

**Developing a Reliable Fluorinated Greenhouse Gas (F-GHG)
Destruction or Removal Efficiency (DRE) Measurement Method for
Electronics Manufacturing: A Cooperative Evaluation with IBM**
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Abbreviations

BE	Back End
DRE	Destruction or Removal Efficiency
CF ₄	Carbon Tetrafluoride
FE	Front End
FTIR	Fourier Transform Infrared
Kr	Krypton
MFC	Mass Flow Controller
NDIR	Non-Dispersive Infrared
NF ₃	Nitrogen Trifluoride
PFC	Perfluorocarbon
PPMV	Parts per million
POU	Point of Use
QMS	Quadrupole Mass Spectrometer
SCCM	cm ³ /min
SF ₆	Sulfur Hexafluoride
SL	Standard Liter
SLM	Standard Liters per Minute
TPU	Thermal Processing Unit

1. Introduction

In 2007, U.S Environmental Protection Agency (EPA) initiated measurements of the Destruction or Removal Efficiency (DRE) of perfluorocarbons (PFC), sulfur hexafluoride (SF_6) and nitrogen trifluoride (NF_3) by Point of Use (POU) abatement systems or scrubbers during semiconductor processing. EPA funded this work in support of the PFC Reduction/Climate Partnership for the Semiconductor Industry and to inform the development of a protocol for measuring DREs of PFCs, SF_6 , and NF_3 . The work presented in this report builds on DRE protocol-development work conducted at two other North American integrated device manufacturing sites in 2007 as well as comments EPA received during review of an initial draft of the DRE measurement protocol.

For the work reported here, testing was conducted at IBM's East Fishkill, New York 300-mm wafer facility on 1 – 5 December, 2008. The tests were performed on two multi-chamber etch process tools. The etch chemistries employed carbon tetrafluoride (CF_4) and sulfur hexafluoride (SF_6), which represent two of the more problematic etchants to abate. One process tool, FE05, enabled a front end (FE) polysilicon etch process with a nitride break through step. The second process tool, FK15, enabled a back end (BE) dielectric etch for dual damascene Cu patterning. Testing was performed during normal multi-chamber wafer processing.

The output of each tool was fed into a POU scrubber. Each etch tool had four chambers feeding the single scrubber. Different experimental configurations, data collection and data reduction methods were tested to identify differences, if any, on the scrubber DRE measurement. In addition, CF_4 scrubber effluents were monitored with a Non-Dispersive Infrared (NDIR) device.

The scrubbers were thermal/wet systems, each containing a natural-gas-fired combustion chamber followed by a post combustion water scrubber. No adjustments were made to the scrubbers and they were tested under normal operating conditions. One scrubber had recently completed its scheduled preventative maintenance.

An essential feature of the protocol under development is the use of a chemical tracer or spiking approach to measure the total scrubber flow, which accounts for the total dilution across the scrubber. Previous tests have demonstrated the efficacy of krypton (Kr) as a spiking agent. Using other spiking agents, such as CF_4 , may require disabling the combustion chamber, which undesirably releases CF_4 directly to the atmosphere.

The analytical equipment deployed to determine DRE values included a Quadrupole Mass Spectrometer (QMS), which was used to monitor Kr emitted by the scrubber after its addition as a tracer at the inlet to the scrubber. Two Fourier Transform Infrared (FTIR) spectrometers were used to monitor process and scrubber emissions. In addition, an (NDIR) detector was deployed to monitor CF_4 emissions from the scrubber.

The report describes two methods for measuring etchant scrubber DRE for the tool/recipe combinations. The first (Method 1) measures scrubber DRE with process plasma off (no wafer

processing), but with etchant gas flowing through the tool. The second method, which may be approached in two ways, measures etchant DRE during actual, multi-wafer processing, typically greater than five wafers. The first of these two approaches (Method 2a), sequentially measures etchant PFC volumes for each chamber while simultaneously measuring the corresponding etchant volumes exiting the scrubber from all chambers. The second approach (Method 2b) measures scrubber effluent etchant volumes while simultaneously extracting a slip-stream of process gases from each chamber, which are then combined and the total etchant volume flow is measured prior to entering the scrubber.¹ The results of all three methods are presented and compared.

This report begins by describing the experimental procedures used during the testing, which is followed by a description of key data necessary for calculating the DREs including the process dilution, scrubber dilution, and process and scrubber emissions during wafer processing. This report then presents and compares results and discussion regarding Method 1, Method 2a, and Method 2b, as well as results from a multiple inlet experiment. This report also presents a comparison of emission profiles for data collected by FTIR and NDIR. This report ends with a summary of methods and results and conclusions based on the testing and results.

2. Experimental Procedures

Sampling was conducted by monitoring process and scrubber emissions simultaneously. Scrubber dilution was determined through the use of 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). The experimental configuration for Methods 1 and 2a is shown in Figure 1 and the two methods are described here. The configuration for Method 2b (the multiple-chamber method) is described in section 3.3 (cf. Figure 11).

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 detectors. The FTIR that measured pre-scrubbed gas concentrations was equipped with a 10 cm path length single pass gas cell. The FTIR used to measure scrubber effluent concentrations was equipped with a 5.6 m path length multi pass gas cell. Both FTIRs were operated at 0.5cm^{-1} resolution. Four scans were co-added for each data point yielding a sampling frequency of 2.2 seconds. Calibration curves for CF_4 , SF_6 and other perfluorinated compounds were developed at Air Products laboratories located in Allentown PA.

A UTI 2221 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 two second sampling frequency was used for each data point. To account for

¹ This sampling approach was implemented following the suggestion of a reviewer of the first draft of the DRE Protocol and an assessment that mixing the gas streams from the different etch chambers during the planned testing posed no safety risks.

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 N_2 .

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 sample 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.

A CS Clean Systems NDIR model CIP1281 was used to monitor CF_4 emissions from the scrubbers. The system used an external sample pump to extract gas through the gas cell. Data were collected and recorded at 1 Hz. CF_4 concentrations were reported as whole number values. The sample configuration of the NDIR sampling is also shown in Figure 1. Sample gas was extracted through 0.25" o.d. PFT tubing. A pre-filter supplied by the vendor was deployed to remove any HF emitted by the scrubber.

The QMS was calibrated to determine its response to Kr on site using a dynamic dilution blending system. Test atmospheres containing Kr were created by blending a calibration standard containing 1% Kr with N_2 diluent. These calibration standards are specified with an accuracy of $\pm 5\%$ or better. Figure 2 shows the QMS response to ^{84}Kr during calibration and the calibration curve resulting from a regression analysis of these data. The calibration curve, which showed a small non-zero, positive intercept, was used for the tests on both tools. These data were used to quantify Kr emissions from the scrubber.

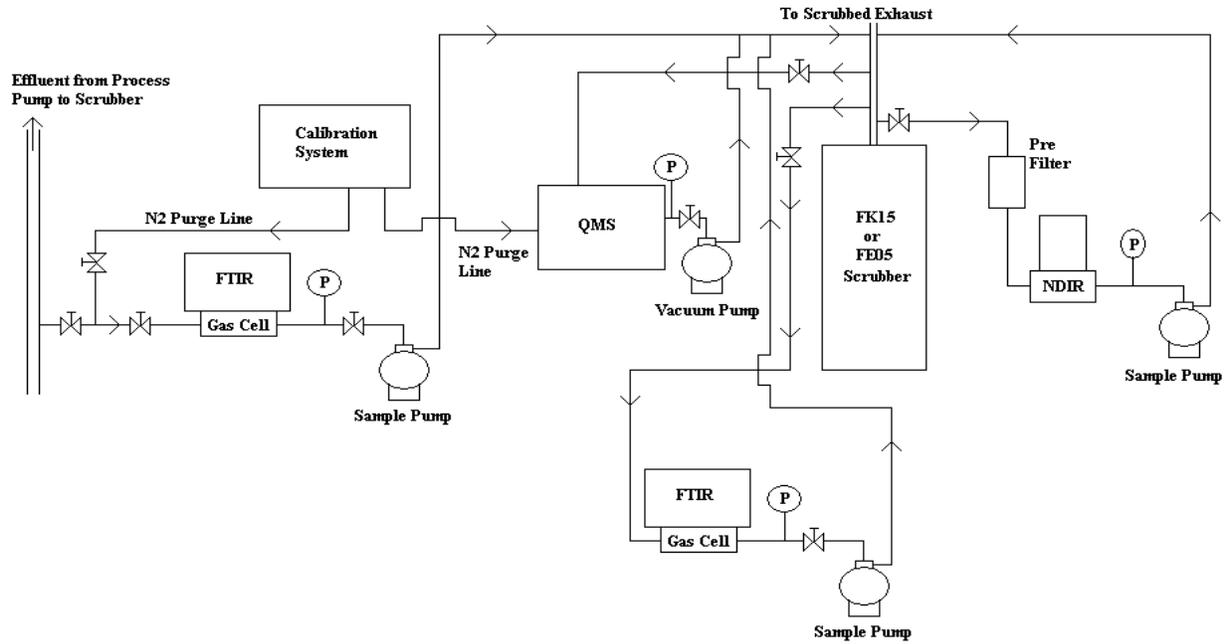


Figure 1: Sampling scheme used to monitor process and scrubber emissions on FK15 and FE05.

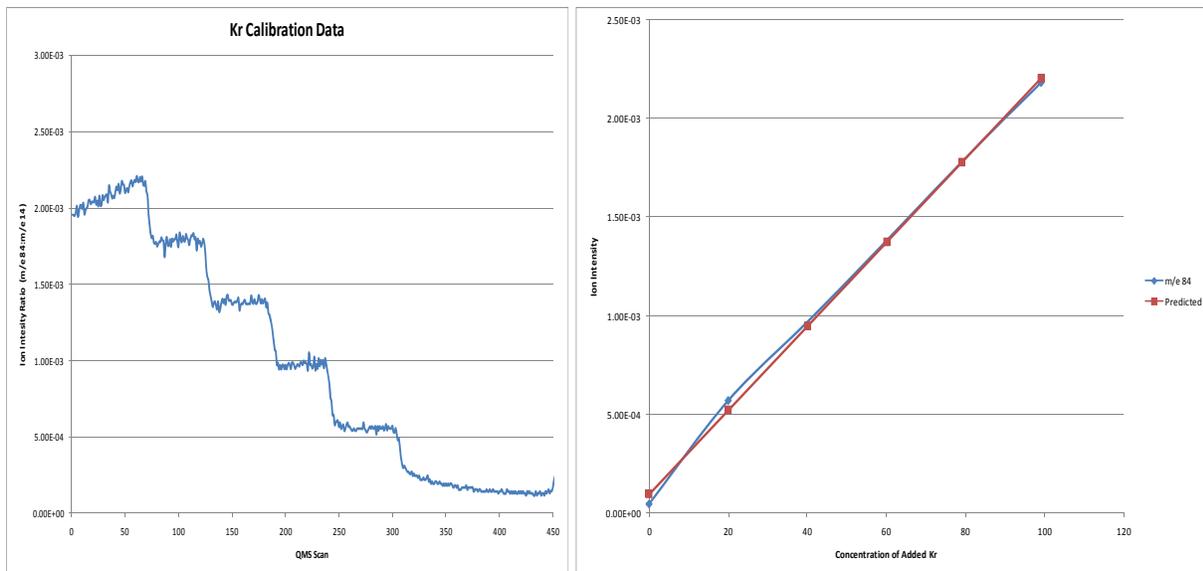


Figure 2: Calibration of QMS response to Kr in nitrogen (right) using the ratio of $^{84}\text{Kr}^+/\text{N}^+$. Regression analysis plot is shown on the left.

