

**Developing a Reliable Fluorinated Greenhouse Gas (F-GHG)
Destruction or Removal Efficiency (DRE) Measurement Method
for Electronics Manufacturing: A Cooperative Evaluation with
NEC Electronics, Inc.
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1.0 Introduction

The purpose of this study was to accurately determine the Destruction or Removal Efficiency (DRE) of two different commercially available Point Of Use (POU) abatement systems or scrubbers for process emissions fluorinated greenhouse gases (F-GHGs) such as perfluorocarbons (PFCs), hydrofluorocarbons (HFCs), sulfur hexafluoride (SF₆), and nitrogen trifluoride (NF₃). A key component in accurately determining DRE was to determine the dilution of process exhaust occurring in each scrubber. This study used an experimental approach to measure the dilution across the scrubber by injecting a chemical tracer that could not react in the scrubber, or be produced as a by-product during scrubber operation. In this study Krypton, Argon and Xenon were used as chemical spiking agents, as they met the requirements for this application.

Testing was conducted in a fully functional semiconductor manufacturing facility, owned and operated by NEC Electronics Inc. in Roseville, CA. Two different process tools, referred to as CVD Tool #1 and CVD Tool #2, each equipped with a POU scrubber, were tested. CVD Tool #1 equipped with a TecHarmonic E-HTVS POU scrubber was tested, and CVD Tool #2 equipped with an Edwards TPU POU abatement device was also tested.

2.0 Experimental Setup

To carry out the objectives of this study it was necessary to monitor both process and scrubber emissions simultaneously, and determine scrubber dilution using chemical spiking. Process and scrubber emissions data were collected in parallel using Fourier Transform Infrared Spectroscopy (FTIR). Data used to determine scrubber dilution were collected using Quadrupole Mass Spectrometry (QMS). A schematic showing the experimental testing set up is shown in Figure 1.

Two FTIRs were used to determine process and scrubber emissions. Both systems were MKS 2010 Multi Gas Analyzers equipped with liquid nitrogen cooled mercury cadmium telluride (MCT) detectors. One FTIR was equipped with a 10 cm path length single pass gas cell, and was used to sample process effluent. The other FTIR was equipped with a 5.6 m path length multi pass gas cell, and was used to sample scrubber effluent. Both FTIR were operated at 0.5cm⁻¹ resolution. Four scans were co-added for each data point yielding a sampling frequency of 2.2 sec.

A Balzers QMS system was used to sample scrubber effluent during dilution determination. The QMS was operated in Selective Ion Monitoring (SIM) mode and a secondary electron multiplier was used to enhance sensitivity. A 1 sec sampling frequency was used for each data point. To account for potential changes in QMS sensitivity, ion signals were normalized to the signal obtained for the nitrogen fragment (N⁺), which is formed during electron impact ionization of N₂.

Sampling of effluent streams was done using metal bellows sampling pumps that were located after the instruments. The sample flow rate was controlled using adjustable flow rate valves. The sample line pressure for both FTIRs and the QMS were monitored using capacitance

manometers. A filter was installed in the sample line used for monitoring scrubber emissions to ensure that particulate emissions from the scrubber would not coat the FTIR internal optics, or the pressure reducing orifice used for the QMS. Since the scrubber DRE determination and the scrubber dilution determination were independent events, it was possible to use the same sample line for both operations. This was accomplished by switching the instrument inlet sample fitting from the FTIR to the QMS.

The QMS was calibrated to determine its response to Xe, Ar and Kr on site using a dynamic dilution blending system. Test atmospheres containing H₂, He, Kr, Ar and Xe were created by blending a calibration standard containing 1% of each species in N₂ with N₂ diluent. The QMS responses to ⁸⁴Kr and ¹³²Xe during calibration are shown in Figure 2. From regression analyses of these data a calibration curve was generated and is shown in Figure 3. These data were used to quantify Kr and Xe emissions from the scrubber.

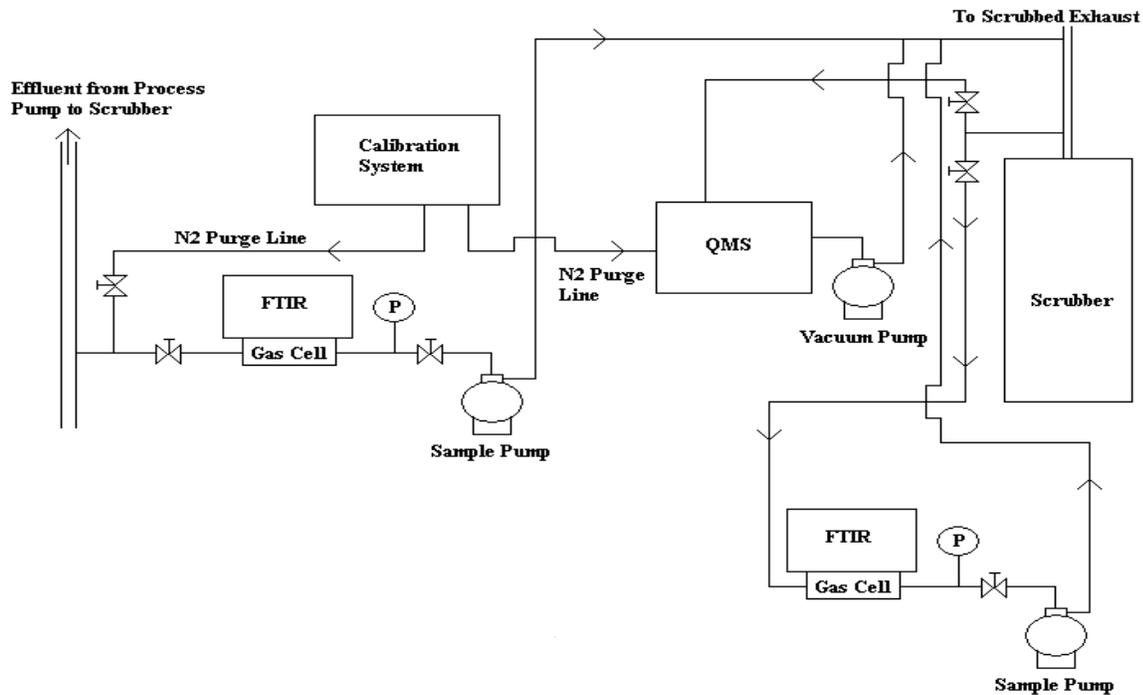


Figure 1: Actual sampling schematic used for E-HTVS and TPU at NEC Electronics Inc. Schematic shows the calibration and sampling capability for each instrument.

