Fate of Fluorine Determination in Exhaust from NF_3-Based CVD Chamber Cleans

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Overview

I. Project Objectives
II. Fluorine Emission Regulatory Issues
III. AMAT Remote Clean™ Technology
IV. Experimental Methodology
V. Data Analysis
VI. Summary
VII. Future Work

Project Objectives

- Determine effect of increased F_2 in exhaust system and effect on emissions treatment infrastructure
- Quantify F_2 in segregated acid exhaust duct (FRP) downstream of tool equipped with Remote Clean™
- Measure emissions using RGA, FTIR, FCS
  - Quantify F_2 emissions and F_2 to HF conversion efficiency
    - as a function of H_2O-to-F_2 ratio (damper position)
    - reaction time (damper position and sampling point)
- Evaluate FCS technology as alternative to RGA/impinger/IC
- Perform materials compatibility study of exhaust duct polymeric coupons placed in exhaust stream (F_2, HF)
- Determine if OF_2 is produced
- Calculate fluorine mass balance

Fluorine Emission Regulatory Issues

- NF_3 chamber clean F_2 emissions are 6X C_2F_6
  - impacts on scrubber efficiency, fluoride ion in wastewater
- F_2 is not a HAP as defined by EPA in 40 CFR 63
  - F_2 regulated by states (TNRCC) New Source Review (NSR)
  - NSR insures ground level concentrations are below ESL
- ESL (Effects Screening Level) evaluates:
  - potential health effects, odor potential, potential effects on vegetation, corrosion potential → *not ambient air standards*
- ESL for F_2 is very low--2 $\mu g/m^3$ (arsine is 1.6 $\mu g/m^3$)
- F_2 is a Toxic Release Inventory (TRI) reportable chemical if used or generated above a certain level
  - current thresholds: 10,000 lb used or 25,000 lb generated
    - ⇨ *included are F_2 from NF_3 cleans and etch emissions*

Fluorine Reactivity

- Highly electronegative, strongest oxidizer
- Small atomic radius
- Reactivity due to small size (0.71Å) high nuclear charge
- Thermodynamically favored reaction with water:

$$F_2 + H_2O \rightarrow HOF + HF$$

$$HOF + H_2O \rightarrow H_2O_2 + HF$$

$$HOF + H_2O_2 \rightarrow HF + H_2O + O_2$$

$$F_2 + H_2O_2 \rightarrow 2HF + O_2$$

  – Net Reaction: $2F_2 + 2H_2O \rightarrow 4HF + O_2$
- In caustic media:

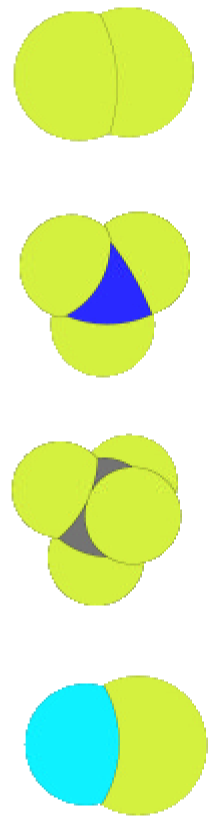
$$2F_2 + H_2O \rightarrow 2HF + OF_2$$

- OF_2 production increases in alkaline solutions (esp. NaOH)

Fluorine Reactivity

Bond Dissociation Energies (kcal/mol)

Increasing bond strength, stability ↓

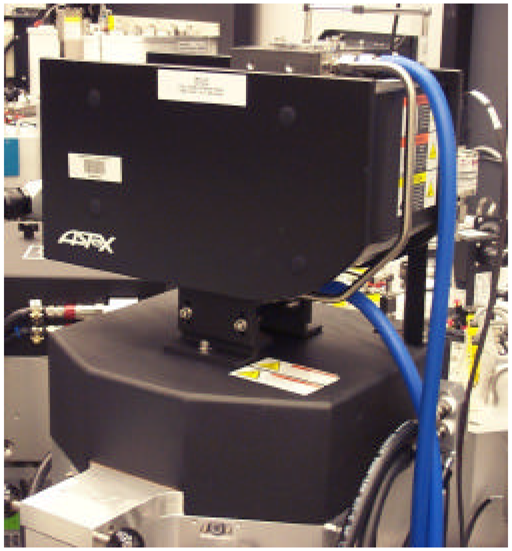


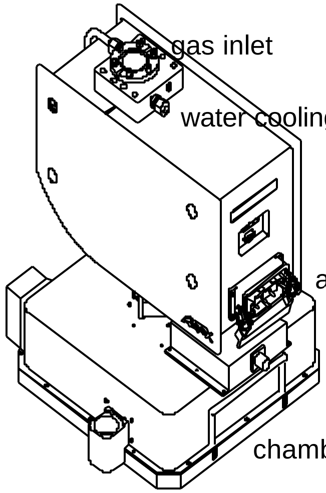
F_2	37.7
NF_3	66.4
CF_4	109.0
HF	136.0

AMAT Remote Clean™ Technology

- Compact, lid-mounted, point of use
- Low-field torroidal microwave (2.45 GHz)
- No consumables
- Converts 95-99% NF_3 to atomic fluorine
- No ion bombardment
  - increased chamber kit longevity
- F_2 cleans remote chamber areas
  - increased time between wet cleans
- Faster clean times (30%--DxZ, 65%--DxL)
  - increased throughput
- Improved film deposition uniformity
- Uses up to 50% NF_3 (Ar balance)
  - 0.1 to 4.0 slm total gas flow, 1-8 Torr