3. Results and Discussion

This section presents the results for measuring process dilution and scrubber dilution as well as measurements of etchant specific DREs. First, etchant-specific DREs are presented without wafer processing for each etching tool. Then, etchant-specific DREs are presented that were measured during normal wafer processing. Finally, DREs are provided for the sequential single-chamber method for FK15 and FE05 etch tools and for the simultaneous multi-chamber method for FK15. Time constraints limited testing the simultaneous multi-chamber method to only FK15.

3.1 Process Dilution

Process dilution is defined as the dilution of a process gas or by-product that occurs in the process chamber and at the process vacuum pump resulting from the addition of N₂. This dilution is experimentally measured by flowing process gas through the chamber with the RF power turned off. The dilution is calculated from the measured concentration and known flow rate. These data are used to integrate process emissions during wafer processing and to measure dilution occurring across the scrubber.

The dilution of each chamber on FK15 and FE05 was determined using CF₄ flows. Figure 3 shows the process emission profile for each chamber on FK15. The concentrations were used to calculate total flows through the exhaust from each of the four process chambers and process pump purge. Those flows are provided in Table I. Also included in Table I are results for the same experiment conducted on FE05. After completing chamber 4 flows, all 4 chambers were set to 200 sccm to provide the highest CF₄ flow challenge possible with the Mass Flow Controllers (MFCs) on FK15

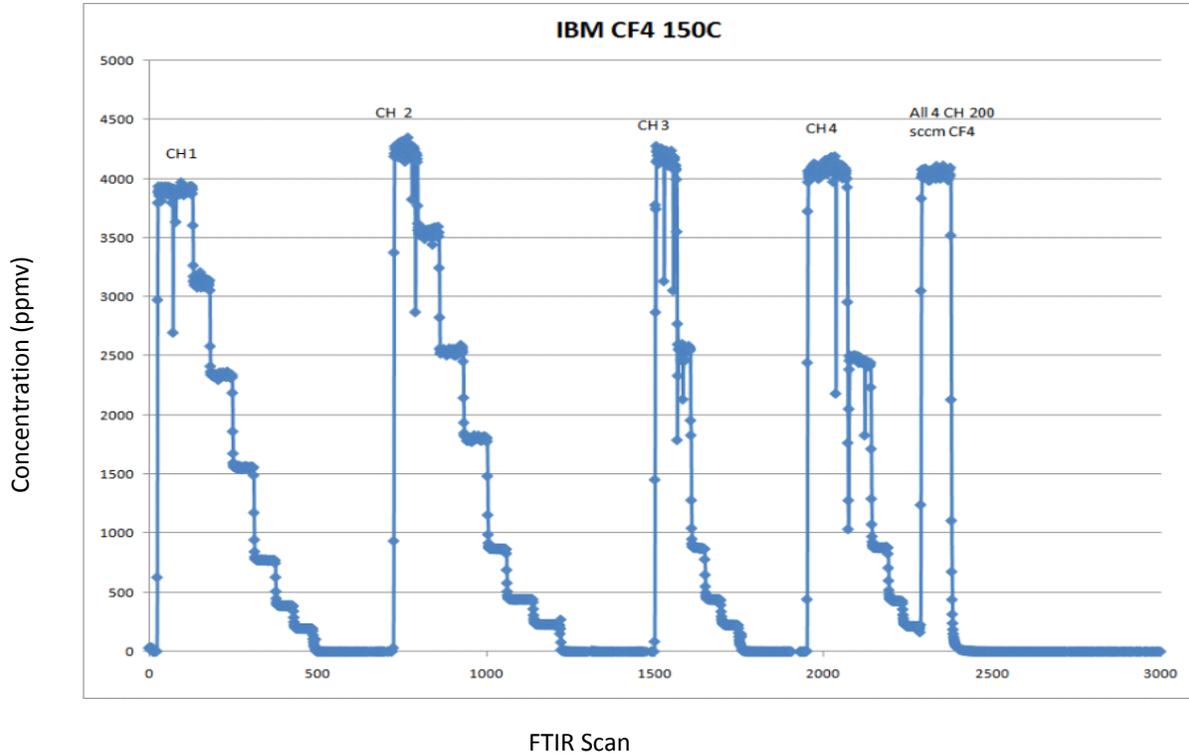


Figure 3: CF₄ emission profile from FK15 during flow calibrations on chambers 1 – 4.

Table I: Process dilution flow determined for chambers 1-4 on FK15 and FE05

FK15 Chamber	Total Flow (slm)	FE05 Chamber	Total Flow (slm)
1	52.3	1	47.3
2	45.0	2	54.0
3	45.5	3	52.7
4	47.3	4	48.5

3.2 Scrubber Dilution

There are several installation-specific sources of scrubber dilution, which, while individually identifiable, are difficult to measure reliably under fab conditions. Dilution can occur from 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 for measuring dilution in these tests was to observe the effective dilution that occurred when a known flow of an inert (spiking) chemical—the analyte—was added to the gas stream entering the scrubber. The measured concentration of the inert analyte, C_{an} , leaving the scrubber provides the means to calculate the total scrubber flow, TF. A total flow from the scrubber can be calculated from the measured concentration and the controlled spike-gas flow rate, S_f , added to the process exhaust duct:

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

Where: the spike gas flow (S_f) is in liters, and the analyte concentration (C_{an}) is in ppmv.

The experiment conducted to determine dilution for the scrubbers on FE05 and FK15 consisted of using the calibration system, shown in Figure 1, to add calibration gas into the process effluent through the FTIR sample line where process effluent was monitored. While calibration gas was being added, the QMS was sampling the scrubber effluent. The flow of calibration gas was controlled with two 0 – 5 slm Mass Flow Controllers (MFC) that were calibrated for nitrogen. Different flow rates were added to the scrubbers. The concentration profile for ^{84}Kr determined from QMS data during spiking is shown in Figure 4 for FE05. From these data total flow data were calculated for each flow rate using Equation 1 and are shown in Table II below. From these data a total flow of 850 ± 3 (95 percent confidence interval)² slm was determined and used subsequently in all DRE calculations.

Table II: Kr spiking results for POU System on FE05: Total flows calculated using Equation 1

Total Calibrated Gas Flow (slm)	^{84}Kr Concentration (ppmv)	Total Flow through Thermal Processing Unit (TPU) (sl)
8.34	98 ± 3	851
6.65	79 ± 2	841
4.98	59 ± 1	844
3.33	39 ± 1	853
1.67	20 ± 1	835
1.00	11 ± 1	909
0.70	8 ± 1	850

² The mean value and confidence interval was estimated using the method of variance, which explains why the figure 850 slm is not the simple mean of the figures given in Table II.

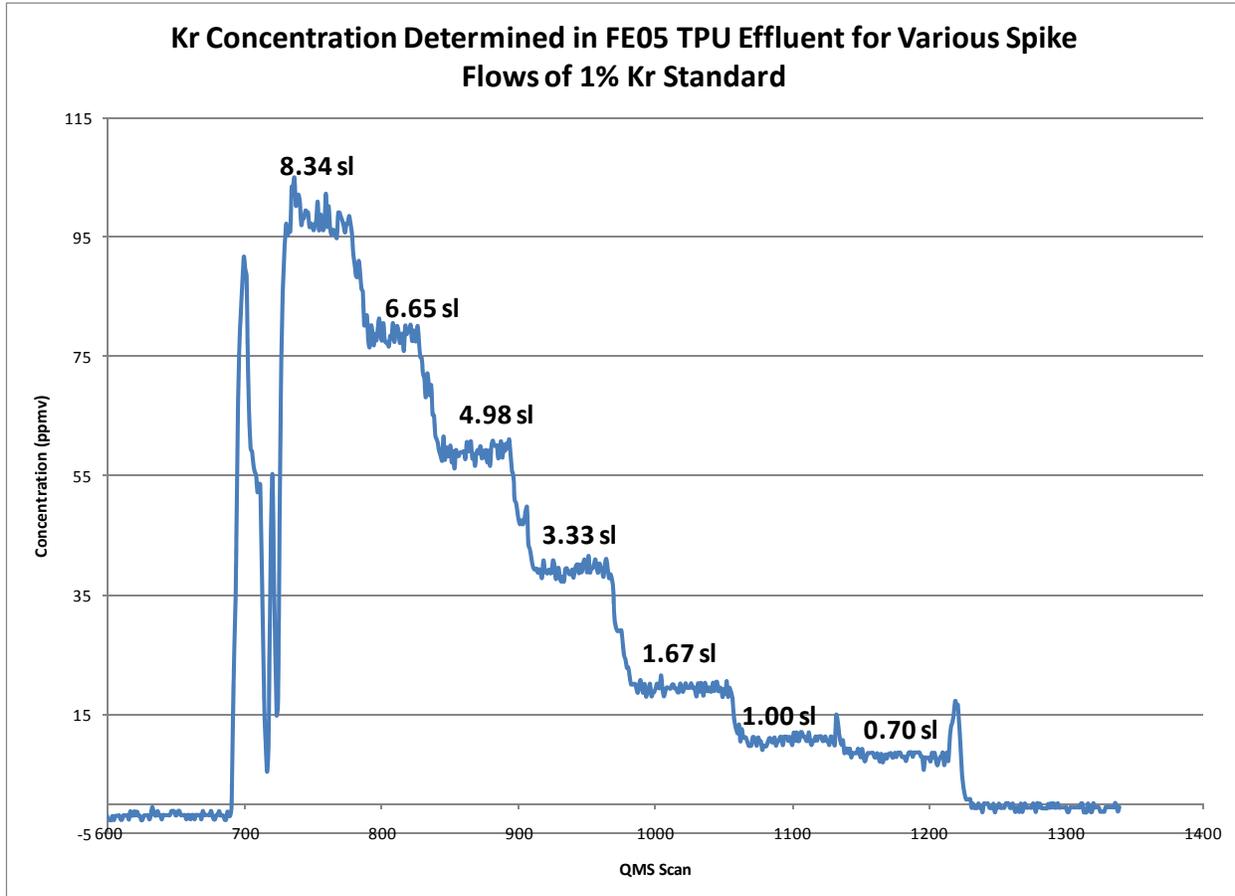


Figure 4: Concentration profile determined for Kr spiking of POU abatement system on FE05.

