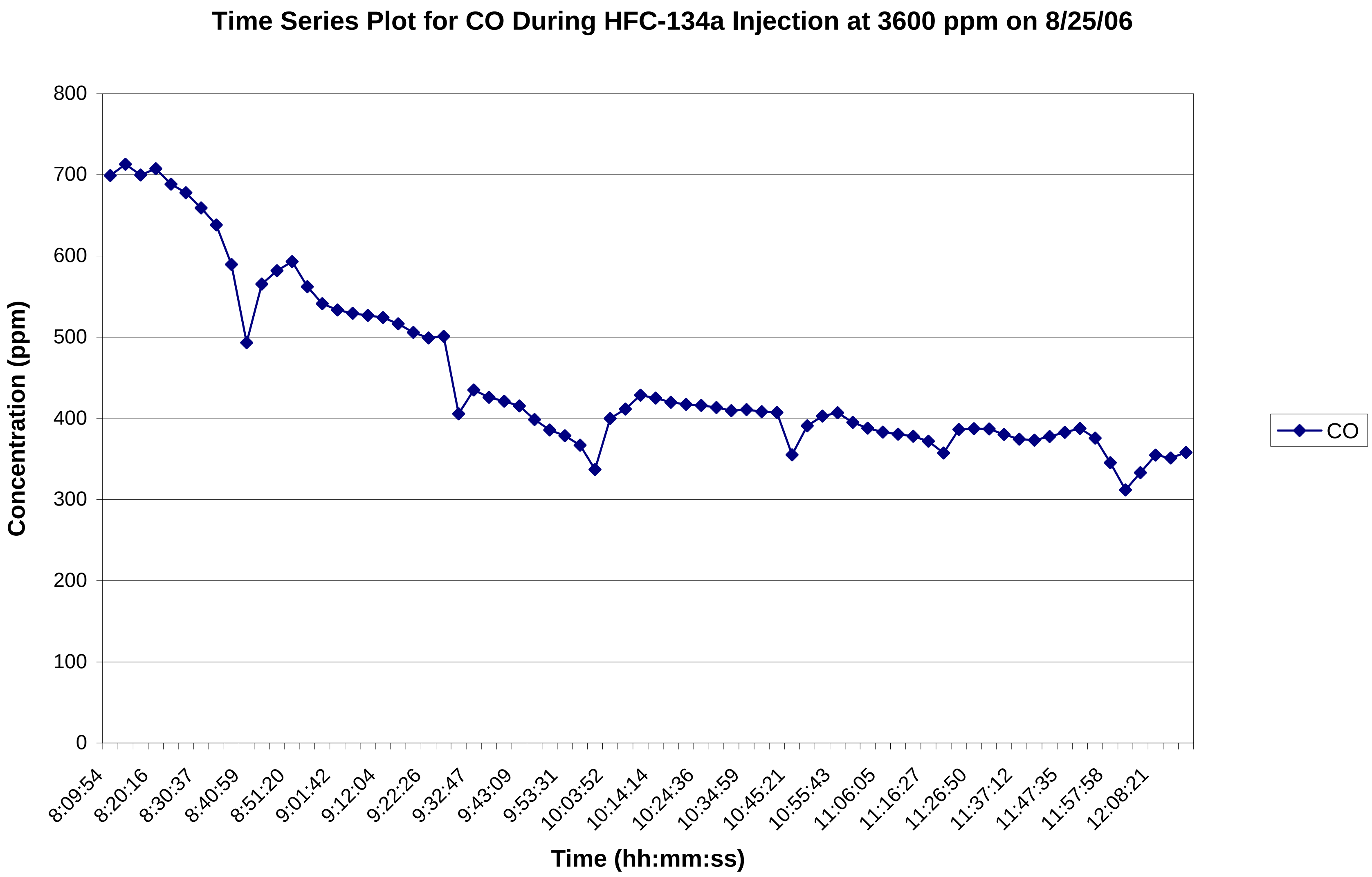


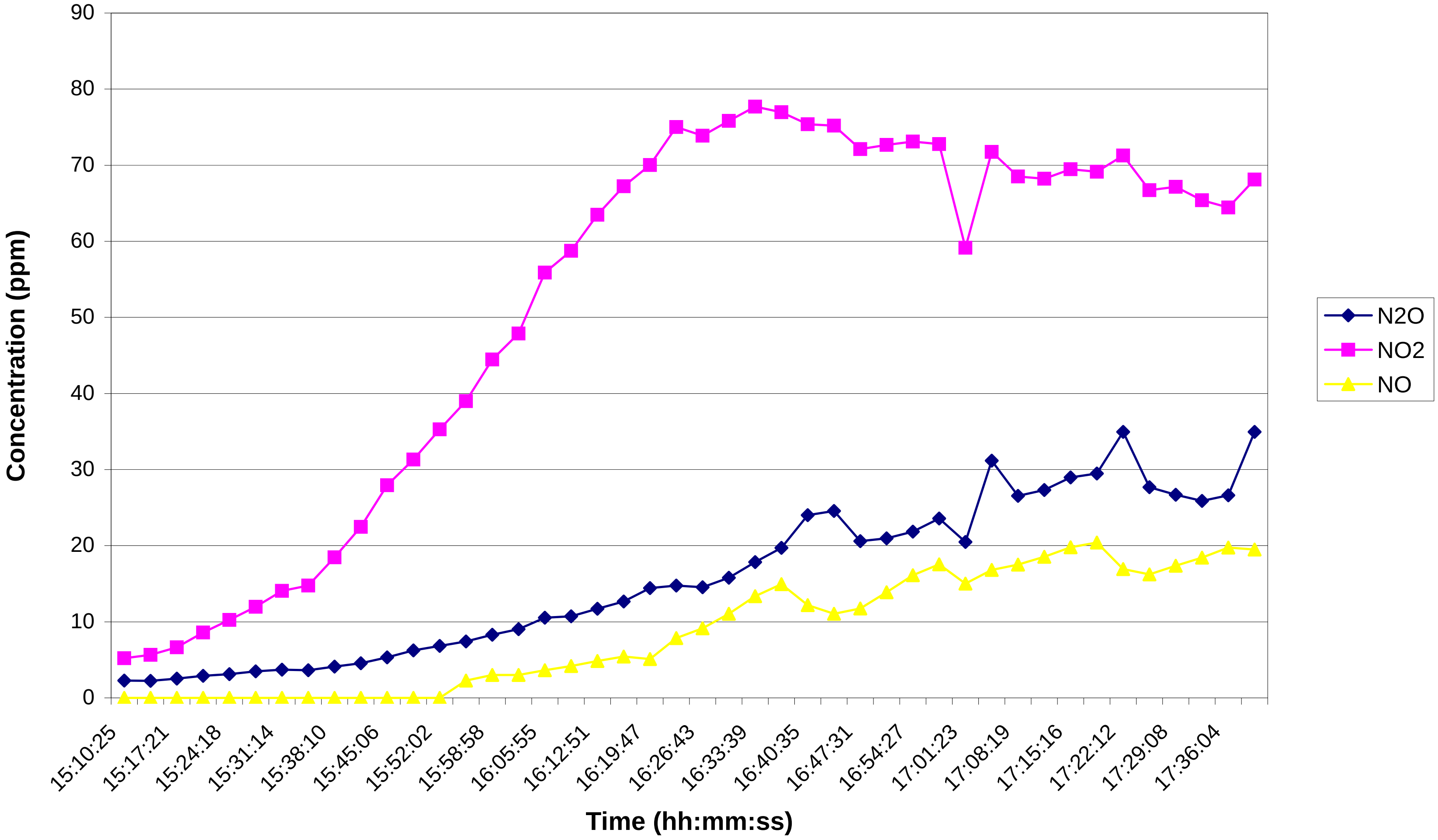


Time Series Plot for HF During HFC-134a Injection at 3600 ppm on 8/25/06

Time Series Plot for CO During HFC-134a Injection at 4200 ppm on 8/24/06

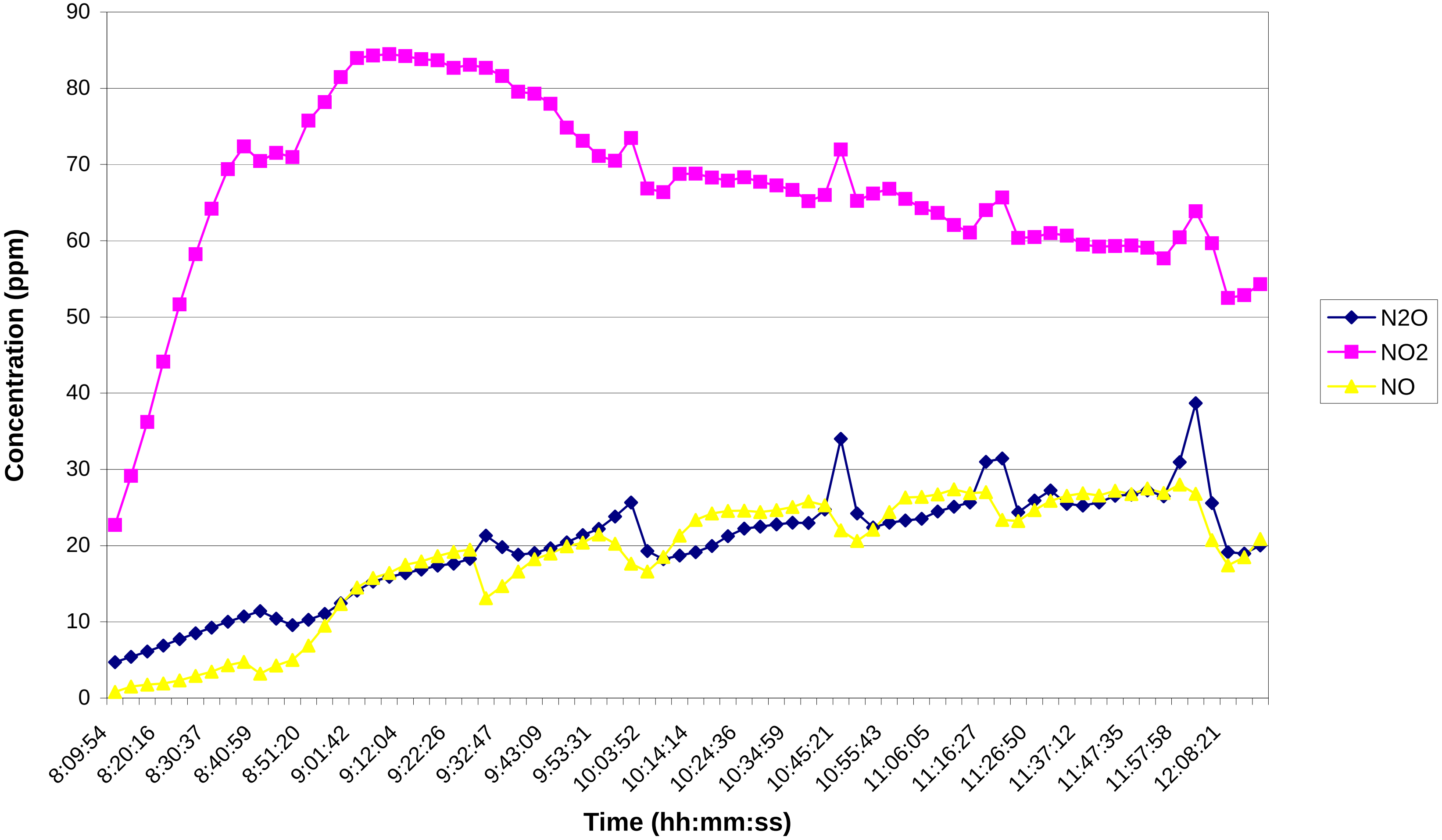



Time Series Plot for CO During HFC-134a Injection at 3600 ppm on 8/25/06
Concentration (ppm)
800
700
600
500
400
300
200
100
0
8:09:54
8:20:16
8:30:37
8:40:59
8:51:20
9:01:42
9:12:04
9:22:26
9:32:47
9:43:09
9:53:31
10:03:52
10:14:14
10:24:36
10:34:59
10:45:21
10:55:43
11:06:05
11:16:27
11:26:50
11:37:12
11:47:35
11:57:58
12:08:21
Time (hh:mm:ss)
CO