Remote Clean™ Unit on DxZ Chamber

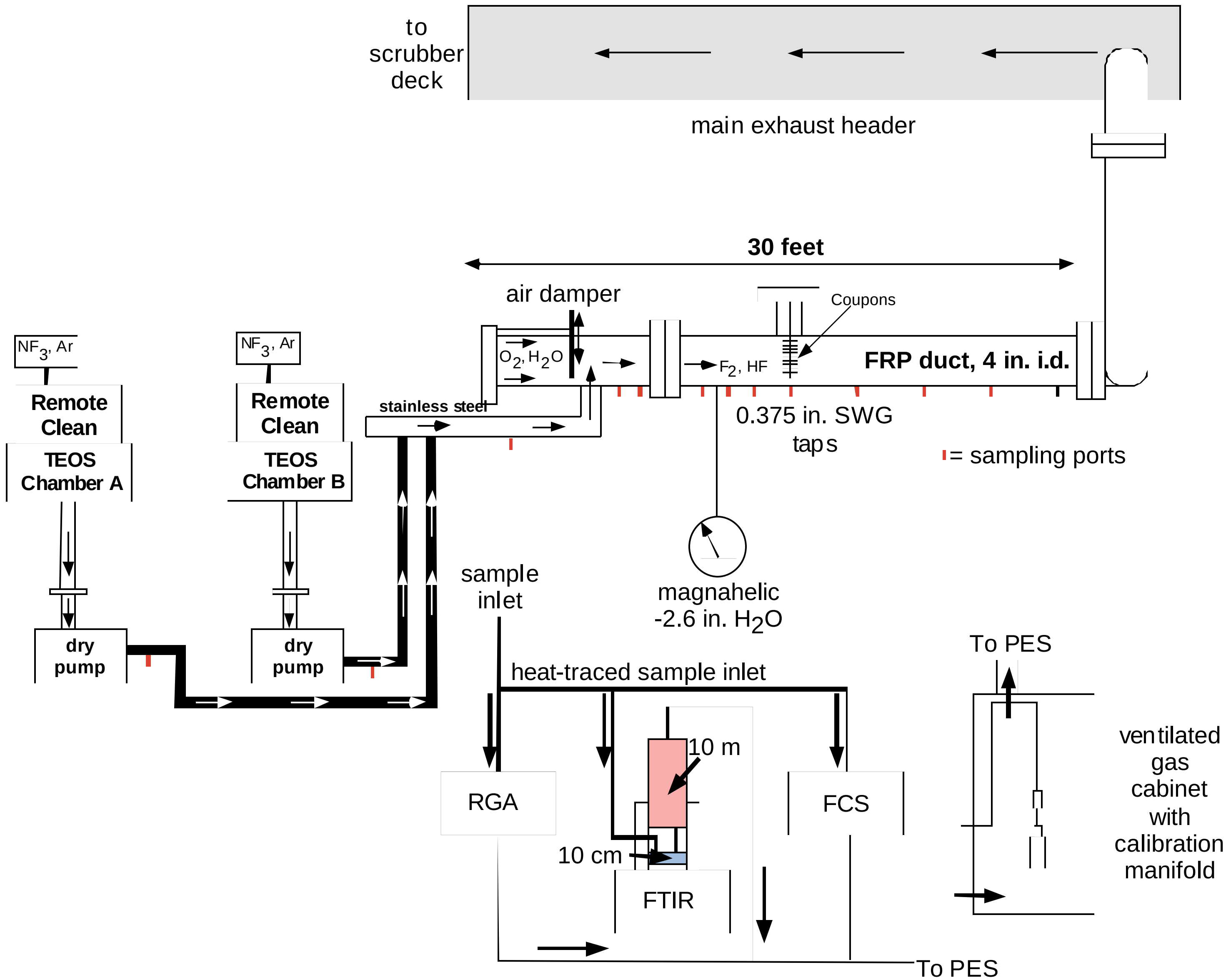




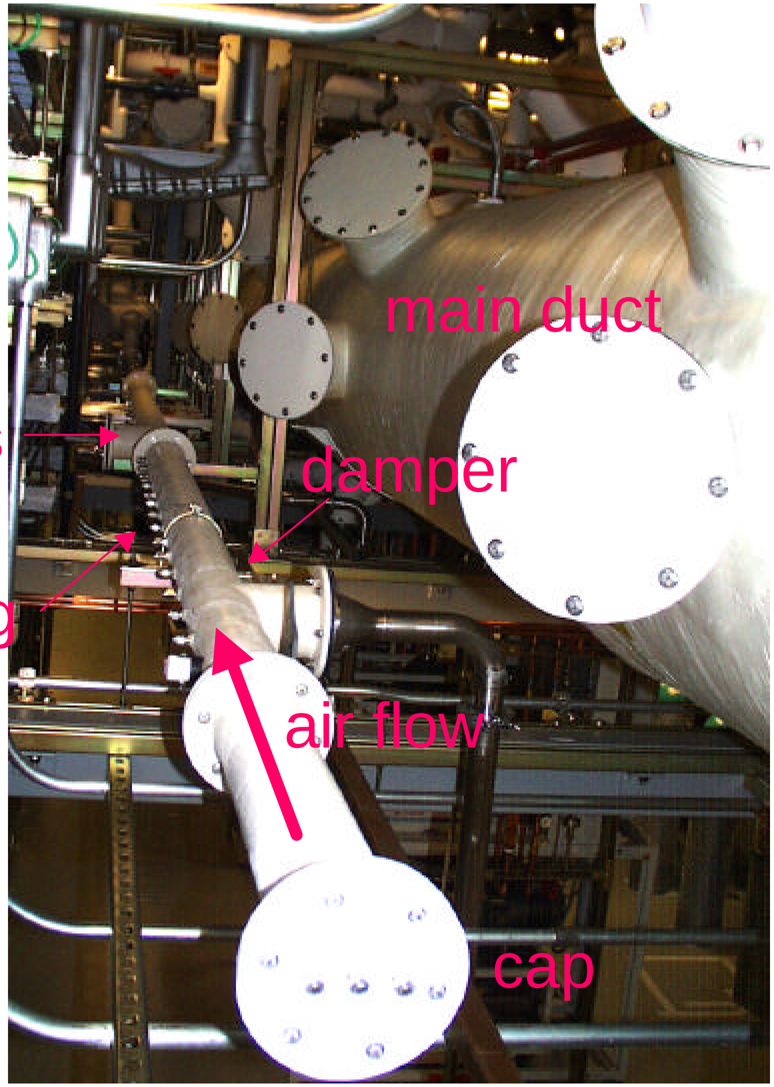
Experimental Methodology

- Continuous air flow measurements made using velocimeter
- Mechanical pump purge regulated by MFC
- Ambient air (45% R.H., 6800 ppm H_2O) introduced to duct
  - Increased H_2O in duct using humidifier
- Damper controls H_2O-to-F_2 ratio and reaction time
  - H_2O-to-F_2 ratio ranges from 4.4-to-1 to 45.8-to-1
  - Reaction time ranges from 0.15 to 5 sec
- Analytical: extractive FTIR, atmospheric pressure RGA, FCS
  - Pneumatically switched dual-cell FTIR (10 cm, 10 m)
  - All instruments have common sampling point
  - Heat-traced and purged transfer lines (except FCS)
  - RGA and FCS calibrated using "dynamic dilution"
- Clean recipe used: 700 sccm NF_3, 1400 sccm Ar, 900 sec