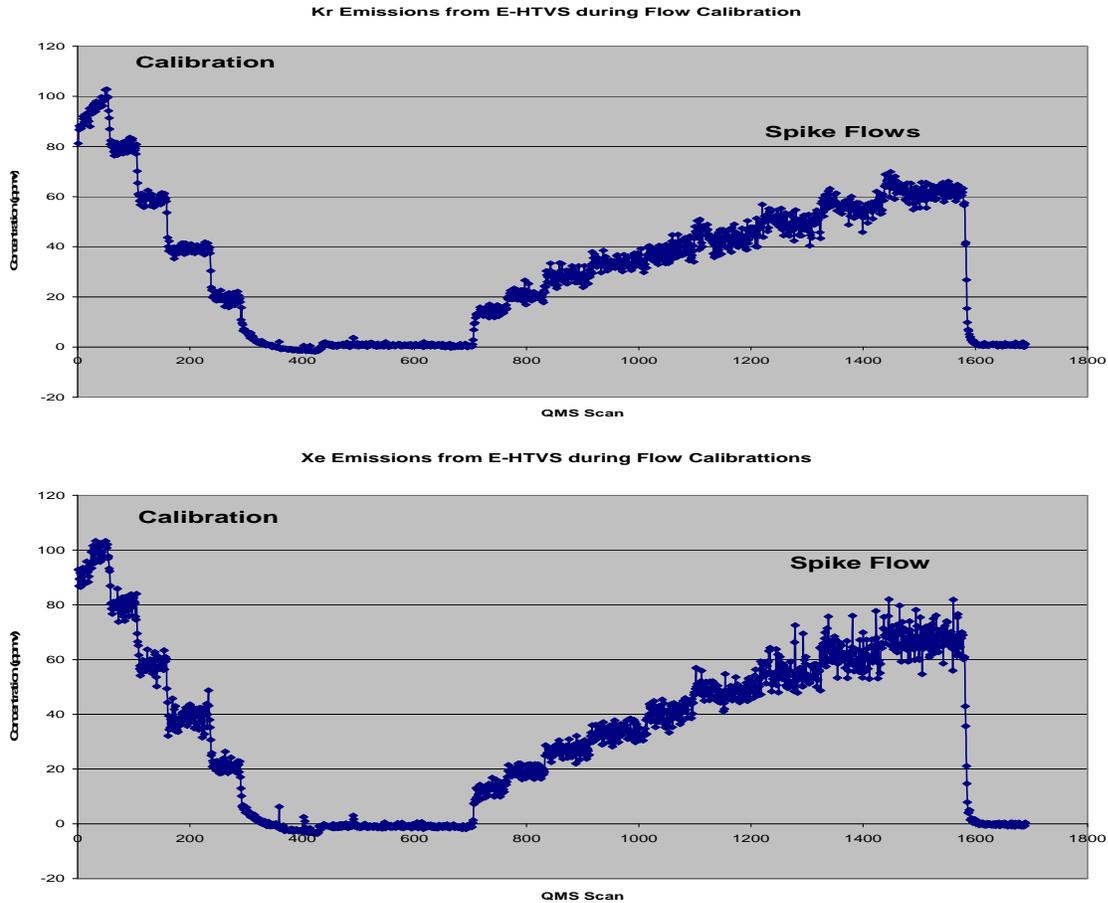


Figure 2: QMS response to Kr (top) and Xe during QMS calibration and E-HTVS spiking of Kr and Xe. (Note: Kr and Xe emissions in the figure titles denote the flow of tracer materials and have nothing to do with process emissions.)

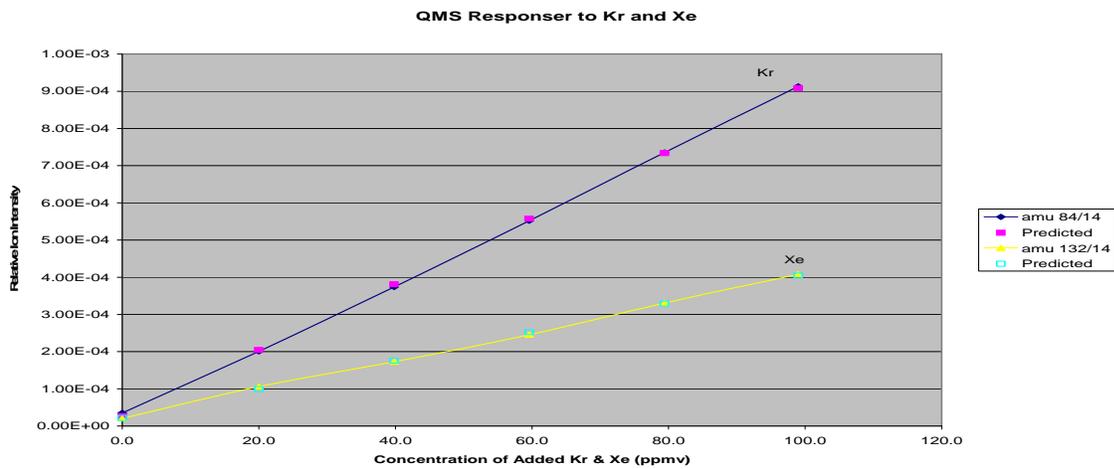


Figure 3: Regression analysis of data obtained during calibration of QMS response to ^{86}Kr and ^{132}Xe in N_2 . These data were used to determine Kr and Xe concentration during chemical spiking of scrubbers.

The FTIR was calibrated on-site using test atmospheres created through dynamic dilution blending of a 1% C₂F₆ in N₂ standard. Several mixtures were created to calibrate the response of the FTIR equipped with the 5.6 m gas cell. Figure 4 shows the calibration curve generated for the CF₃ symmetrical deformation of C₂F₆ (centered at 714 cm⁻¹) as measured by the maximum absorbance of the R branch for each calibration point. The relative error of this calibration was determined to be 3.1 %.

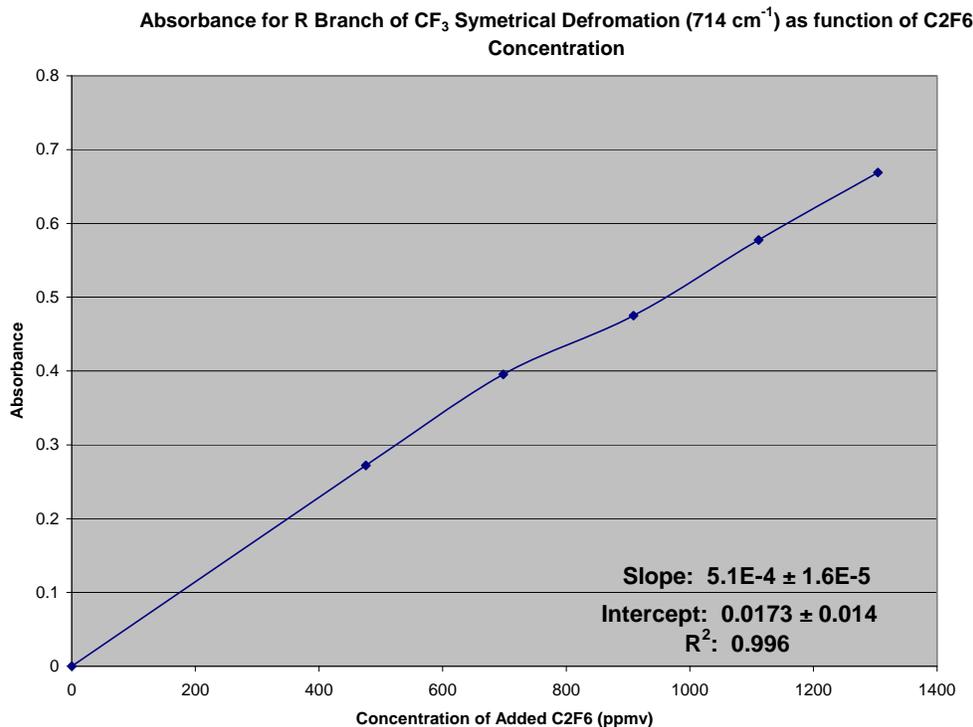


Figure 4: Calibration of FTIR response to C₂F₆. Note 1: These data were generated on-site at NEC Electronics Inc. using a 1% C₂F₆ in N₂ standard. Note 2: The least squares line is *not* shown in Figure, but the relevant parameters of regression line and statistics are presented.

3.0 Data Analysis

3.1 Determination of Scrubber Dilution

One of the primary goals of this study was to accurately determine the dilution that occurs when gas emitted from the process chamber passes through the scrubber. Dilution can occur from many sources including effluents from other chambers, combustion gases and by-products added to and generated within the scrubber, vapors added as the gas stream passes through the water scrubber portion of the system, in-board leaks, and back diffusion from main headers. The method of determining dilution in this study was to use a purely experimental approach where a chemical was spiked into the gas stream entering the scrubber at a known flow rate, and determined in the scrubber effluent stream. From the determined concentration and the

controlled flow rate added to the process exhaust duct, a total flow from the scrubber could be calculated:

$$\mathbf{TF = S_f / (C_{an} \times 10^{-6})} \quad \mathbf{(1)}$$

Where S_f represents the spike gas flow and is reported in liters, and C_{an} represents the analyte concentration reported in ppmv.

The experiment conducted to determine total flow from the E-HTVS scrubber consisted of using the calibration system shown in Figure 1 to add calibration gas into the process effluent through the FTIR sample line where the process effluent was monitored. While calibration gas was being added, the QMS was used to sample scrubber effluent. The flow of calibration gas was controlled with a 0 – 5 slm MFC that was calibrated for nitrogen. Five flow rates were added to the scrubber: 1, 2, 3, 4 and 5 slm. At 1% concentration, each of these flows corresponded to Kr and Xe flows of 0.01, 0.02, 0.03, 0.04 and 0.05 slm, respectively. Concentration profiles for Xe and Kr determined from QMS data during this experiment are shown in Figure 5 for CVD Tool #1, which was the tool used for testing the E-HTVS scrubber.

