



**Evaluation of the Applied Materials  $\mu$ Clean Technology for  
DxZ Chamber Clean for Perfluorocompound (PFC) Emissions  
Reduction**

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# Evaluation of the Applied Materials $\mu$ Clean Technology for DxZ Chamber Clean for Perfluorocompound (PFC) Emissions Reduction

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**Abstract:** This report presents the results of an evaluation of Applied Materials'  $\mu$ Clean technology to clean a 200 mm DxZ plasma enhanced TEOS (PETEOS) chamber in an actual manufacturing environment at Motorola. Both quadrupole mass spectrometry (QMS) and Fourier transform infrared spectroscopy (FTIR) were used to quantify the major fluorinated gases in the process effluent. A 500-wafer marathon collected data on particle counts, performance, film thickness uniformity, and film stress and refractive index. Designed experiments determined the effects of helium addition on clean time and  $\text{NF}_3$  utilization efficiencies. Process pressure and total gas flow were also included as variables. The revision includes additional input from the supplier about design considerations.

**Keywords:** Emissions Reduction, Perfluorocompounds, Chamber Cleaning, Design of Experiments, Fourier Transform Infrared Spectroscopy, TEOS, PETEOS, Marathon Runs

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## 1 EXECUTIVE SUMMARY

The concern over global warming and emissions of gases, such as perfluorocompounds (PFCs), that may contribute to this phenomenon has driven semiconductor manufacturers to endeavor to reduce their emissions of PFCs. Applied Materials has developed a new chamber cleaning technology that has the potential to dramatically reduce PFC emissions from chamber cleaning on their DxZ platform. Their prototype product, known as  $\mu$ Clean, is a remote microwave clean using  $\text{NF}_3$  that can be retrofitted to a DxZ chamber.

Recent tests of the  $\mu$ Clean technology conducted by Air Products and Chemicals, Inc. at Applied Materials have demonstrated the high utilization efficiencies of  $\text{NF}_3$  (>90%) and reduced clean times. To confirm these results in an actual manufacturing environment, Motorola installed a prototype unit on a 200 mm Applied Materials DxZ plasma enhanced TEOS (PETEOS) chamber. Both quadrupole mass spectrometry (QMS) and Fourier transform infrared spectroscopy (FTIR) were used to quantify the major fluorinated gases in the process effluent. Impact on the process was determined by clean times, particle generation, and film thickness uniformity in the tool.

The Applied Materials  $\mu$ Clean technology has been shown to be effective for 200 mm DxZ TEOS chamber cleaning. Throughout a 500-wafer marathon and during subsequent product processing of more than 13,000 wafers, no negative effect on manufacturing parameters has been noted. There is no evidence of particle generation, and film properties are seemingly unaffected by the remote  $\text{NF}_3$  clean.

The  $\text{NF}_3$  utilization of the Applied Materials  $\mu$ Clean—also referred to as remote microwave clean—has been shown to be 90% in a manufacturing environment with a one-second  $\text{NF}_3$  stabilization flow. Greater utilization efficiencies have been demonstrated with no stabilization flow. The volumetric emissions ( $\text{NF}_3$ ,  $\text{SiF}_4$ ,  $\text{F}_2$ , and  $\text{HF}$ ) for this process have been quantified and a fluorine balance of 99% achieved. This fluorine balance was compared with the standard in situ  $\text{C}_2\text{F}_6/\text{NF}_3$  clean. The remote microwave clean generates nearly six times more fluorine than the  $\text{C}_2\text{F}_6/\text{NF}_3$  clean. However, for a 0.5  $\mu\text{m}$  (200 mm wafer) TEOS film, the environmental impact of the remote  $\text{NF}_3$  is  $0.40 \times 10^{-9}$  million metric tons of carbon equivalent (MMTCE). This compares to a measured MMTCE value of  $4.34 \times 10^{-9}$  for the in situ  $\text{C}_2\text{F}_6/\text{NF}_3$  RF clean in a manufacturing operation. It indicates that the microwave clean can significantly reduce MMTCE emissions. The MMTCE reduction would be even greater if the  $\text{NF}_3$  stabilization flow were eliminated.

The results of the design of experiments (DOE) indicate that some helium can be added to the  $\mu$ Clean process to reduce the  $\text{NF}_3$  required. An 80:20  $\text{NF}_3$ :He ratio showed no significant decrease in the clean time. Clean times were also compared. While the remote microwave clean is only a few seconds faster for thinner films, the clean time difference is much greater for thicker films. This may translate to increased throughput with the  $\mu$ Clean unit. The DOE results have been revised to include additional input from the supplier about design considerations.

The Applied Materials  $\mu$ Clean technology has been demonstrated to be a viable alternative to the standard  $\text{C}_2\text{F}_6/\text{NF}_3$  clean used in 200 mm DxZ TEOS chambers. PFC emissions are virtually eliminated without affecting the manufacturing process.

## 2 INTRODUCTION

The *National Technology Roadmap for Semiconductors* (1997 edition) calls for proactive reduction of emissions that may cause global climate change. Perfluorocompounds (PFCs), such as  $\text{CF}_4$ ,  $\text{C}_2\text{F}_6$ ,  $\text{SF}_6$  and  $\text{NF}_3$ , are anthropogenic gases that are currently used in semiconductor manufacturing operations for chamber cleaning and plasma etching. All of the SEMATECH member companies have signed a voluntary agreement with the U.S. Environmental Protection Agency that calls for the companies to endeavor to reduce PFC emissions.

Concern over the fate of atmospherically persistent PFCs and the desire to address industry calls for reduced PFC emissions has motivated the development of a new chamber cleaning technology. Applied Materials proposes a potential solution that may be retrofitted to their existing line of DxZ chambers. Unlike current chamber cleans (using  $\text{C}_2\text{F}_6$ ,  $\text{O}_2$ , and  $\text{NF}_3$ ) where the gaseous discharge is sustained by radio frequency (RF) power applied to electrodes inside the reactor, this technology uses microwave excitation of  $\text{NF}_3$  in a resonant cavity directly upstream of the deposition reactor. The advantages of this approach stem from the ability of the microwave discharge to achieve near complete dissociation of the source gas. Not only does this eliminate the concern over the fate of unreacted perfluorinated gas, but it also leads to faster clean rates with an associated increase in wafer throughput and extended lifetime of process hardware. Although it is possible for in situ  $\text{NF}_3$  cleans to achieve similar destruction efficiencies, they are often plagued by long-term process drift associated with energetic ion formation in the reactor from unoptimized processes.

Applied Materials currently offers three separate microwave-based chamber cleaning products for dielectric deposition. The tests reported here are for the DxZ plasma enhanced TEOS (PETEOS) deposition prototype product known as  $\mu\text{Clean}$ . This source is an unusually compact design that holds promise as a cost-effective retrofit for the installed base of DxZ PETEOS chambers. The PETEOS microwave clean is differentiated from the sub-atmospheric chemical vapor deposition (SaCVD) and high density plasma (HDP) chamber clean products by a lower operating power and very compact design.

## 3 PROJECT OVERVIEW/BACKGROUND

Recent tests of the  $\mu\text{Clean}$  technology conducted by Air Products and Chemicals, Inc. at Applied Materials have demonstrated the high utilization efficiencies of  $\text{NF}_3$  (>90%) and reduced clean times associated with this external source. The purpose of this study was to again confirm high  $\text{NF}_3$  utilization efficiencies in an actual manufacturing environment at Motorola on a 200 mm Applied Materials DxZ PETEOS chamber while demonstrating the absence of negative impacts on manufacturing parameters. A fluorine balance was also conducted on both the baseline  $\text{C}_2\text{F}_6/\text{NF}_3$  clean and the  $\mu\text{Clean}$  using  $\text{NF}_3$ . Both QMS and FTIR were used to quantify the major fluorinated gases in the process effluent. Process impact was determined by clean times, particle generation, and film parameters, including thickness, uniformity, stress, and refractive index.

## 4 EXPERIMENTAL DATA

### 4.1 Test Method Overview

The first phase of the study was a 500-wafer marathon of 2  $\mu\text{m}$  TEOS oxide film depositions followed by the baseline  $\mu\text{Clean}$  using  $\text{NF}_3$  as determined by Applied Materials. The following data was collected during the marathon:

- Particle count performance
- Film thickness and uniformity
- Film stress and refractive index

Once the marathon was completed, Air Products performed a complete emissions characterization and fluorine mass balance for the  $\mu\text{Clean}$  process for a 0.5  $\mu\text{m}$  (5500  $\text{\AA}$ ) film. For comparison purposes, the same characterization was performed for the standard  $\text{C}_2\text{F}_6/\text{NF}_3$  clean for a 0.5  $\mu\text{m}$  film.

The third phase of this study was a designed experiment to determine the effects of helium addition on clean time and  $\text{NF}_3$  utilization efficiencies. Process pressure and total gas flow were also included as variables.

### 4.2 Equipment Information

The Applied Materials  $\mu\text{Clean}$  system is a chamber-mounted, air-cooled remote microwave plasma source with manual tuning. The remote microwave plasma source is a self-contained plasma generation unit; the ceramic applicator tube, resonator cavity, waveguide, tuning stubs, directional loop couplers, magnetron (microwave source), filament transformer, gas inlet and outlets, plasma detector, and interlock board are all assembled within one containment. This unit can be mounted on a DxZ chamber using KF type fittings. Figure 1 (Appendix A) shows a cross-sectional front view of a DxZ chamber with the  $\mu\text{Clean}$  unit mounted on top. The microwaves generated using a water-cooled 2.45 GHz microwave source (magnetron) are propagated through a wave launcher into a very short waveguide section. This wave guide opens into a resonator cavity. Within this cavity, the microwaves traverse across an air-cooled ceramic applicator tube in which  $\text{NF}_3$  gas strikes a high density plasma generating fluorine radicals. These radicals flow through the gasbox, blocker plate, and conical hole showerhead into the process chamber, cleaning residue as they flow through. The flow is radially outwards and the radicals etch the film in the same pattern.

QMS was used to monitor  $\text{NF}_3$ ,  $\text{F}_2$ , and  $\text{SiF}_4$  concentrations, whereas, FTIR spectroscopy was used for HF measurements. Measurements were made downstream of the process pump at ambient pressure using QMS and FTIR. The QMS instrument was used for  $\text{NF}_3$ ,  $\text{SiF}_4$ , and  $\text{F}_2$  determinations while the FTIR measured HF concentrations.

Wafers were processed in a 200 mm Applied Materials DxZ PECVD chamber on a Centura mainframe. Particle analysis was conducted on a Tencor 6200 using particle monitor wafers at 2.5 K  $\text{\AA}$  film thickness. Film thickness, uniformity, and stress were measured on a Prometrix UV1250 using a 5 mm edge exclusion. Refractive index was measured on a Tencor Flexus 7200.

### 4.3 Marathon Results

The 500-wafer marathon was conducted using blanket test wafers and particle monitors. Cassettes of 25 wafers were run through the PECVD TEOS deposition process with a remote microwave clean between each wafer. The test wafer matrix is illustrated in Table 1. Three particle monitors at a film thickness of 2.5K Å were run. Film thickness and uniformity were measured on five wafers of varying thickness: 1K Å, 4K Å, 6 K Å, and 10K Å. Stress and refractive index were measured on two wafers at 4K Å film thickness. This matrix was repeated for each cassette of 25 wafers throughout the marathon.

**Table 1 Marathon Test Matrix**

Wafer #	Film Type	Thickness (Å)	Particles	Stress	RI	Thickness	Uniformity
1	Blanket	20K					
2	Particle	2.5K	X				
3	Blanket	20K					
4	Stress/RI	4K		X	X	X	X
5	Blanket	20K					
6	Blanket	20K					
7	Blanket	20K					
8	Blanket	20K					
9	Blanket	20K					
10	Blanket	20K					
11	Blanket	20K					
12	Blanket	20K					
13	Blanket	20K					
14	Blanket	20K					
15	Particle	2.5K	X				
16	Blanket	20K					
17	Blanket	20K					
18	Bright Light	20K					
19	Blanket	20K					
20	Stress/RI	4K		X	X	X	X
21	Thickness	10K				X	X
22	Thickness	1K				X	X
23	Thickness	6.5K				X	X
24	Blanket	20K					
25	Particle	2.5K	X				

Particle measurements for the 500-wafer test are plotted in Figure 2 (Appendix B). Three particle monitors were included in each run of 25 wafers. With a few exceptions, including a scratch on the wafers, the particles were well below the acceptable level of 22 adders. This indicates that the remote microwave unit was able to completely clear the residue in the chamber after each wafer, thus preventing particles from building up. It also indicates that the design of the unit itself does not cause particle generation during normal operation.

Figure 3 through Figure 6 (Appendix B) present the film thickness and uniformity data for the four different film thicknesses routinely used for such measurements: 1K Å, 4K Å, 6.5 K Å and 10 KÅ. The film thicknesses throughout the test were within the normal range, always slightly higher than the nominal deposition thickness. There was also no significant variability (gradual increase or decrease) in actual thickness over the 500 wafers. The film thickness uniformity was also within the acceptable range at approximately 1.5% for all four thicknesses. As with thickness, there was no noticeable variability in the uniformity over the 500 wafers. This indicates that the remote microwave clean did not affect the deposition process with respect to these film parameters.

The film stress and refractive index measurements are shown in Figure 7 (Appendix B). As with the other film parameters, these are within the acceptable range. The film stress was approximately -112 to -115 MPa throughout the marathon. The refractive index was also constant at 1.45 or 1.455. It should be noted that there appears to be great variability in the refractive index, measuring 1.45 and 1.455. This variability is due to differences in operator readings (i.e., one operator read four significant digits, while another read only three). Again, the remote microwave clean did not affect the deposition process with respect to these film properties.

Based on the results of the 500-wafer marathon, it can be concluded that the remote microwave clean does not have any negative affect on the deposition process, as is indicated by the film properties, and does not cause particle generation during normal operation.