Fluorine Test Lateral Schematic



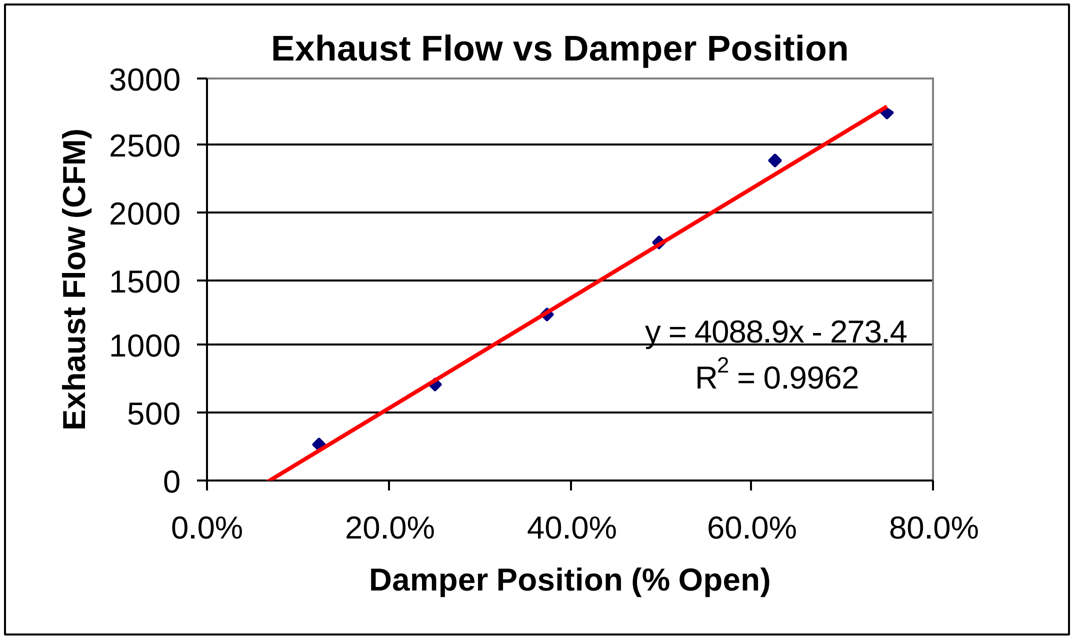
FRP Test Lateral



Air Flow Measurements

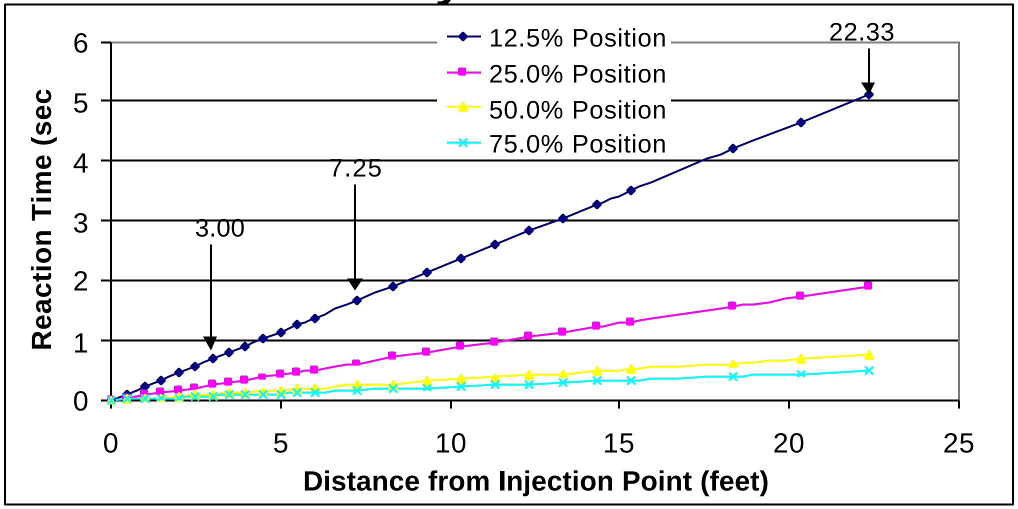
Damper Position (% Open)	Velocity (feet/min)	CFM	Liter/min	Negative Static Pressure (in. H_2O)	*H_2O-to-fluorine ratio
0.0%	NA	NA	NA	2.600	NA
12.5%	262	23	651	2.600	4.43
25.0%	705	62	1756	2.536	11.94
37.5%	1243	109	3087	2.556	20.99
50.0%	1773	155	4390	2.498	29.85
62.5%	2383	209	5919	2.576	40.25
75.0%	2727	238	6740	2.430	45.83
100.0%	2721	238	6740	2.439	45.83