Applying Eq. 1 to the data shown in Figure 5 for the E-HTVS scrubber yielded the total equivalent flows determined for both Xe and Kr, which are contained in Table I. The average total flow for each species was:

Xe: 741 ± 3

Kr: 765 ± 3

Here the reported standard deviations are the best estimate of the standard deviations of the mean for total flows contained in Table I. Combining the data for Kr and Xe yielded a best estimate of effective flow of 757 ± 2 slm, which is the variance weighted average of the mean.

The precision of these measurements were ± 0.3 %. The differences between the flow values (3%) obtained for Kr and Xe could be attributable to other factors affecting accuracy, such as the accuracy of the Kr and Xe concentrations in the calibration standards.

Table I: Total equivalent flow measurements from E-HTVS determined using Xe and Kr.

Xe/Kr Flow (slm)	Xe Conc (ppmv)	Total Equivalent Flow (slm)	Kr Conc (ppmv)	Total Equivalent Flow (slm)
0.010	12.7 ± 1.7	787 ± 122	14.4 ± 1.3	694 ± 63
0.020	26.9 ± 2.0	744 ± 52	28.1 ± 2.3	712 ± 58
0.030	40.1 ± 3.1	748 ± 58	37.8 ± 2.7	794 ± 57
0.040	55.4 ± 4.5	722 ± 59	50.2 ± 2.8	797 ± 44
0.050	67.6 ± 4.7	740 ± 51	64.8 ± 2.4	772 ± 29

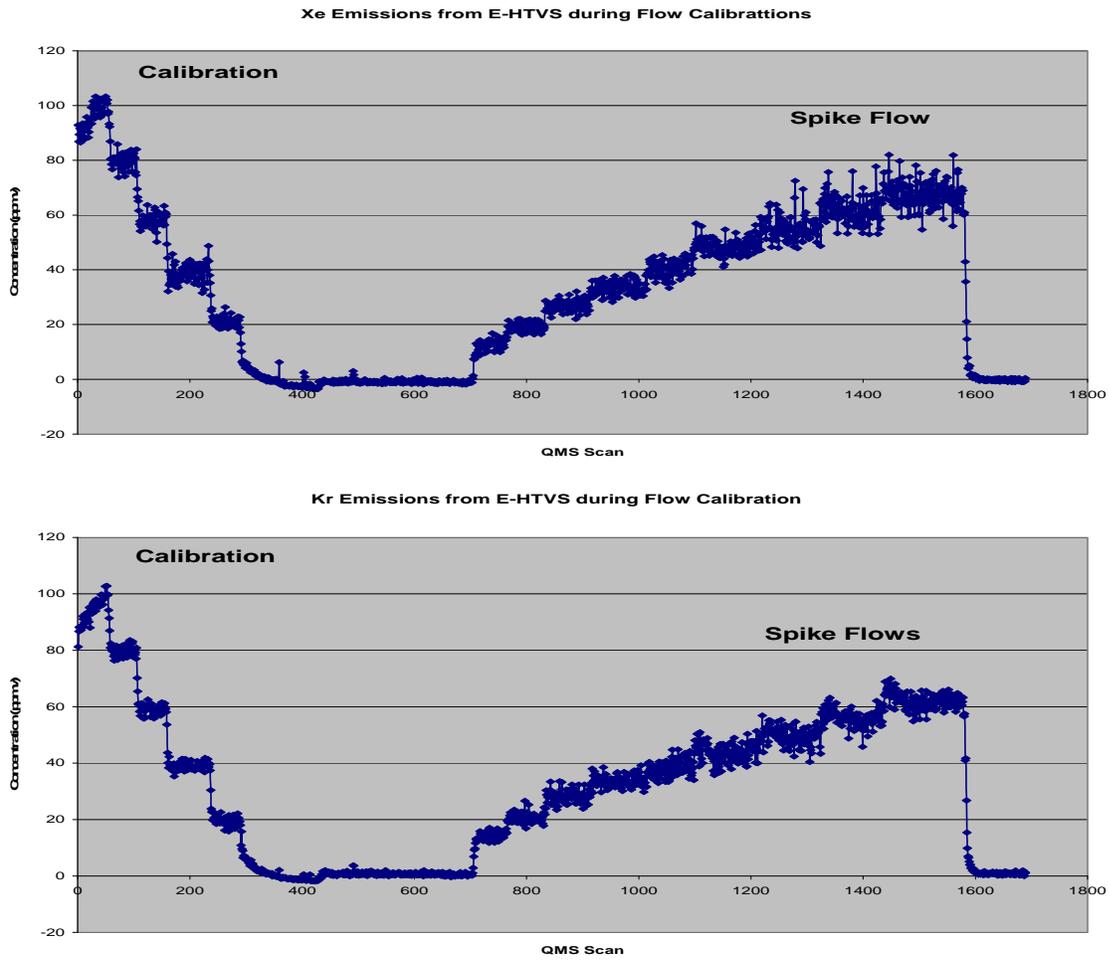


Figure 5: Xe (top) and Kr (bottom) emissions from E-HTVS during spike calibration. Calibration data were generated using test atmospheres as described above.

The same approach was used for determining flow from the TPU. Figure 6 shows Xe and Kr emissions from the TPU during spiking of the scrubber. The same Xe and Kr flow rates of 0.01, 0.02, 0.03, 0.04, and 0.05 slm were used. Table II contains the total flow determined for each species at each spike flow rate. The average total flow for each species was:

Xe: 751 ± 3

Kr: 838 ± 2

Here the reported standard deviations are the best estimate of the standard deviations of the mean for total flows contained in Table II. Combining the data for Kr and Xe yielded a best estimate of effective flow of 815 ± 2 slm, which is the variance weighted average of the mean.

The precision of these measurements were ± 0.3 %. The difference between the flow values observed for Kr and Xe on the TPU (11%) were greater than those observed on the E-HTVS (3%). An additional flow determination method was deployed.

An additional experiment using Ar was conducted on the TPU. The experiment consisted of flowing Ar from the CVD Tool #2 through the scrubber and determining the Ar concentration emitted from the scrubber. Figure 7 shows the Ar emission profile for 4 process flows: 2.0, 1.5, 1.0 and 0.5 slm. As indicated in Figure 7, Ar background concentration was relatively high due to the natural atmospheric abundance of 0.94 %. This background was subtracted from the measured Ar concentration during the Ar flows to yield a concentration that could be attributable to the added Ar. Table III contains the data from this experiment. The data in Table III was used to determine the TPU flow by dividing the Ar process flow (in sl) by the differential Ar concentration (ΔAr). The weighted average total flow determined during this experiment was **826 ± 2 slm**. This value is in close agreement (± 1.5%) with the reported effective dilution for the Kr spike test (838 slm).

Table II: Total flow measurements from TPU determined using Xe and Kr.

Xe/Kr Flow (slm)	Xe Conc (ppmv)	Total Equivalent Flow (slm)	Kr Conc (ppmv)	Total Equivalent Flow (slm)
0.010	12.3 ± 1.3	813 ± 86	12.7 ± 0.9	787 ± 56
0.020	27.2 ± 2.2	735 ± 60	22.8 ± 2.5	877 ± 95
0.030	42.2 ± 2.7	711 ± 45	35.0 ± 1.5	857 ± 37
0.040	51.6 ± 4.1	775 ± 62	47.6 ± 1.6	840 ± 28
0.050	63.6 ± 5.0	786 ± 62	59.9 ± 1.9	835 ± 26

Table III: Ar concentration determined in TPU effluent during Ar flow testing. ΔAr concentration is the measured concentration minus the baseline.