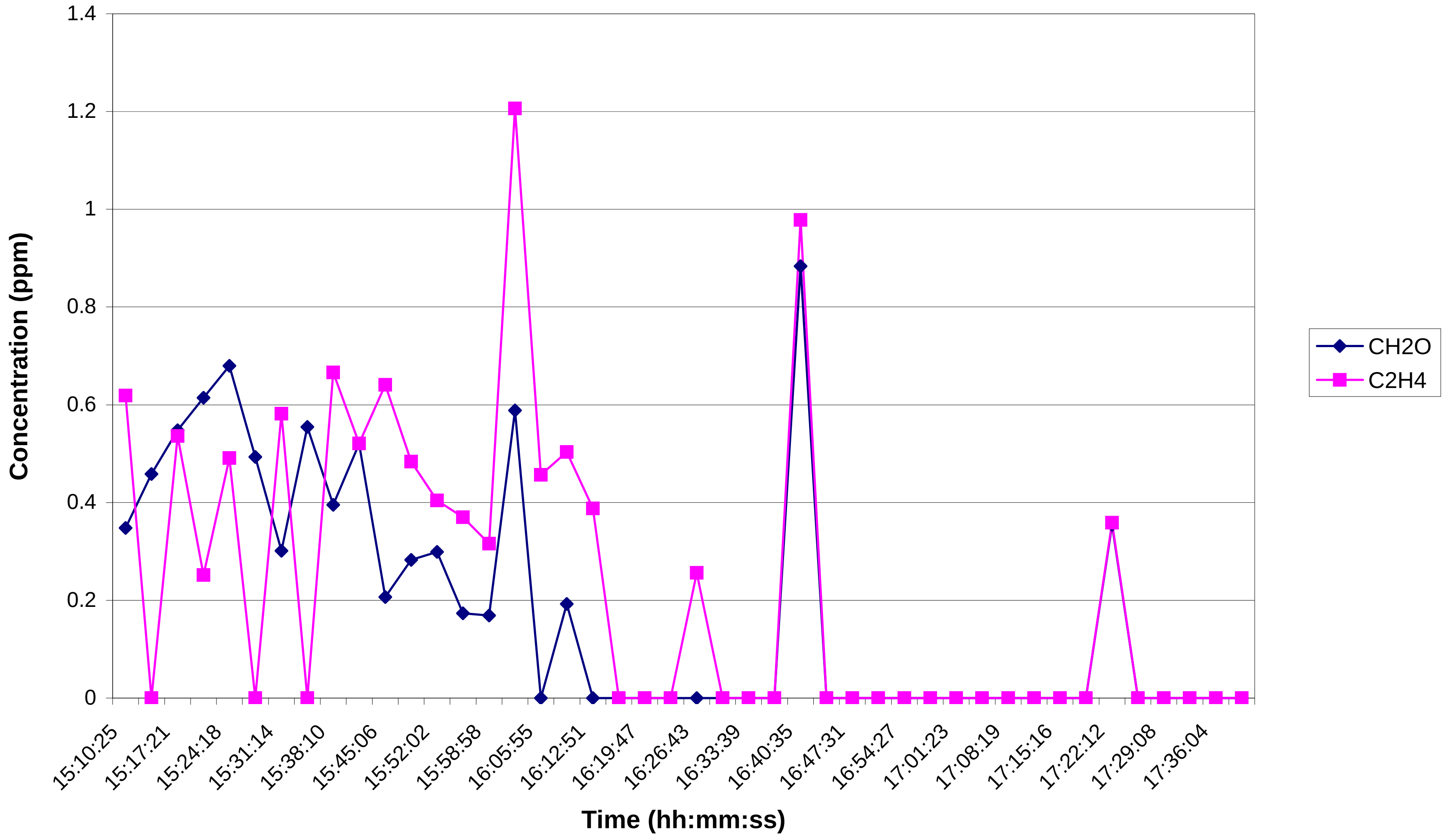


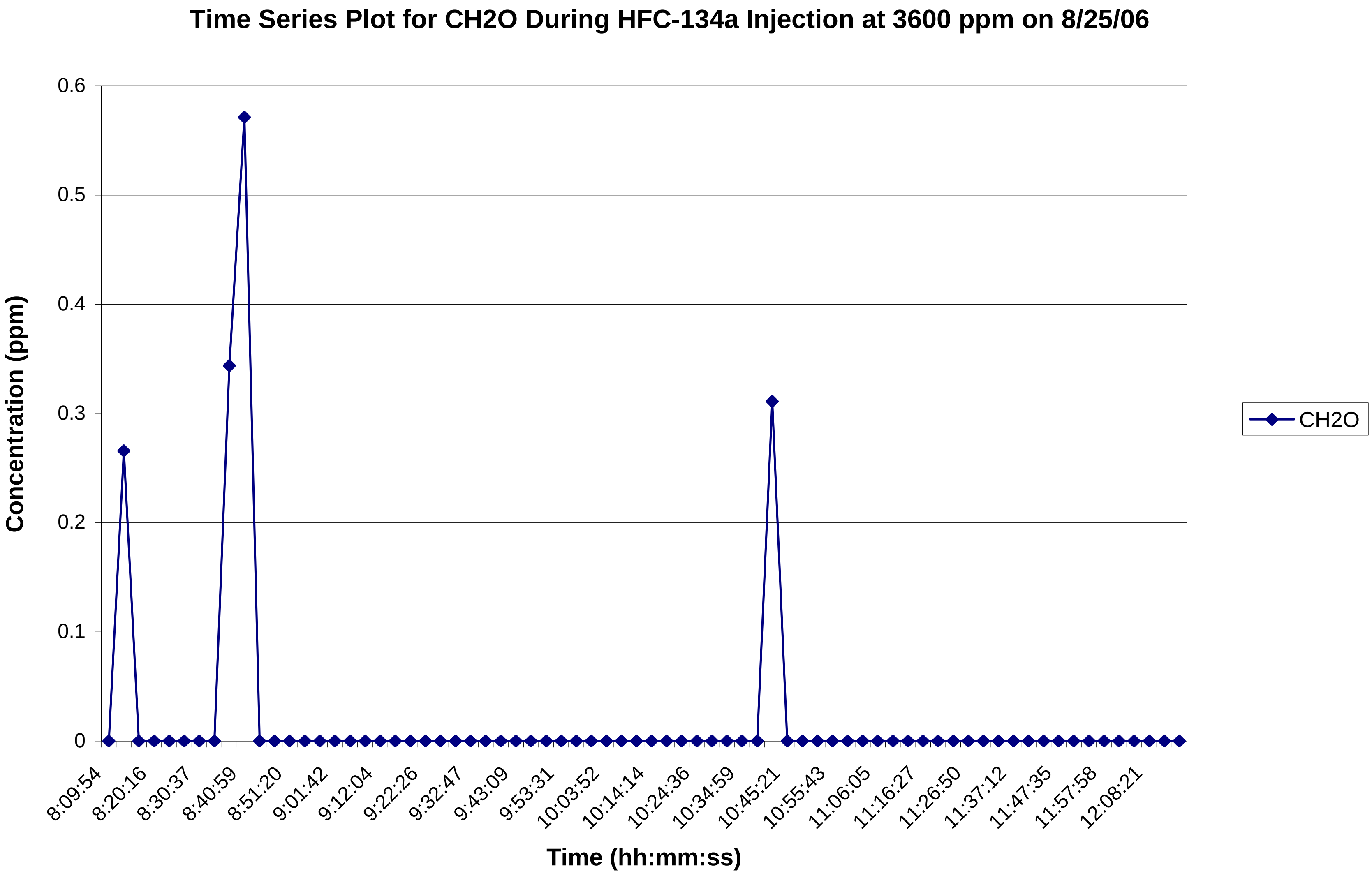
Time Series Plot for Nitrogen Oxide By-Products
During HFC-134a Injection at 4200 ppm on 8/24/06

Time Series Plot for Nitrogen Oxide By-Products During HFC-134a Injection at 3600 ppm on 8/25/06