## **4.4 Emissions Characterization Results**

### **4.4.1 Instrument Calibration**

#### **4.4.1.1 QMS Measurements of $\text{NF}_3$ , $\text{SiF}_4$ , and $\text{F}_2$**

The processes were monitored with a UTI Qualitorr QMS having a 200 amu mass filter. The QMS features a closed ion source (CIS) for high pressure process analysis. The sample inlet was differentially pumped to quickly sample a slightly subambient atmosphere; i.e., the QMS response time must be much shorter than changes in the gas composition of each process step. The QMS sampled the process through a 1/4-inch VCR compression fitting welded to the exhaust elbow of the process pump as shown in Figure 8 (Appendix C). The gases of interest are therefore diluted by any pump purge. Since the QMS measures concentration, it is important to know the pump purge flow to make reliable estimates of the PFC emissions (i.e., effluent gas flow). This  $\text{N}_2$  gas flow was estimated by flowing  $\text{NF}_3$  (106, 413, 770, and 1029 sccm) using the gas panel on the process tool. The  $\text{NF}_3$  concentration at the pump exhaust was measured using the mass spectrometer, which had been independently calibrated for  $\text{NF}_3$  measurements. The pump purge calculated from the slope of Figure 9 (Appendix C) was 42.7 slm. The QMS sample inlet pressure was 700 torr throughout as measured by a capacitance manometer. All sample lines were 1/8-inch stainless steel GC tubing heat traced to  $\sim 100^\circ\text{C}$ .

The mass locations were determined using N<sub>2</sub> (7, 14, 28 amu) and NF<sub>3</sub> (71 and 52 amu). The QMS instrument was directly calibrated for NF<sub>3</sub>, SiF<sub>4</sub>, and F<sub>2</sub> using 1% gas standards as shown in Figure 10 through Figure 14 (Appendix C). Five-point or better calibration curves were measured using dynamic dilution methods to generate concentrations <10,000 ppm. Because a C<sub>2</sub>F<sub>6</sub> gas standard was unavailable, the QMS was calibrated using C<sub>2</sub>F<sub>6</sub> from the gas panel on the tool. C<sub>2</sub>F<sub>6</sub> from the process chamber (0, 119, 328, and 532 sccm) was diluted by the pump purge (42.7 slm) to generate the C<sub>2</sub>F<sub>6</sub> calibration shown in Figure 15 (Appendix C) (Note: a tool mass flow controller [MFC] verification was performed after testing). Because CF<sub>4</sub> and CHF<sub>3</sub> standards were also unavailable, previously generated calibration data (1/16/98) were used as shown in Figure 16 and Figure 17 (Appendix C). The change in the sensitivity of the QMS (7%) was accounted for through the C<sub>2</sub>F<sub>6</sub> calibration. The QMS was calibrated before and after the emissions measurements (4% change in sensitivity). In addition, changes in QMS sensitivity were monitored by a single-point NF<sub>3</sub> calibration immediately before and after each process.

#### 4.4.1.2 FTIR Measurements of HF

HF concentrations were determined using a Midac I2000 FTIR spectrometer with an MCT detector and a 0.1 m Axiom gas cell. Absorbance from the rotational-vibrational transitions at 4038 cm<sup>-1</sup> was used as a monitor of the HF concentrations. The FTIR spectrometer was directly calibrated for ex situ HF measurement using a 0.5% HF gas standard. These concentrations were determined from a single-point calibration; however, the chosen calibration point (540 ppm) was within 20% of the measured value.

#### 4.4.1.3 Error Estimation

The errors contributing to the overall uncertainty of the QMS calibration are summarized in the table below.

Source	Error
Gas standards	1 %
MFC	1 % (full scale)
Inlet pressure	1 %

### 4.4.2 Baseline Clean Comparison

#### 4.4.2.1 Remote NF<sub>3</sub> Microwave Clean Process

##### *Emissions from the Standard NF<sub>3</sub> Clean Process*

The 200 amu mass spectrum during the standard remote microwave clean process (following a 5500 Å or 0.5 μm deposition) using NF<sub>3</sub> (700 sccm, 1.5 Torr, 60 s) is shown in Figure 18 (Appendix D) along with the peak assignments. The major byproducts are SiF<sub>4</sub>, HF, F<sub>2</sub>, and unreacted NF<sub>3</sub>. Trace amounts of perfluorocarbon (69, 119, and 169 amu) compounds and Si<sub>2</sub>F<sub>3</sub> (113 amu) were observed.

Figure 19 (Appendix D) shows the concentration of NF<sub>3</sub>, SiF<sub>4</sub>, and F<sub>2</sub> while processing ten wafers using the remote microwave clean. These concentrations were obtained by independently calibrating the QMS for NF<sub>3</sub>, F<sub>2</sub>, and SiF<sub>4</sub> (Section 4.4.1). The F<sub>2</sub> signal is shown to steadily increase while the first three wafers are processed as the sample lines are passivated. Because of the short (1 s) stabilization step, the NF<sub>3</sub> concentration remains low (<2000 ppm) throughout the

process. Once the MW power is applied, the SiF<sub>4</sub> concentration sharply increases as the chamber is cleaned. At endpoint, the F<sub>2</sub> concentration levels off and the SiF<sub>4</sub> signal drops to baseline levels. The HF concentration, measured by FTIR during wafer processing, is shown in the first ten wafers of Figure 20 (Appendix D). The HF emissions reflect hydrogen in the TEOS films. Note that there is an HF spike during the seasoning step because of the residual F in the process chamber after the clean.

### ***Fluorine Balance and NF<sub>3</sub> Utilization***

Integrating under the concentration profiles (Figure 19 and Figure 20, Appendix D) allows the volumetric emissions to be calculated. The NF<sub>3</sub>, SiF<sub>4</sub>, F<sub>2</sub>, and HF emissions for nine of the processed wafers are summarized in Table 2 (Note: a static QMS spectrum was collected while the tenth wafer was running).

**Table 2 Volumetric Emissions During the NF<sub>3</sub> Remote Microwave Clean**

Wafer #	1	2	3	4	5	6	7	8	9	Avg.
NF <sub>3</sub> in (scc)	578	578	578	578	578	578	578	578	578	578
NF <sub>3</sub> out (scc)	59	55	56	58	55	62	59	57	54	57
SiF <sub>4</sub> out (scc)	69	94	88	94	94	96	94	88	64	89
F <sub>2</sub> out (scc)	413	480	481	500	495	501	493	507	498	499
HF out (scc)	201	204	202	198	203	199	204	194	203	200
F Balance	0.85	0.98	0.97	1.01	1.00	1.02	1.00	1.00	0.93	0.99
Utilization(%)	90	90	90	90	91	89	90	90	91	90

The first row (NF<sub>3</sub> in) represents the amount of NF<sub>3</sub> supplied during the clean. This value was obtained by running the clean recipe with no MW power applied and measuring the NF<sub>3</sub> emission profile with the QMS. Rows 3–6 summarize the NF<sub>3</sub>, SiF<sub>4</sub>, F<sub>2</sub>, and HF emissions, respectively. The major byproduct is F<sub>2</sub>. Indeed, for the TEOS clean, almost one F<sub>2</sub> molecule is formed from each NF<sub>3</sub> molecule.

Using the volumetric emissions of NF<sub>3</sub> and ratioing this to the NF<sub>3</sub> in value, the NF<sub>3</sub> utilization is calculated to be 90% (row 10). Previously, the NF<sub>3</sub> utilization had been calculated only for the main etch. The NF<sub>3</sub> utilization calculated from the volumetric emissions includes both the gas stabilization and overetch steps. If the stabilization flow of NF<sub>3</sub> were omitted, the utilization efficiency would be greater.

Using the volumetric emissions of the fluorine byproducts and their molecular formulae, the total amount of fluorine emitted can be calculated. Comparing this value to the fluorine influent (NF<sub>3</sub> in) gives the fluorine balance. For the nine processed wafers, the fluorine balance is 99% thus verifying that all of the fluorine byproducts have been accounted for.

#### **4.4.2.2 In Situ C<sub>2</sub>F<sub>6</sub> RF Clean Process**

Current practice for cleaning the PECVD TEOS chamber following a 0.5 μm (5500 Å) deposition is an in situ C<sub>2</sub>F<sub>6</sub> (400 sccm)/NF<sub>3</sub> (60 sccm) RF process. The emissions from this C<sub>2</sub>F<sub>6</sub> clean were also quantified to provide a basis for comparing the remote NF<sub>3</sub> clean emissions.

### ***Emissions from the Standard C<sub>2</sub>F<sub>6</sub> RF Clean Process***

The 200 amu mass spectrum during the standard C<sub>2</sub>F<sub>6</sub> (400 sccm)/NF<sub>3</sub> (60 sccm) process is shown in Figure 21 (Appendix D) along with the peak assignments. The major byproducts are CF<sub>4</sub>, SiF<sub>4</sub>, HF, F<sub>2</sub>, and unreacted C<sub>2</sub>F<sub>6</sub> and NF<sub>3</sub>. Figure 22 (Appendix D) shows the concentration of C<sub>2</sub>F<sub>6</sub>, NF<sub>3</sub>, CF<sub>4</sub>, CHF<sub>3</sub>, SiF<sub>4</sub>, and F<sub>2</sub> while processing five wafers. The HF concentration measured by FTIR while processing the five wafers is shown in Figure 20 (Appendix D).

#### **4.5 Fluorine Balance**

Integrating under the concentration profiles (Figure 20 and Figure 22, Appendix D) allows the volumetric emissions to be calculated. The C<sub>2</sub>F<sub>6</sub>, NF<sub>3</sub>, CF<sub>4</sub>, CHF<sub>3</sub>, SiF<sub>4</sub>, F<sub>2</sub>, and HF emissions for the five wafers processed are summarized in Table 3.

**Table 3 Volumetric Emissions During the C<sub>2</sub>F<sub>6</sub> RF Clean**

Wafer #	1	2	3	4	5	Avg.
NF <sub>3</sub> in (scc)	60	60	60	60	60	60
C <sub>2</sub> F <sub>6</sub> in (scc)	400	400	400	400	400	400
NF <sub>3</sub> out (scc)	21	24	23	21	21	22
C <sub>2</sub> F <sub>6</sub> out (scc)	235	217	231	203	216	220
CF <sub>4</sub> out (scc)	108	113	123	118	90	110
CHF <sub>3</sub> out (scc)	2	2	2	2	2	2
SiF <sub>4</sub> out (scc)	77	73	73	74	81	76
F <sub>2</sub> out (scc)	77	78	85	82	83	81
HF out (scc)	180	170	167	169	164	170
F Balance	0.99	0.95	1.00	0.92	0.92	0.96

Based upon these volumetric emissions, the C<sub>2</sub>F<sub>6</sub> and NF<sub>3</sub> utilization is 45% and 63%, respectively. The major by product, besides unreacted C<sub>2</sub>F<sub>6</sub> and NF<sub>3</sub>, is CF<sub>4</sub>; 28% of the influent C<sub>2</sub>F<sub>6</sub> molecules result in a CF<sub>4</sub> molecule. For the five processed wafers, the fluorine balance is 96% verifying that all of the fluorine byproducts have been accounted for. Table 4 compares the fluorine balance of the two clean processes.

**Table 4 Fluorine Balance Summary (all values scc)**

	μClean	Baseline C <sub>2</sub> F <sub>6</sub> /NF <sub>3</sub>
C <sub>2</sub> F <sub>6</sub> in	0	400
NF <sub>3</sub> in	578	60
C <sub>2</sub> F <sub>6</sub> out	0	220
NF <sub>3</sub> out	57	22
CF <sub>4</sub> out	0	110
CHF <sub>3</sub> out	0	2
SiF <sub>4</sub> out	89	76
HF out	200	170
F <sub>2</sub> out	499	81

The amount of SiF<sub>4</sub> generated in the C<sub>2</sub>F<sub>6</sub> process (76 scc) is lower than for the remote NF<sub>3</sub> process (89 scc). Since the deposition processes are identical (0.5 μm), this is evidence that the remote NF<sub>3</sub> process is cleaning further in the downstream areas of the process chamber/foreline than the in situ C<sub>2</sub>F<sub>6</sub> process. The fluorine generation by the remote microwave clean is six times greater than the baseline C<sub>2</sub>F<sub>6</sub> process.

#### 4.5.1 Design of Experiments Results

One concern of the remote microwave clean is the amount of NF<sub>3</sub> required in the baseline clean. Not only is NF<sub>3</sub> a costly gas, but a significant amount of fluorine is generated as a byproduct of the clean (see Table 4). To determine if an effective clean could be achieved with a reduced total NF<sub>3</sub> requirement, helium was added as a diluting gas in hopes that some amount of helium can maintain distribution of the free fluorine throughout the chamber. A statistical design of experiments was run to establish the sensitivity of the emissions and clean time to the process variables pressure, NF<sub>3</sub>/He diluent ratio, and total gas flow. The methodology was to deposit 5500 Å of TEOS oxide then run the experimental clean (DOE) after the wafer had been removed from the chamber. The clean was run for 100 seconds in hopes of achieving endpoint. Since an experimental clean may not achieve endpoint, a standard NF<sub>3</sub> clean (STD) was run for another 100 seconds before the next deposition. This eliminated any hysteresis concerns compounding the DOE. The experimental design is summarized in Table 5.

**Table 5 Experimental Helium Addition**

Expt.	P (Torr)	NF <sub>3</sub> /He (%)	Gas Flow (sccm)
1	1.5	25.0	500
2	1.5	62.5	1000
3	1.5	100.0	750
4	2.0	25.0	1000
5	2.0	62.5	750
6	2.0	100.0	500
7	2.5	25.0	750
8	2.5	62.5	500
9	2.5	100.0	1000
10	1.5	100.0	750
11	2.5	62.5	500

The concentrations of NF<sub>3</sub>, SiF<sub>4</sub>, F<sub>2</sub>, and HF during the DOE are shown in Figure 23 and Figure 24 (Appendix D). Two standard clean processes were run first to eliminate first-wafer effects and repassivate the sample lines. Results for the 11-experiment DOE and subsequent standard processes are summarized in Table 6 (DOE results in the first half; standard process in the second half). The point at which the F<sub>2</sub> signal levels off was used as an arbitrary measure of endpoint. All but one of the experimental cleans reached endpoint using this criterion. The 13 standard processes demonstrate an NF<sub>3</sub> utilization of 93% in agreement with the earlier ten-wafer marathon (Section 4.4.2.1) The fluorine balance of 1.04 also agrees very well with the earlier results (Section 4.4.2.2).