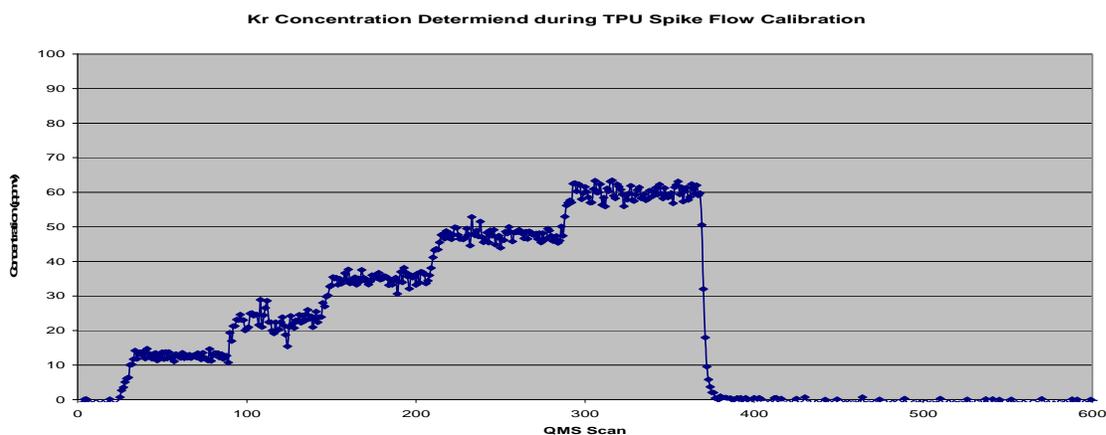
Ar Process Flow (slm)	Ave. Ar Conc. (ppmv)	ΔAr Conc (ppmv)	Total TPU Flow (slm)
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Baseline (0)	8685 ± 22	–	–
2.0	11,098 ± 154	2413 ± 156	828 ± 53
1.5	10,302 ± 33	1617 ± 40	927 ± 23
1.0	9996 ± 27	1311 ± 35	762 ± 20
0.5	9321 ± 18	636 ± 28	786 ± 35
Baseline (0)	8655 ± 18	–	–

A summary comparing total flows determined for both scrubbers is contained in Table IV. Results for Kr and Xe on the E-HTVS scrubber were within 3%, while on the TPU system the difference was 11 %. In both cases the Kr based determination was higher than Xe determination. The dilution determined using Ar on the TPU was found to be within 1.5 % of the value determined using Kr. Both values were > 10 % higher than the value determined using Xe. Considering that using Ar supplied by the process tool is independent of the calibration standard accuracy for the spiking process, this result suggests that inaccuracies in the Xe determination may more likely have occurred. Given the relative close agreement in results for all flow determinations, this was not further investigated. However, the Xe discrepancy warrants further investigation in subsequent evaluation of the methodology.

Table IV: Summary of the average total flow determinations for E-HTVS and TPU at NEC Electronics Inc. All flows reported as slm.

POU System	Xe Spike	Kr Spike	Ar On-Tool
E-HTVS	741 ± 3	765 ± 3	N/A
TPU	751 ± 3	838 ± 2	826 ± 2



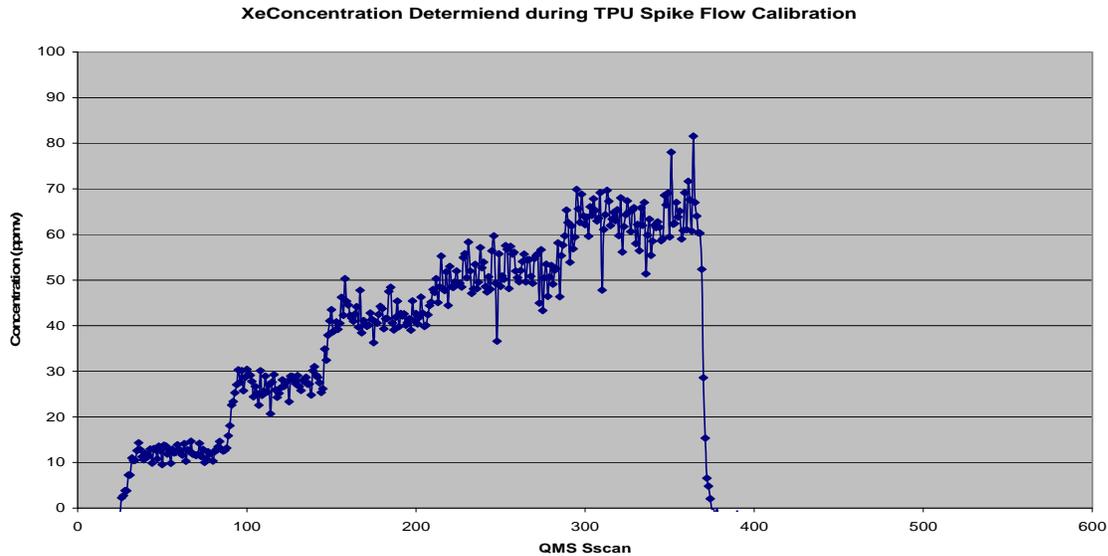


Figure 6: Kr (top) and Xe (bottom) emissions from TPU during chemical spiking of scrubbers.

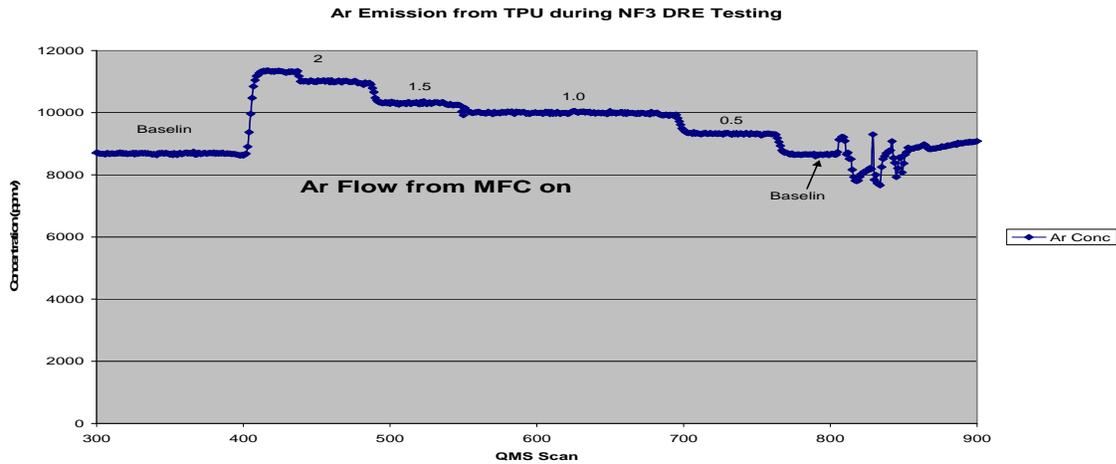


Figure 7: Ar emission from TPU while Ar was being flowed through the process chamber on CVD Tool #2. Baseline Ar concentration was close to that expected in air.

Once the total flow from the scrubbers has been determined it was then possible to determine the dilution of process effluent occurring across the scrubbers. This calculation requires measuring the dilution that occurs as gases from the process chamber are pumped out of the chamber and fore line and sent into the corrosive scrubbed exhaust. The experiment to measure the dilution of CVD Tool #1 and CVD Tool #2 chamber effluent consisted of flowing C_2F_6 into the CVD Tool #1 chamber and NF_3 into the CVD Tool #2 chamber, with the radio frequency (RF) power in the chambers turned off, at several flow rates. The determined C_2F_6 and NF_3 concentrations in the chamber effluent could be used to calculate the total process flow entering the scrubber from the following equation:

$$T_{PF} = PG_f / (C_{PG} \times 10^{-6}) \quad (2)$$

Here the total process flow (T_{PF}) is determined from the ratio of the process gas flow (PG_f) in slm divided by the measured concentration (C_{PG}) in ppmv.

Process flow data for the E-HTVS system were obtained by flowing C_2F_6 through the CVD Tool #1 chamber at several flows with the RF power turned off. Figure 8 shows the C_2F_6 emission profile for 5 different flows. From these data the total process flow was determined and is contained in Table V. The average total process flow was **83.58 ± 0.03 slm**. Combining this value with the total scrubber flow yielded the effective dilution of influent gas across the E-HTVS:

$$\text{Dilution Factor} = (757 \pm 2) / (83.58 \pm 0.03) = 9.05 \pm 0.02$$

This value was used for all subsequent DRE calculations. This value represents the effective dilution that was determined for the E-HTVS. These data do not necessarily imply a total flow of 757 slm was flowing through the abatement device, but do imply that the chemical spiking agents were diluted to an equivalent flow of 757 slm. The source of this dilution was not determined, but could be attributable to factors such as in-board leaks in the duct work between the scrubber outlet and the sample location or mixing at the sample location from the main header of the scrubbed corrosive exhaust system. Having an accurate determination of this effective dilution is critical in determining an accurate DRE for the scrubber.