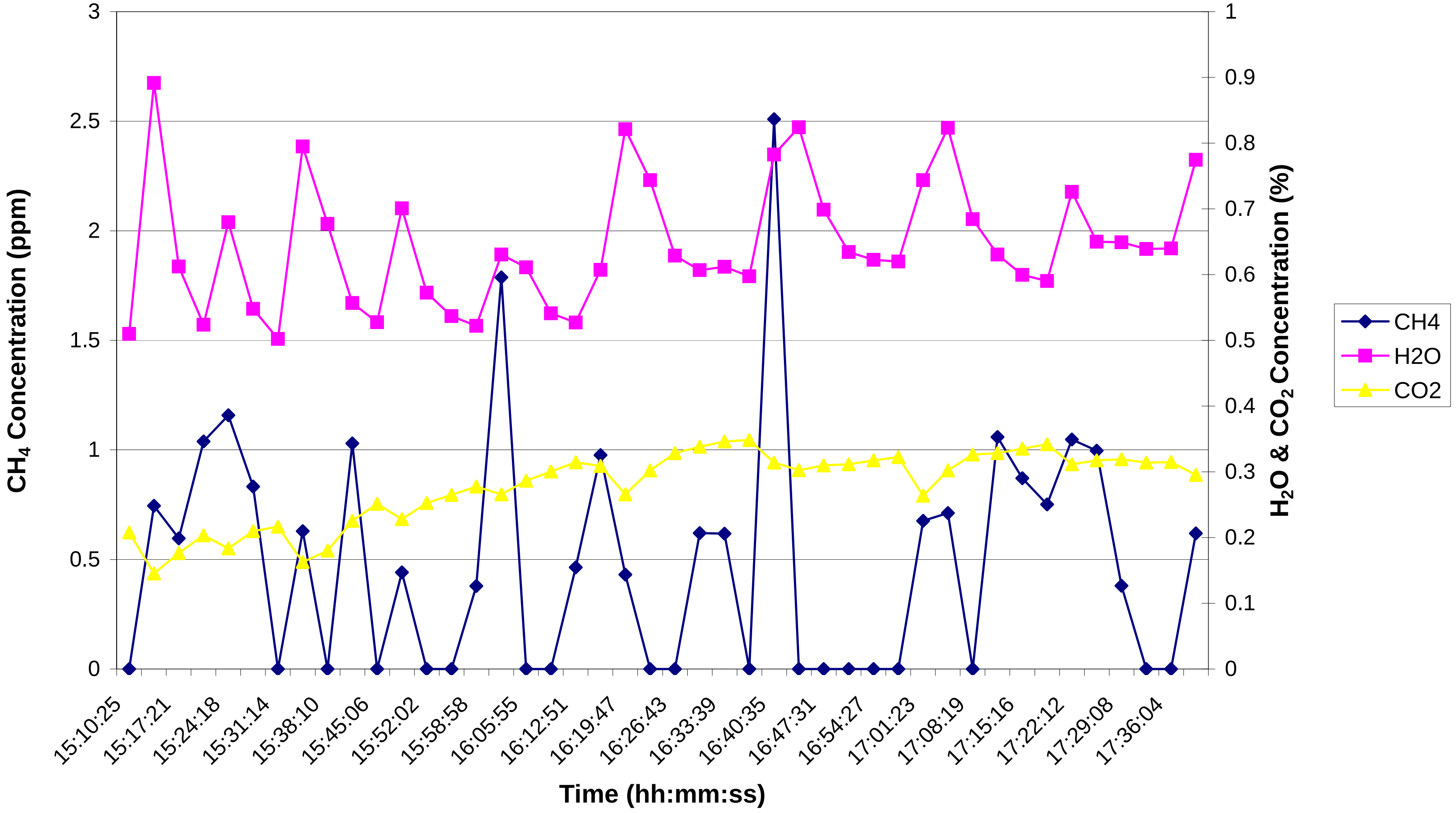


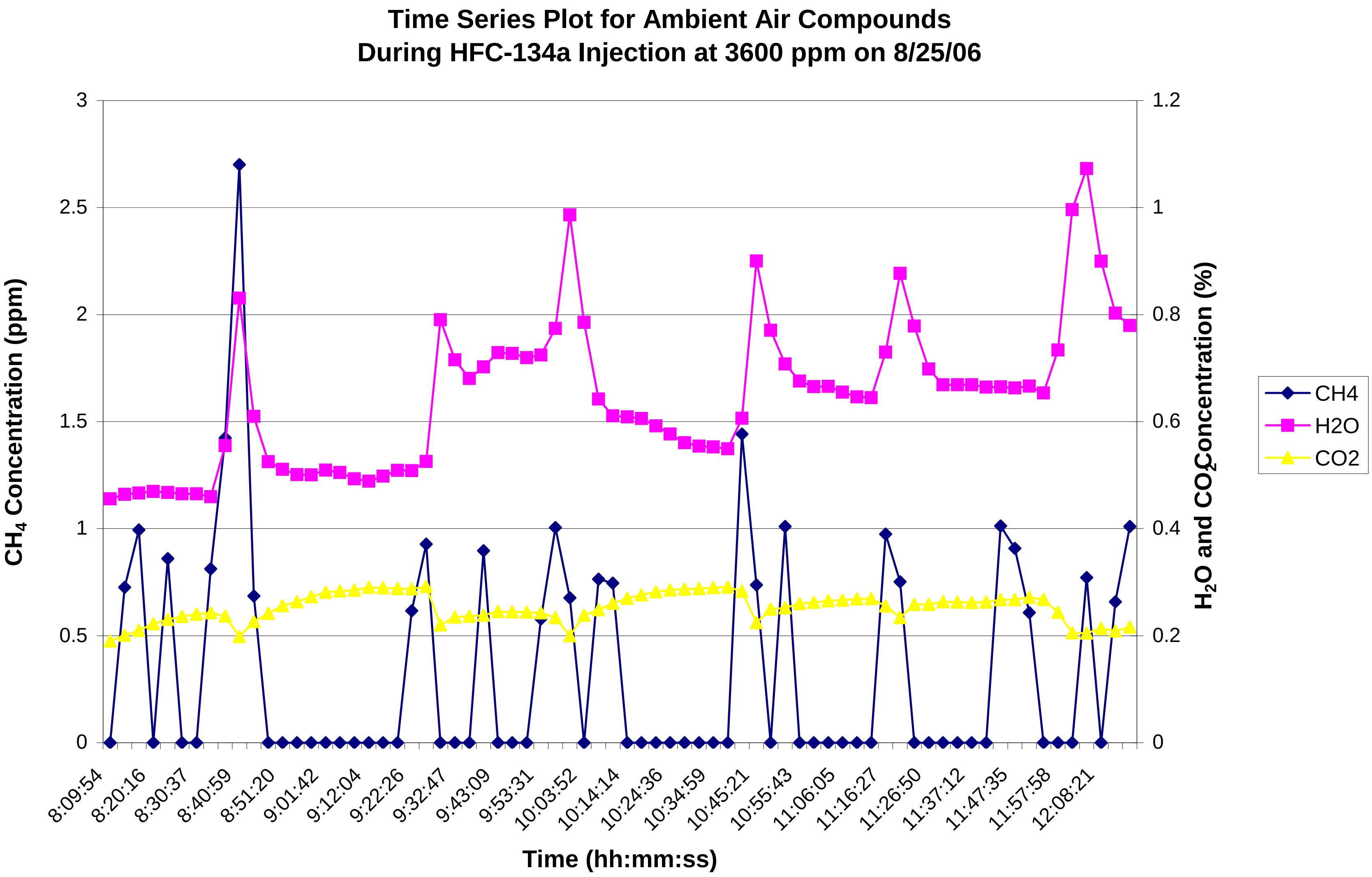
Time Series Plot for CH_2O and C_2H_4 During HFC-134a Injection at 4200 ppm on 8/24/06




Time Series Plot for CH2O During HFC-134a Injection at 3600 ppm on 8/25/06
Concentration (ppm)
0.6
0.5
0.4
0.3
0.2
0.1
0
8:09:54
8:20:16
8:30:37
8:40:59
8:51:20
9:01:42
9:12:04
9:22:26
9:32:47
9:43:09
9:53:31
10:03:52
10:14:14
10:24:36
10:34:59
10:45:21
10:55:43
11:06:05
11:16:27
11:26:50
11:37:12
11:47:35
11:57:58
12:08:21
Time (hh:mm:ss)
CH2O

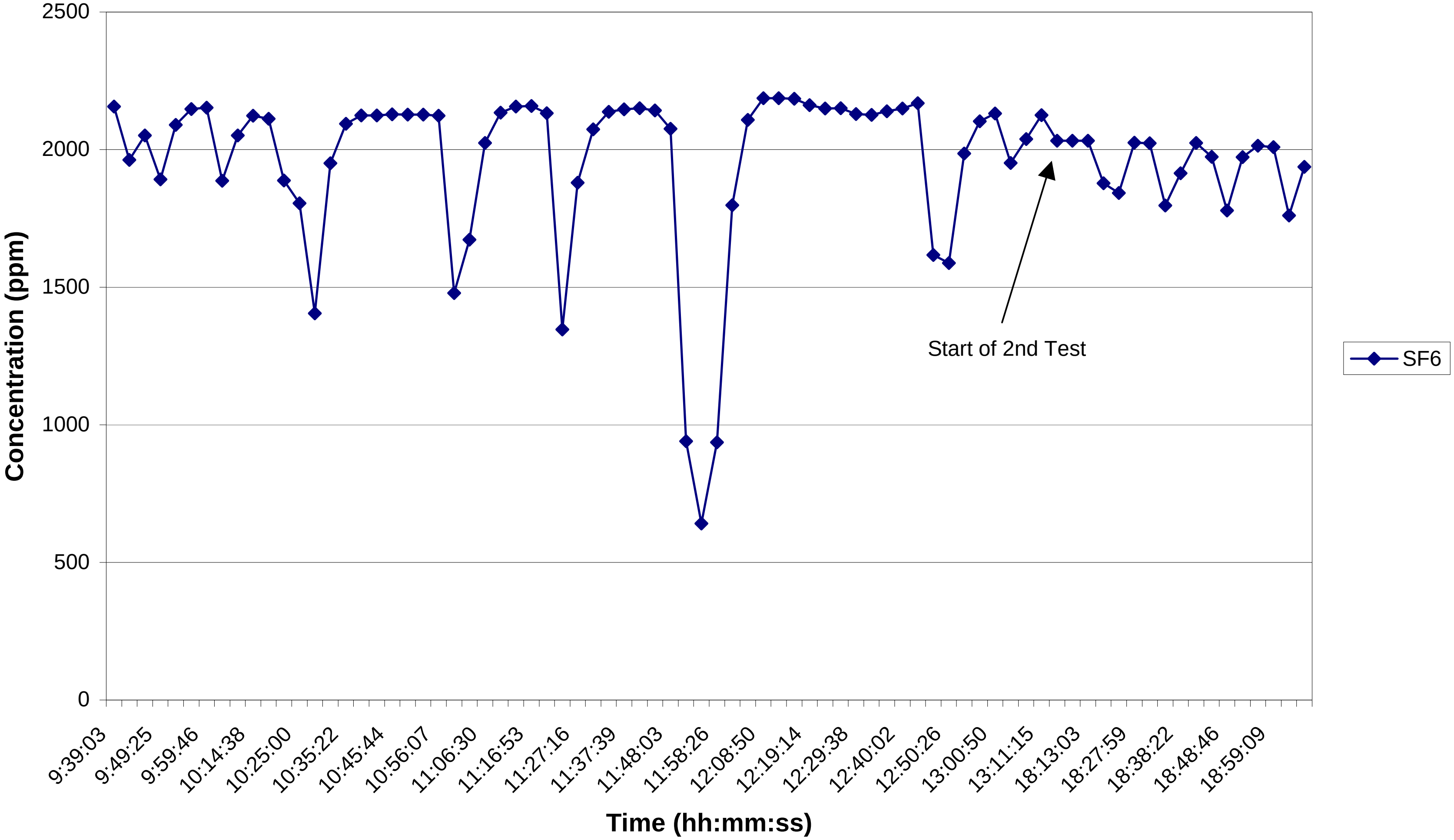
Time Series Plot for Ambient Air Compounds During HFC-134a Injection at 4200 ppm on 8/24/06

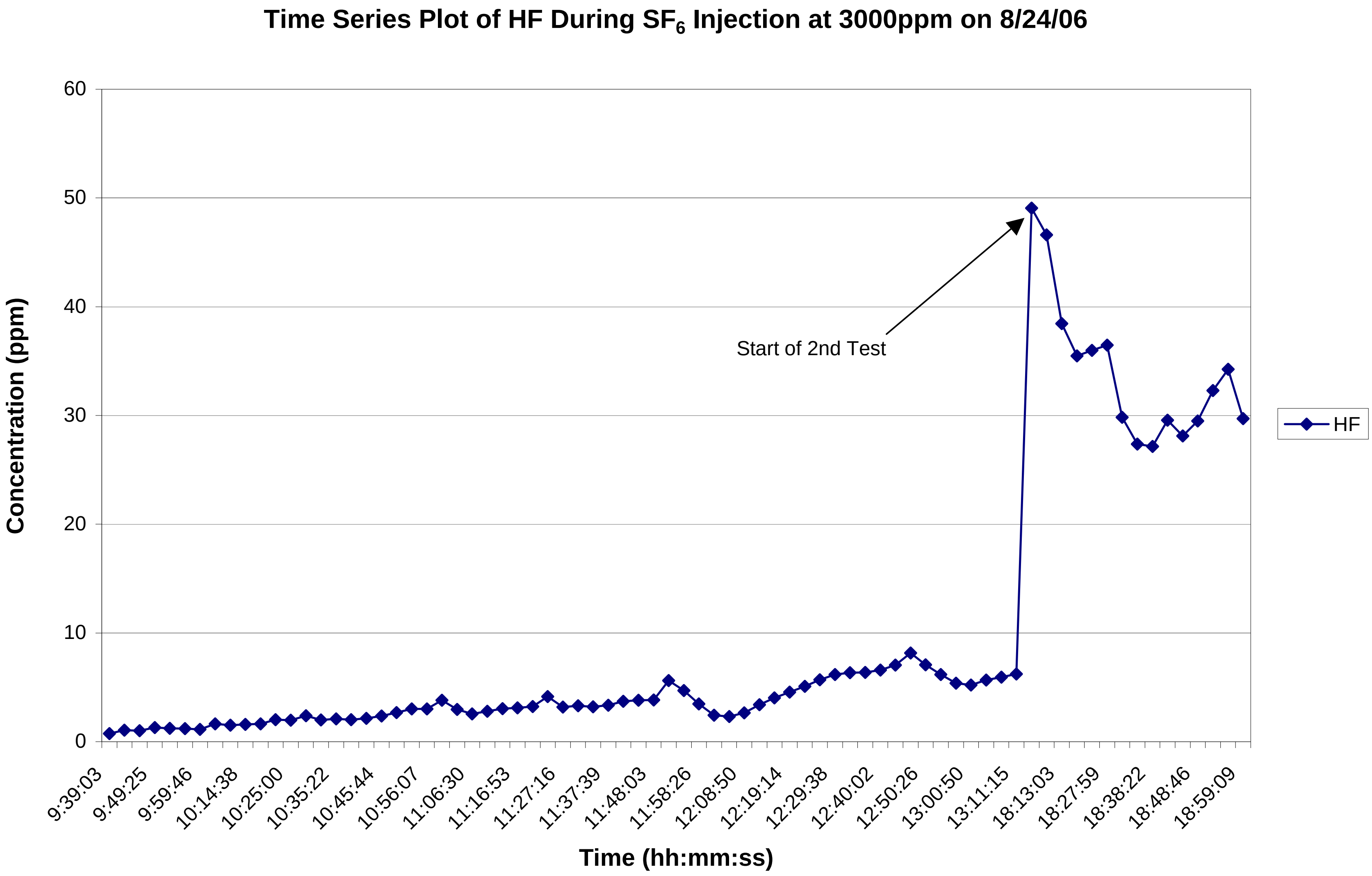



Time Series Plot for Ambient Air Compounds
During HFC-134a Injection at 3600 ppm on 8/25/06
CH_4 Concentration (ppm)
H_2O and CO_2 Concentration (%)
Time (hh:mm:ss)
3
2.5
2
1.5
1
0.5
0
1.2
1
0.8
0.6
0.4
0.2
0
8:09:54
8:20:16
8:30:37
8:40:59
8:51:20
9:01:42
9:12:04
9:22:26
9:32:47
9:43:09
9:53:31
10:03:52
10:14:14
10:24:36
10:34:59
10:45:21
10:55:43
11:06:05
11:16:27
11:26:50
11:37:12
11:47:35
11:57:58
12:08:21
CH4
H2O
CO2