**Table 6 Summary of Emissions and Clean Time Data for the 11-Experiment DOE**

Wafer #	1	2	3	4	5	6	7	8	9	10	11	12	13
DOE	Std.	Std.	1	2	3	4	5	6	7	8	9	10	11
NF <sub>3</sub> IN (sccm)	700	700	131	644	772	259	484	516	196	324	1028	772	324
NF <sub>3</sub> DOE IN (scc)	700	700	218	1073	1287	432	807	860	327	540	1713	1287	540
NF <sub>3</sub> DOE (scc)	59	57	3	61	100	7	13	10	8	5	483	114	5
SiF <sub>4</sub> DOE (scc)	75	80	69	77	67	76	74	74	72	70	74	73	71
F <sub>2</sub> DOE (scc)	529	577	89	1194	1443	366	889	964	225	533	1448	1452	528
HF DOE (scc)	181	169	146	160	162	154	169	163	158	168	168	168	168
DOE U (%)	92	92	99	94	92	98	98	99	98	99	72	91	99
DOE F Balance	0.82	0.86	0.93	0.94	0.94	0.93	0.94	0.94	0.94	0.94	0.94	0.96	0.94
EP (sec)	No EP	53	No EP	53	47	85	63	55	No EP	65	51	48	83
NF <sub>3</sub> STD IN (scc)	578	578	578	578	578	578	578	578	578	578	578	578	578
NF <sub>3</sub> STD (scc)	49	50	45	40	41	42	43	42	41	43	41	42	41
SiF <sub>4</sub> STD (scc)	28	28	19	10	11	11	10	11	13	15	1	13	14
F <sub>2</sub> STD (scc)	688	719	726	780	803	784	817	812	790	778	801	785	780
HF STD (scc)	112	115	69	56	62	68	57	65	72	67	32	56	69
STD U (%)	92	91	92	93	93	93	93	93	93	93	93	93	93
DOE F Balance	1.00	1.05	1.00	1.03	1.06	1.04	1.07	1.07	1.05	1.04	1.01	1.04	1.04

Where U = NF<sub>3</sub> utilization and EP = endpoint

Results of the DOE model fit are summarized in Appendix E. These results indicate that there is no significant effect on clean time if an 80:20 NF<sub>3</sub>:He ratio is used for the remote microwave clean. Such a dilution can result in a 20% reduction in the total amount of NF<sub>3</sub> required to achieve the clean, resulting in reduced cost and fluorine generation. The DOE data also indicate that increasing the flow of NF<sub>3</sub> beyond the baseline of 700 sccm actually results in a significant decrease in NF<sub>3</sub> utilization efficiency (down to 72%) without a corresponding decrease in clean time. This is due to the limit of available power. Efficiency is decreased with increasing flow without the ability to increase available power. This suggests that the rated flow of 700 sccm is optimum for the design of this unit.

#### 4.5.2 Subsequent Manufacturing Results

After the marathon, clean comparison, and DOE, the microwave unit continued to operate on the TEOS chamber, performing the remote NF<sub>3</sub> clean in place of the standard C<sub>2</sub>F<sub>6</sub> clean. The chamber processed non-priority product with no detrimental effects noted from the microwave clean. Although complete film parameter and particle data were not taken (as was during the marathon), qualifications on particles and film parameters were performed on the routine schedule. After approximately 3200 wafers were processed, the microwave was taken off-line for some maintenance. It was returned to service later for continued processing. At the time of this report, more than 13,000 wafers of non-priority product have been processed with a remote microwave clean performed between each wafer.

Figure 25 (Appendix D) compares clean times for the remote microwave  $\text{NF}_3$  clean and the standard in situ  $\text{C}_2\text{F}_6/\text{NF}_3$  clean. Although the clean time difference is only a few seconds different for thinner films, with the remote microwave clean being faster, the difference becomes much more significant for thicker films. With a decrease in clean time, wafer throughput may be increased with the remote microwave clean.

## 5 SUMMARY/CONCLUSIONS

The Applied Materials  $\mu$ Clean technology has been shown to be effective for 200 mm DxZ TEOS chamber cleaning. Throughout the 500-wafer marathon and during subsequent product processing of more than 13,000 wafers, no negative effect on manufacturing parameters has been noted. There is no evidence of particle generation, and film properties are seemingly unaffected by the remote  $\text{NF}_3$  clean.

The  $\text{NF}_3$  utilization of the Applied Materials remote microwave clean has been shown to be 90% in a manufacturing environment with the one-second  $\text{NF}_3$  stabilization flow. Greater utilization efficiencies have been demonstrated with no stabilization flow. The volumetric emissions ( $\text{NF}_3$ ,  $\text{SiF}_4$ ,  $\text{F}_2$ , and  $\text{HF}$ ) for this process have been quantified and a fluorine balance of 99% achieved. The mass balance expressed in grams for the remote  $\text{NF}_3$  clean and the in situ  $\text{C}_2\text{F}_6$  clean are summarized in Table 7.

**Table 7 Fluorine Balance (in grams) for Remote  $\text{NF}_3$  and In Situ  $\text{C}_2\text{F}_6$  Cleans**

(g/wafer)	Remote $\text{NF}_3$	In Situ $\text{C}_2\text{F}_6$
$\text{NF}_3$	0.18	0.07
$\text{C}_2\text{F}_6$	0.00	1.36
$\text{CF}_4$	0.00	0.43
$\text{CHF}_3$	0.00	0.01
$\text{SiF}_4$	0.41	0.35
$\text{F}_2$	0.85	0.14
$\text{HF}$	0.18	0.15

For a 0.5  $\mu\text{m}$  (200 mm wafer) TEOS film, the environmental impact of the remote  $\text{NF}_3$  is  $0.40 \times 10^{-9}$  MMTCE. This compares to a measured MMTCE value of  $4.34 \times 10^{-9}$  for the in situ  $\text{C}_2\text{F}_6/\text{NF}_3$  RF clean in a manufacturing operation. This indicates that the remote microwave clean can significantly reduce MMTCE emissions (> 90%). The MMTCE reduction would be even greater if the  $\text{NF}_3$  stabilization flow were eliminated.

The results of the DOE indicate that some helium can be added to reduce the  $\text{NF}_3$  required and thus the fluorine generated as a byproduct. An 80:20  $\text{NF}_3$ :He ratio showed no significant decrease in the clean time compared to using 100%  $\text{NF}_3$ .

The Applied Materials  $\mu$ Clean technology has been demonstrated to be a viable alternative to the standard  $\text{C}_2\text{F}_6/\text{NF}_3$  clean used in 200 mm DxZ TEOS chambers. PFC emissions are virtually eliminated without affecting the manufacturing process.

APPENDIX A  
Schematics of Applied Materials  $\mu$ Clean Unit

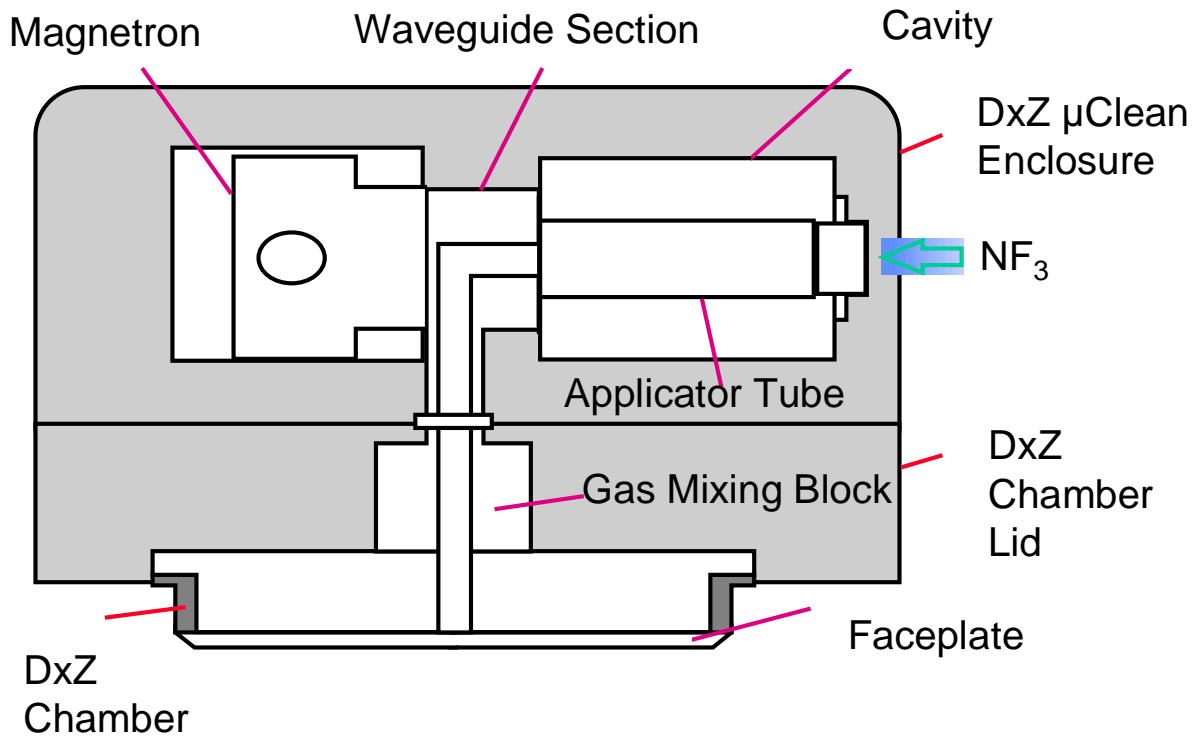
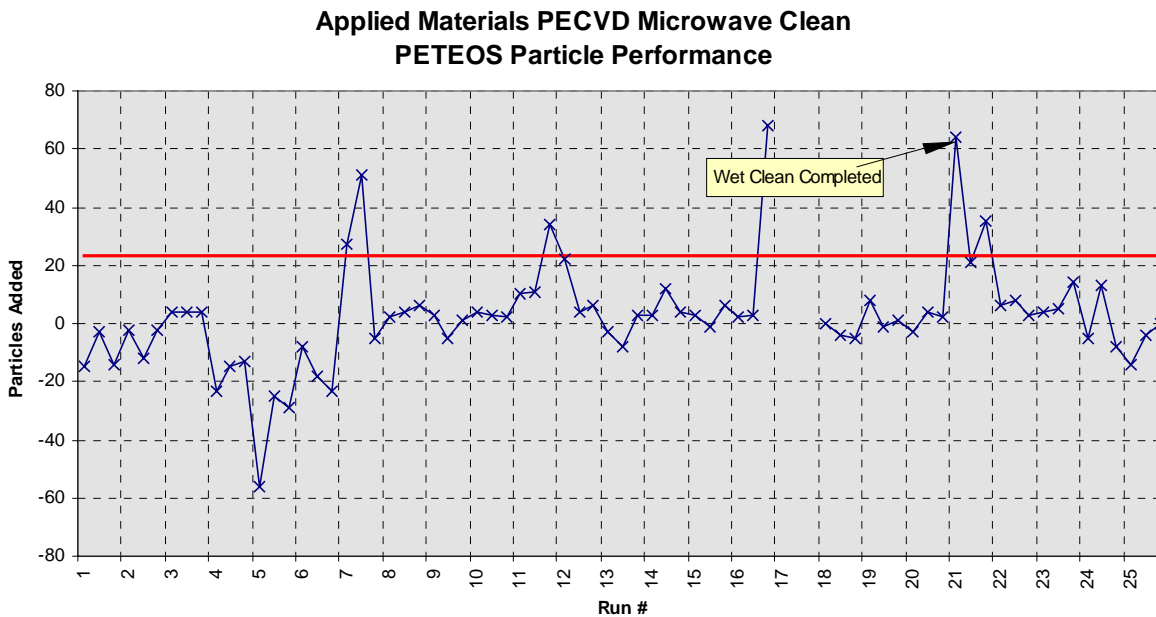
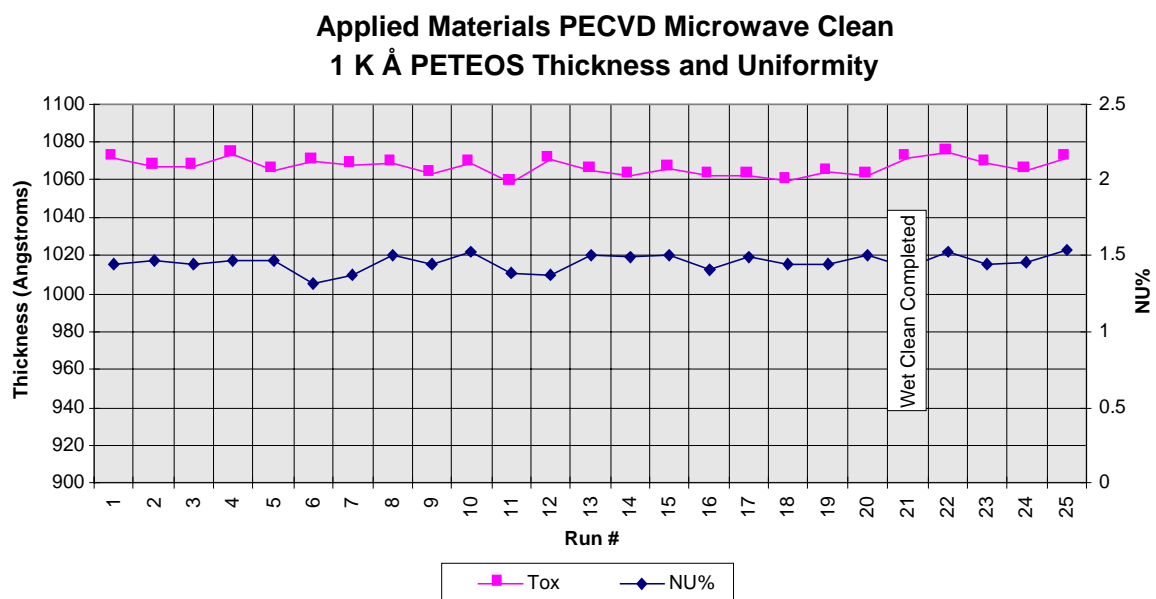