*Based on 45% r.h., 6800 ppmv H_2O in air

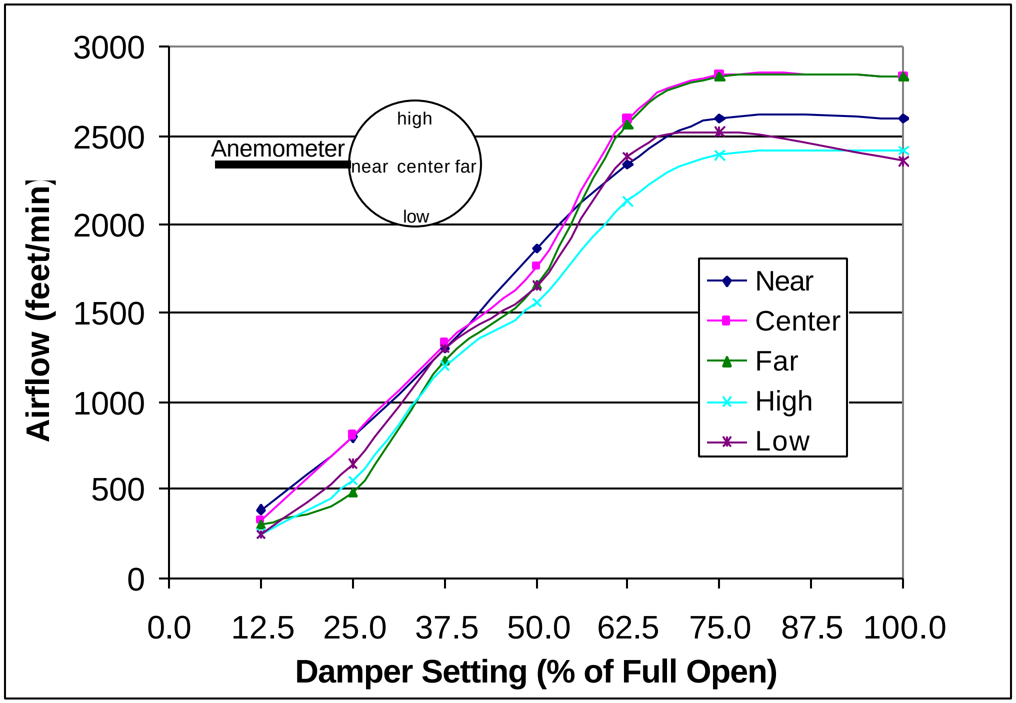


Air Velocity Measurements

Reaction Time as a Function of Distance from F_2 Injection Point



Air Velocity as a Function of Radial Position



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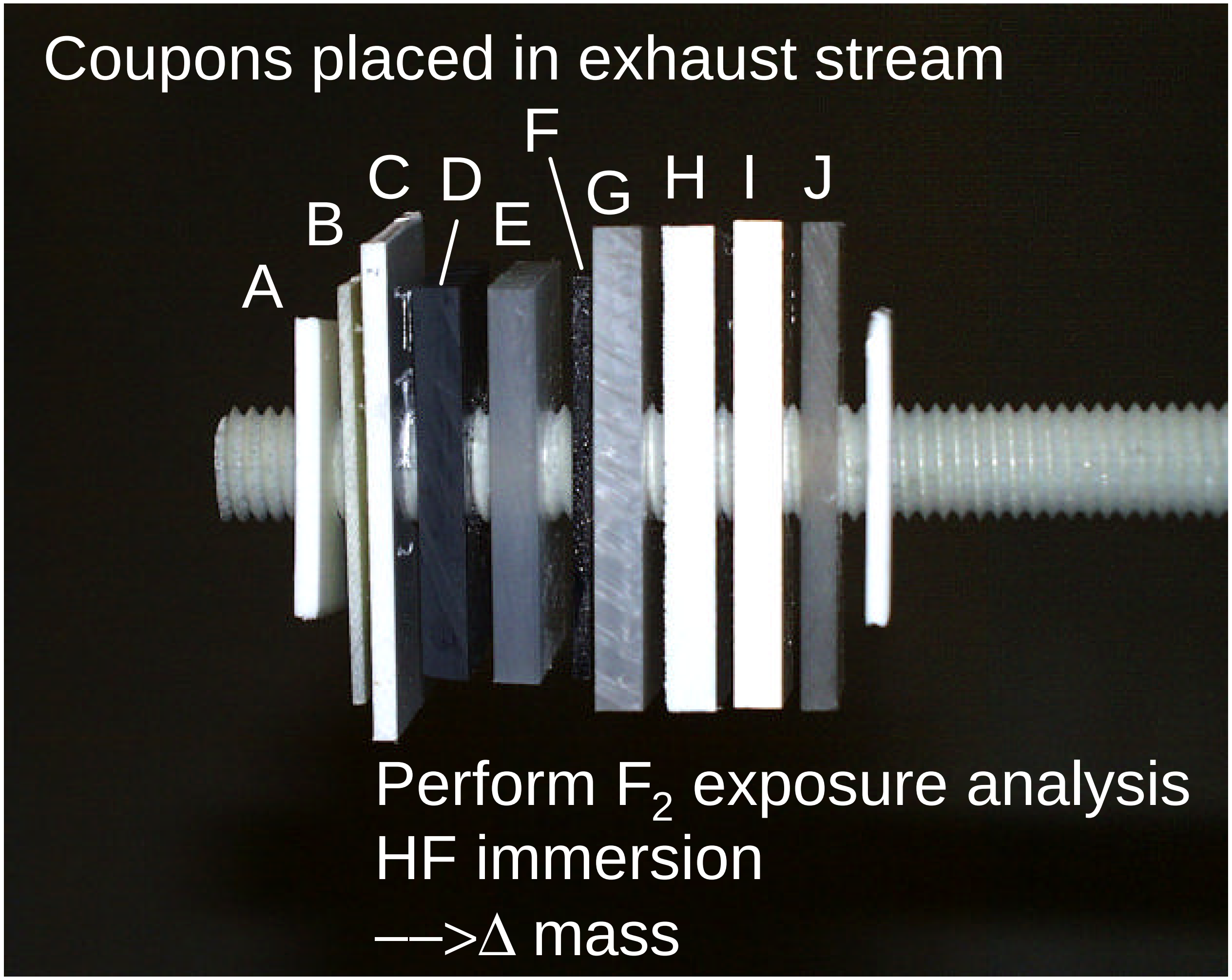
Duct Material Evaluation



A: PTFE (Teflon)

B: FRP (Fiberglass Reinforced Plastic)

C: FRPP (Flame Retardant Polypropylene)

D:PVC (Polyvinylchloride)

E: PP (Polypropylene)

F: ATS (Air Tight Systems brand of FRP)

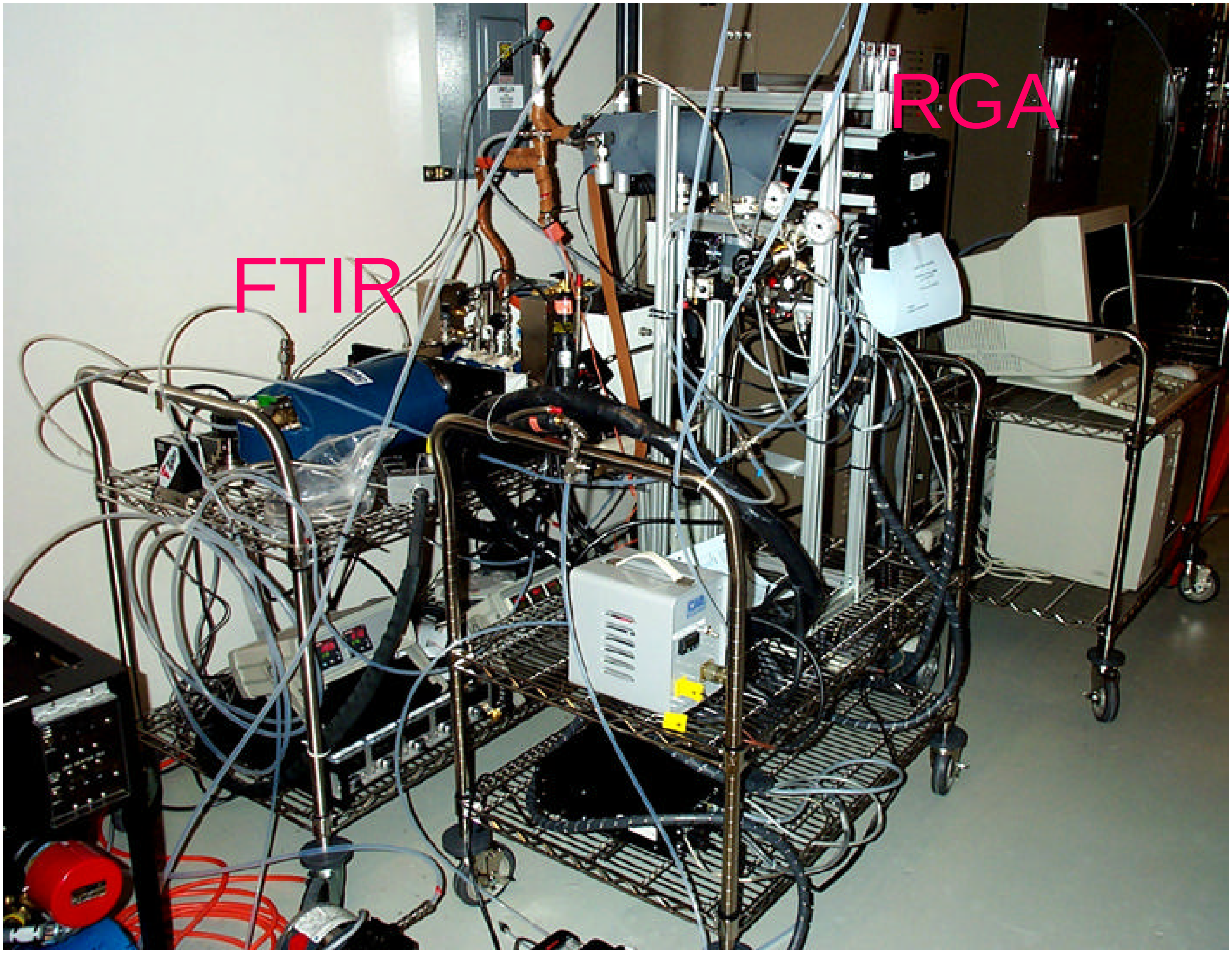
G: PVDF (Polyvinylidene fluoride or Kynar)