A similar experiment on FK15 yielded a total flow of 780 ± 3 (95 percent confidence interval) slm. Data for this flow determination are shown in Table III.³ This total flow was used for all subsequent DRE calculations.

Table III: Kr spiking results for POU System on FK15: Total flows calculated using Equation 1)

Total Calibration Gas Flow (slm)	⁸⁴Kr Concentration (ppmv)	Total Flow through Thermal Processing Unit (TPU) (sl)
8.34	108 ± 3	772
6.65	87 ± 2	764
4.98	62 ± 2	803
3.33	44 ± 2	757
1.67	21 ± 2	795

³ See footnote 3, p.10 replacing Table II with Table III.

3.2.1 Scrubber DRE While Measuring Process Dilution Determination—No Wafer Processing

While measuring process dilution, scrubber PFC abatement performance may also be measured. These measurements permit DRE measurements on each of the four chambers for each etchant. However, because power to the plasma is turned off during these experiments, the gas mixture entering the scrubber differs from the gas mixture during wafer processing.

Figure 5 shows the CF_4 emission profile from the scrubber on FK15 during the process dilution experiments. The DRE was calculated as one minus the ratio of average CF_4 inlet concentration to the corresponding dilution adjusted scrubber (emission) concentration. DREs and dilution factors for CF_4 for each one of the four chambers and each tool are provided in Table IV. Results for SF_6 , which was used on FE05, are also provided in Table IV. Note that chamber-specific dilution factors varied by as much as 13 percent for FK15 and FE05 (17 percent for chambers 2 or 3 for FK15 vs. 15 percent for chamber 1.) It is also interesting to note that when all four chambers were flowing maximum CF_4 flows of 200 sccm each, an increase in DRE was observed relative to when CF_4 was flowed through the individual chambers. This effect was more pronounced for the scrubber on FK15 than for the scrubber on FE05.

Other PFCs evaluated during the process dilution flow testing on FK15 included CHF_3 , CH_2F_2 and CH_3F . CH_2F_2 and CH_3F were not detected in the scrubber effluent. A low concentration of CHF_3 was detected in the scrubber effluent of FK15 during CHF_3 flows through the tool and scrubber. The CHF_3 DRE was determined to be greater than 99 percent based on detecting 0.5 ppmv CHF_3 when flowing 100 sccm through chamber 2.

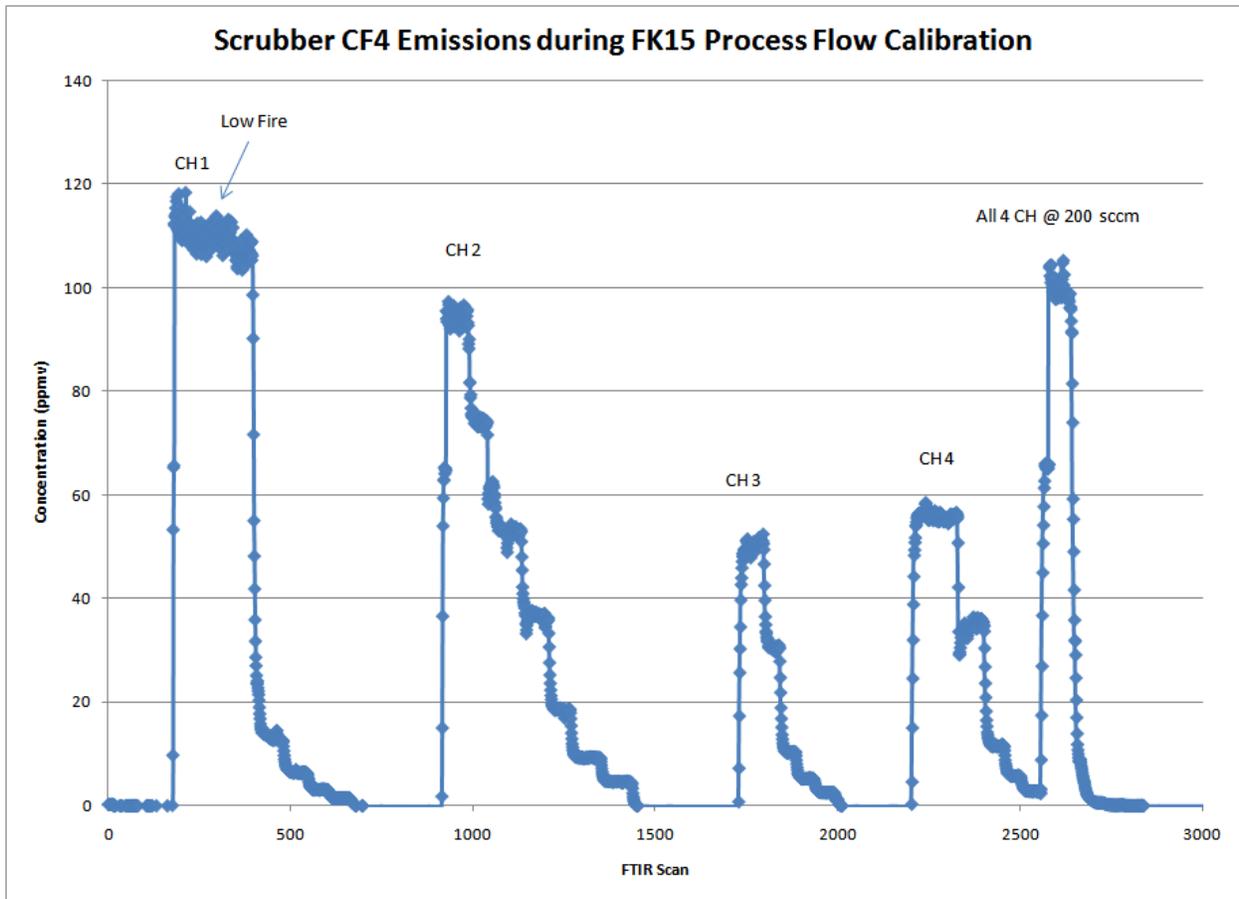


Figure 5: CF₄ emissions from scrubber on FK15 during process flow calibration experiments. The initial high CF₄ concentration observed on chamber 1 was attributed to the scrubber being in low fire mode.

Table IV: Scrubber DRE values for CF₄ and SF₆ during process flow calibrations on chambers 1-4 of each etch tool. SF₆ was only available on FE05.

<u>Tool: Chamber</u>	<u>Dilution Factor</u>	<u>CF₄ DRE</u>	<u>SF₆ DRE</u>
FK15 #1	14.9	87.5 %	Na
FK15 #2	17.3	63.1 %	Na
FK15 #3	17.2	79.4 %	Na
FK15 #4	16.5	77.4 %	Na
All 4 Chambers	4.1	89.3 %	Na
FE05 #1	18.0	84.5 %	99.0 %
FE05#2	15.7	82.2 %	98.9 %
FE05 #3	16.1	91.7 %	99.0 %
FE05 #4	17.5	96.0 %	99.0 %
All 4 Chambers	4.2	92.7 %	Na

3.2.2 Etch Process Emissions and Scrubber DRE Measurements during Wafer Processing

In this section, measurements of DRE during actual wafer processing are presented for FK15 and then FE05. For FK15, measured (integrated) CF₄ emission volumes are provided during wafer processing for each etch process, each chamber, each wafer (and averaged over all wafers) together with the corresponding measured (integrated) scrubber emissions of CF₄. Using these measurements DREs for CF₄ are calculated. For FE05, the same procedure was followed for both CF₄ and SF₆ measurements and the average DRE over all wafers are provided for CF₄ and SF₆. Process and scrubber dilutions are reflected in the reported CF₄ and SF₆ gas volumes.

Process emissions on etch tool FK15 were monitored and emission volumes were determined for CF₄ process gases and by-products. Effluent was monitored on chambers 1 and 3; these were the chambers operating during production. CF₄ emission volumes were determined per wafer for two etch processes, trench and via etch, on each chamber. Figure 6 shows the CF₄ emission profile observed for the monitored Back End (BE) trench etch for several wafers monitored on each chamber. Integration of the CF₄ emission peaks yielded volumes contained in Table V. The emission volumes from each chamber were similar (0.184 sl vs. 0.186 sl).

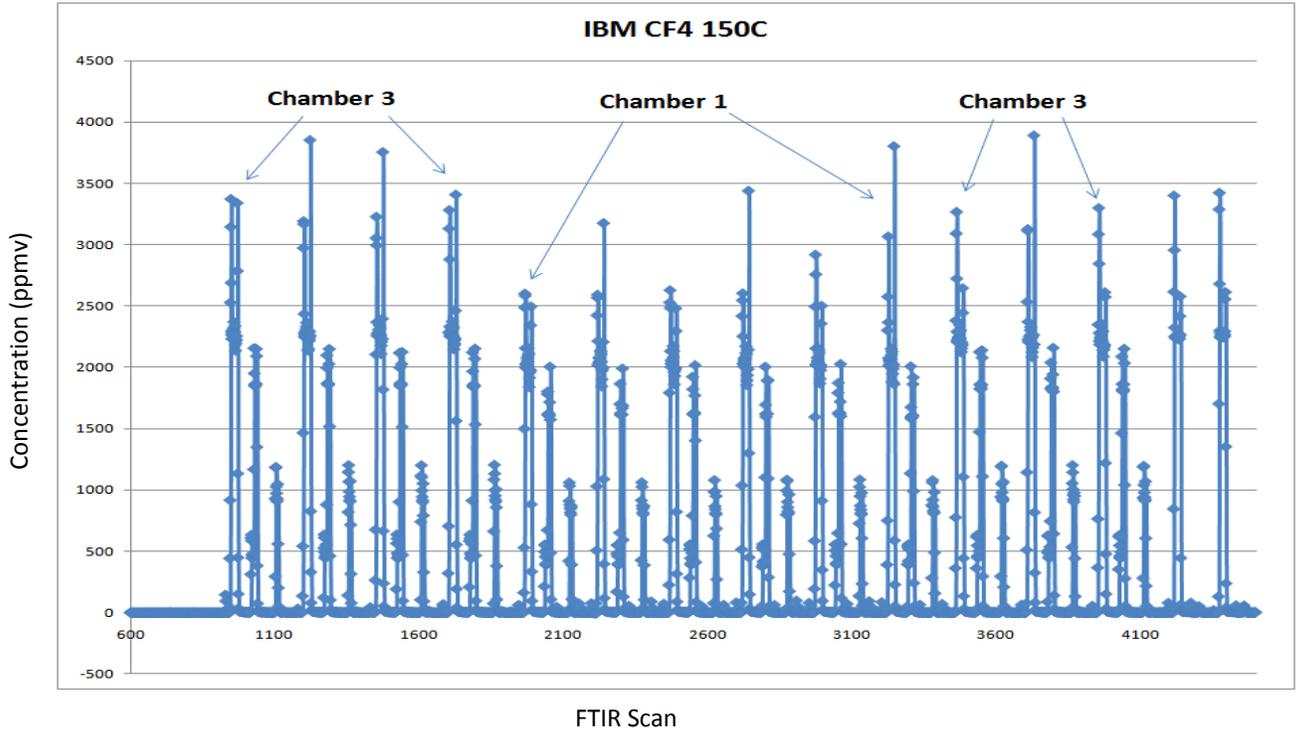


Figure 6: CF₄ emission profile observed for a back end trench etch process on FK15