Table V: Total process flow determination for CVD Tool #1 using C_2F_6 tool flows.

C_2F_6 Flow (slm)	Ave. C_2F_6 Concentration (ppmv)	Total Process Flow (slm)
1.0	$11,714 \pm 61$	85.4 ± 0.4
0.8	9461 ± 50	84.6 ± 0.4
0.6	7232 ± 43	83.0 ± 0.5
0.4	4889 ± 32	81.8 ± 0.5
0.2	2500 ± 26	80.0 ± 0.8

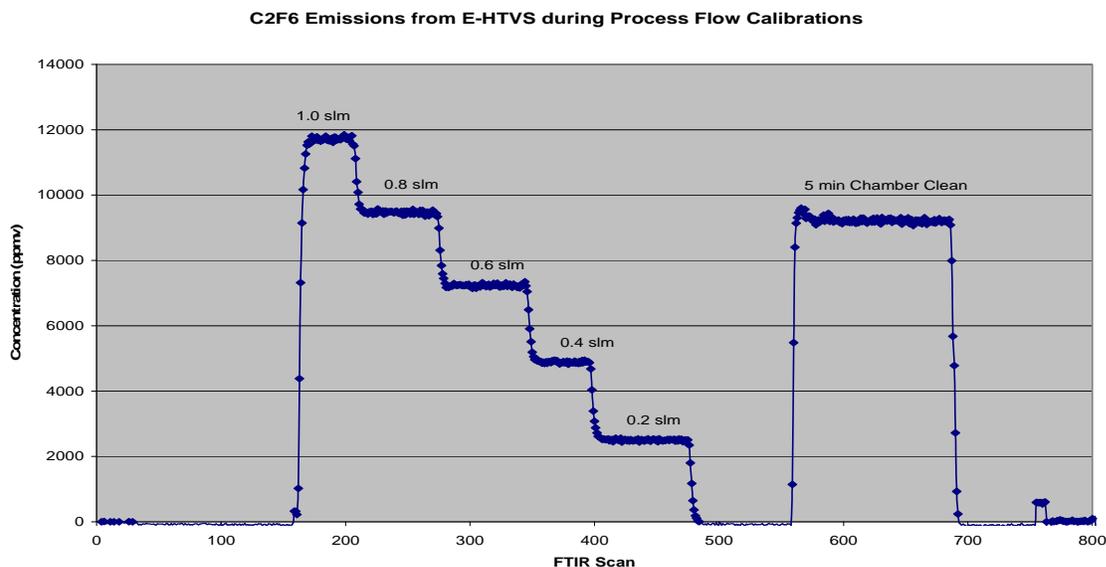


Figure 8: C₂F₆ emission profile for CVD Tool #1 during process flow calibration. C₂F₆ emissions from a 5 minute chamber clean are also shown.

Total process flow into the TPU was determined by flowing NF₃ from the chamber with RF power off. Process emissions from six flows are shown in Figure 9. From these data the total process flow was determined to be **15.50 ± 0.01 slm**. Table VI contains NF₃ concentrations determined for each flow. The total process flow and total TPU exhaust flow were used to calculate the dilution occurring in the TPU:

$$\text{Dilution Factor} = (831 \pm 1) / (15.50 \pm 0.01) = 53.6 \pm 0.1$$

Having determined the total process flow for each tool and scrubber allows determination of the dilution occurring across the scrubber. These data were used to determine the scrubber F-GHG DRE.

Table VI: Total process flow determination for CVD Tool #2 using NF₃ tool flows.

NF ₃ Flow (slm)	Ave. NF ₃ Concentration (ppmv)	Total Process Flow (slm)
0.50	31,735 ± 157	15.8 ± 0.1
1.00	67,886 ± 974	14.7 ± 0.1
1.50	93,964 ± 685	16.0 ± 0.1
0.20	13,098 ± 83	15.3 ± 0.1
0.25	16,147 ± 50	15.5 ± 0.1
0.30	19,020 ± 41	15.8 ± 0.1

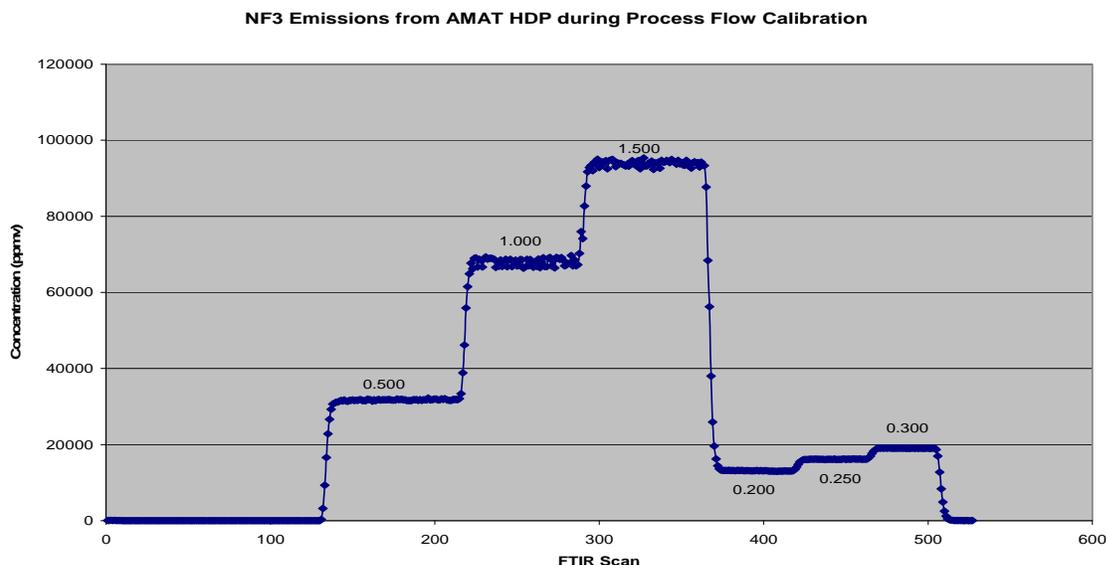


Figure 9: NF₃ emission profile from CVD Tool #2 during NF₃ process flow calibration.

3.2 Scrubber DRE Determinations

Determination of the E-HTVS scrubber performance was performed using two different testing conditions. The first was to measure the scrubber effluent of C₂F₆ during the total process flow calibrations and the second was to measure the scrubber effluent during C₂F₆/O₂ chamber cleans. Two chamber cleans were monitored. The first was a short 5-minute clean of a chamber that was relatively clean (little tungsten accumulation in the chamber). The second clean was longer and was performed after an accumulation of approximately (ca.) 20 μm of film that had built up in the chamber. This clean used an optical end-point mechanism to determine the length of the clean. The process recipe for the chamber clean was to flow 1.2 slm C₂F₆ and 1.2 slm O₂.

Determination of the TPU performance could only be done using NF₃ flows from the tool gas delivery system, as the tool chosen for this project was not operational at the time of testing. Several NF₃ flows were sent through the process chamber to determine NF₃ DRE. However, no process wafers could be run and the system could not be evaluated under manufacturing conditions.

3.2.1 TecHarmonic E-HTVS DRE

The E-HTVS DRE for C₂F₆ was determined during process flow calibrations. Figure 10 shows C₂F₆ emissions from process and scrubber during the flow calibration. Using the average measured C₂F₆ concentration for both inlet and outlet samples from each step and applying the dilution correction yields the C₂F₆ DRE for the E-HTVS scrubber during process flow determination. These averages for each C₂F₆ flow are contained in Table VII. The associated DRE values for each C₂F₆ flow are also contained in Table VII.

Table VII: C₂F₆ DRE in E-HTVS during process flow calibrations. Dilution adjustment was based total measured flows into and out of the scrubber.