H: Flametec (KYTEC PVDF)

I:Corzan

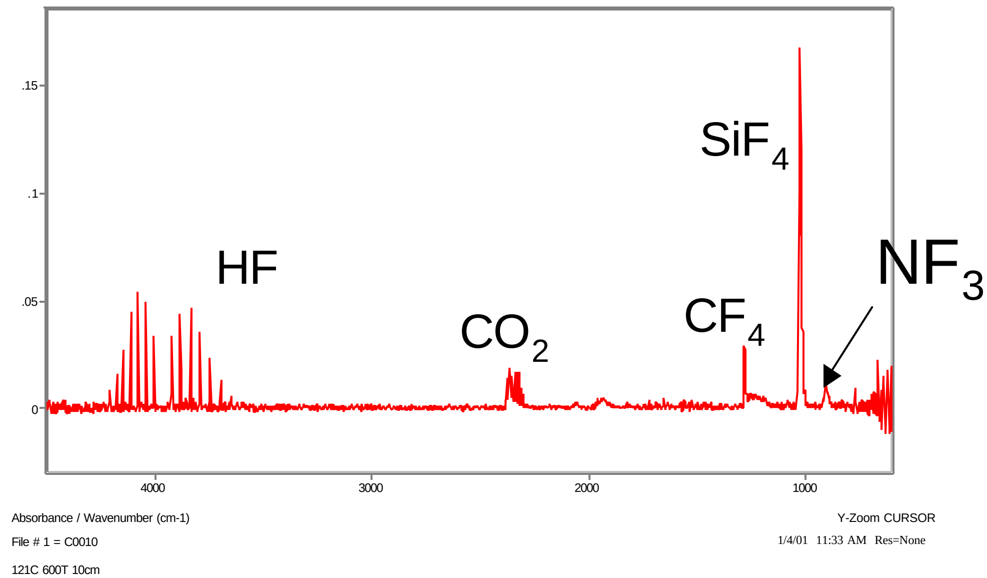
J: Halar

FTIR, RGA Sampling Arrangement

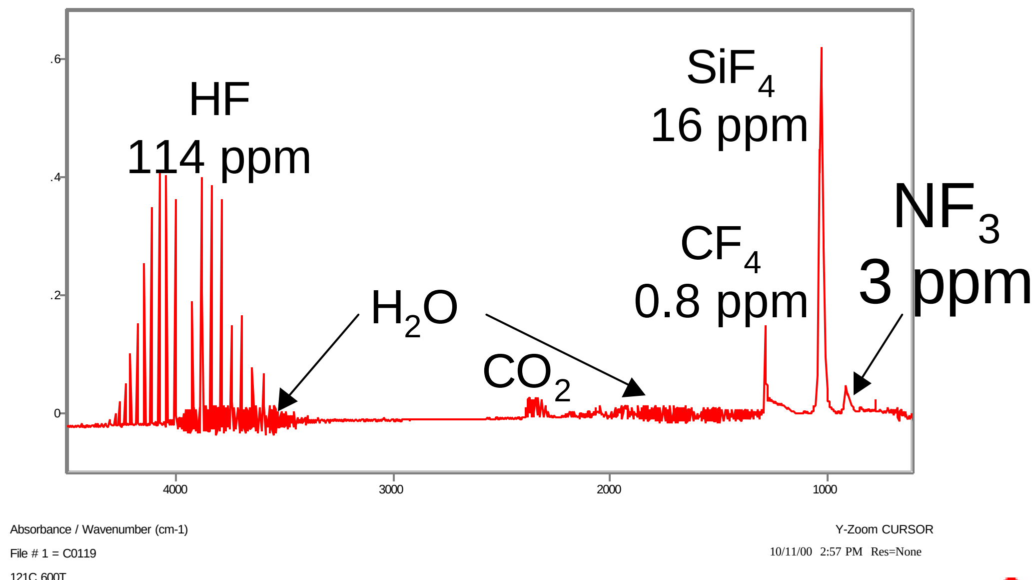


FTIR NF_3 Chamber Clean Emissions

Stainless steel duct 10 cm



FRP duct 10 m



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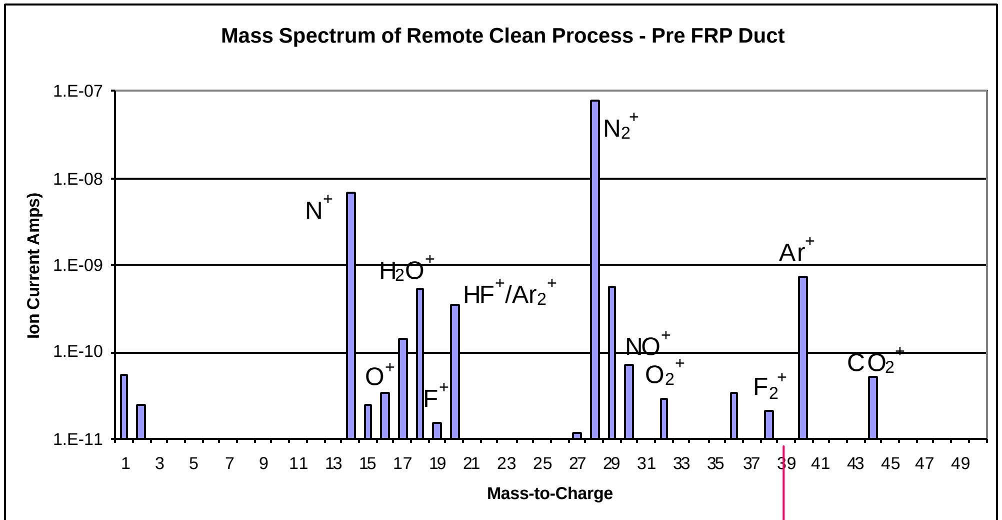
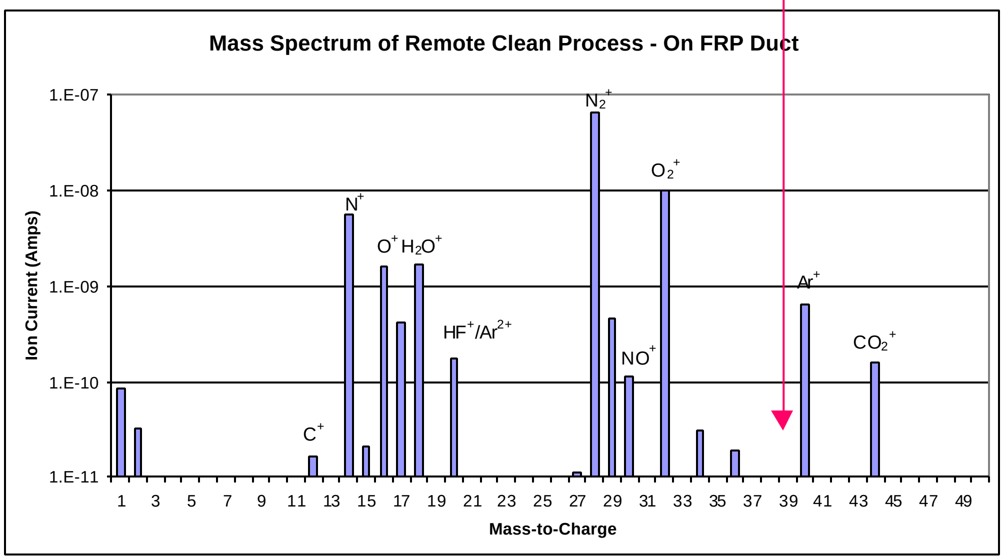
RGA NF_3 Chamber Clean Emissions