Appendix A-3
SF$_6$ with CDA Carrier Gas
Plots

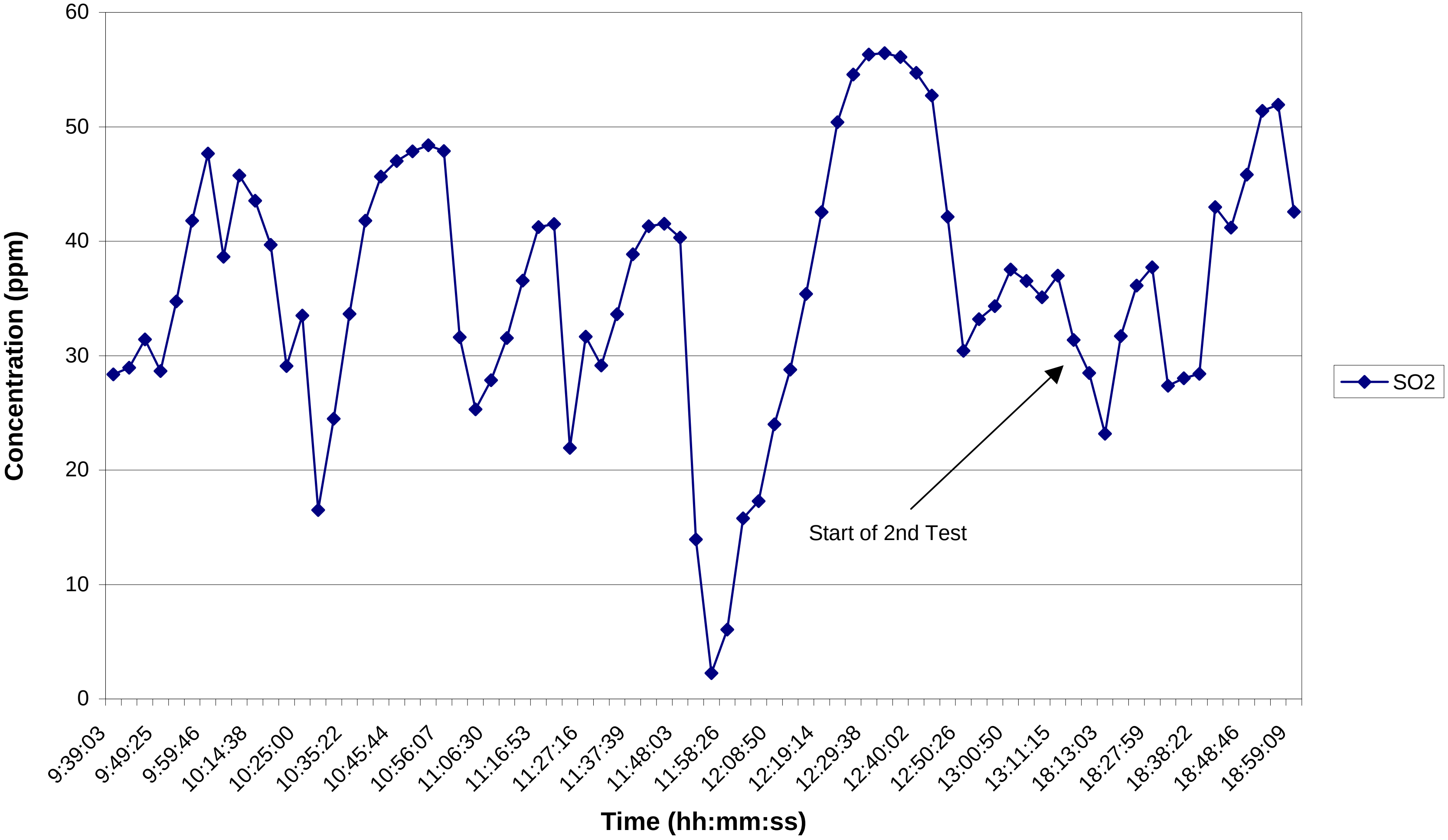
Time Series Plot of SF_6 During SF_6 Injection at 3000ppm on 8/24/06



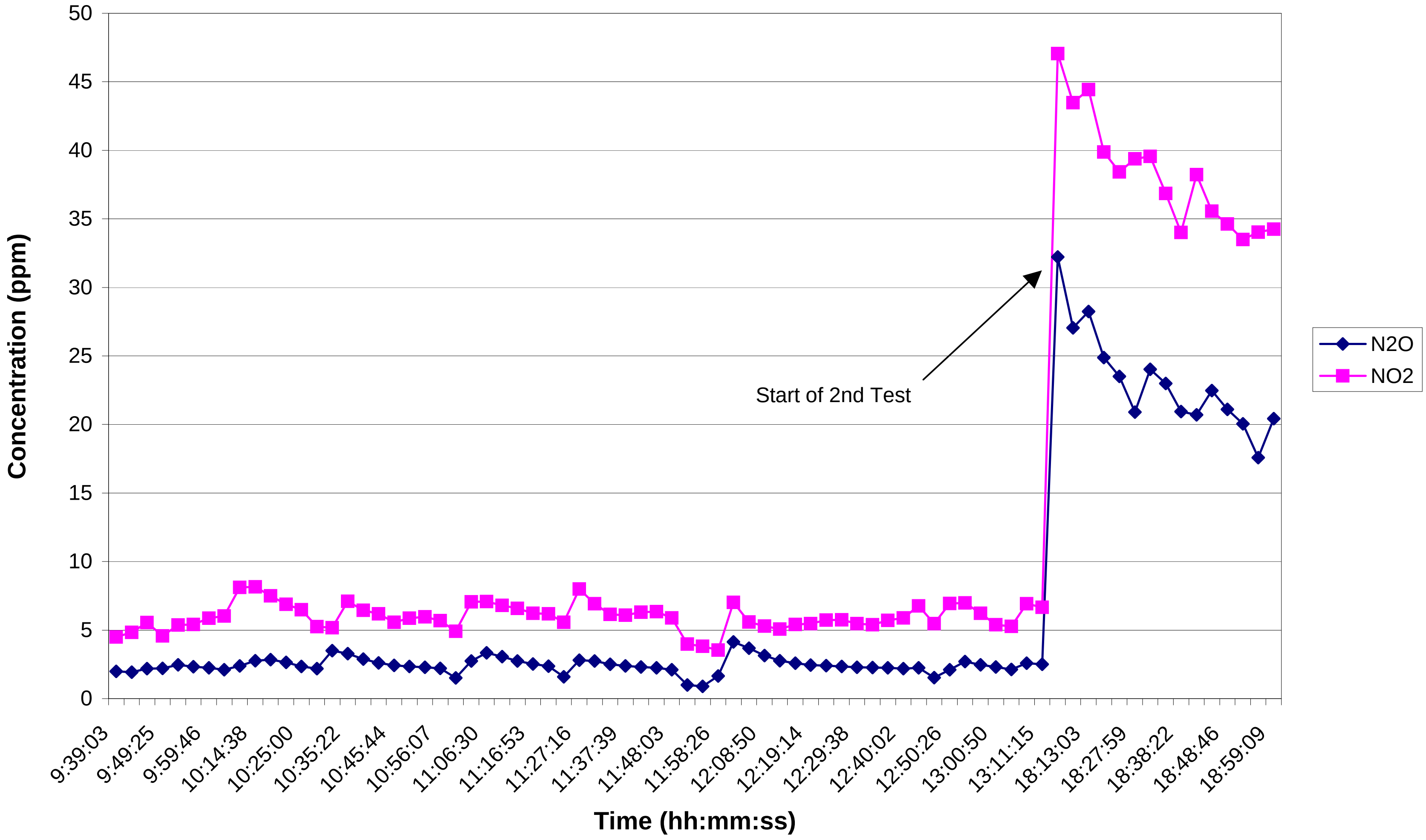


Time Series Plot of HF During SF_6 Injection at 3000ppm on 8/24/06

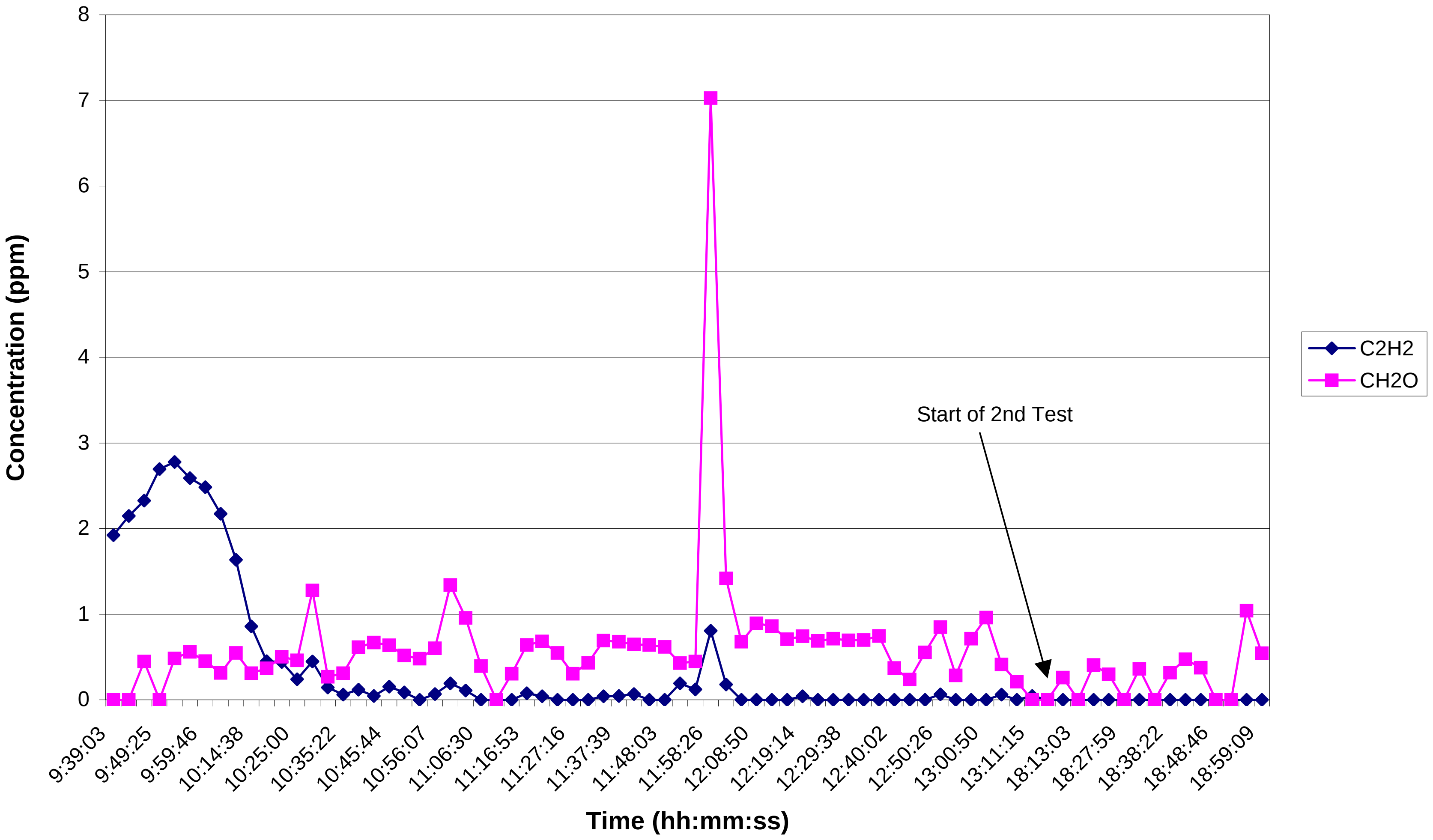
Time Series Plot of SO_2 During SF_6 Injection at 3000ppm on 8/24/06