Table V: Integrated CF₄ emissions from trench etch process run on FK15

Trench Etch Chamber 1	Integrated CF ₄ Emissions (sl)	Trench Etch Chamber 3	Integrated CF ₄ Emissions (sl)
Wafer 1	0.181	Wafer 1	0.188
2	0.183	2	0.188
3	0.183	3	0.188
4	0.185	4	0.187
5	0.185	5	0.182
6	0.187	6	0.184
Ave	0.184	Ave	0.186

A second etch process, a BE via etch, was also monitored on Chambers 1 and 3. The CF₄ emission profile for this process is shown in Figure 7. From these data integrated emissions were determined for chambers 1 and 3, and are shown in Table VI. A difference of 5 % in CF₄ emission volume was observed between the chambers.

Table VI: Integrated CF₄ emissions from via etch process run on FK15

Via Etch Chamber 1	Integrated CF ₄ Emissions (sl)	Via Etch Chamber 3	Integrated CF ₄ Emissions (sl)
Wafer 1	0.114	1	0.107
2	0.115	2	0.109
3	0.112	3	0.109
4	0.114	4	0.108
5	0.113	5	0.108
Ave	0.114	Ave	0.108

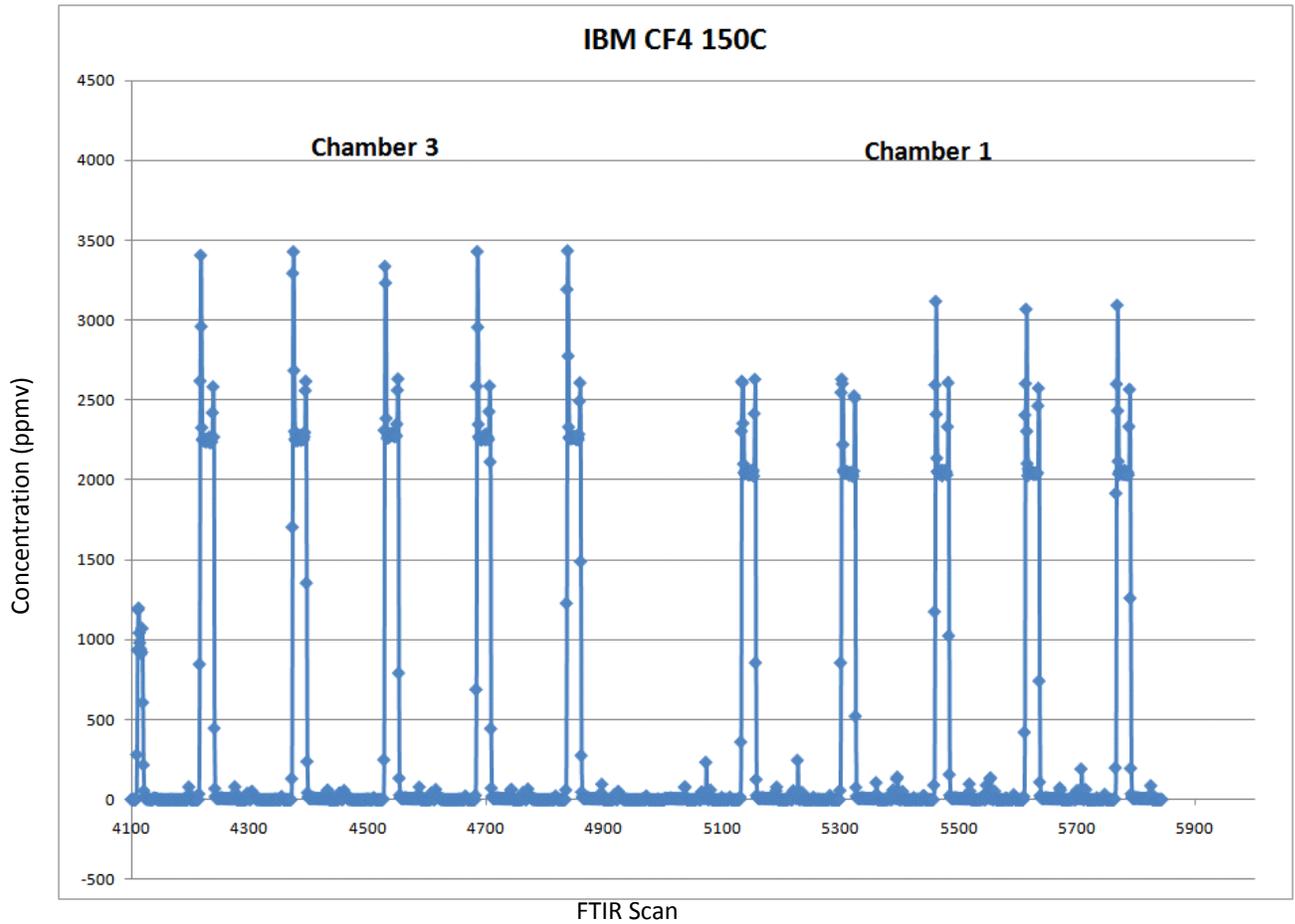
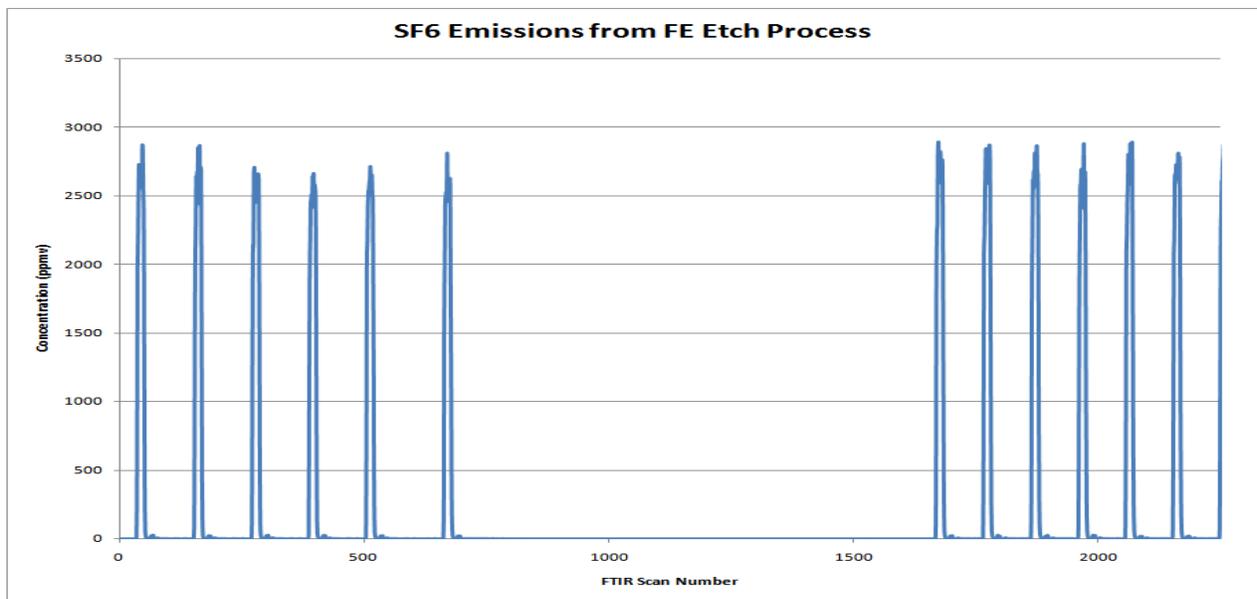
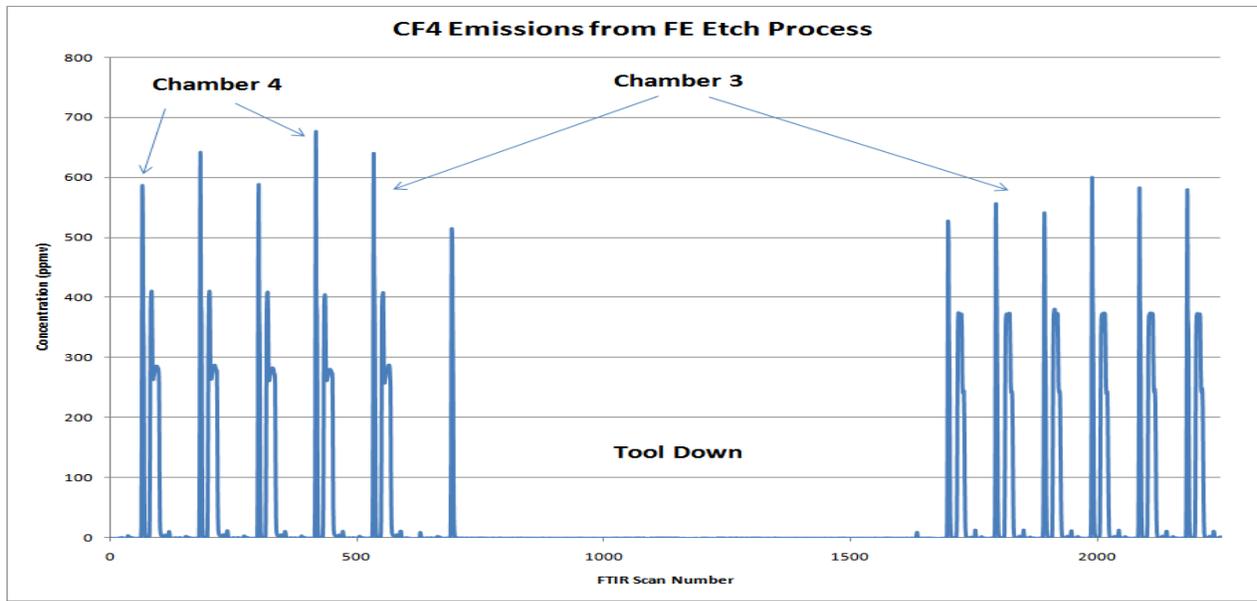


Figure 7: CF₄ emission profile observed during BE Via etch on FK15 chambers 1 & 3.