C ₂ F ₆ Flow (slm)	C ₂ F ₆ Conc. In Process Effluent (ppmv)	C ₂ F ₆ Conc. In E-HTVS Effluent (ppmv)	Dilution Adjusted C ₂ F ₆ Concentration (9.05X in ppmv)	DRE (%)
1.0	11,714 ± 61	1288 ± 10	11,656	0 %
0.8	9461 ± 50	1064 ± 10	9629	-2 %
0.6	7232 ± 43	736 ± 10	6661	8 %
0.4	4889 ± 32	505 ± 8	4570	7 %
0.2	2500 ± 26	250 ± 4	2263	9 %

From the data contained in Table VII above, a 95% Confidence Interval (CI) is determined to be 5.0 ± 4.4 % indicating that all values in Table VII are statistically zero at the 95 % CI.

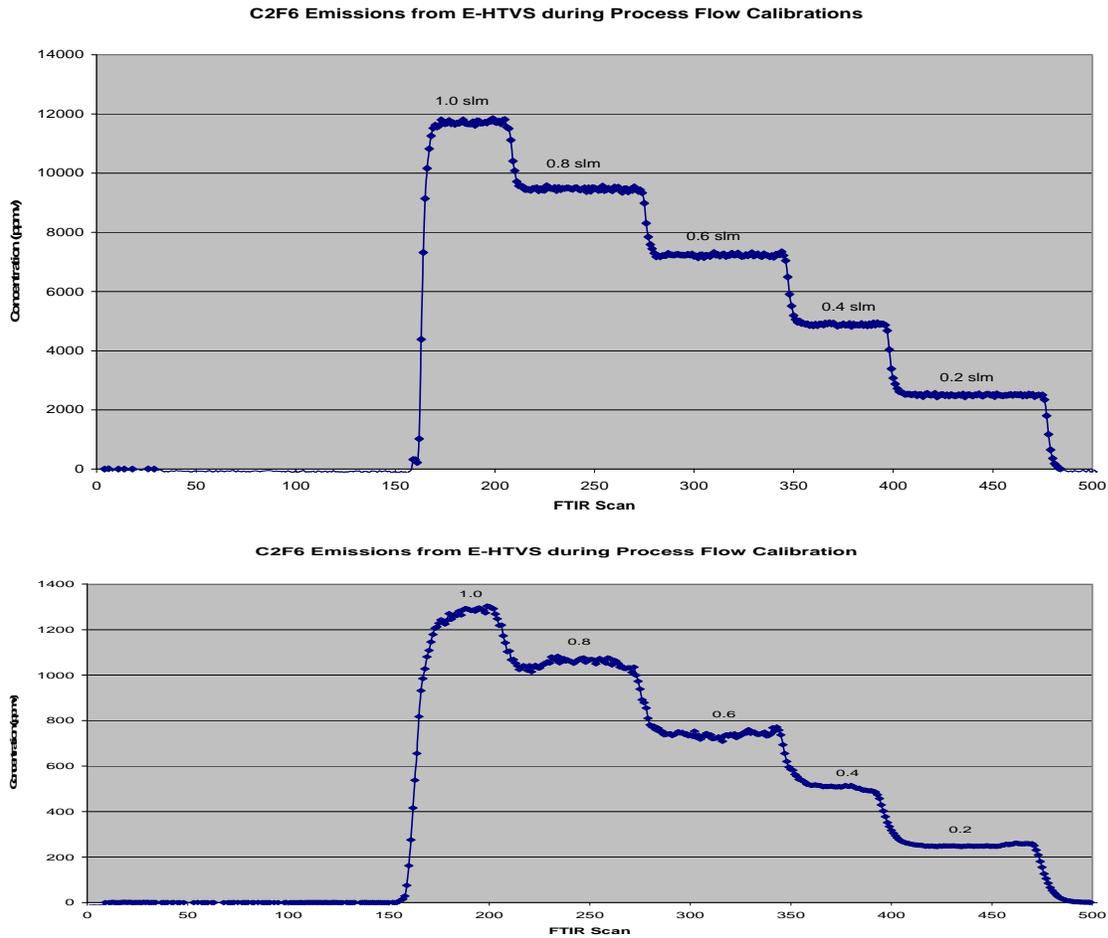


Figure 10: Inlet and outlet C₂F₆ emission profiles for E-HTVS during process flow calibration.

The E-HTVS DRE for C_2F_6 was also determined during chamber cleans. Emissions from the chamber clean included significant levels of tetrafluoromethane (CF_4), which was formed as by-product. Other chamber clean by-products included carbonyl fluoride (COF_2), tungsten hexafluoride (WF_6) and carbon monoxide (CO) as identified in the FTIR spectrum shown in Figure 11. Emission profiles of CF_4 and C_2F_6 for two chamber cleans are shown in Figure 12. Emission profiles of CF_4 and C_2F_6 from the E-HTVS are also shown in Figure 12. These data were numerically integrated over time to yield emission volumes. Comparison of the CF_4 and C_2F_6 emission volume entering the scrubber with that emitted from the scrubber can be used to directly calculate DRE for each compound.

To convert measured concentrations into volumes, the following equation was used:

$$V_{EM} = \Sigma C_i T_f \Delta t \quad (5)$$

Where the total emission volume (V_{EM}) is the summation of each FTIR data point where the concentration of analyte C_i is determined during time interval Δt and multiplied by the total flow (T_f). The summation of the entire emission profile provides an emission volume for a given analyte during the process. During this study, these calculations were performed using standard spreadsheet software (Microsoft Excel). Use of this technique reinforces the importance of accurately determining the total process and scrubber flows as described in the sections above.

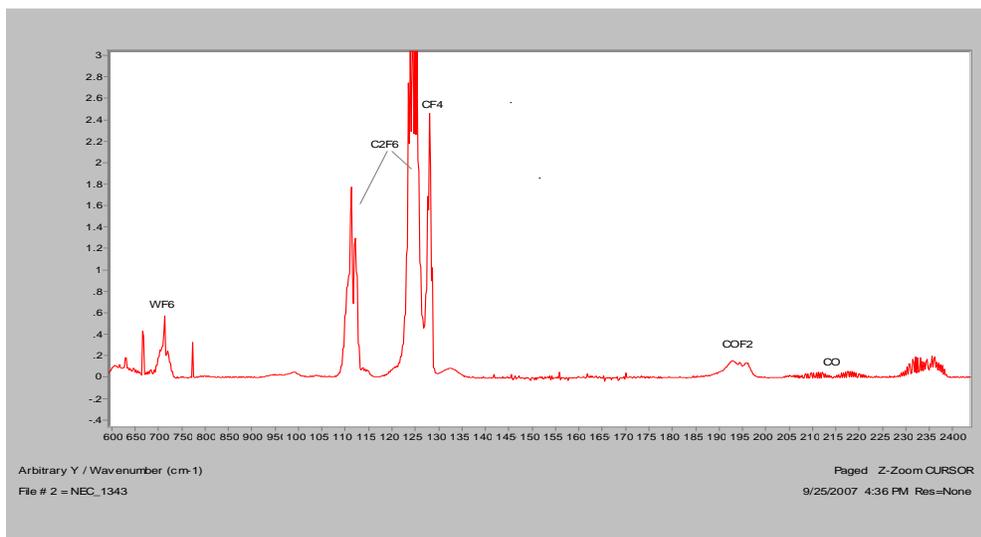


Figure 11: FTIR spectrum of process emissions during C_2F_6/O_2 chamber clean on CVD Tool #1.