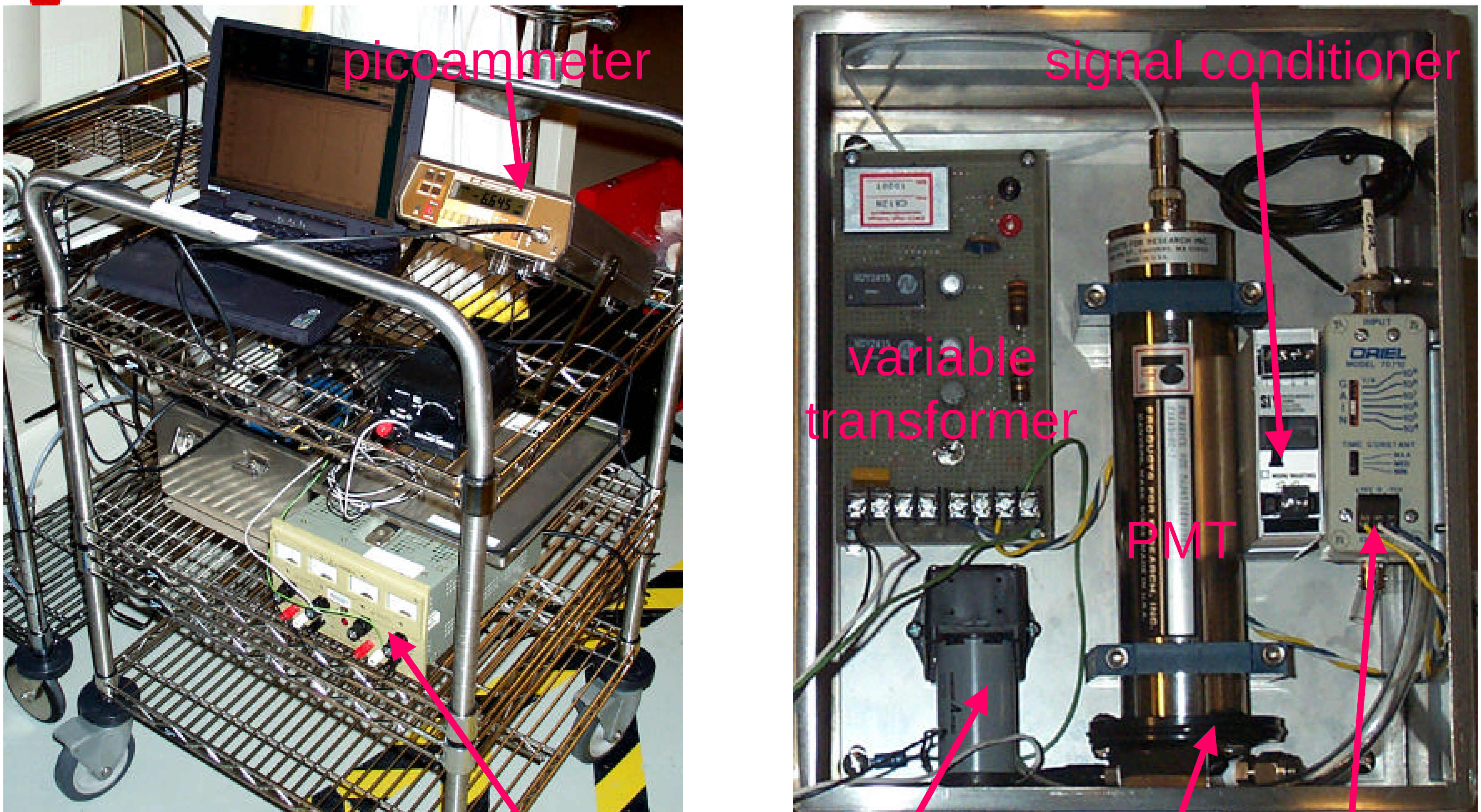
Post-pump measurement



Higher CO_2, H_2O

FRP duct measurement --F_2 below detection limit

URS Radian Fluorine Chemical Sensor



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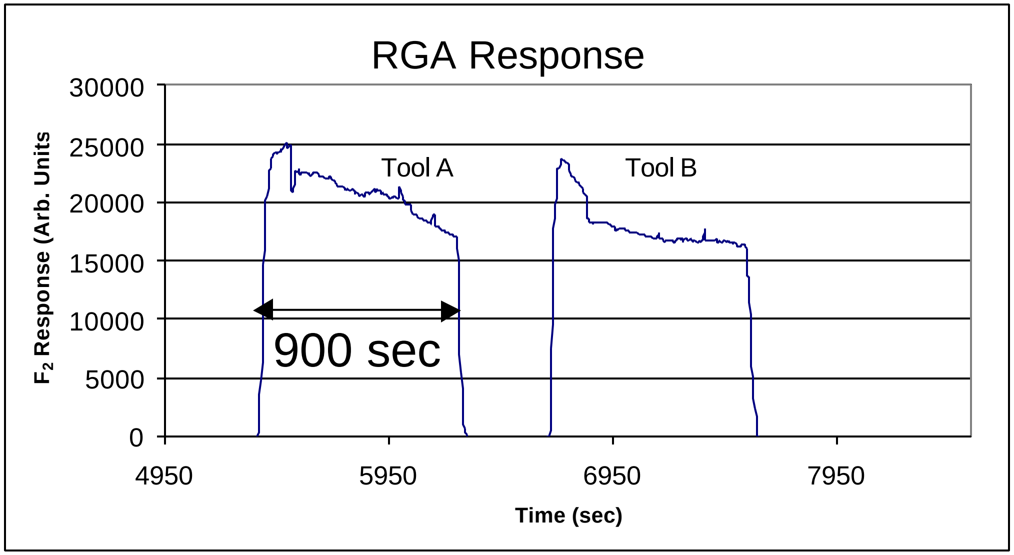
URS Radian
Fluorine Chemical Sensor (FCS)