Process emissions for a Front End (FE) etch were monitored on etch tool FE05 to determine emission volumes for PFC process gases and by-products. Effluents from chambers 3 and 4 were monitored as these were the chambers operating during production. The emission volumes were determined per wafer for a single process on each chamber. Figures 8a-b show the CF₄ and SF₆ emission profiles observed for the etching of several wafers monitored on each chamber. Integration of the CF₄ and SF₆ emissions yielded volumes shown in Table VII. These data were used to calculate CF₄ and SF₆ loading on the scrubber.

Table VII: Integrated CF₄ and SF₆ emissions from FE etch process run on FE05

<u>Chamber 4</u>	CF₄ Emission Volume (sl)	SF₆ Emission Volume (sl)	<u>Chamber 3</u>	CF₄ Emission Volume (sl)	SF₆ Emission Volume (sl)
Wafer 1	0.015	0.077	Wafer 1	0.015	0.081
2	0.016	0.078	2	0.015	0.085
3	0.015	0.078	3	0.015	0.085
4	0.015	0.077	4	0.015	0.085
Ave	0.015	0.078	Ave	0.015	0.085



Figures 8a - b: Emission profiles for CF_4 and SF_6 on Chambers 3 & 4 of FE05.

Table V, Table VI, and Table VII contain data that were used to calculate loading of CF_4 and SF_6 on the scrubbers while simultaneously monitoring the scrubber effluent for CF_4 and SF_6 .

Figures 9a - b show CF_4 emissions from the scrubber on FK15 during the BE trench and via etching. Integration of emissions as indicated by the arrows provided emission volumes from the scrubber for a set number of wafers processed. These volumes were used to calculate the CF_4 DRE for the scrubber during each process. The total volume of CF_4 loading on the scrubber was determined from the product of the total number of wafers monitored and the CF_4 emission volume per wafer. For the trench etch,

0.185 sl CF_4 was emitted from the process per wafer yielding a total loading for 25 wafers of 4.63 sl (= 25 X 0.185). The via etch emitted 0.11 sl CF_4 per wafer yielding a total loading of 2.20 sl for the 20 wafers processed (= 20 X 0.11).

The DRE was calculated from the ratio of CF_4 scrubber emissions to loading volumes. DRE values of 83 percent and 85 percent for the trench and via etch, respectively, were consistent with the average of the CF_4 DRE determined for chambers 1 and 3 during CF_4 process flow calibrations (see Table IV; using CF_4 DREs for chambers 1 and 3 gives an average DRE of 84 percent [= {88 + 79}/2]). In this instance, scrubber performance appears robust over the different gas mixtures entering the scrubber.

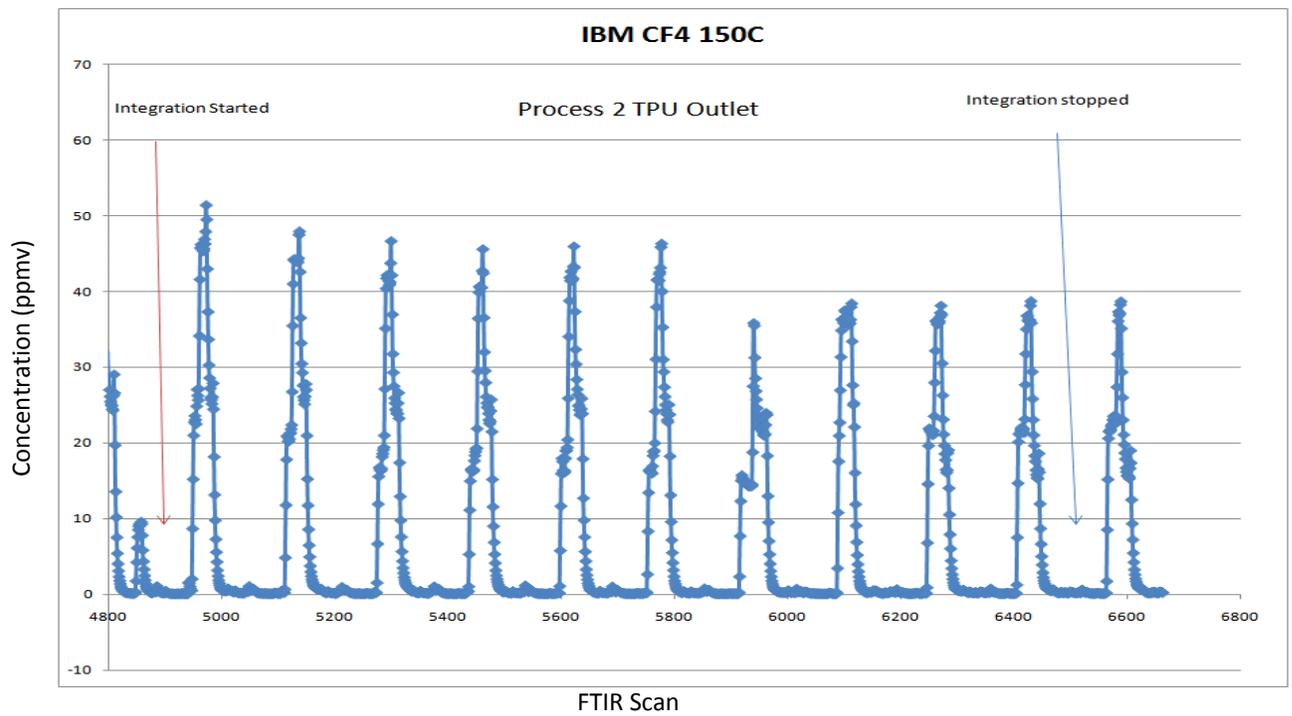
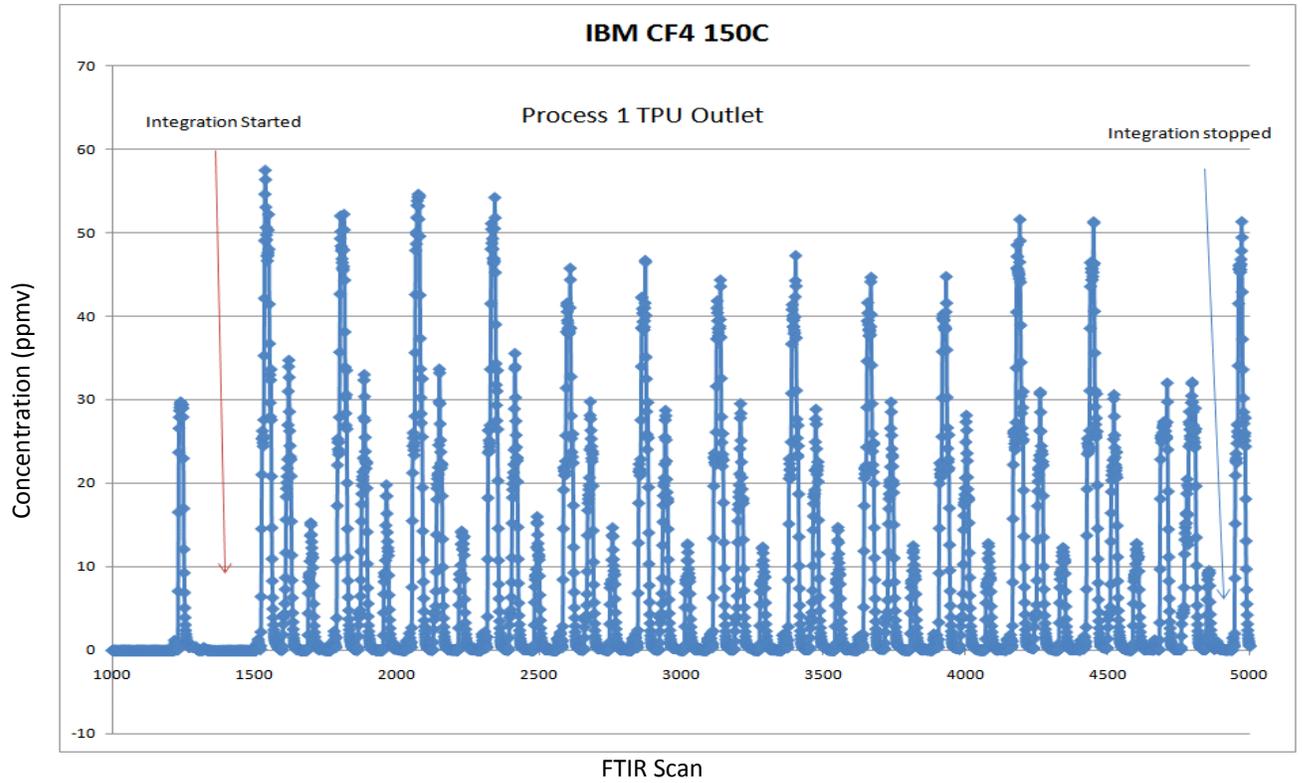
The FE etch process ran on FE05, using chambers 3 and 4, produced CF_4 and SF_6 emissions which were detected in the scrubber effluent. The emission profiles for CF_4 and SF_6 from the scrubber are shown in Figures 10a-b. These emission profiles correspond to the process emissions shown in Figures 8a-b. Scrubber emissions were integrated over 20 wafers and the volumes were divided by the corresponding process emission volumes to determine the CF_4 and SF_6 DRE. These data, presented in Table IX, indicate a CF_4 DRE of 90 percent and an SF_6 DRE of greater than 99 percent. These results are also consistent with the scrubber performance during the process dilution flow experiments when wafers were not being processed. Using a simple average from the process flow experiments for chambers 3 and 4 gives an average DRE of 94 percent (see Table IV for chambers 3 and 4) compared to the 90 percent DRE obtained during actual wafer processing. For SF_6 , the process flow experiments for chambers 3 and 4 gives an average SF_6 DRE of 99 percent (see Table IV, chambers 3 and 4).