Figure 1 Cross Section of  $\mu$ Clean Unit

**APPENDIX B  
500-Wafer Marathon Data**

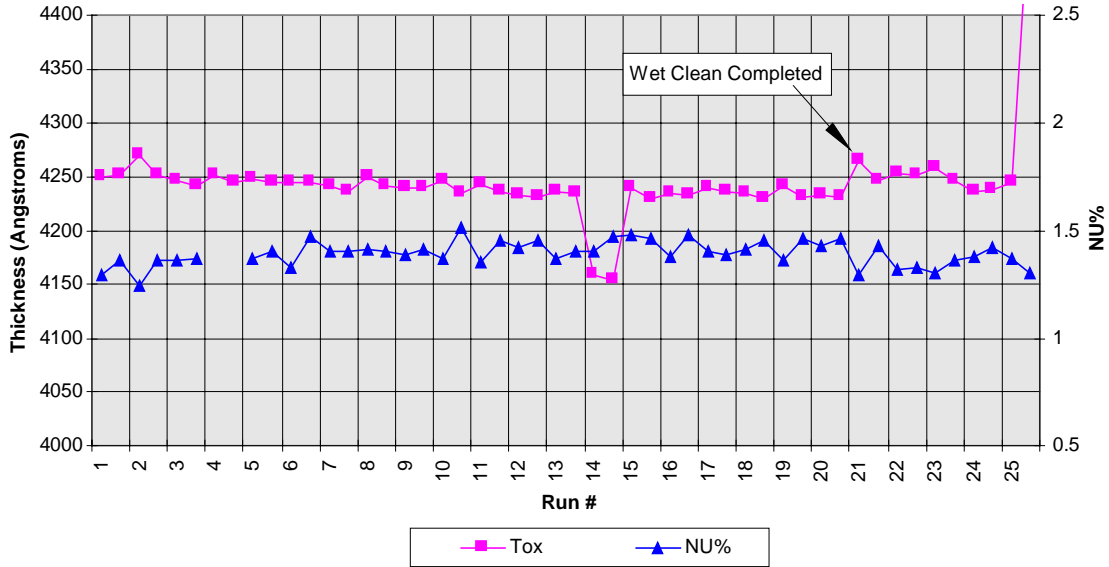


**Figure 2 PETEOS Particle Performance**



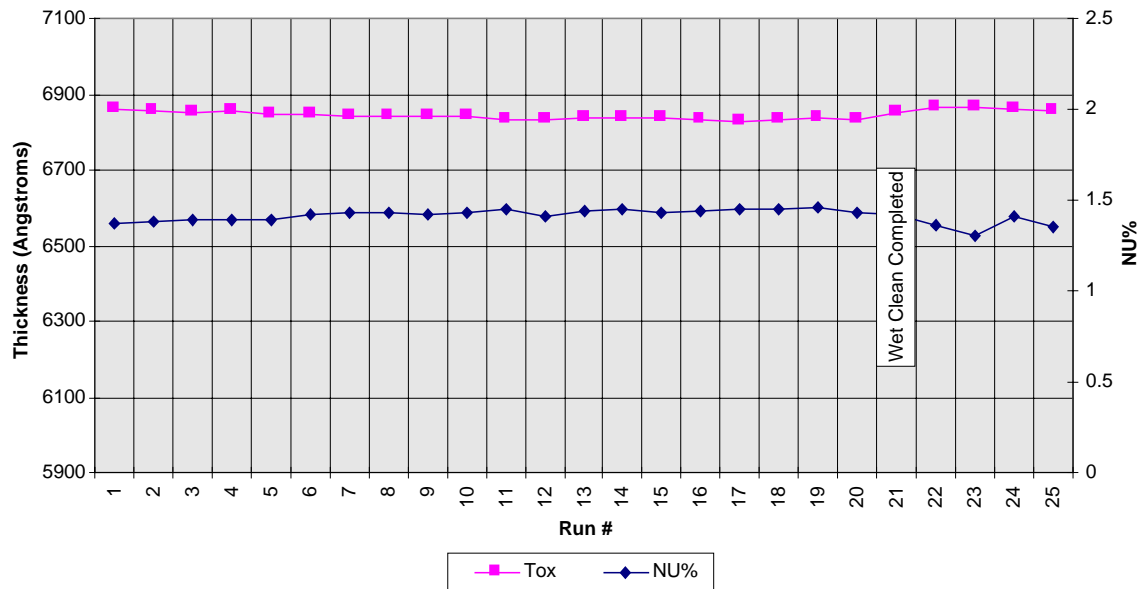
**Figure 3 1K Å PETEOS Thickness and Uniformity**

**Applied Materials PECVD Microwave Clean  
4 K Å PETEOS Thickness and Uniformity**



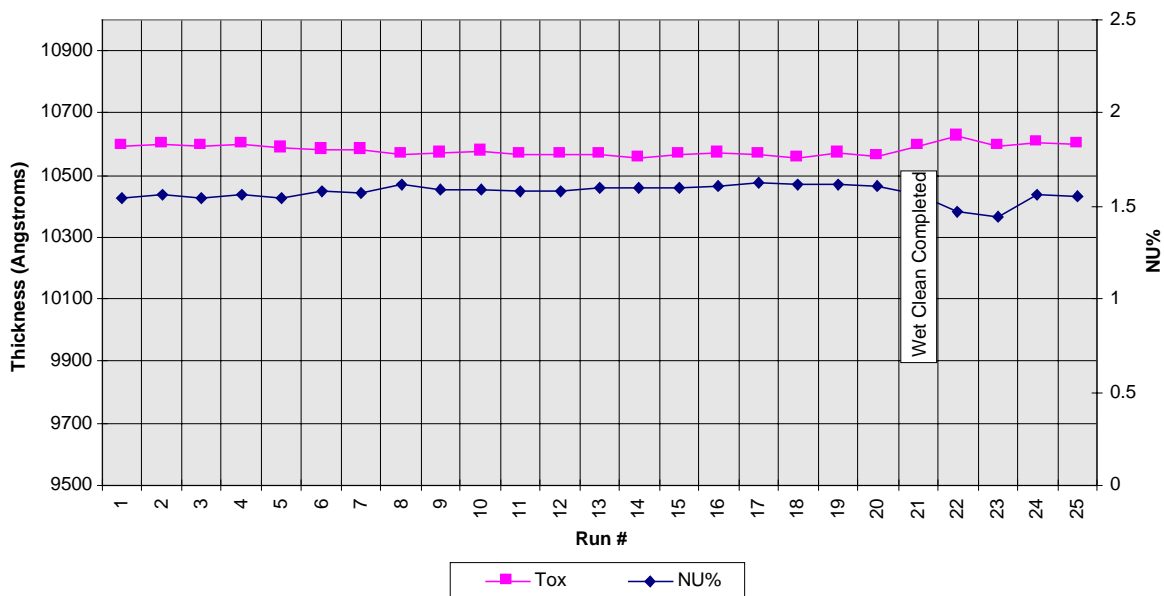
**Figure 4 4K Å PETEOS Thickness and Uniformity**