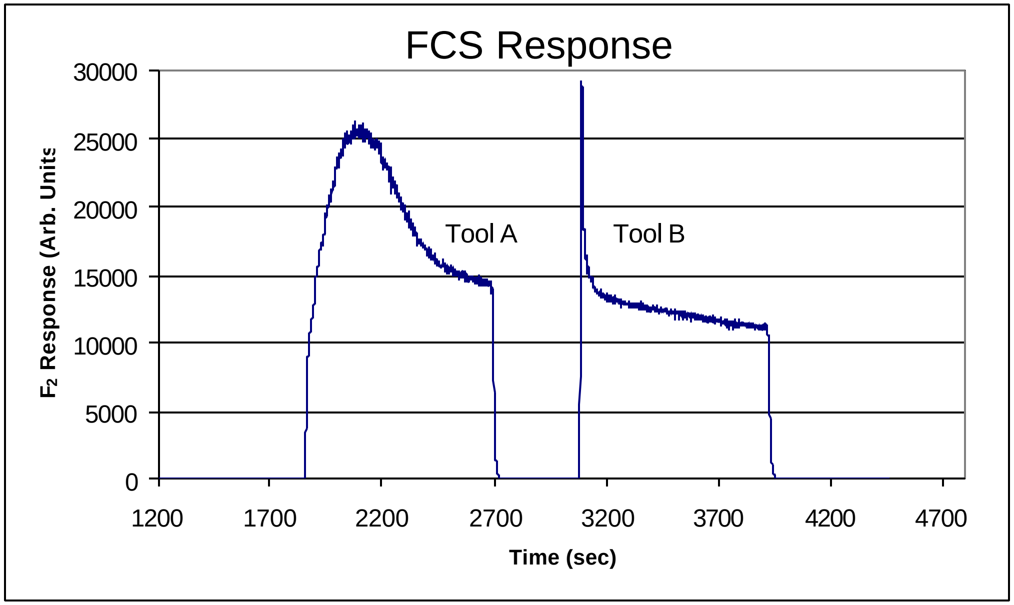
- Real-time, solid-state gas sensing device with ppb-level sensitivity and wide measurement range
- Applicability ranges from ambient air (scrubber) to dry nitrogen (tool effluent) characterizations
- Based on the chemical interaction of F_2 with organic substrate; no known cross interferents
- Fast response, small footprint, no vacuum system required
- Calibration performed at constant flow

FCS Operation and Performance Specifications

Measurement range	**0 to percentage levels (>10000 ppmv)**
Measurement precision	$\pm$ **2%**
Minimum detection limit	**10 ppbv**
Detector response time	**msec**
Sample cell operating pressures	**mTorr to several atm**
Footprint	**cell/detector: 12”x 3”x 3”**
Weight	**cell/detector: 2 lbs**
Electrical requirements	**24 VDC**
Applicable sample matrices	**Ambient air, tool effluent (low pressure or N_2 diluted), water saturated air or nitrogen streams (wet scrubber outlets)**
Chemical interferences	**None observed for mixtures containing SiF_4, HF, O_2, Cl_2, HCl, PFCs and H_2O**

RGA and FCS Comparison During Clean





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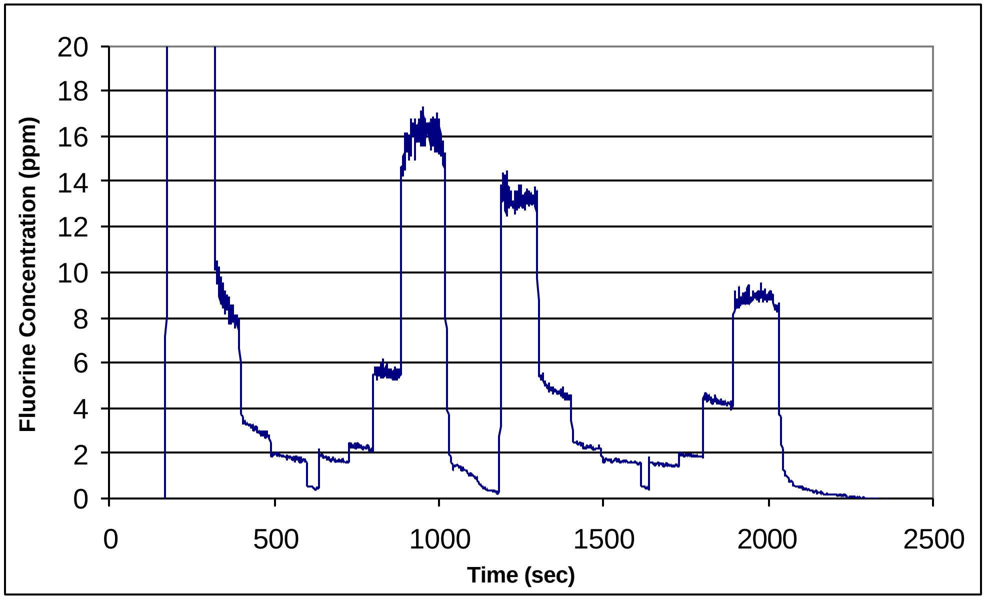
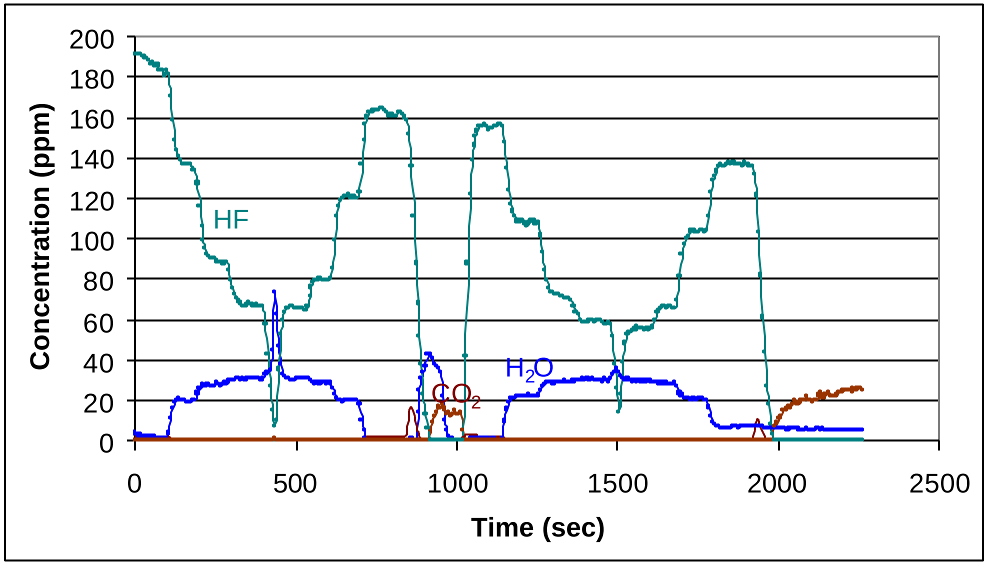
FCS and FTIR NF_3 Chamber Clean Emissions