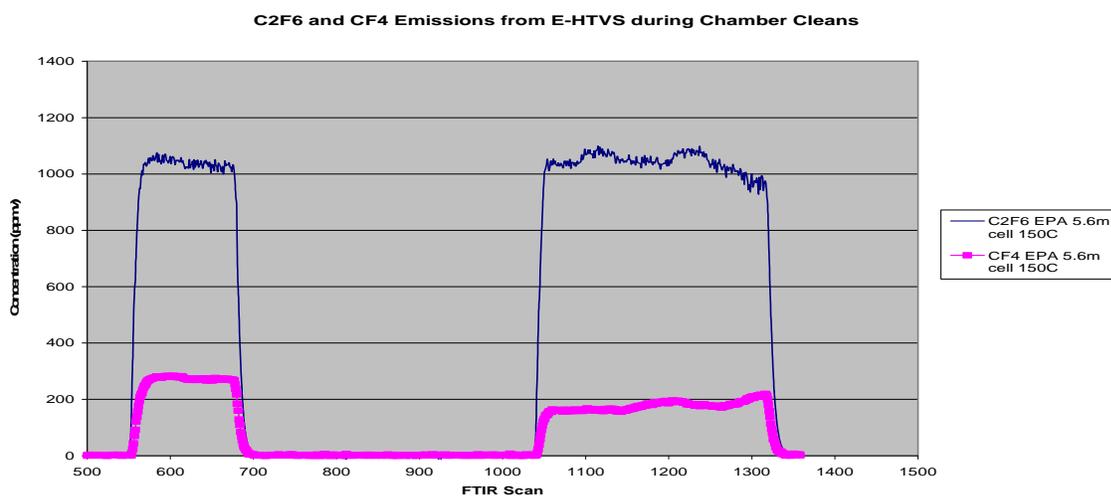
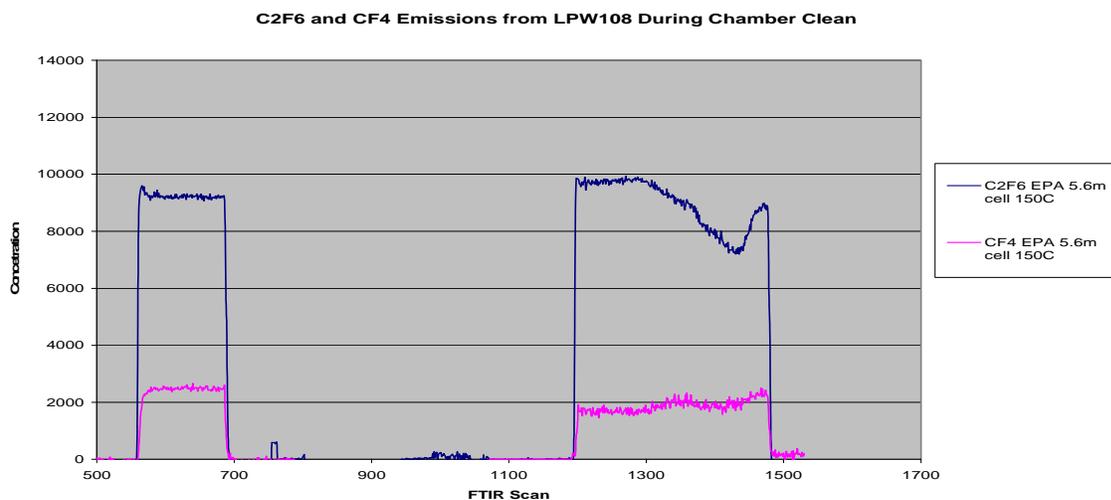


Figure 12: C₂F₆ and CF₄ emissions from CVD Tool #1 (top) and E-HTVS scrubber during chamber cleans. The first clean was timed for 5 minutes. The second clean was for a tungsten accumulation of ca. 20µm and was run until end point.

Integration of the emission profiles shown in Figure 12 yielded emission volumes contained in Table VIII for both process and scrubber emissions. These integrated emission volumes were compared directly to determine F-GHG DRE during the chamber cleans, which are also included in Table VIII. The results are close in value to those presented for C₂F₆ during the process flow calibrations shown above.

The results for CF₄ yielded an average DRE of 9.5 % with a 95 % CI of ± 9.8 %. Use of these two data points yields DRE's in the range of -0.3 – 19.3 %, which includes zero. Therefore, we cannot reject the hypothesis that the DRE equals zero. Given that CF₄ is more difficult to abate than C₂F₆ due to higher bond energy of C-F compared to C-C, a zero DRE would be expected and the data indicates statistically that this is the case. The actual deviation from a zero DRE as

determined in this study can be attributable to the propagation of errors associated with all the factors used in calculating the values contained in Table VIII.

Table VIII: Integrated F-GHG process and scrubber emissions for CVD Tool #1 (process) and E-HTVS during chamber cleans. Details on the cleans provided in text

	Clean #1	Clean #2
C₂F₆ Process Emission (sl)	3.914	8.266
C₂F₆ E-HTVS Emission (sl)	3.723	8.802
C₂F₆ DRE	5 %	-5 %
CF₄ Process Emission (sl)	1.011	1.730
CF₄ E-HTVS Emission (sl)	0.952	1.494
CF₄ DRE	6 %	13 %

The data contained in Table VIII can also be used to determine the process DRE for C₂F₆ and the process emission factor for CF₄. The process DRE is defined as the ratio of C₂F₆ emitted from the process to the total C₂F₆ added to the process. For clean #1 the total C₂F₆ added to the process was 6.0 sl based on a 1.2 slm process flow and 5 minute chamber clean, thus the C₂F₆ process DRE was 35 % for this clean. For clean #2, which reached end point at 11.1 minutes, the C₂F₆ process DRE was 38% based on a total process flow of 13.3 sl.

The CF₄ emission factor is defined as the ratio of CF₄ volume emitted from the process to the C₂F₆ volume added to the process. For cleans #1 and #2 these values were 17 and 13%, respectively. The slight differences between cleans 1 and 2 were attributed to clean #2 being done when the chamber had more tungsten film accumulation in the chamber.

All of the DRE values reported for C₂F₆ and CF₄ indicate that the E-HTVS system does not abate these gases under the operating conditions tested. The result obtained for CF₄ is statistically equivalent to zero at the 95 % CI.

3.2.2. Edwards TPU DRE

As stated above the CVD Tool #2 was not operational. This prevented evaluating the performance of the TPU during wafer processing. It was possible to flow NF₃ from the process chamber through the TPU. The five flow rates used to collect the data in Figure 9 (data collected at the inlet to the TPU) yielded undetectable levels of NF₃ in the TPU effluent. Figure 13 shows FTIR spectra obtained at the inlet and outlet of the TPU while 1.5 slm NF₃ was flowing from the process chamber. These data can be used to report a TPU DRE of **> 99.9 %** based on an estimated FTIR detection limit of 0.5 ppmv, an average inlet concentration of 93,964 ± 685 ppmv and a dilution factor of 53.6 X:

Diluted NF₃: **93,964/53.6 = 1750 ppmv fully diluted**
Undetected NF₃: **0.5/1750 = 0.00029**
DRE **(1.000 – 0.00029)x100 = 0.99971 = 99.971%**

The TPU was proven to be effective at abating any NF₃ potentially emitted from the process under the conditions with which it was operated. The TPU thermocouple temperature gauge reported an operating temperature of ca. 820° C. An experiment was conducted to determine if the NF₃ DRE would be reduced if the TPU operating temperature was reduced. Temperature reduction was done by reducing the natural gas flow by ca. 10 and 20 %, which yielded operating conditions of 665° C and 480° C, respectively. Under these operating conditions NF₃ was not detected in the TPU effluent suggesting that it may be possible to operate the TPU at lower temperatures if its sole purpose is to abate NF₃. One observed consequence of operating at lower temperatures was an increase in CO and CH₄ emissions from the TPU relative to those observed at 820° C. Figure 14 shows CO and CH₄ increased emissions while the temperature was reduced.

Another by-product observed during NF₃ abatement was nitric oxide (NO). Figure 15 shows NO emission profile during testing. NO emissions are correlated with NF₃ flows from the tool.

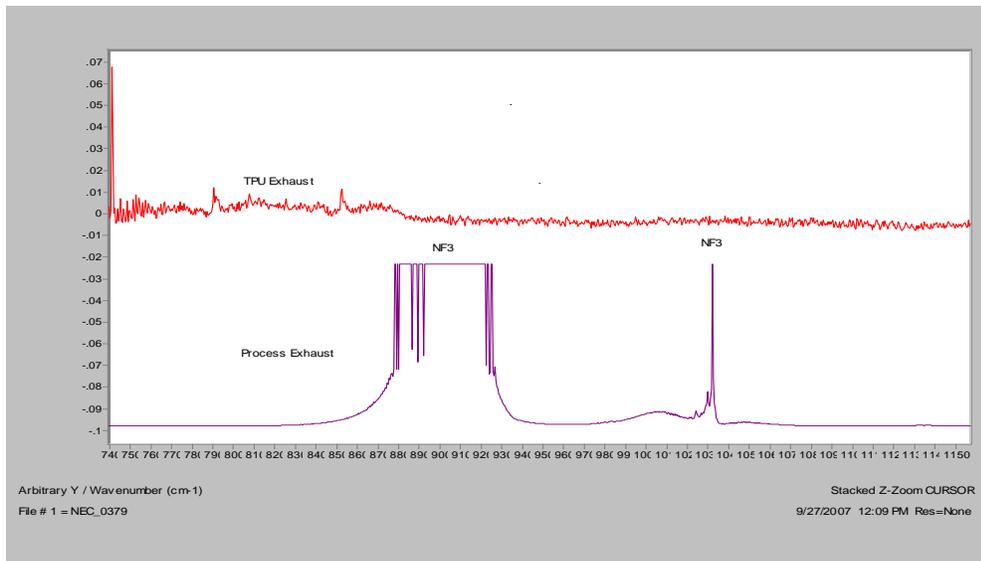


Figure 13: FTIR spectra of TPU exhaust (top) and CVD Tool #2 process exhaust (bottom) while 1.5 slm NF₃ was flowing through the chamber. NF₃ emissions from TPU were below the detection limit of the FTIR (0.5 ppmv). The process emissions were ca. 94,000 ppmv.