**Applied Materials PECVD Microwave Clean  
6.5 K Å PETEOS Thickness and Uniformity**

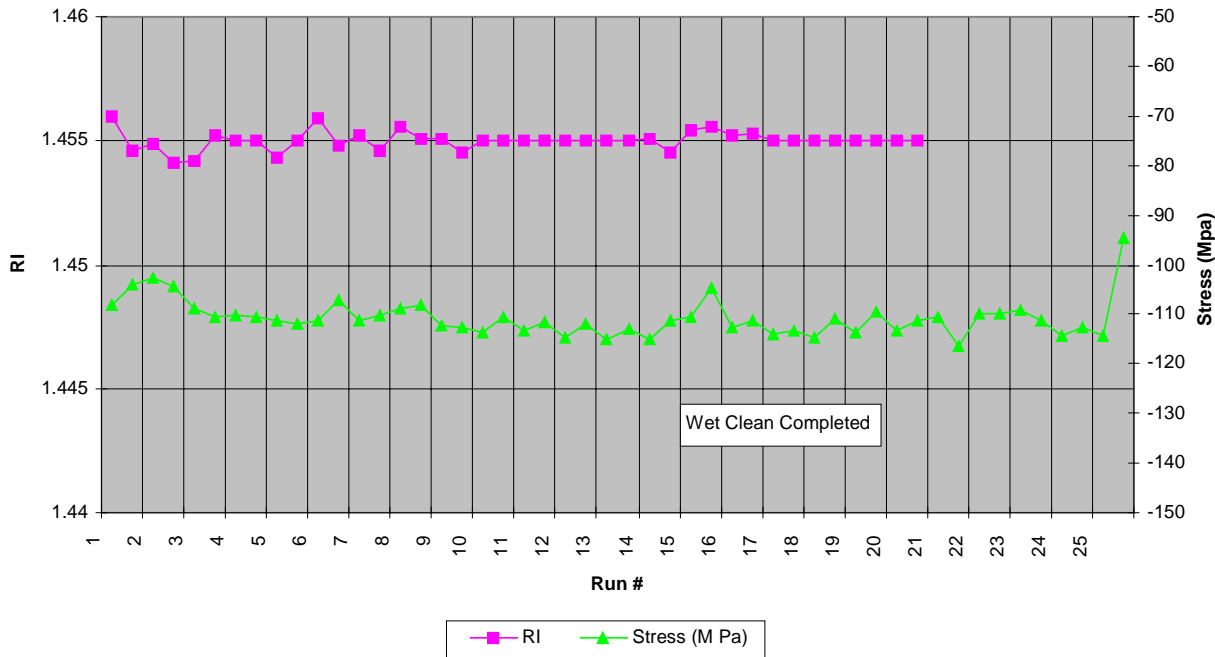


**Figure 5 6.5K Å PETEOS Thickness and Uniformity**

**Applied Materials PECVD Microwave Clean  
10 K Å PETEOS Thickness and Uniformity**

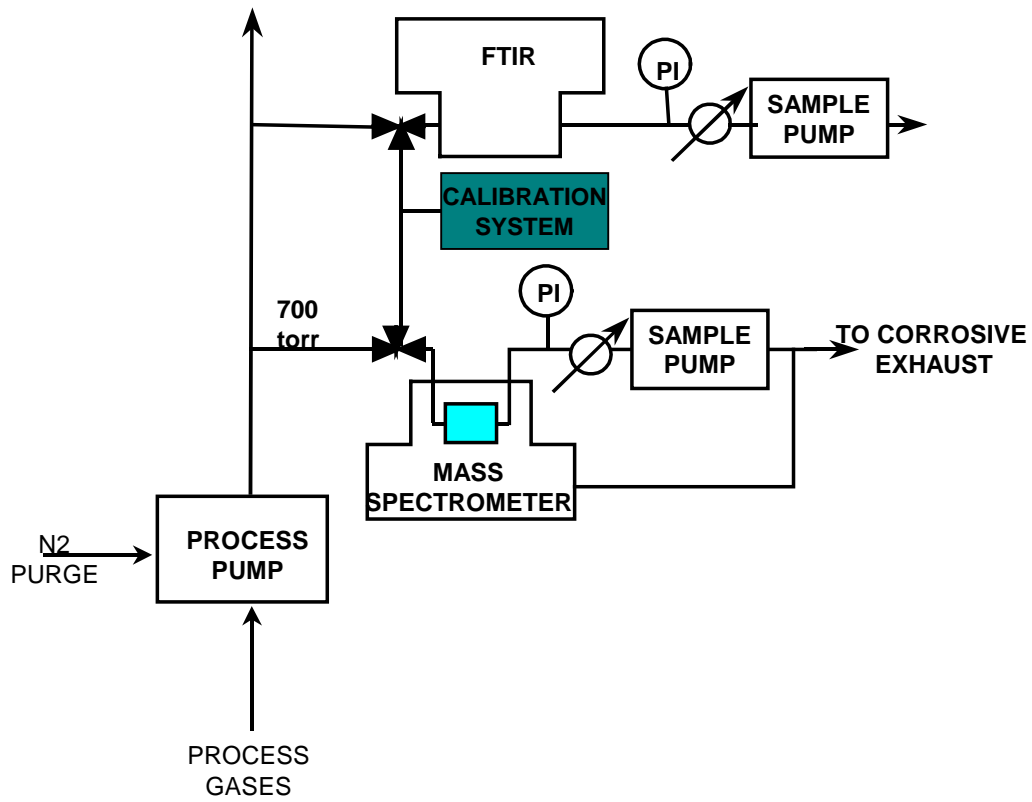


**Figure 6 10K Å PETEOS Thickness and Uniformity**

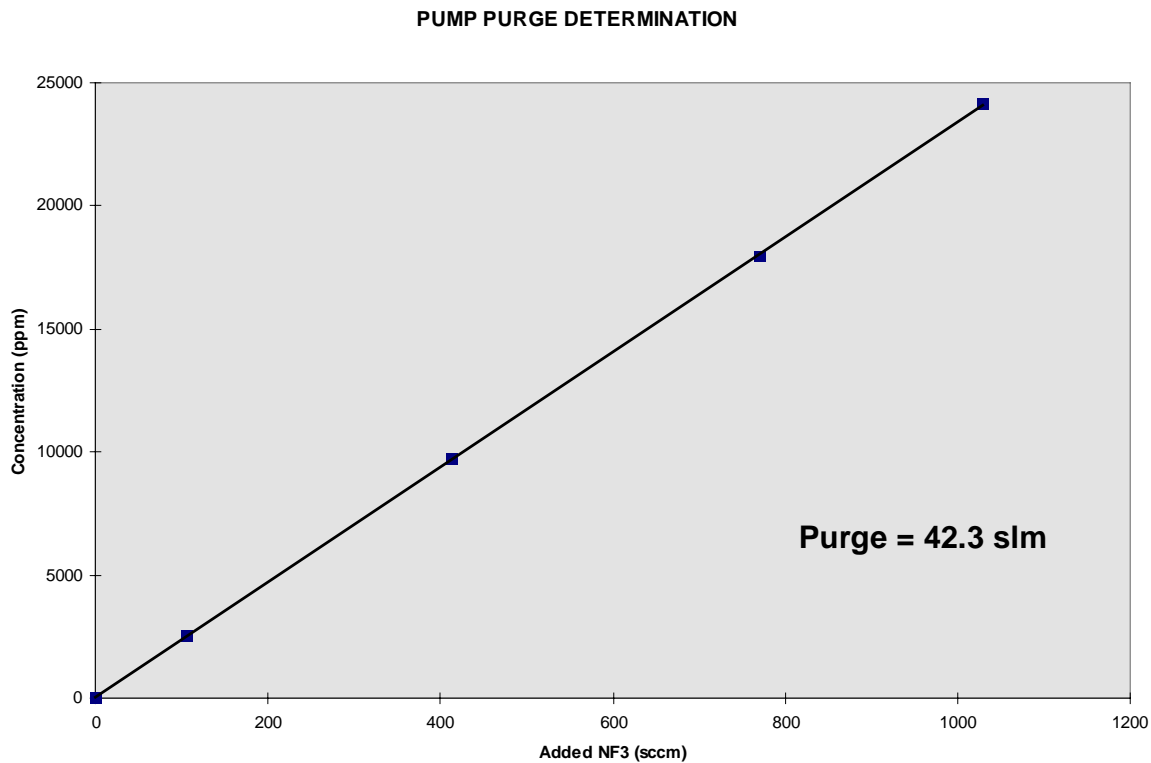


**Figure 7 PETEOS Refractive Index and Stress**

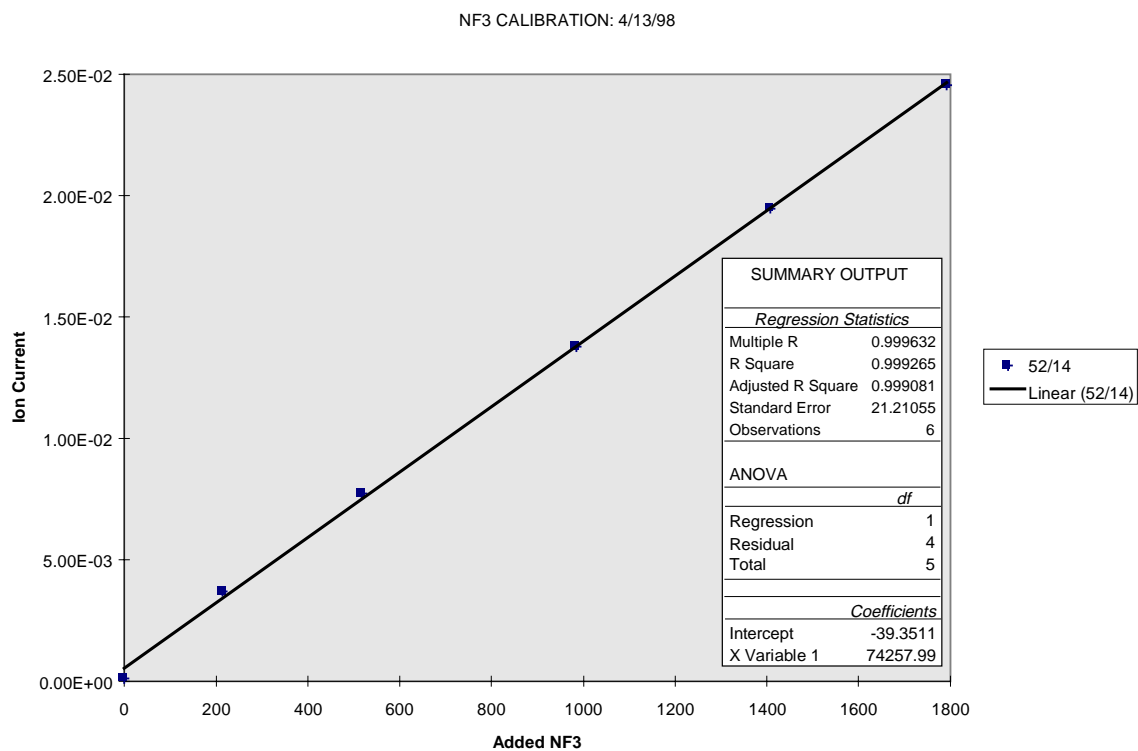
**APPENDIX C**  
**Instrument Calibration Data**



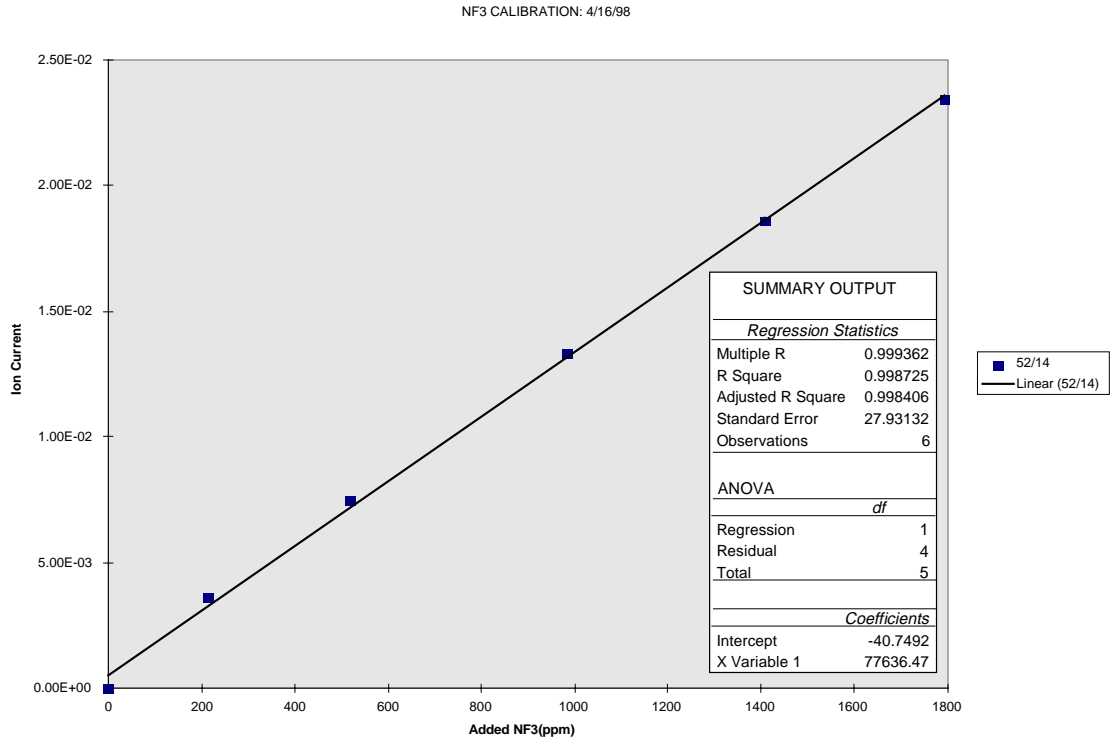
**Figure 8**      **Sampling Apparatus Configuration**



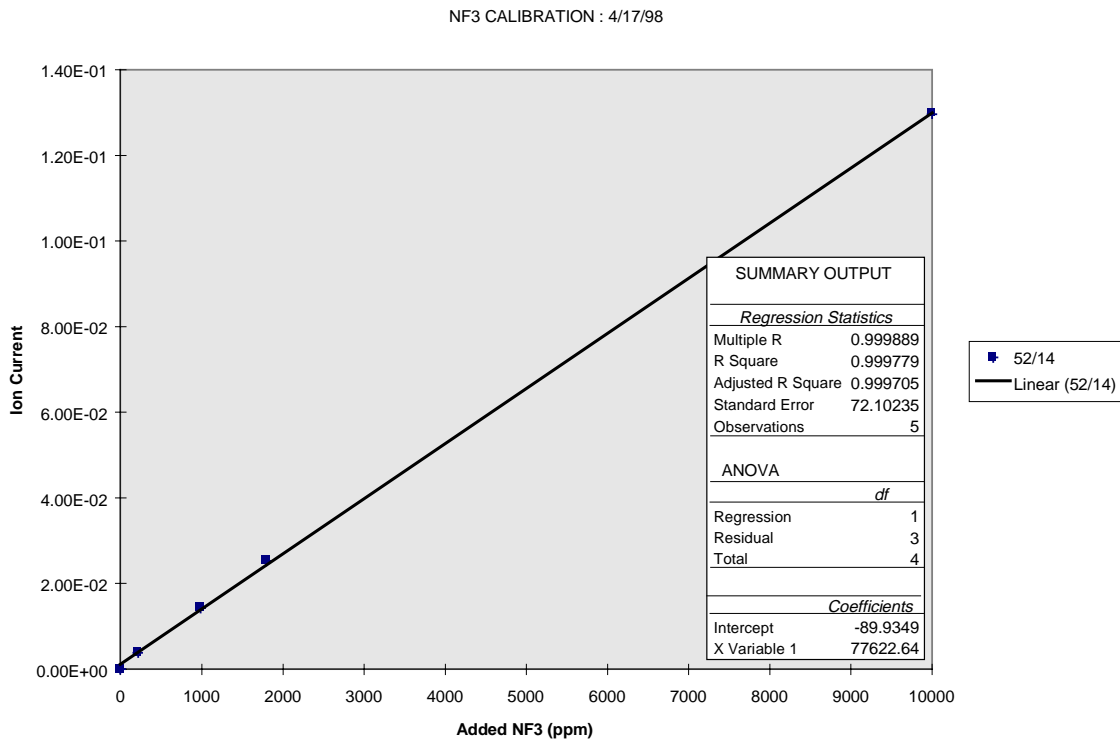
**Figure 9 Pump Purge Determination**



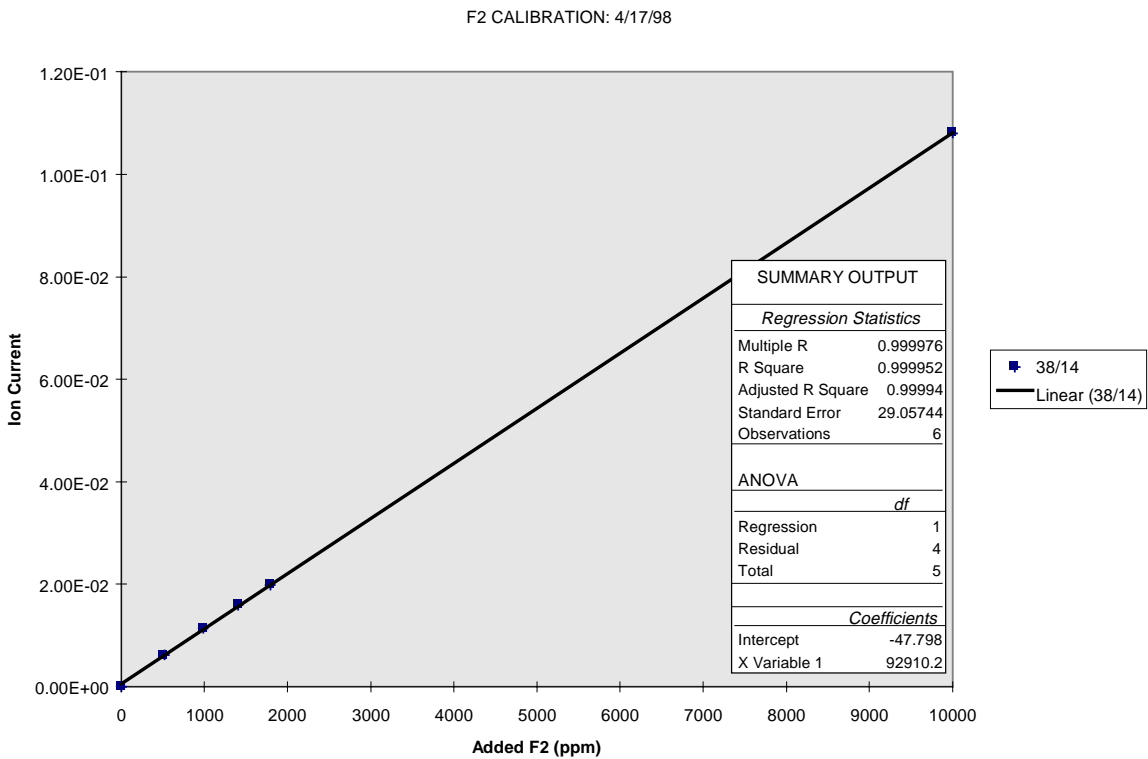
**Figure 10 NF<sub>3</sub> Calibration 4/13/98**