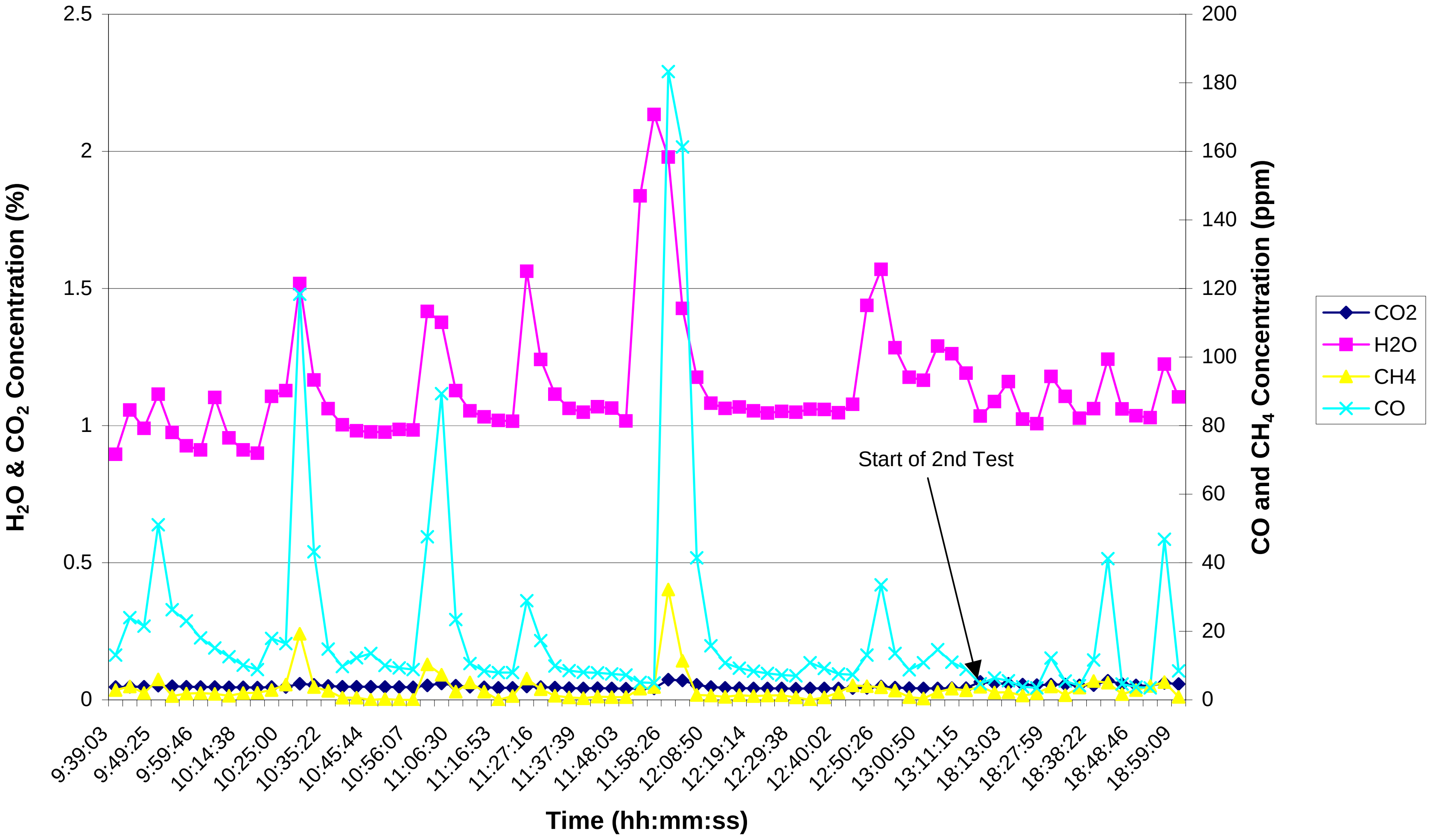
Time Series Plot of N_2O and NO_2 During SF_6 Injection at 3000ppm on 8/24/06



Time Series Plot of C_2H_2 and CH_2O During SF_6 Injection at 3000ppm on 8/24/06

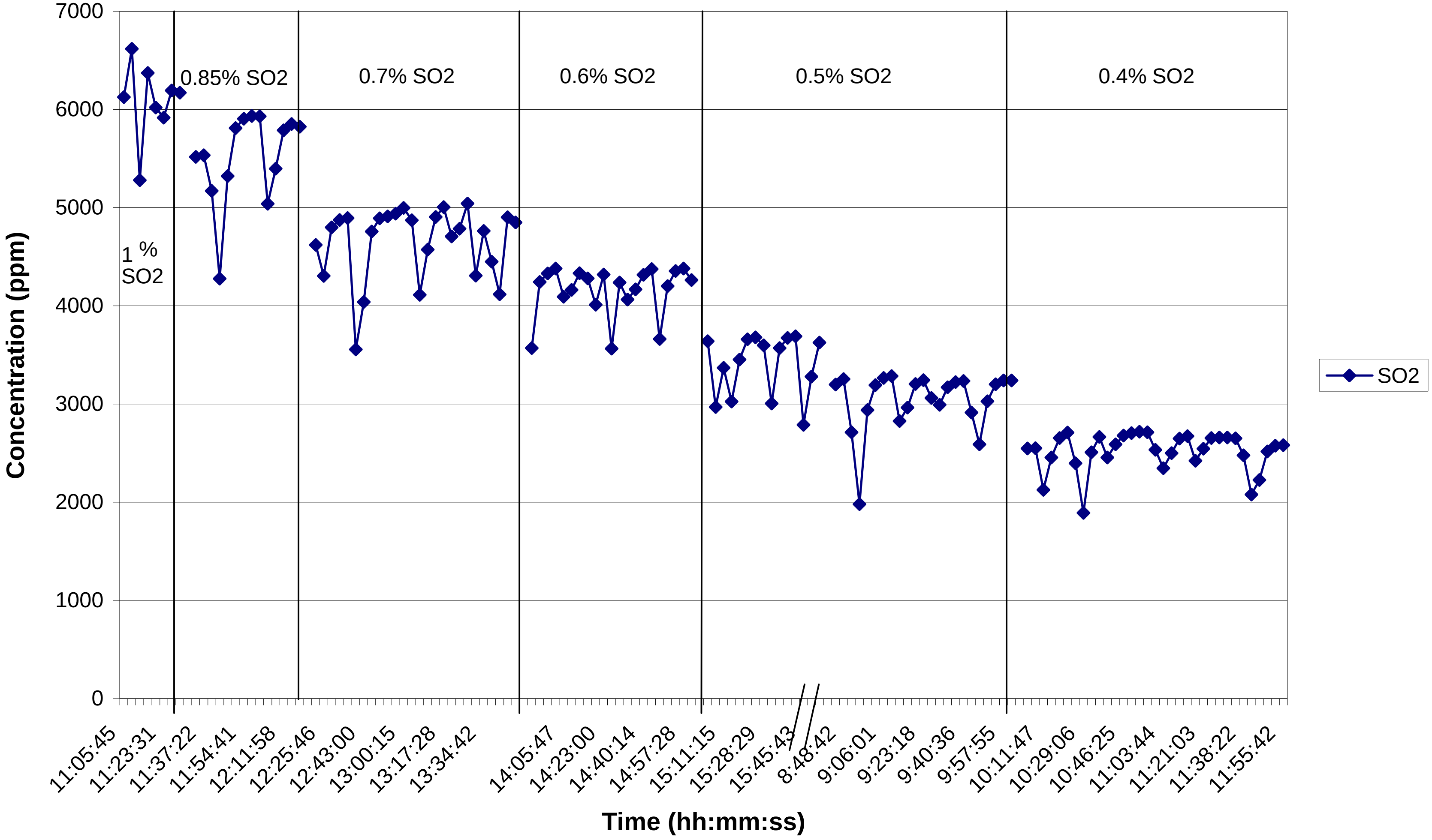


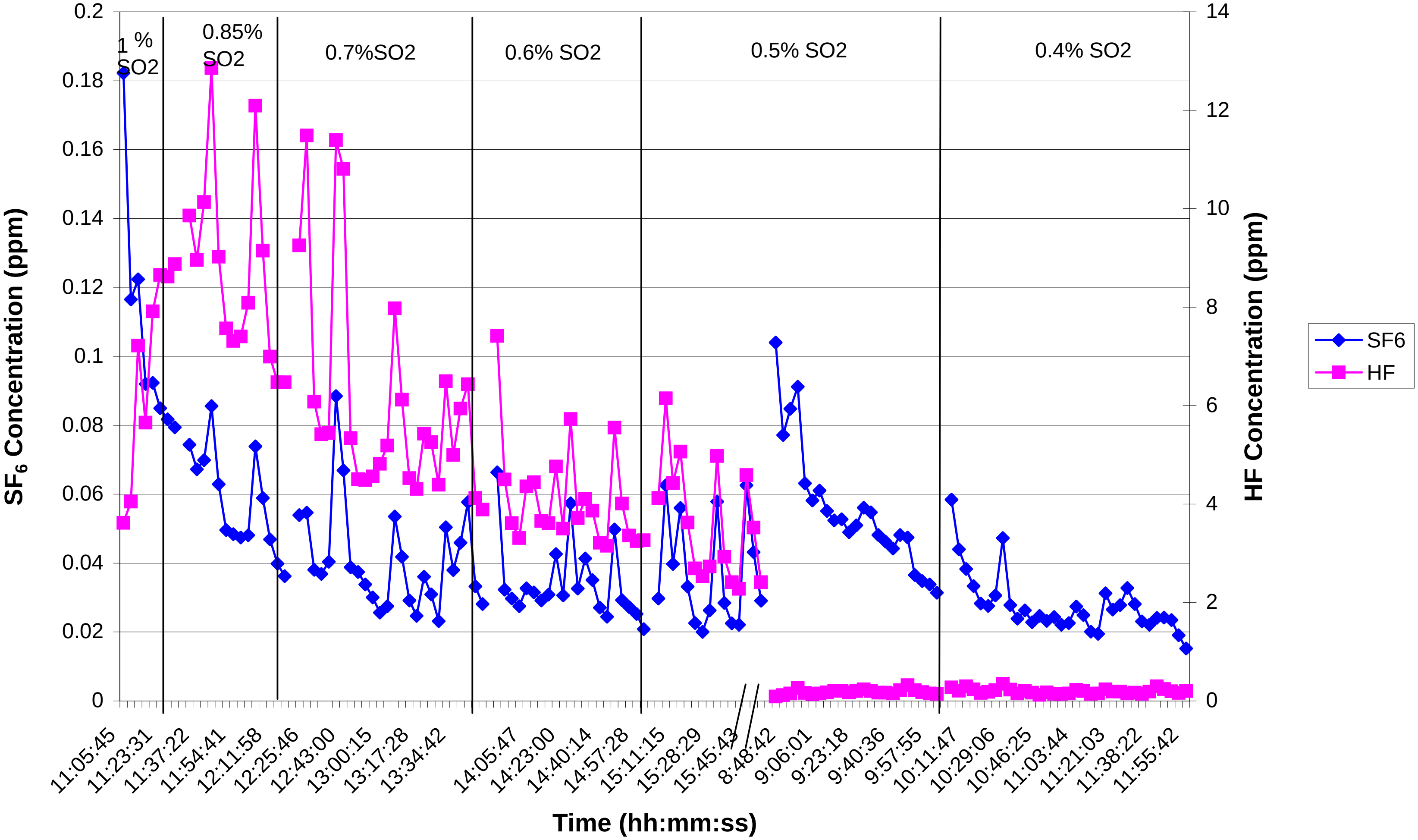
Time Series Plot of Ambient Compounds During SF_6 Injection at 3000ppm on 8/24/06