4.0 Conclusion

The purpose of this study was to accurately determine the DRE of F-GHGs in two commercially available POU abatement systems used in semiconductor manufacturing. A critical component of an accurate DRE was to determine the dilution of process effluent occurring in the scrubbers. Chemical spiking of inert gases was used to determine the dilution. Kr and Xe were used for the TecHarmonic E-HTVS scrubber. It was determined that both Xe and Kr yielded statistically equivalent effective dilution for the E-HTVS. Kr, Ar and Xe were used to determine the effective dilution occurring in the Edwards TPU scrubber. All three chemicals yielded similar results. The effective dilution for each system was combined with the process emission data to determine the DRE of each scrubber for F-GHGs C_2F_6 and CF_4 on the E-HTVS and for NF_3 on the TPU.

The DRE determined for C_2F_6 and CF_4 on the E-HTVS were very low. The results indicate a statistically zero DRE was obtained for both C_2F_6 and CF_4 on the E-HTVS.

The TPU was determined to have a very high DRE, > 99.9%, for NF_3 when accounting for the dilution occurring in the scrubber. The data also demonstrated that the TPU can be operated at lower temperatures while maintaining a high DRE for NF_3 . While other process and operating parameters may need to be considered before reducing the temperature, it could be possible to operate at lower natural gas flows and maintain a high NF_3 DRE.

The process DRE for C_2F_6 during tungsten chamber clean was determined to be 35 - 38 %, which was in close agreement with the 2006 IPCC reported value of 40 %. A CF_4 emission factor of 13 – 17 % was determined, which was also in close agreement to the 2006 IPCC reported value of 20 %.

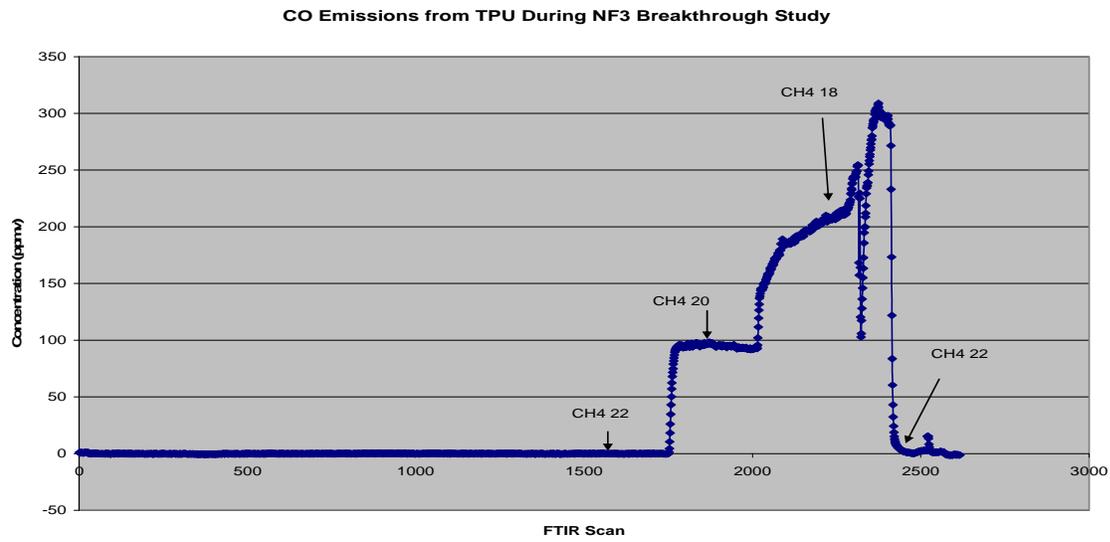
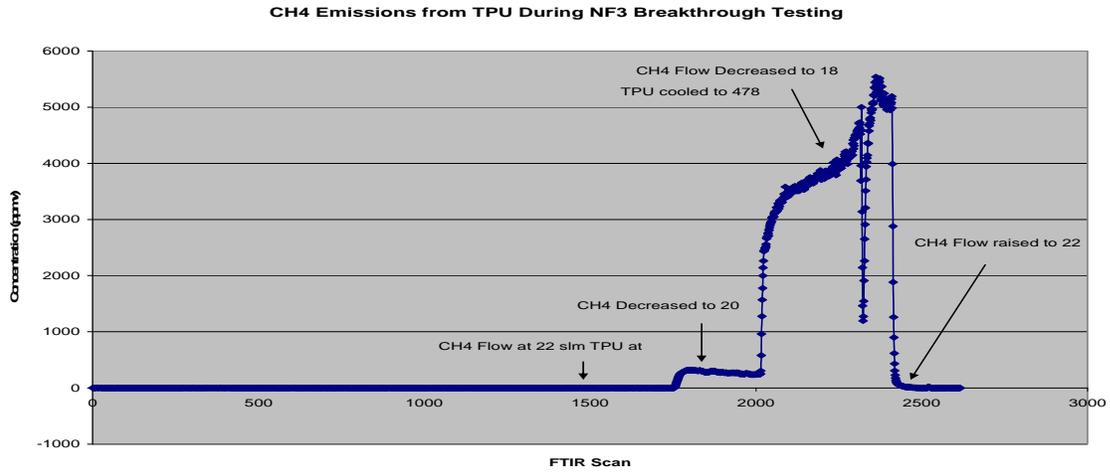


Figure 14: Relative CH₄ and CO emissions from TPU during reduced temperature operation. The temperature was reduced by lowering the CH₄ flow into the system.

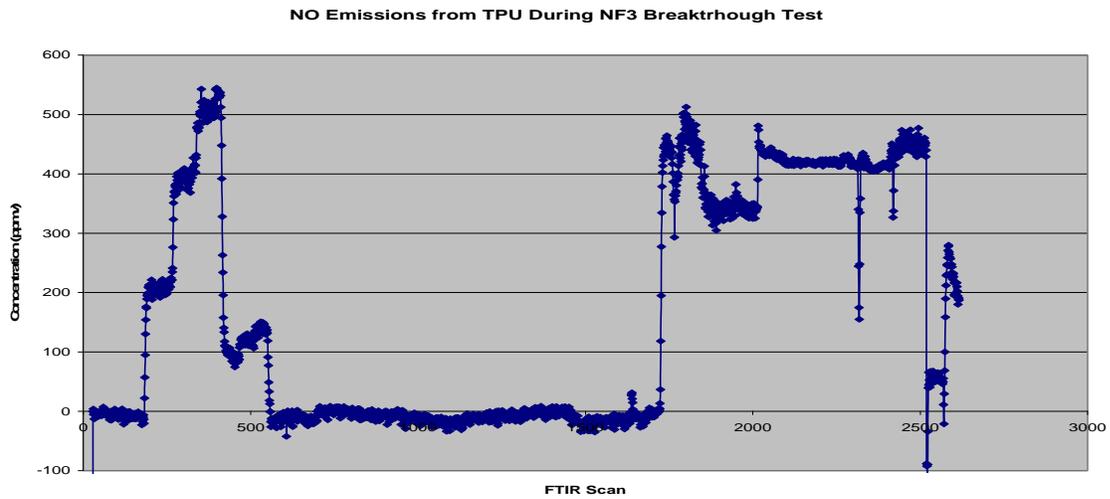


Figure 15: Nitric oxide emission profile during NF₃ flows from CVD Tool #2 chamber through the TPU. NO emissions are correlated with NF₃ flow rate