Table VIII: Scrubber CF₄ DRE determined for BE trench and via etch on FK15

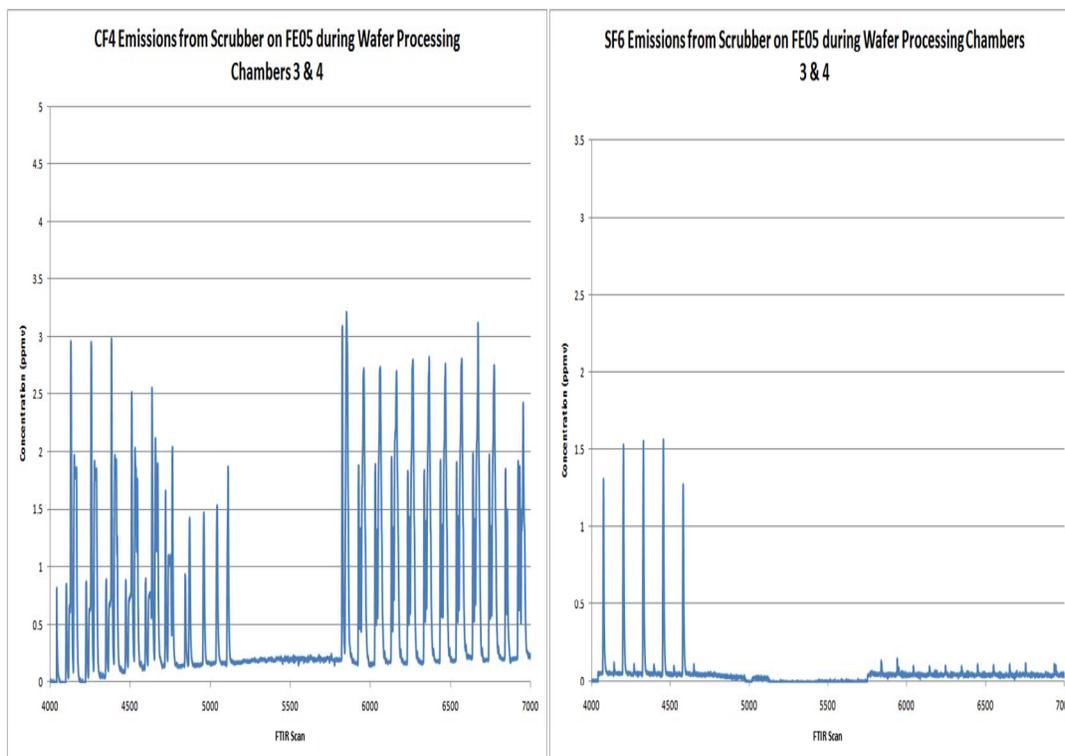
	Total # Wafers Monitored	CF₄ Loading on Scrubber (sl)	CF₄ Scrubber Emissions (sl)	CF₄ DRE (%)
Trench Etch	25	4.63	0.81	83
Via Etch	20	2.20	0.34	85

Table IX: Scrubber CF₄ and SF₆ DRE determined for FE etch on FE05

	Total # Wafers Monitored	CF₄ loading on Scrubber (sl)	CF₄ Scrubber Emissions (sl)	CF₄ DRE (%)	SF₆ loading on Scrubber (sl)	SF₆ Scrubber Emissions (sl)	SF₆ DRE (%)
FE Etch	20	0.300	0.029	90	1.64	0.004	> 99



Figures 9a - b: CF₄ emissions from scrubber during trench etch (top) and via etch



Figures 10a-b: CF_4 and SF_6 emission profiles from scrubber on FE05 during FE etch

3.3 Multiple Inlet Experiment—Simultaneous Multi-chamber Monitoring During Wafer Processing

An experiment was conducted to determine the efficacy of sampling a combined slip stream from each chamber running process on FK15, while simultaneously monitoring the outlet concentration of the scrubber (Method 2b). The purpose of this experiment was to determine if it is possible to get a sample representative of the actual gas composition in the scrubber. The experiment consisted of drawing controlled flows of process emissions from each operating chamber (1 and 3) from FK15, and combining these into a common sample line, which pumps them through the FTIR gas cell. (See Figure 11 for illustration of the experimental set-up used to conduct this experiment.) The Mass Flow Controllers (MFCs) were used to measure the sample flow from each chamber's exhaust. Needle valves were used to control the flow. The ratio of sample flow was set equal to the ratio of process dilution for each chamber. For this experiment, the ratio of process flow for chambers 1 and 3 was 1.15 (52 slm chamber 1, 45 slm chamber 3, cf. Table I). The sample flows were adjusted to 210 sccm and 240 sccm for chambers 1 and 3 respectively. These flows were combined and drawn through the FTIR gas cell using 0.25" unheated Teflon tubing.

Data were collected for several processed wafer lots during testing. The CF_4 process and scrubber emission profiles observed for one lot are shown in

Figures 12a-b. It is evident that the scrubber emission profile was significantly different than the inlet profile observed for the combined streams. It was determined that chamber 2 was running in addition to chambers 1 and 3 during the time these data were collected. Because of the confounding influence of the operation of chamber 2, these data could not be used for measuring CF₄ DRE for FK15.

Figures 13a-b show emission profiles for CF₄ when only chambers 1 and 3 were running process. These emissions were integrated to yield CF₄ loading and scrubber emission volumes. The CF₄ DRE was calculated from the ratio of these integrated volumes. Integration of process emissions from chambers 1 and 3 required using the total flow through both chambers, which was 98 slm. The CF₄ emitted during 16 wafers processed was 0.881 sl. The corresponding CF₄ scrubber volume was 0.133 sl of CF₄ yielding a DRE of 85 percent, which compares favorably to the DREs measured during the process flow experiments (84%, Table IV for chambers 1 and 3) and process emissions experiments (83% and 85% for the trench and via etch processes, respectively).

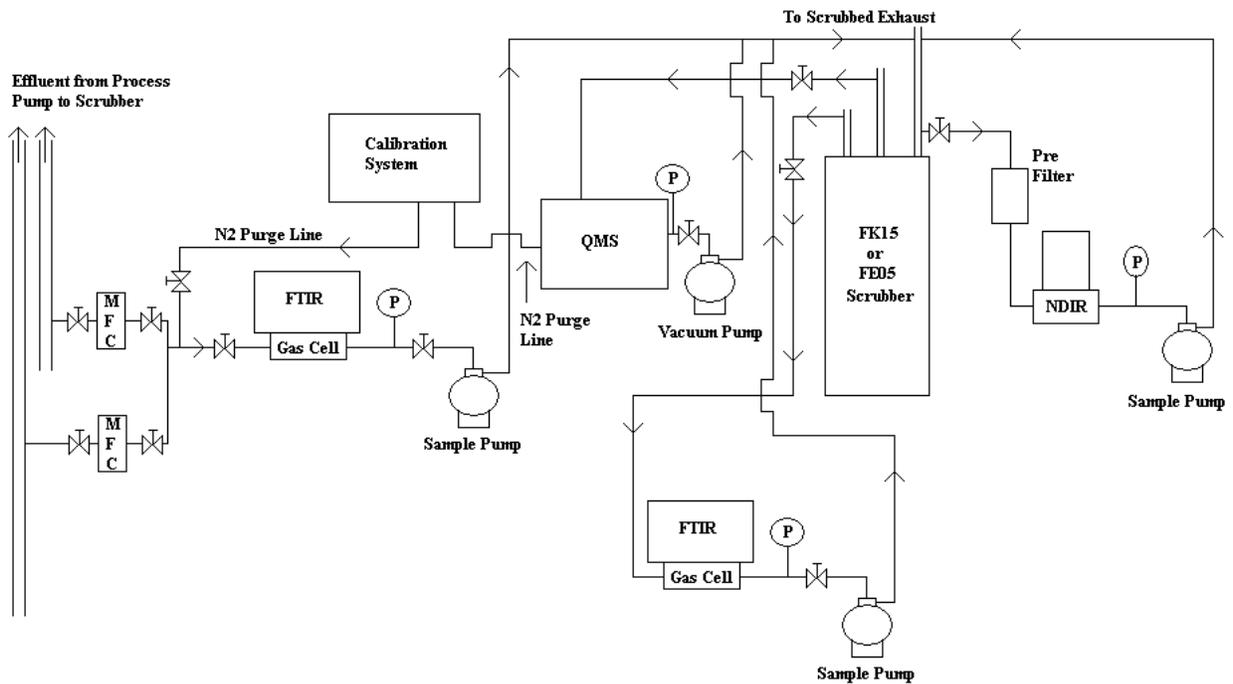
The data shown in Figures 14a-b were averaged in order to compare DRE values obtained from the ratio of dilution corrected emission concentrations with those obtained via emissions integration described in the previous paragraph. Averages may constitute a simpler method for processing concentration data under relatively simple, highly repetitive process and scrubber emissions profiles.

Two methods of averaging were used. The first consisted of averaging just the emission peaks observed in both inlet and outlet profiles, as indicated in Figures 14a-b. The CF₄ DRE obtained via peak-averaging was 87 percent. The second method averaged the CF₄ concentration over the entire collection period from the start of the first peak to the conclusion of the last peak in the emission profiles. This method gave 85 percent. These results indicate that for this process with two chambers running simultaneously it is possible to determine CF₄ DRE using concentration averaging or integrated emission volumes.