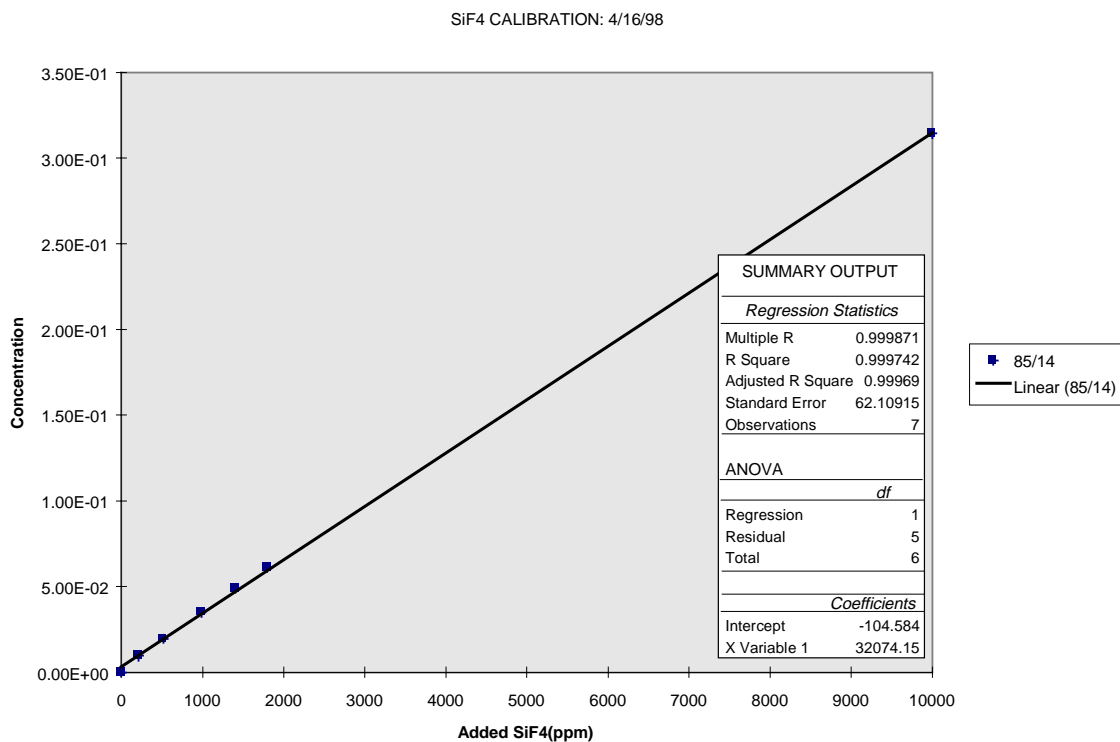
**Figure 11 NF<sub>3</sub> Calibration 4/16/98**



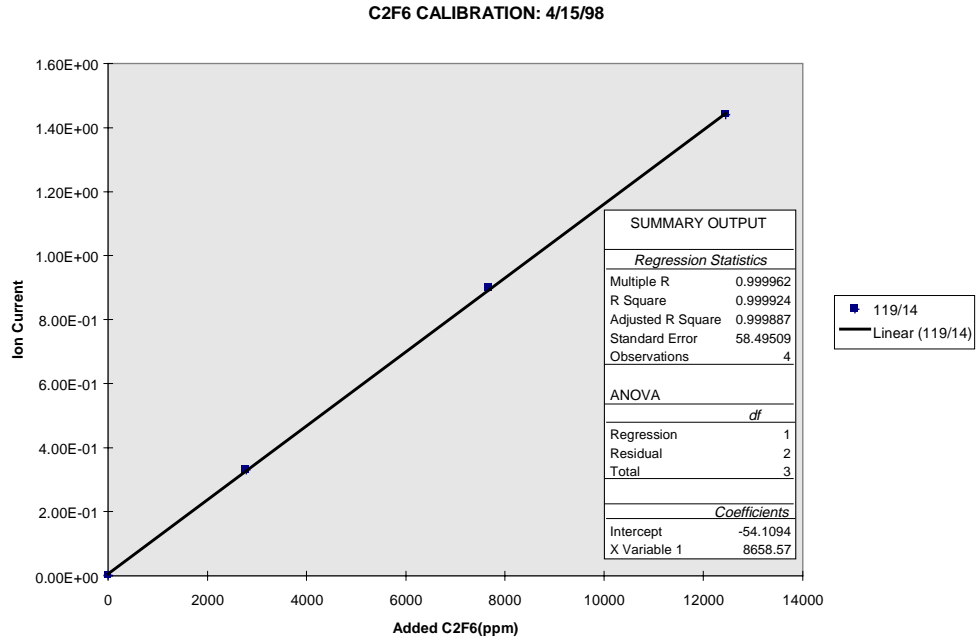
**Figure 12 NF<sub>3</sub> Calibration 4/17/98**



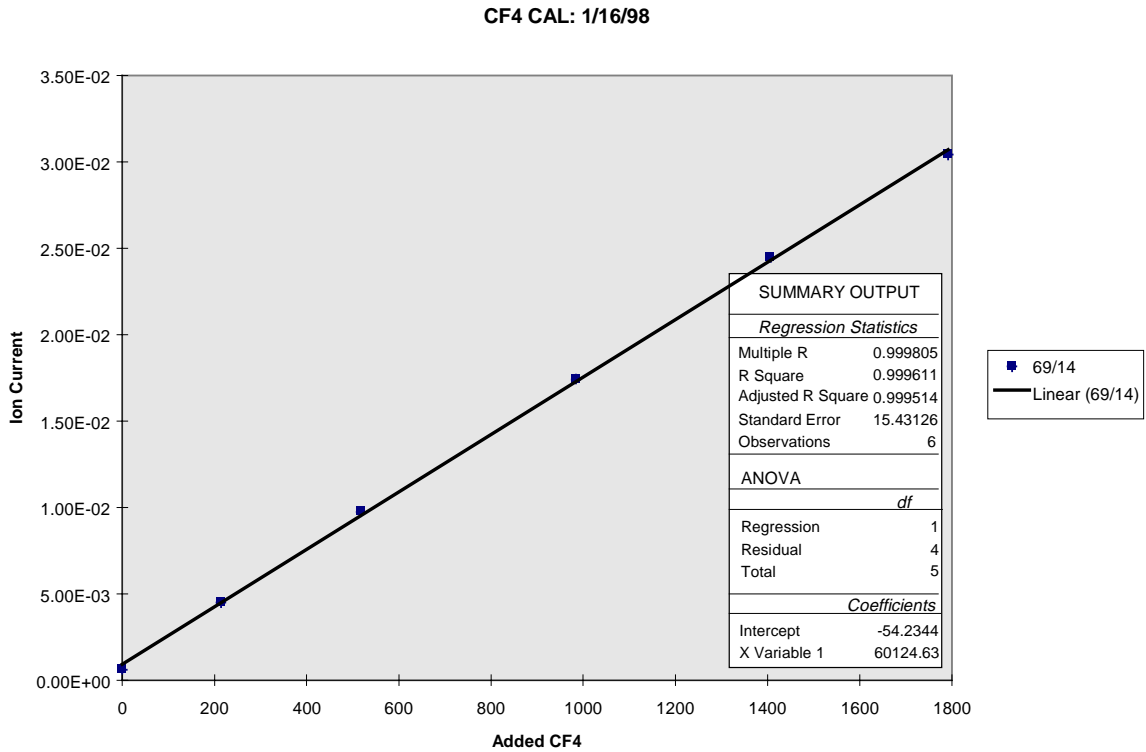
**Figure 13 F<sub>2</sub> Calibration 4/17/98**



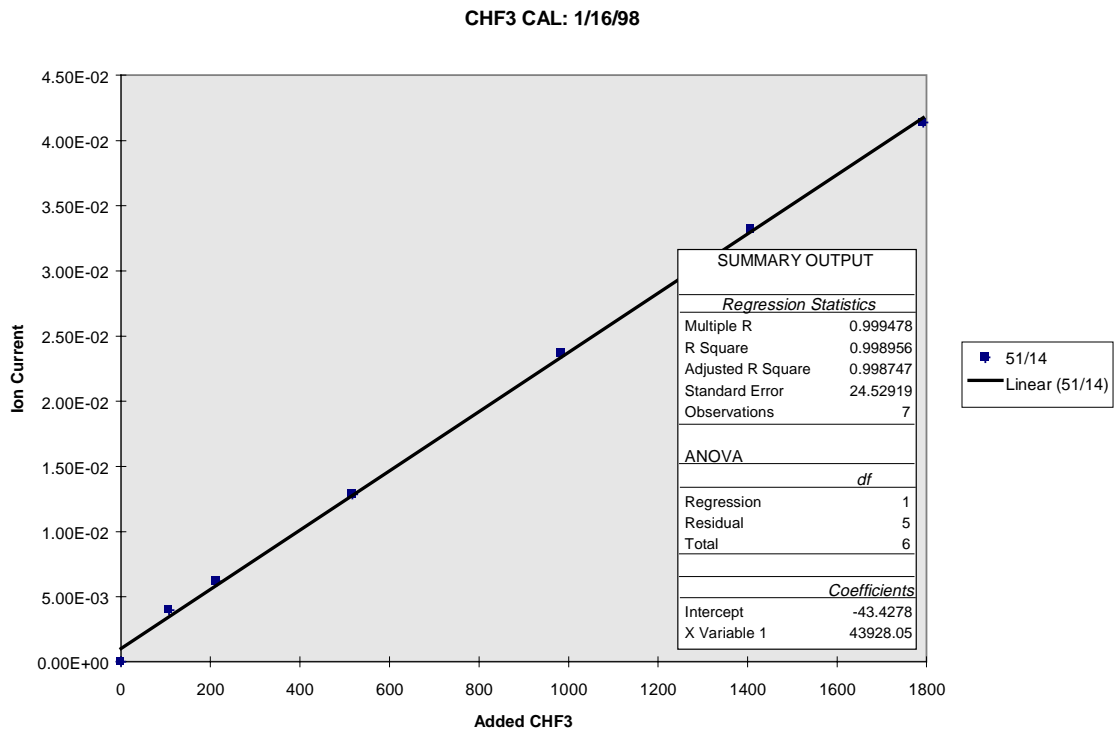
**Figure 14 SiF<sub>4</sub> Calibration 4/16/98**