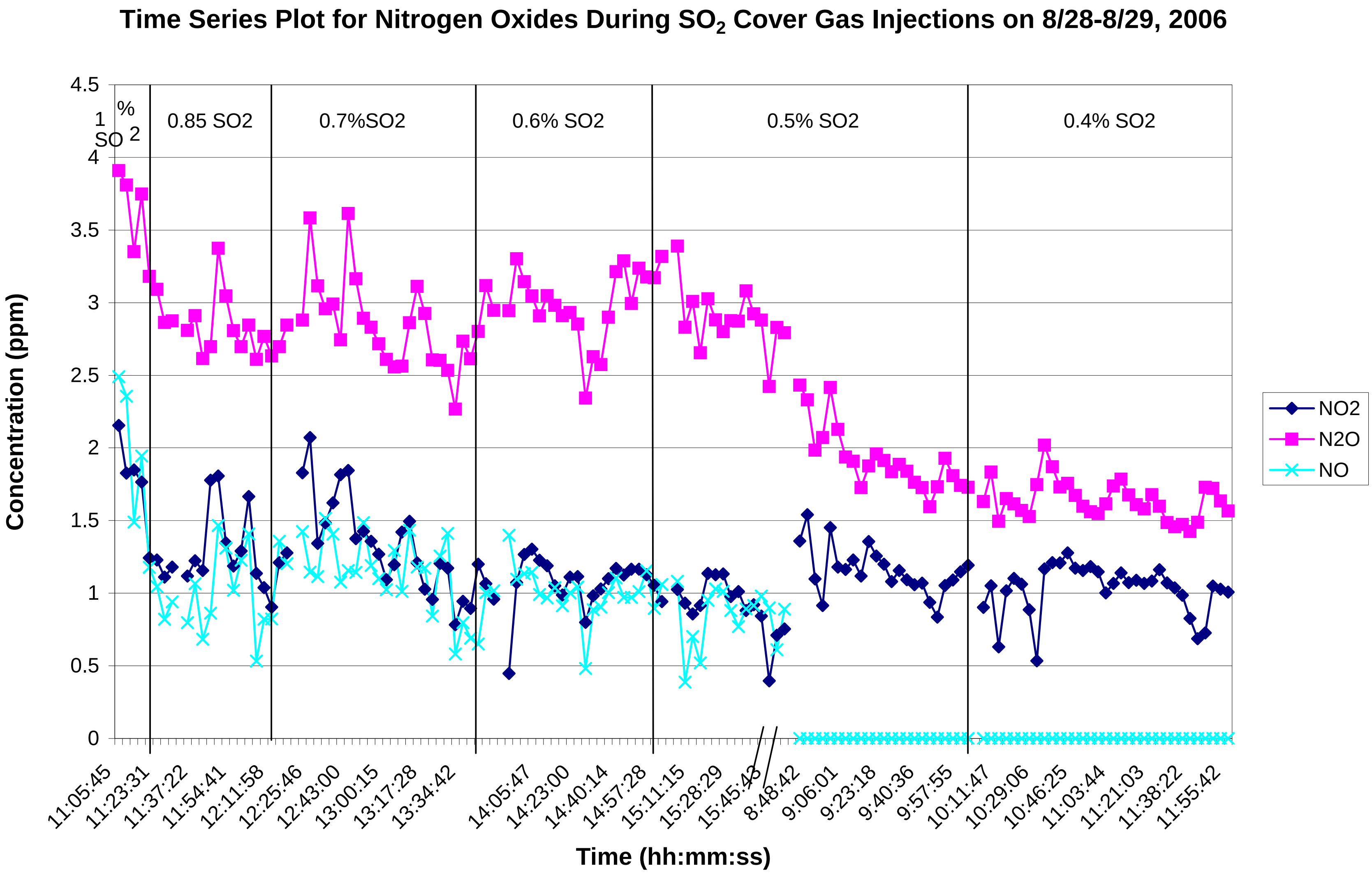
Appendix A-4
Dilute SO_2 with CDA Carrier Gas
Plots

Time Series Plot for SO_2 During SO_2 Cover Gas Injections on 8/28-8/29, 2006

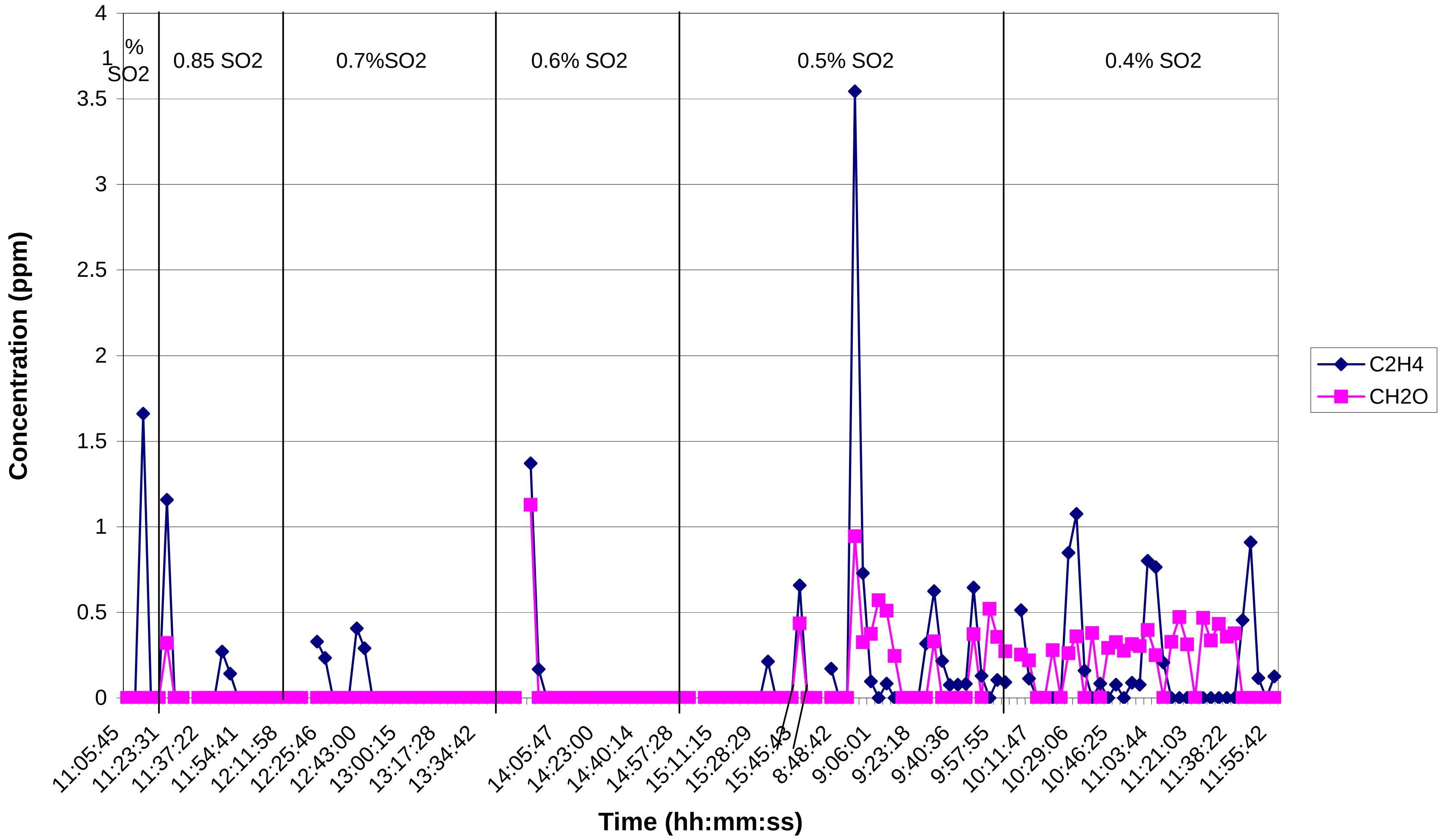




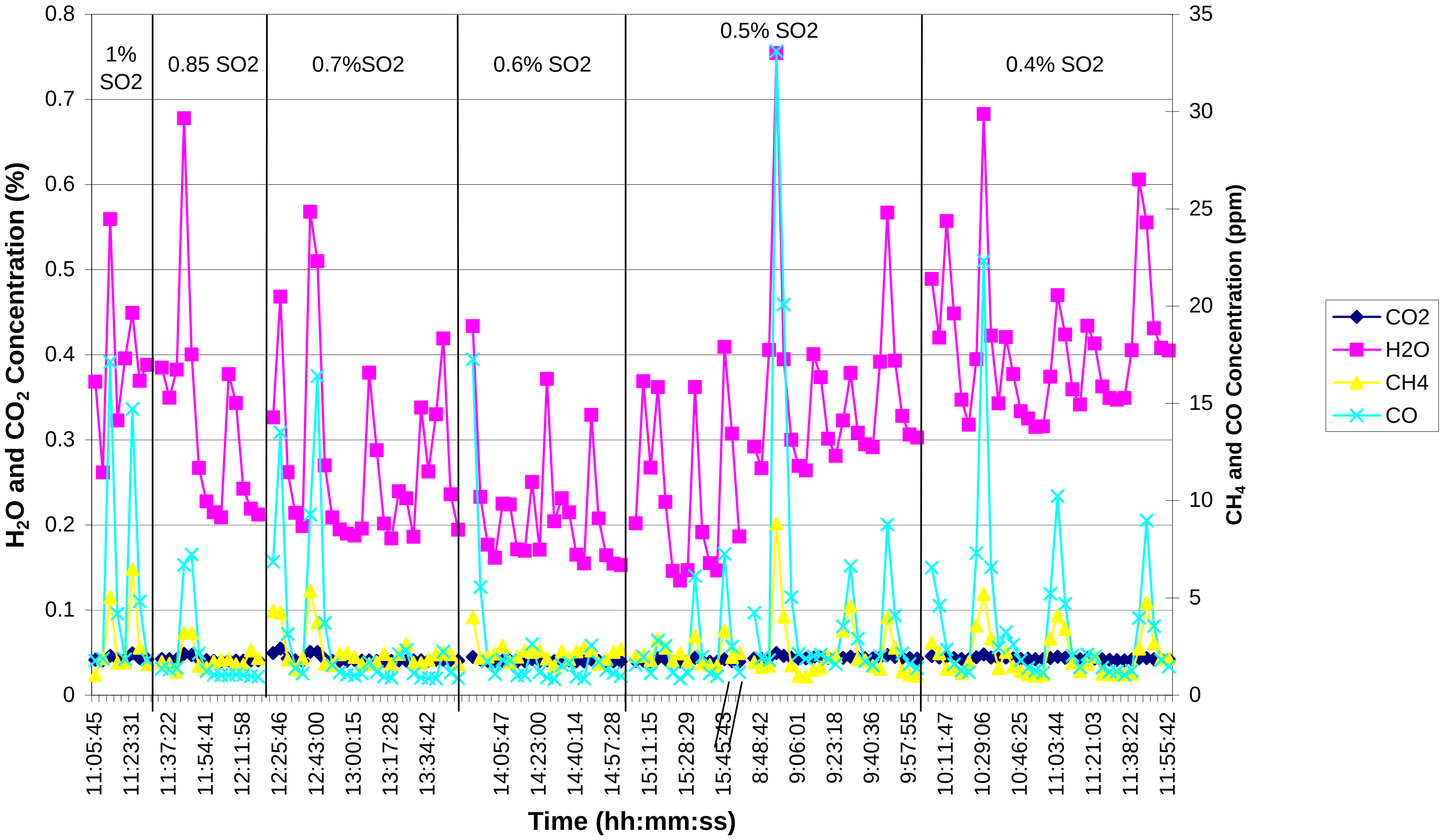
Time Series Plot for SF_6 and HF During SO_2 Cover Gas Injections on 8/28-8/29, 2006


Time Series Plot for Nitrogen Oxides During SO$_2$ Cover Gas Injections on 8/28-8/29, 2006
Concentration (ppm)
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
1% SO2
0.85 SO2
0.7%SO2
0.6% SO2
0.5% SO2
0.4% SO2
11:05:45
11:23:31
11:37:22
11:54:41
12:11:58
12:25:46
12:43:00
13:00:15
13:17:28
13:34:42
14:05:47
14:23:00
14:40:14
14:57:28
15:11:15
15:28:29
15:45:43
8:48:42
9:06:01
9:23:18
9:40:36
9:57:55
10:11:47
10:29:06
10:46:25
11:03:44
11:21:03
11:38:22
11:55:42
Time (hh:mm:ss)
NO2
N2O
NO