Table X: Comparison of CF₄ DRE values obtained for differing methods of data analysis during the multiple inlet experiment

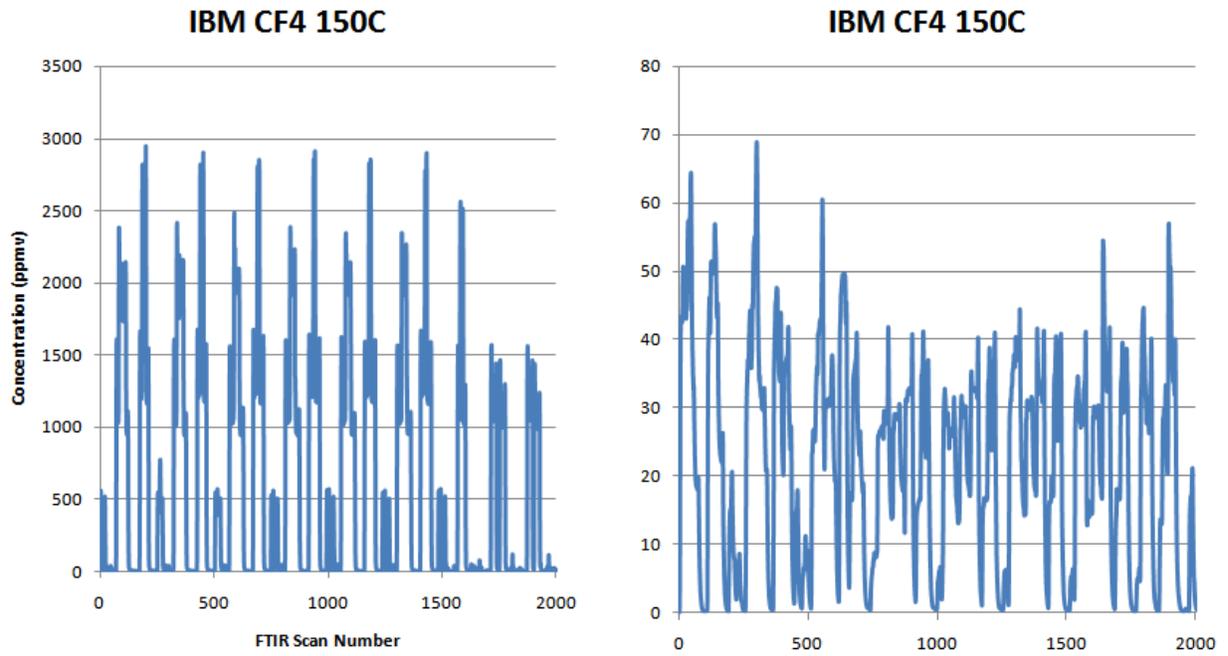
Method	CF₄ In	CF₄ Out	Dilution Adjusted CF₄ Out	CF₄ DRE (%)
Integrated Emissions	0.881 sl	0.133 sl	na	85
Average of Peaks	1094 ppmv	18.3 ppmv	146	87
Average of Emission Profile	381 ppmv	7.3 ppmv	58	85

One important comment about safety is required concerning the multiple sample inlet experiment. In these tests, etch emissions from different chambers were mixed together and pulled through the FTIR gas cell with a metal bellows pump. It was safe, in these tests, to mix effluents from these processes. Other processes, such as CVD processes, should be carefully reviewed prior to executing this type of procedure to ensure that mixing gases at various stages within the process cycle will not lead to an unsafe condition in the sample system. One example would be mixing deposition gas, such as silane, from one chamber with effluent from another chamber being cleaned and containing potentially high levels of molecular fluorine. The incompatibility of these gases could lead to a rapid exothermic reaction, potentially presenting a safety risk.

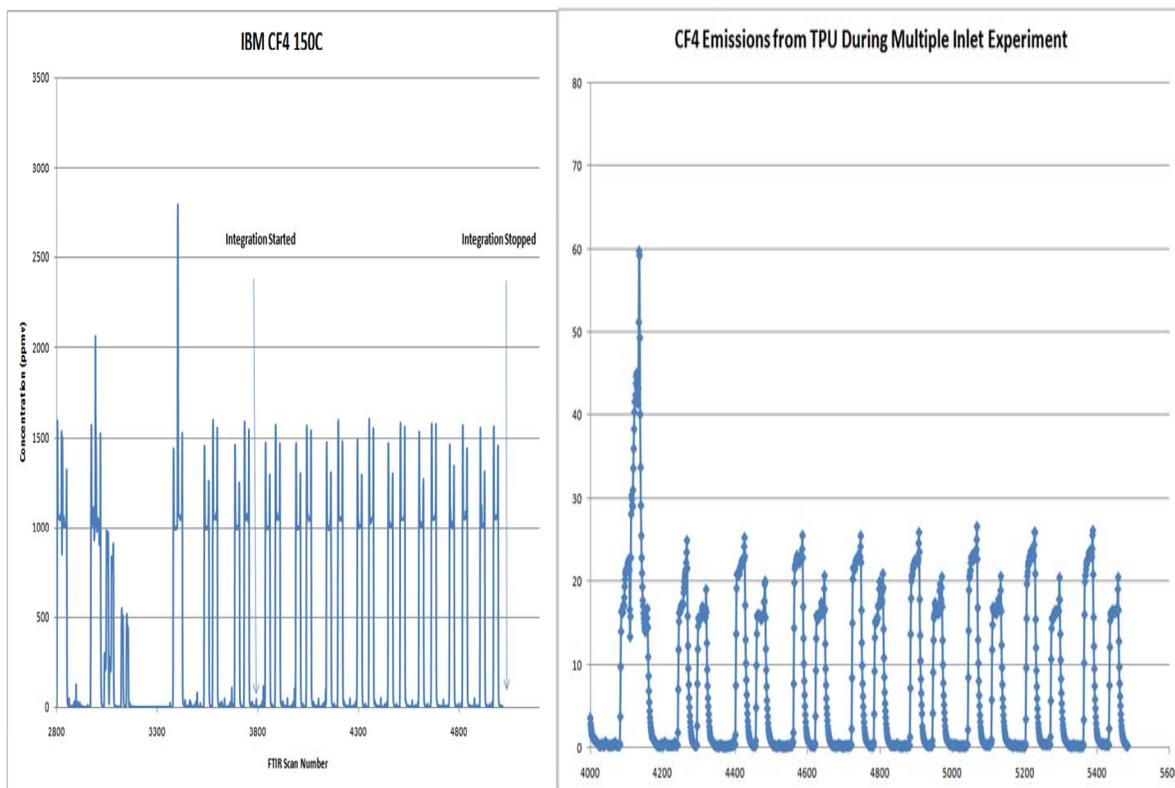


Schematic for effluent analysis during multiple inlet set-up on FK15 tool set for EPA study at IBM

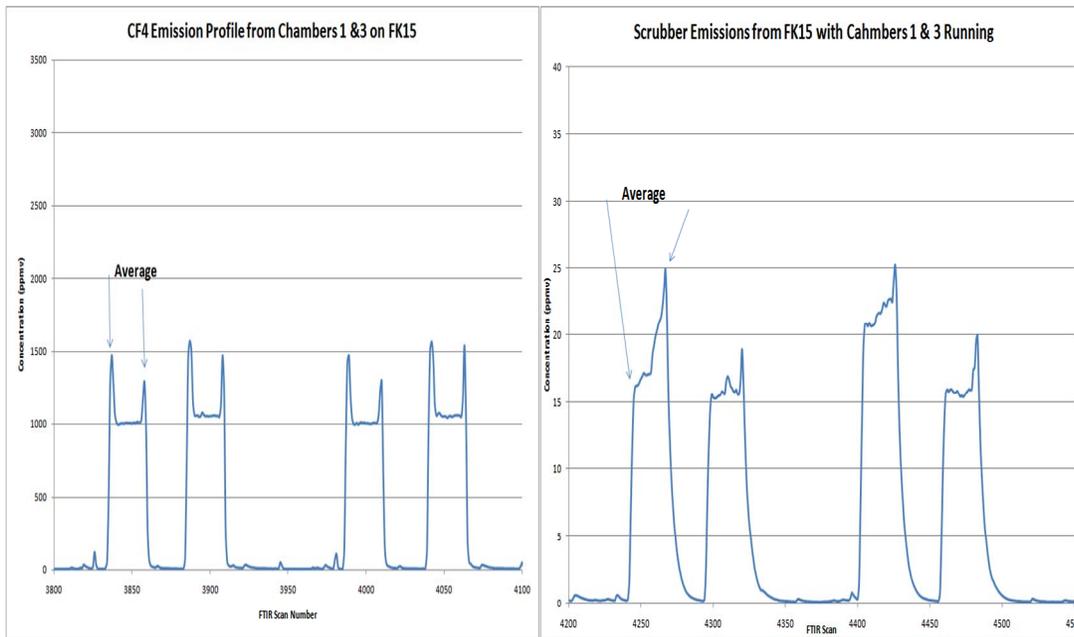
Figure 11: Sampling scheme used to monitor process and scrubber emissions on FK15 during multiple inlet experiment.



Figures 12a - b: CF₄ emission profile for combined effluent of chambers 1 & 3 on FK 15 (left) and scrubber effluent (right). Note: chamber 2 was also processing wafers (see text).



Figures 13a - b: CF₄ emission profile from combined process flows on chambers 1 &3 (left) and from scrubber (right) during wafer processing on FK15. Note: These data were used to determine the scrubber CF₄ DRE.



Figures 14a - b: Expanded view of process and scrubber CF_4 emissions during multiple inlet experiment. Note: Peak concentrations were individually averaged and used to calculate DRE.

3.4 *NDIR-FTIR Comparison*

One objective of these tests was to benchmark the performance of a Non-Dispersive Infrared (NDIR) analyzer for continuously monitoring F-gas scrubber emissions. NDIR is a relatively cost-effective means for continuously monitoring scrubber emissions and performance. It may also indicate, for example, the onset of changing CF_4 destruction which, in turn, may indicate process change(s), need for scrubber repair/maintenance or both. These tests were accomplished by sampling scrubber effluent with FTIR and NDIR simultaneously. Extractive techniques were employed for both instruments and each had a separate sample port as shown in Figure 1. The NDIR was configured to measure only CF_4 concentrations.

3.4.1 **NDIR Data Collected on FK15**

Carbon tetrafluoride concentrations monitored with both FTIR and NDIR from the FK15 scrubber during wafer processing, are shown in Figures 15a-b. Inspection of the concentration profiles for the NDIR (Figure a) and FTIR (Figure b) provides a qualitative indication of close agreement in the measured concentration profiles for the NDIR and FTIR. Note the different scales in Figures 15a and 15b.

A quantitative comparison of the two monitoring systems was accomplished by integrating the NDIR and FTIR profiles over identical periods. The result is the measured total volume of CF_4 emitted over the period of integration for each monitor. The integration was performed during a more complex wafer processing sequence than shown in Figures 15a-b, which shows two peaks of somewhat differing magnitudes.