**Figure 15 C<sub>2</sub>F<sub>6</sub> Calibration 4/15/98**

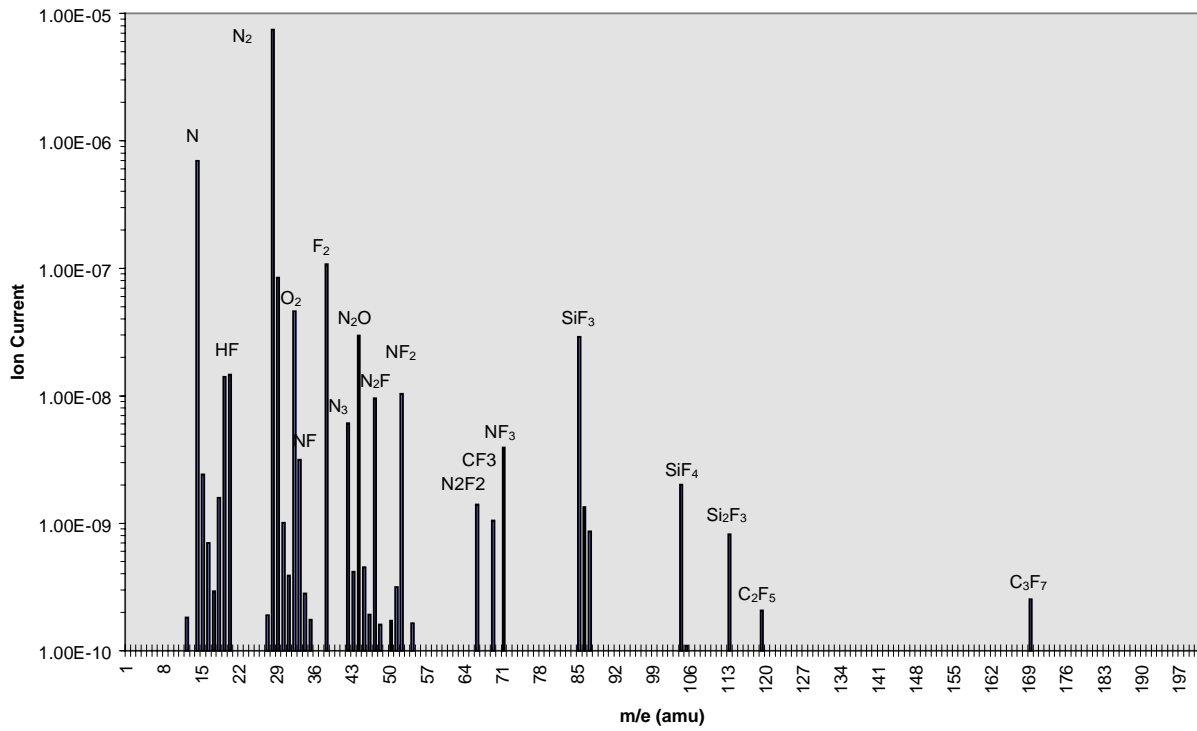


**Figure 16 CF<sub>4</sub> Calibration 1/16/98**

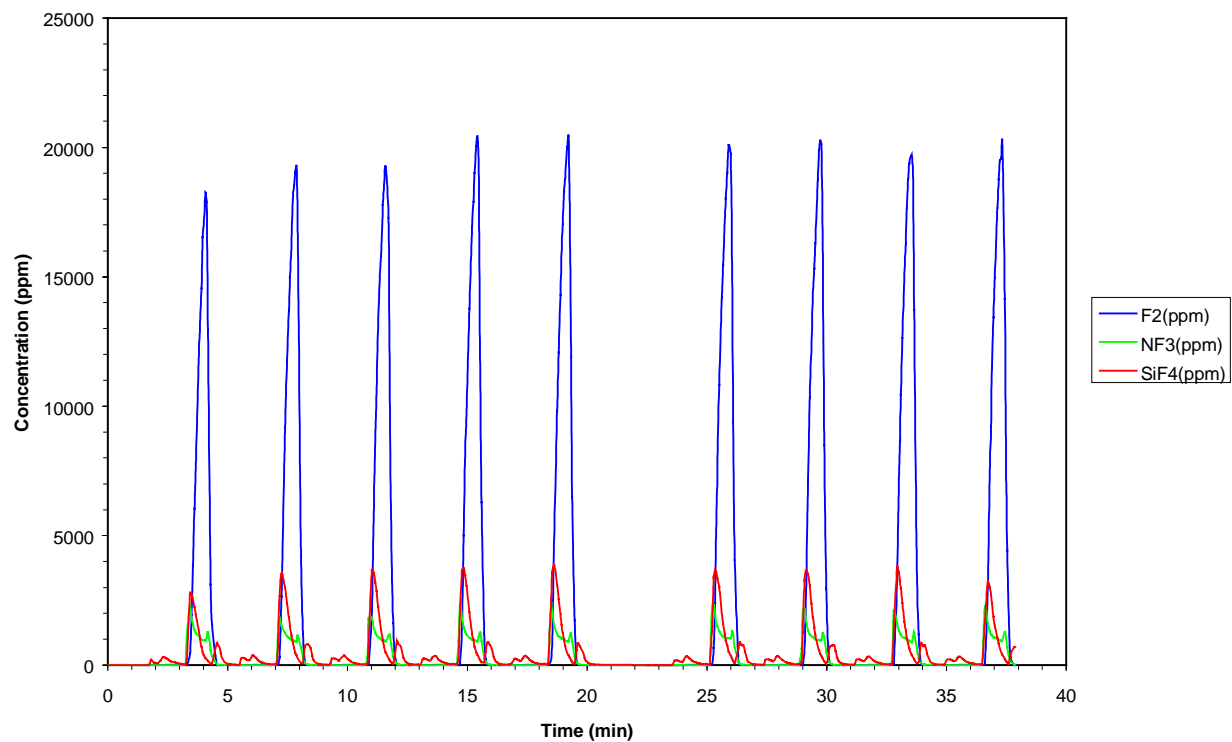


**Figure 17 CHF<sub>3</sub> Calibration 1/16/98**

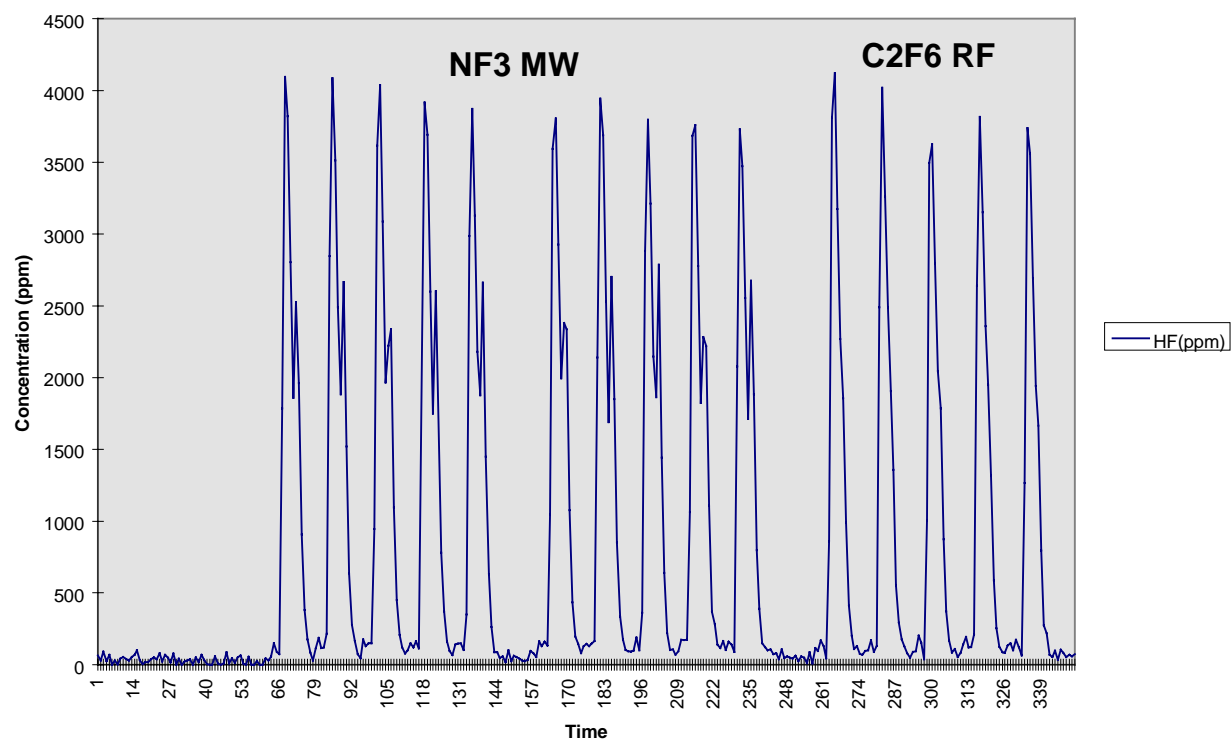
**APPENDIX D**  
**Emissions Characterization Data**



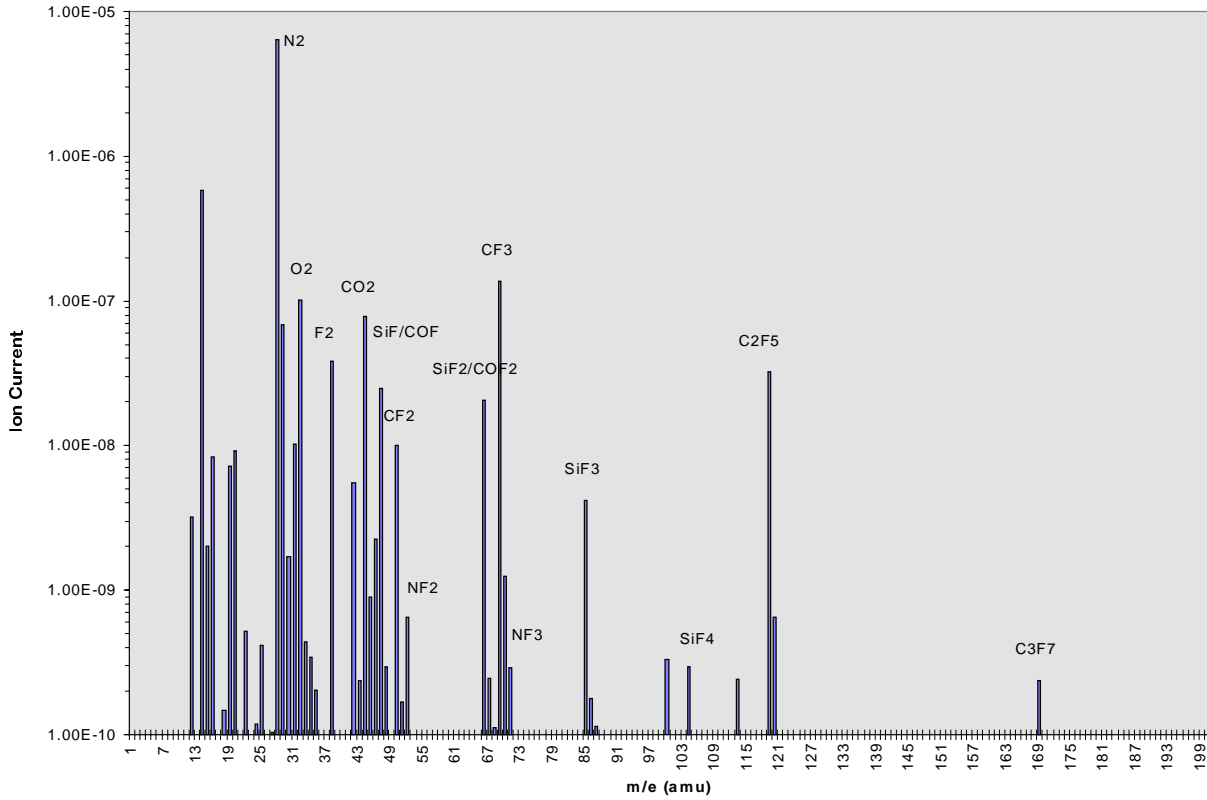
**Figure 18    Mass Spectrum of  $NF_3$  Remote Clean**



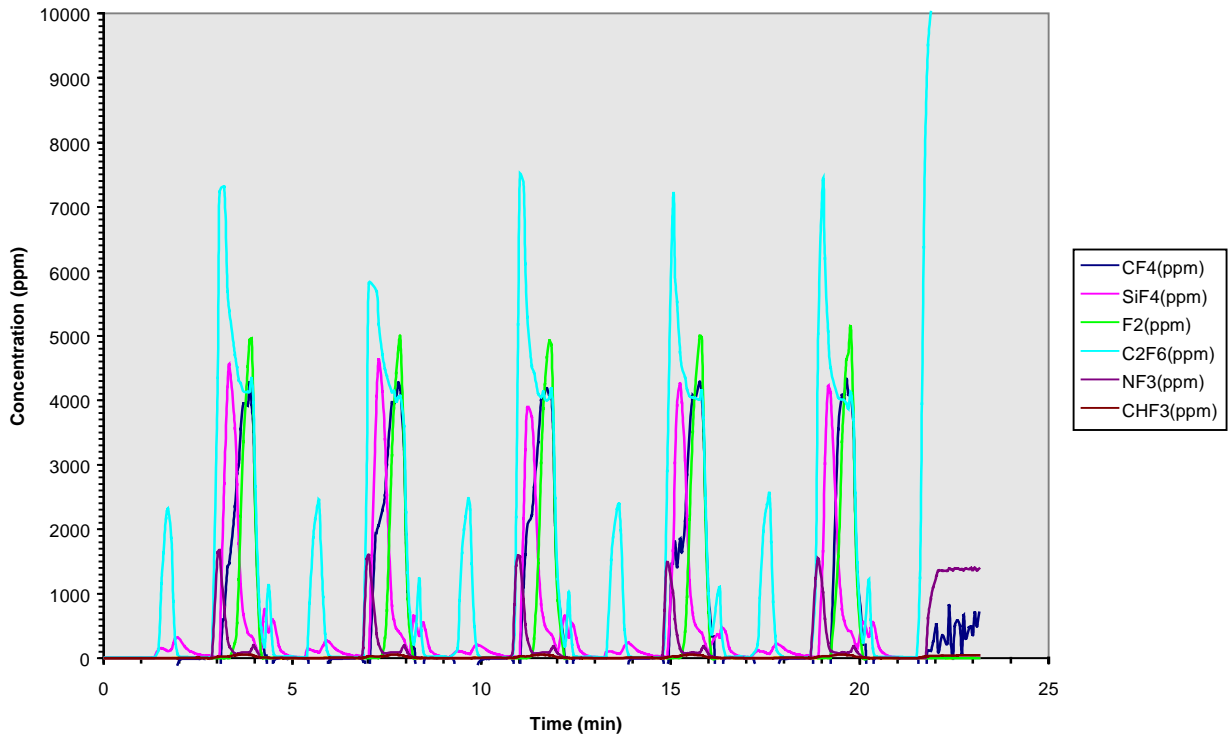
**Figure 19** TEOS PECVD:  $\text{NF}_3$  MW Clean



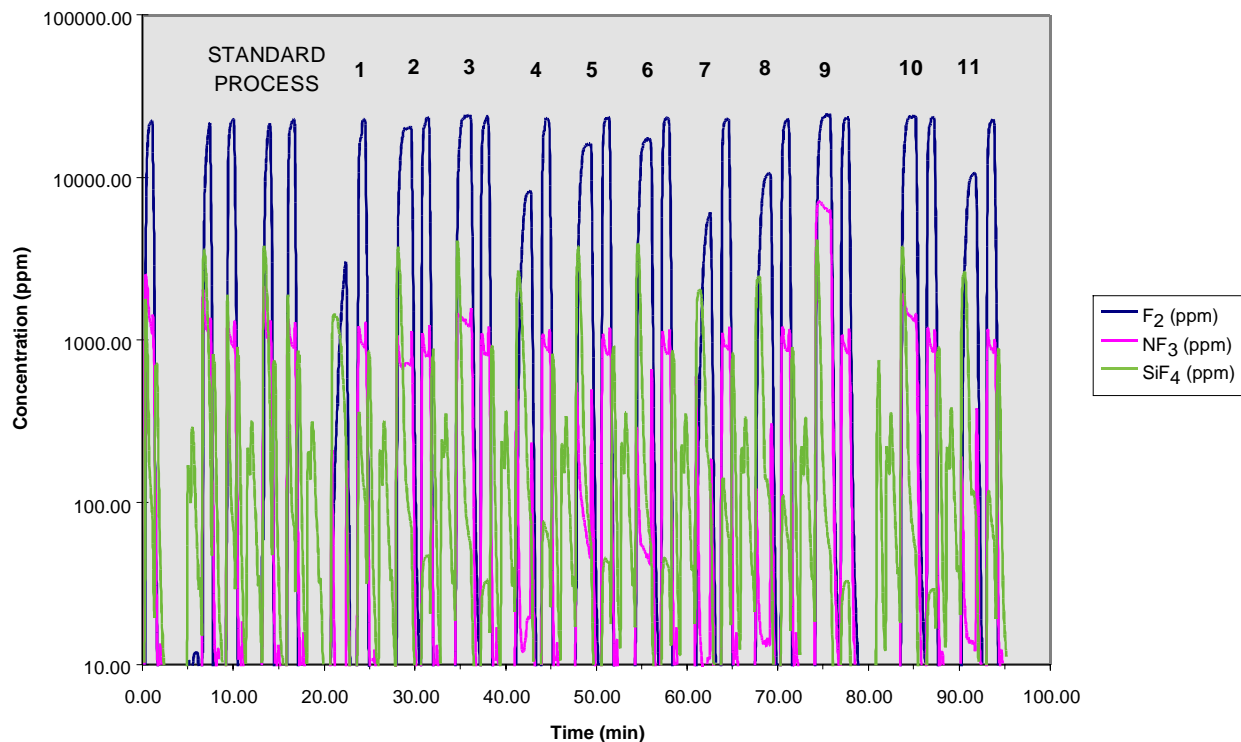
**Figure 20** HF Measurements for  $\text{NF}_3$  MW and  $\text{C}_2\text{F}_6$  RF