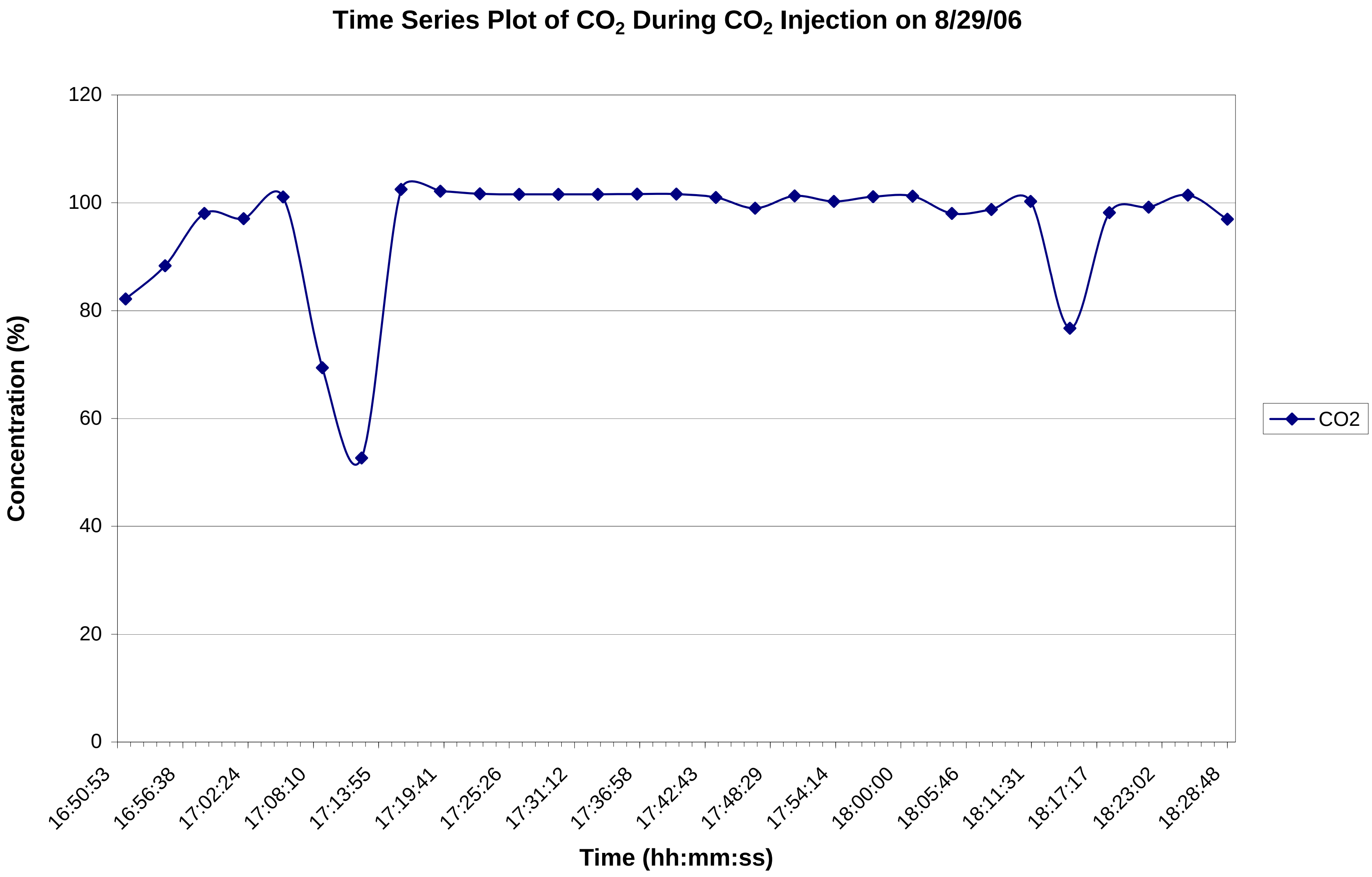
Time Series Plot for C_2H_4 and CH_2O During SO_2 Cover Gas Injections on 8/28-8/29, 2006



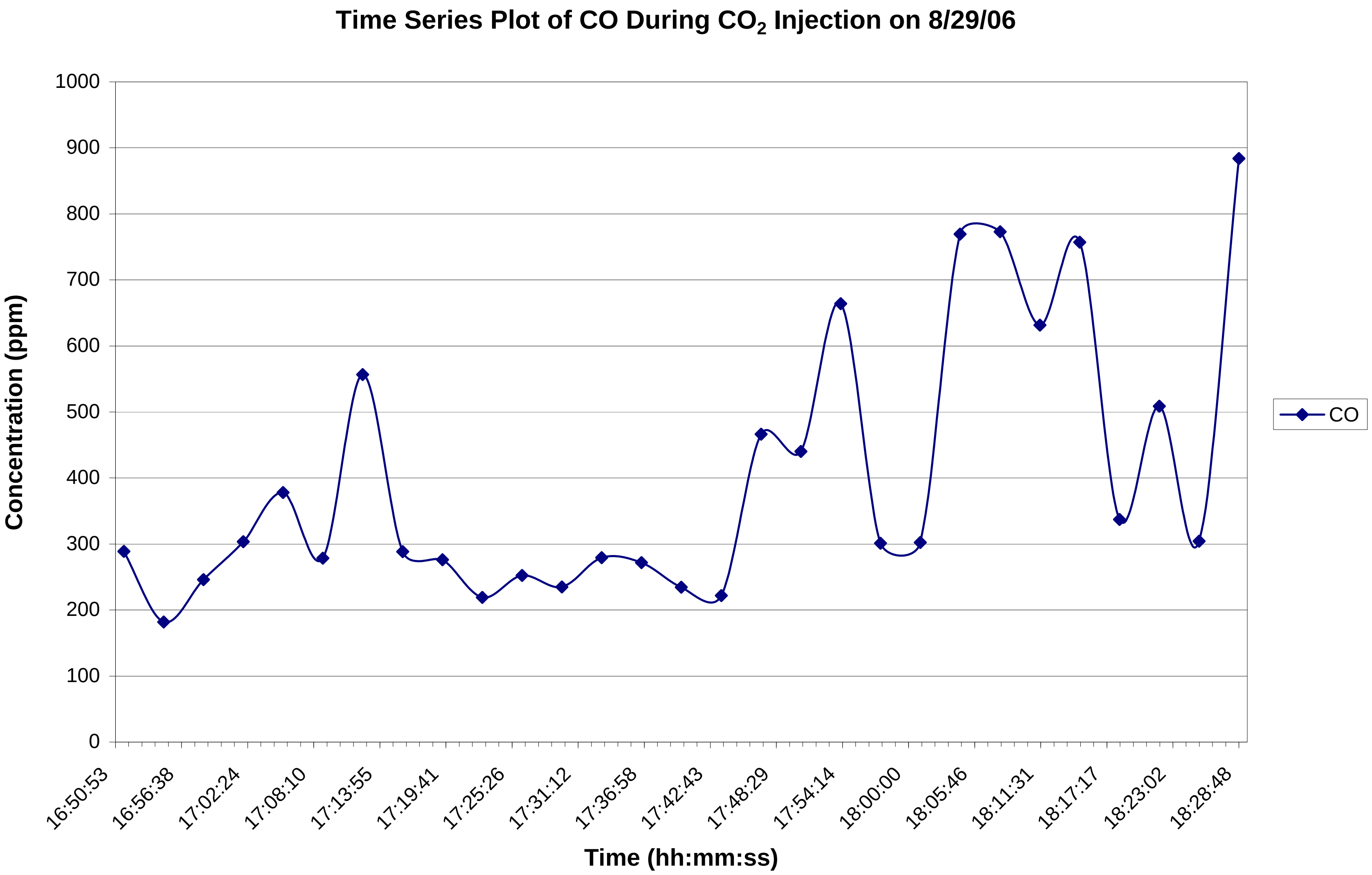
Time Series Plot for Ambient Compounds During SO_2 Cover Gas Injections on 8/28-8/29, 2006