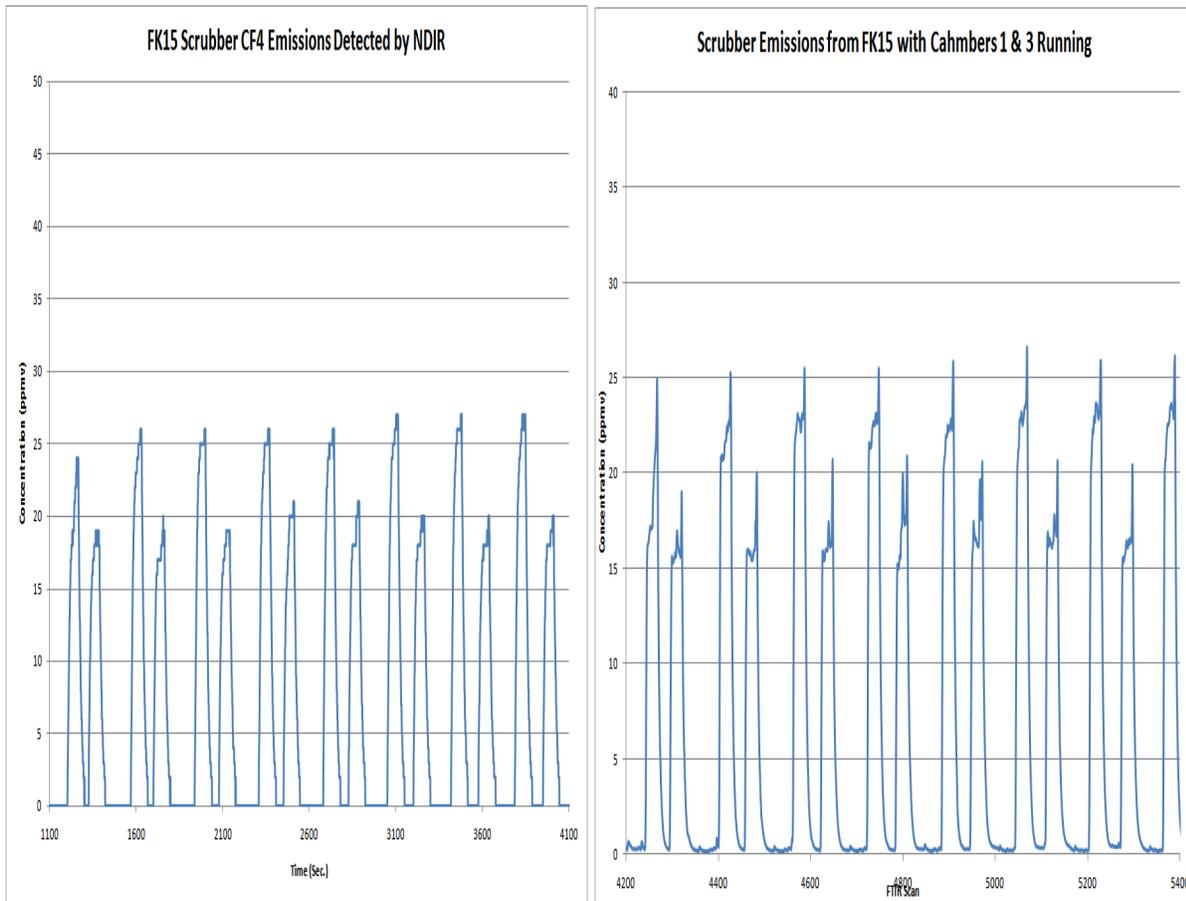
The results of the integration are presented in Table VIII for two etching profiles, one comprised of three peaks, which was repeated 13 times, and the second of a single peak, which was repeated 11 times. The fractional difference $[= (NDIR - FTIR)/0.5 (NDIR + FTIR)]$ is +11 percent for both etching profiles, which confirms the qualitative agreement evident in Figures 15a-b. Note also that the NDIR was used as it was received from the manufacturer, e.g., the manufacturer's calibration was accepted.

The scrubber DRE can also be calculated using the measured (FTIR) influent volumes, 5.85 sl, during these tests and the measured scrubber effluent volumes given in Table VIII for the NDIR and FTIR. The DRE for the FTIR measurement is 85 percent, while the DRE based on NDIR measured scrubber effluent is 83 percent.

Given the experimental errors of these tests, the results are considered equal. Furthermore, it appears the NDIR may be considered a relatively cost-effective means for monitoring CF_4 destruction in, as well as CF_4 emissions from, these scrubbers. Additional trials would be needed to better evaluate suitability for continuous monitoring over long periods.

Table XI: Comparison of measured NDIR and FTIR emitted CF_4 volumes (sl) during wafer processing on FE15

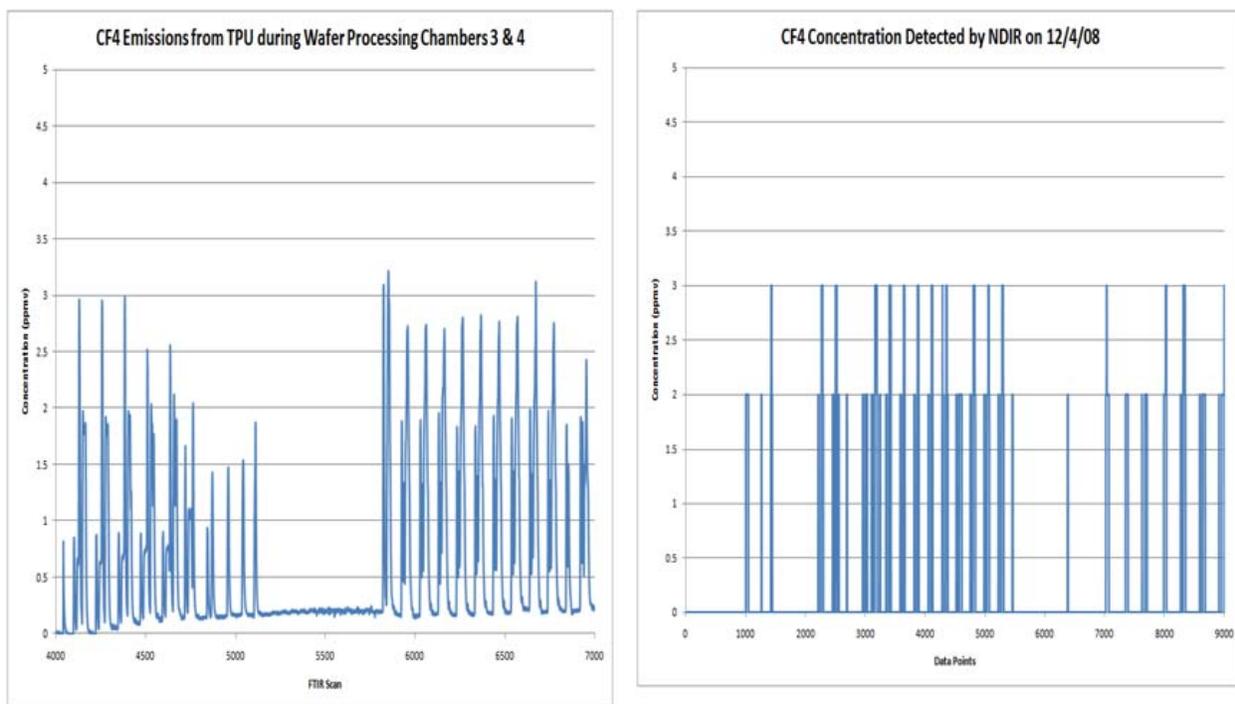
Etching Profile	NDIR, sl	FTIR, sl	Fractional difference, %
Triple peaks	0.99	0.89	11
Single peak	0.46	0.41	11



Figures 15a - b: Comparison of FTIR vs. NDIR determined CF₄ emissions from FK15 scrubber during wafer processing. Note the difference scales in the two figures.

3.4.2 NDIR Data Collected on FE05

CF₄ emissions from FE05 were also monitored with the FTIR and NDIR during wafer processing. Emission profiles for both instruments are shown in Figures 16a-b. The CF₄ emission concentrations were lower than those observed on FK15. As was the case with FK15, the emission concentrations for FE05 were nearly identical, again demonstrating that NDIR is a potentially viable alternative for scrubber emission monitoring.



Figures 16a - b: CF_4 emissions from scrubber on FE05 determined by FTIR (right) and NDIR during wafer processing.

4. Summary and Conclusions

The results of this study have shown that chemical spiking of POU abatement systems is an effective method for reliably measuring the DRE of PFCs used during semiconductor manufacturing. In these tests QMS was effectively combined with FTIR to measure the DREs of PFCs used during normal semiconductor wafer manufacturing and normal scrubber operation. The chemical spiking agent (Kr) was added at the inlet to the scrubber in one of the chamber exhaust lines, and the concentration was determined at the outlet of the scrubber in the combined effluent stream. The total effective flow through the scrubber was calculated from these data, and used to correct for the dilution occurring across the scrubber.

It was also demonstrated that NDIR can be used to reliably monitor scrubber effluent CF_4 concentrations during semiconductor manufacture. If this technology is subsequently shown to be robust through longer term evaluations, it would provide a relatively cost-effective method for monitoring CF_4 (and other PFC) emissions.

Scrubbers on two multi-chamber etch tools were tested. Results gave DRE values of greater than 98 percent for all PFCs except CF₄. The non-CF₄ process gases included CHF₃, SF₆, CH₂F₂ and CH₃F; the non-CF₄ process by-product gases included C₂F₄ and C₂F₆.

CF₄ had a sufficiently low DRE to serve as a prime example for protocol development and validation. The DRE values for each etcher/scrubber pair were measured using two different methods: comparing integrated emission volumes from the etcher during manufacturing, and comparing the corresponding measured inlet and outlet CF₄ concentrations with no process or plasma. Both methods yielded similar DRE values for CF₄. The measured CF₄ DRE for each etcher/scrubber pair differed, with an average DRE across two etch processes and chambers for FE15 of 84 percent and the corresponding value for FE05 of 90 percent.

An experiment was conducted to assess the performance of an alternative process sampling procedure that continuously extracted and monitored gas concentration samples from multiple inlet flows while simultaneously monitoring the corresponding scrubber effluent concentrations. This alternative method drew slip streams from each process chamber from their respective exhausts, combined them in the FTIR sample inlet line, and pulled that combined flow through the FTIR gas cell for analysis. The potential advantage of this method is that it allows direct determination of the actual process atmosphere entering the scrubber, eliminating the need to know the PFC emissions for each chamber. This approach requires measuring the individual process dilutions for each chamber, and employing additional experimental controls on sample flow. The approach also requires assurance of the safety of mixing chamber exhausts. Both sampling methods gave similar results for the DRE of CF₄.

These results, when coupled with the results obtained during prior studies⁴ at two fabs with different PFC-based processes using the same experimental methodology, demonstrate the robustness of the measurement procedures to accurately and precisely measure the performance of POU abatement systems under operating fab conditions for PFCs, SF₆ and NF₃.

⁴Ridgeway, R.G., and T. Strencosky (2008a) Developing a reliable method for estimating abatement system dilution and DRE: Evaluation in an IC Mfg Environment (Fab A). Draft report prepared for the USEPA by Air Products & Chemicals Inc. March 2008

Ridgeway, R.G., and T. Strencosky (2008b) Developing a reliable method for estimating abatement system dilution and DRE: Evaluation in an IC Mfg Environment (Fab B). Draft report prepared for the USEPA by Air Products & Chemicals Inc. March 2008