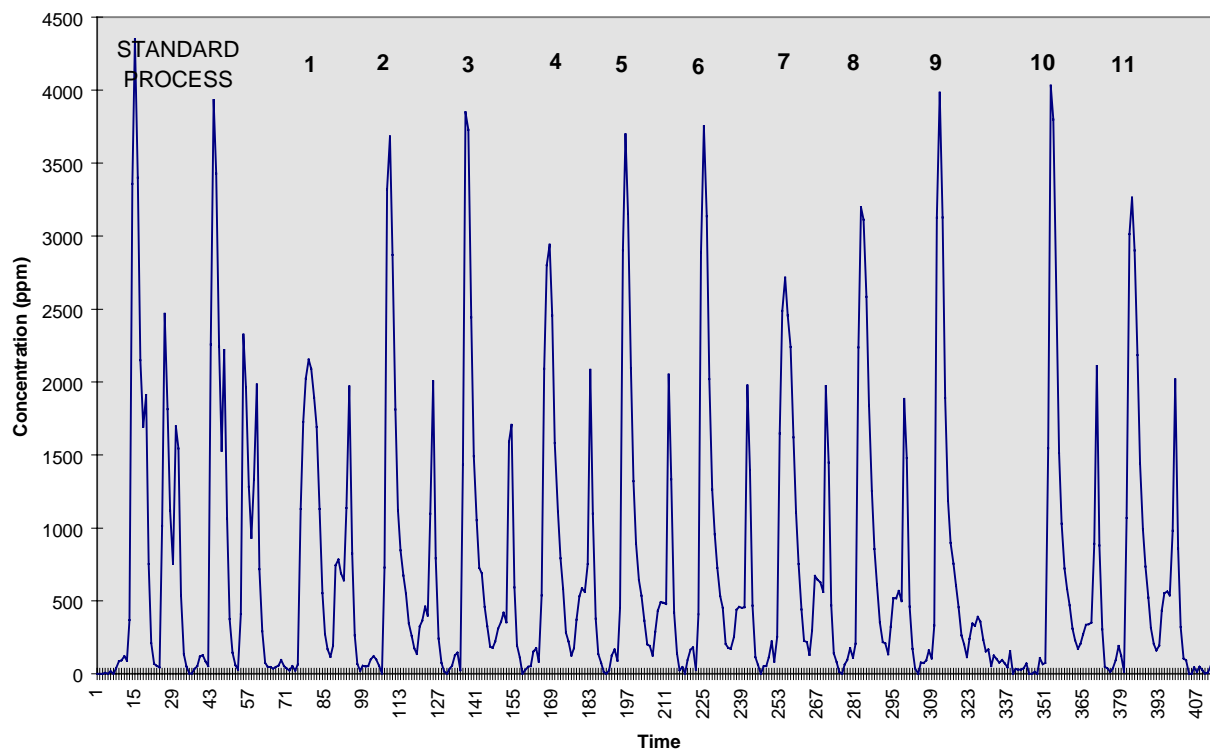
**Figure 21** Mass Spectrum of C<sub>2</sub>F<sub>6</sub> RF Clean



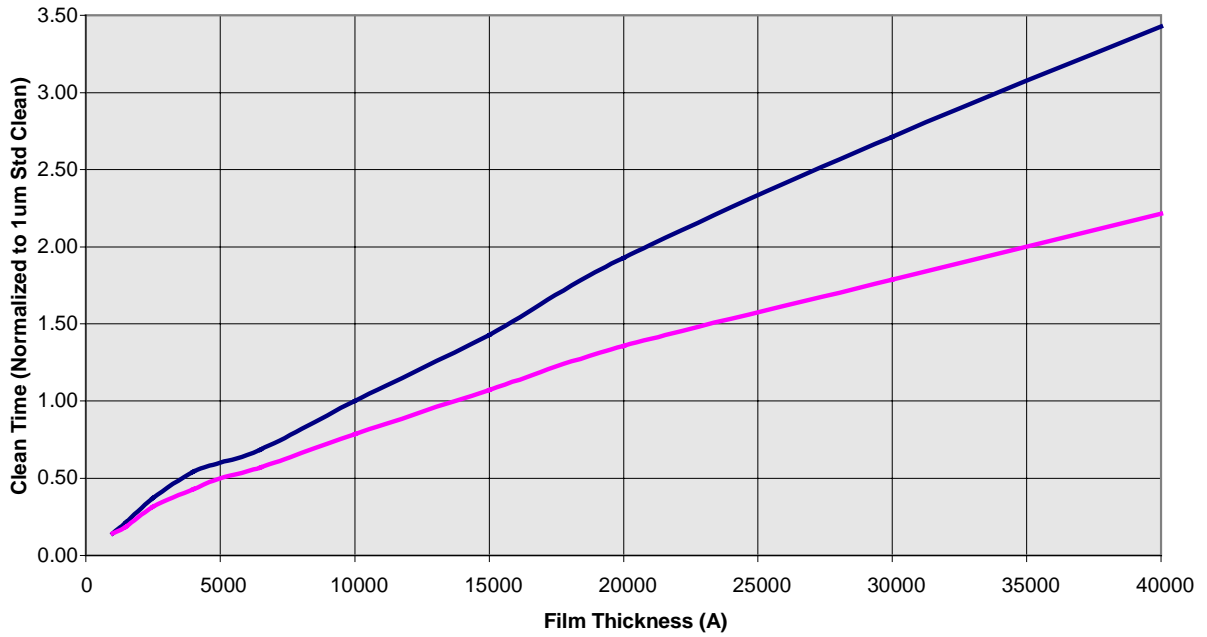
**Figure 22** C<sub>2</sub>F<sub>6</sub> RF Clean



**Figure 23 DOE Matrix**



**Figure 24 Standard NF<sub>3</sub> MW Process During DOE**

**Applied Materials Microwave Clean**

Standard in-situ C<sub>2</sub>F<sub>6</sub>/NF<sub>3</sub> clean  
Remote microwave clean (µClean)

**Figure 25 Clean Time Comparison**

## APPENDIX E DOE Summary

### Screening Fit Endpt

RSquare	0.998395
RSquare Adj	0.995988
Root Mean Square Error	0.987722
Mean of Response	64.18182
Observations (or Sum Wgts)	11

### Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	6	2427.7940	404.632	414.7543
Error	4	3.9024	0.976	Prob>F
C Total	10	2431.6964		<.0001

### Lack of Fit

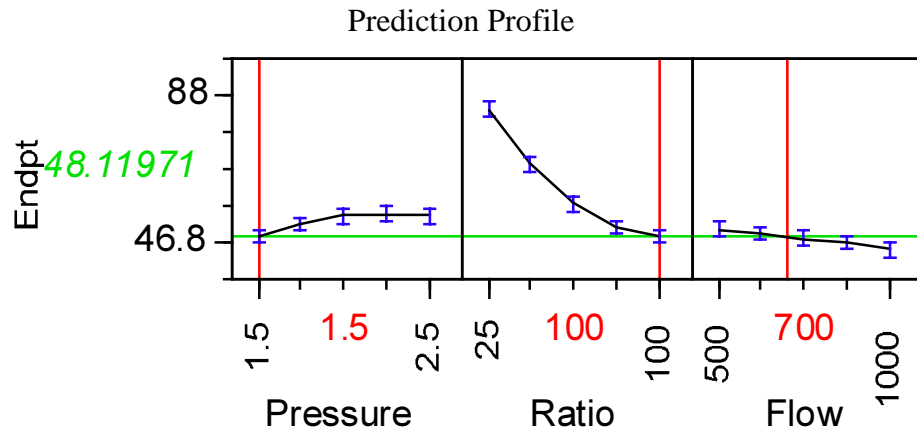
Source	DF	Sum of Squares	Mean Square	F Ratio
Lack of Fit	2	2.9223810	1.46119	2.9820
Pure Error	2	0.9800000	0.49000	Prob>F
Total Error	4	3.9023810		0.2511
Max RSq				0.9996

### Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob> t
Intercept	62.619841	12.21491	5.13	0.0069
Pressure	51.495238	10.79345	4.77	0.0088
Pressure*Pressure	-11.45714	2.692077	-4.26	0.0131
Ratio	-1.220603	0.05885	-20.74	<.0001
Ratio*Ratio	0.0059962	0.00046	13.04	0.0002
Flow	-0.000843	0.015523	-0.05	0.9593
Flow*Flow	-0.000007	0.00001	-0.65	0.5533

### Effect Test

Source	Nparm	DF	Sum of Squares	F Ratio	Prob>F
Pressure	1	1	22.20668	22.7622	0.0088
Pressure*Pressure	1	1	17.67044	18.1125	0.0131
Ratio	1	1	419.69271	430.1914	<.0001
Ratio*Ratio	1	1	165.90241	170.0525	0.0002
Flow	1	1	0.00288	0.0029	0.9593
Flow*Flow	1	1	0.40741	0.4176	0.5533



## Effect Screening

Response: Endpt

The estimates are correlated and need a transformation.  
The estimates have different variances and need scaling.

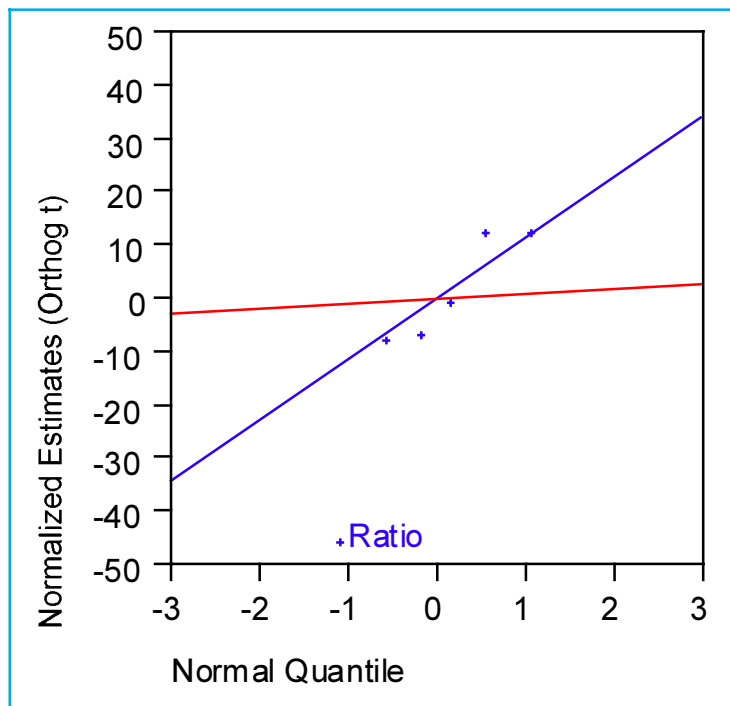
Lenth PSE  
11.365487

## Transformed Parameter Estimates

Term	Original	Orthog Coded	Orthog t-Test	Prob> t
Intercept	62.61984	64.18182	215.5130	<.0001
Pressure	51.49524	3.64573	12.2418	0.0003
Pressure*Pressure	-11.45714	-2.25650	-7.5770	0.0016
Ratio	-1.22060	-13.56935	-45.5639	<.0001
Ratio*Ratio	0.00600	3.70621	12.4449	0.0002
Flow	-0.00084	-2.10357	-7.0635	0.0021
Flow*Flow	-0.00001	-0.19245	-0.6462	0.5533

Each Orthog Estimate is conditioned on the effects before it

## Normal Plot

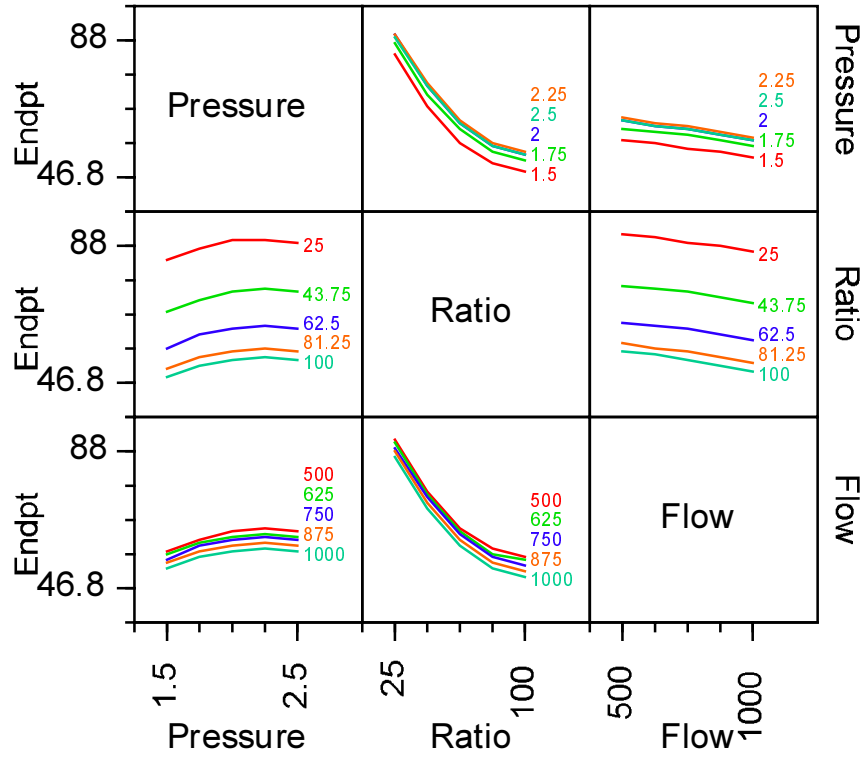


Blue line is Lenth's PSE.

Red line is RMSE.

Interaction Profiles

Response: Endpt





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