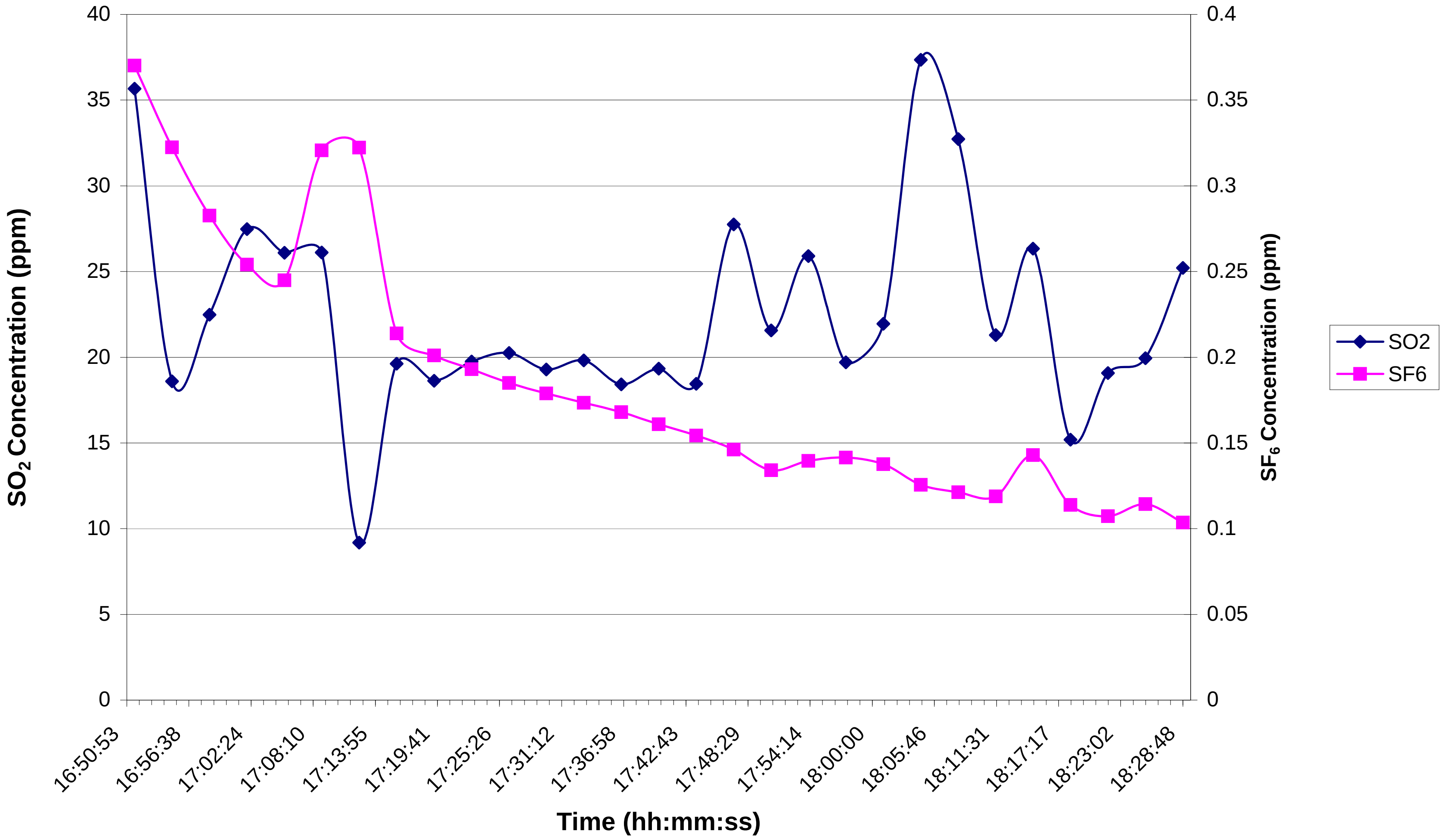


Appendix A-5
Frozen CO_2 Plots

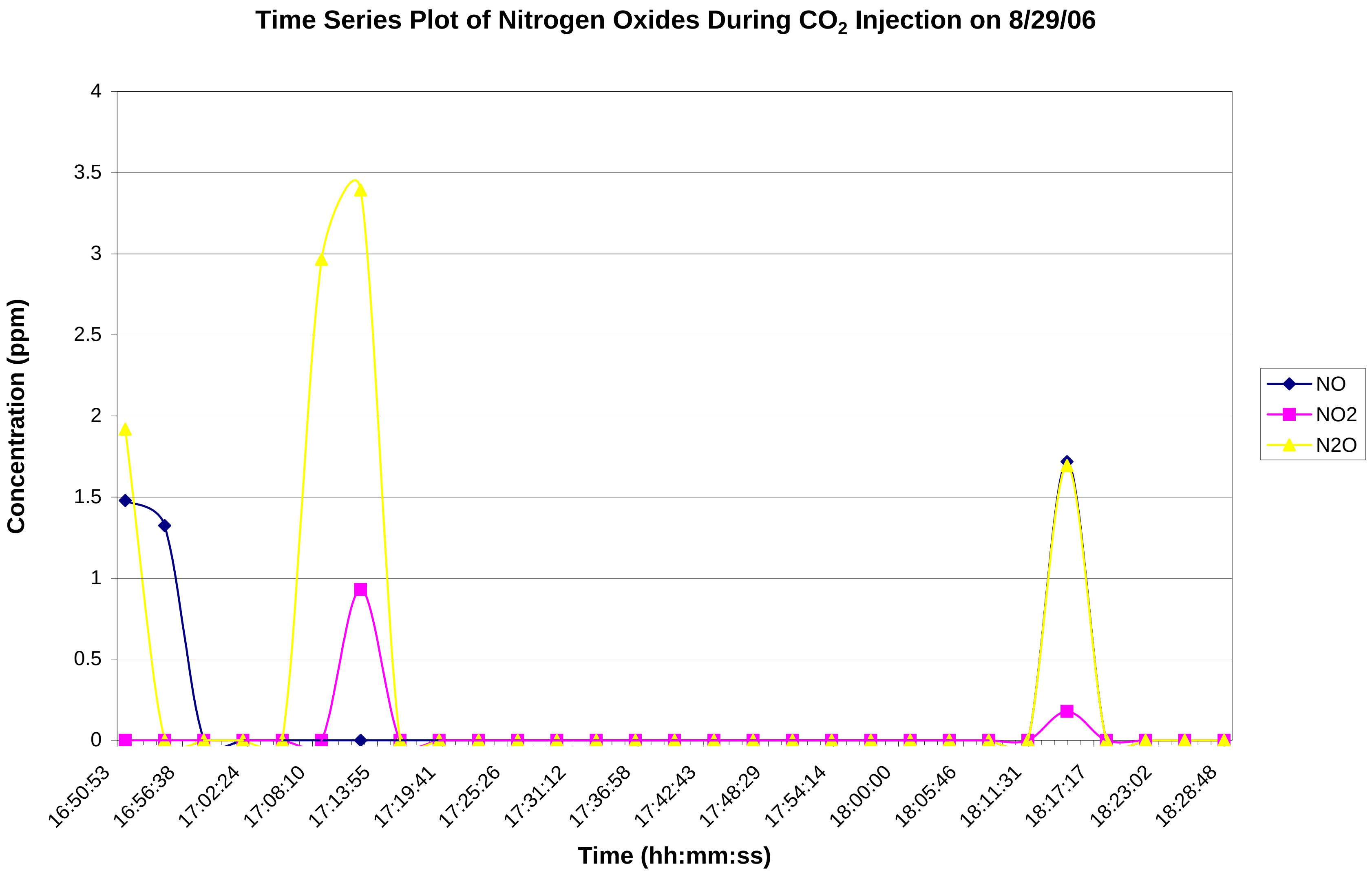


Time Series Plot of CO_2 During CO_2 Injection on 8/29/06

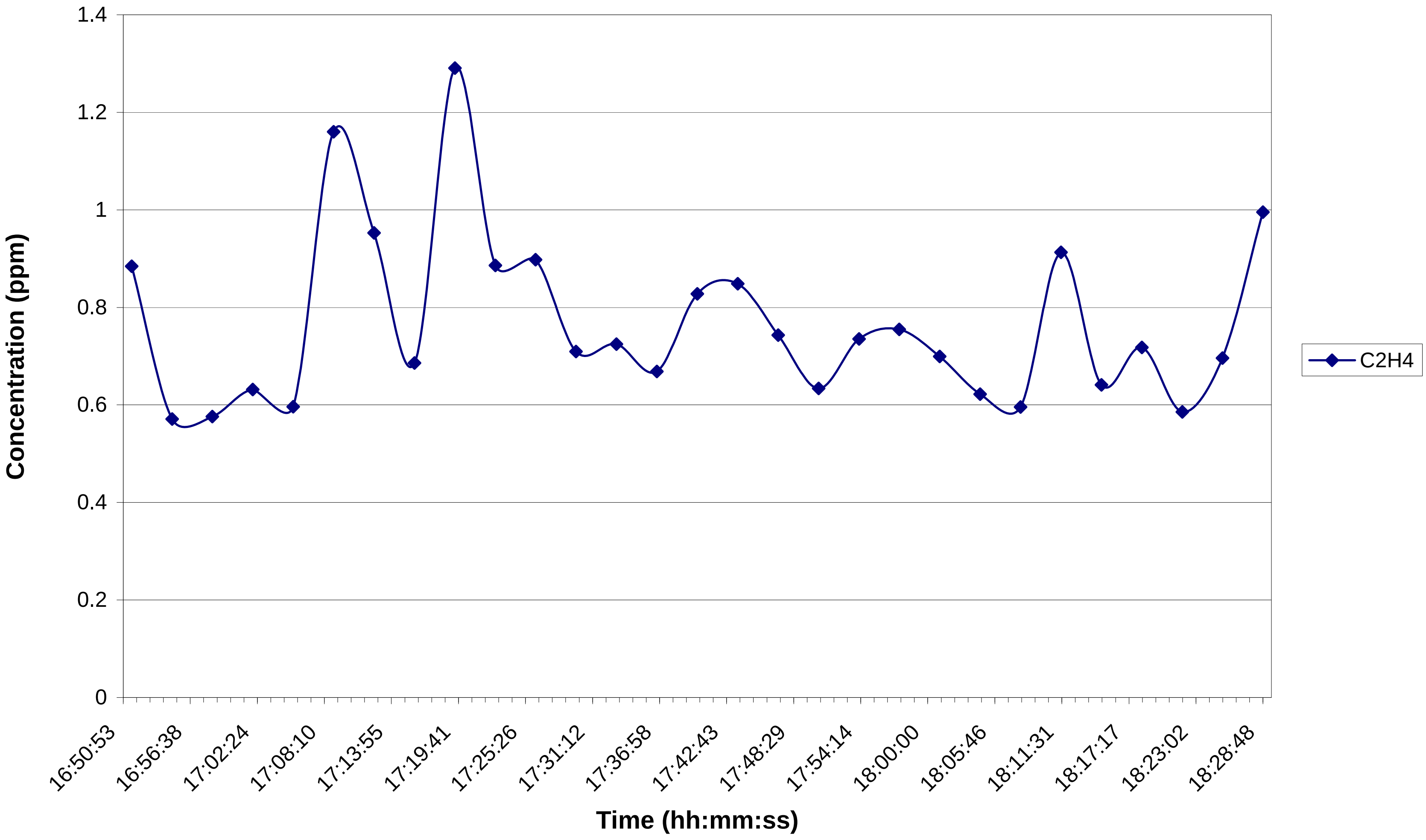

Time Series Plot of CO During CO$_2$ Injection on 8/29/06
Concentration (ppm)
0
100
200
300
400
500
600
700
800
900
1000
Time (hh:mm:ss)
16:50:53
16:56:38
17:02:24
17:08:10
17:13:55
17:19:41
17:25:26
17:31:12
17:36:58
17:42:43
17:48:29
17:54:14
18:00:00
18:05:46
18:11:31
18:17:17
18:23:02
18:28:48
CO

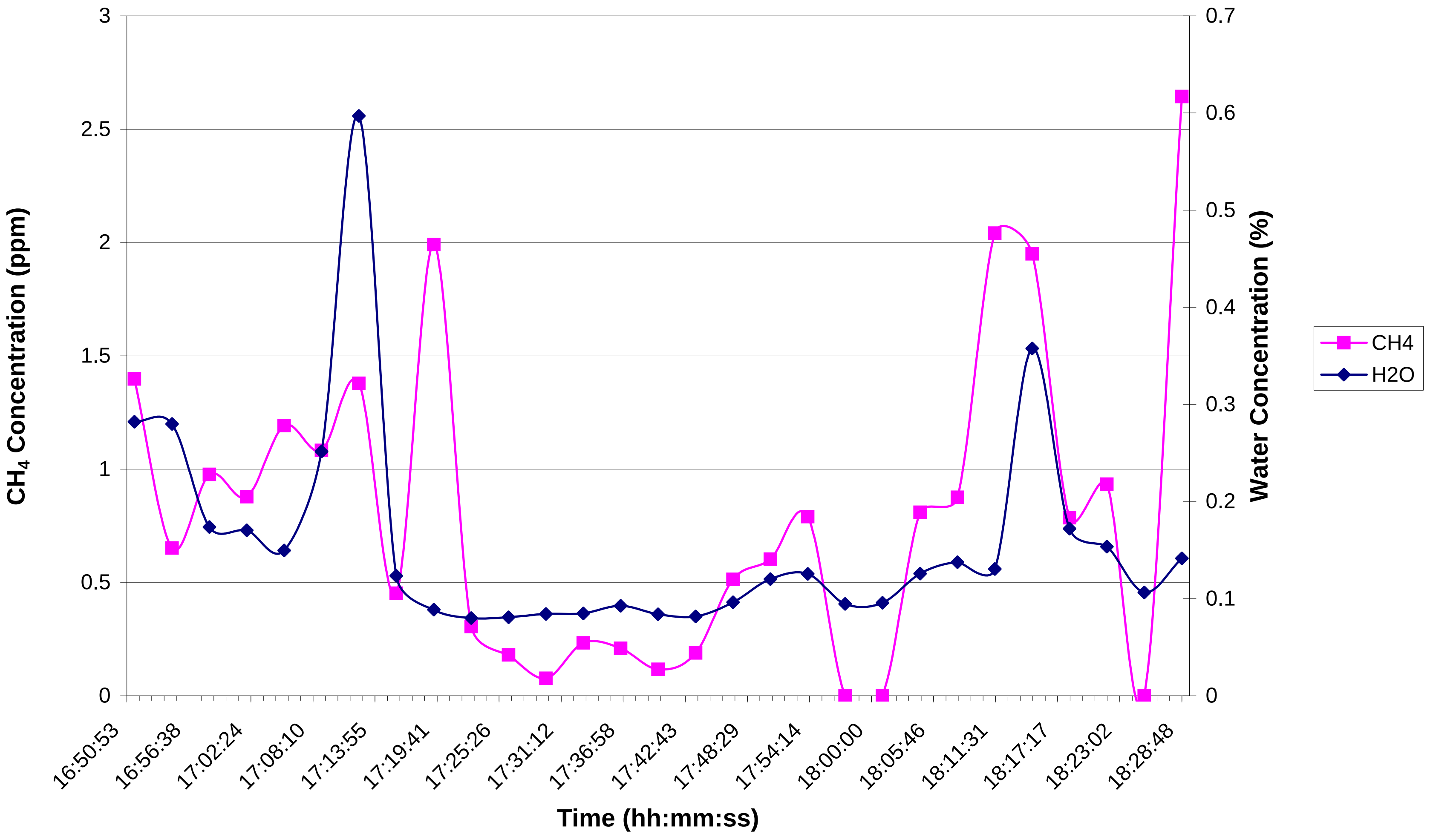


Time Series Plot of SO_2 and SF_6 During CO_2 Injection on 8/29/06


Time Series Plot of Nitrogen Oxides During CO_2 Injection on 8/29/06
Concentration (ppm)
4
3.5
3
2.5
2
1.5
1
0.5
0
16:50:53
16:56:38
17:02:24
17:08:10
17:13:55
17:19:41
17:25:26
17:31:12
17:36:58
17:42:43
17:48:29
17:54:14
18:00:00
18:05:46
18:11:31
18:17:17
18:23:02
18:28:48
Time (hh:mm:ss)
NO
NO2
N2O

Time Series Plot of C_2H_4 During CO_2 Injection on 8/29/06





Time Series Plot of CH_4 and H_2O During CO_2 Injection on 8/29/06