FCS



FTIR



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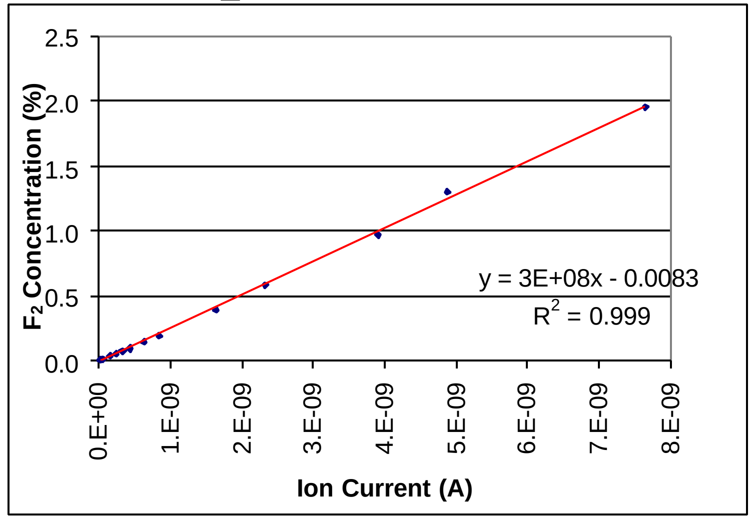
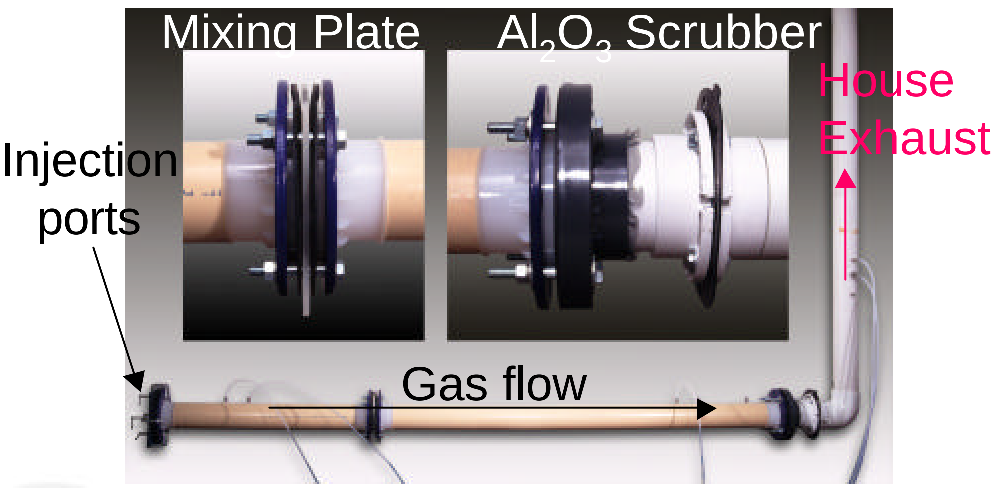
Analytical Calibration of Fluorine

3 analyte panels, 1 N_2 panel

Exhausted Gas Cabinet "Dynamic Dilution" Manifold

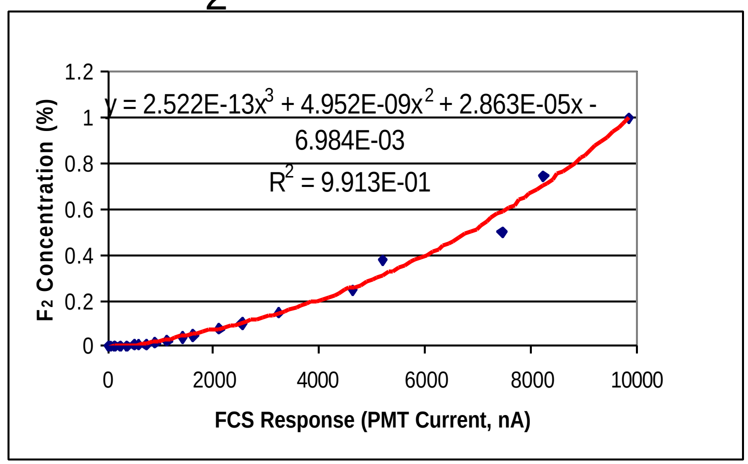
RGA F_2 Calibration Curve





URS Radian FCS PFA Calibration Duct

FCS F_2 Calibration Curve



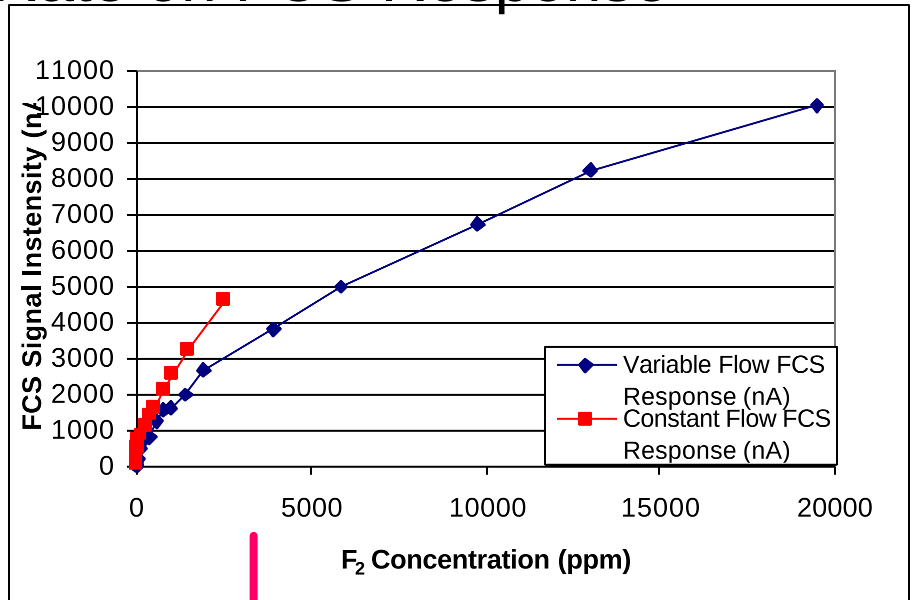
Effect of Calibrant Flow Rate on FCS Response

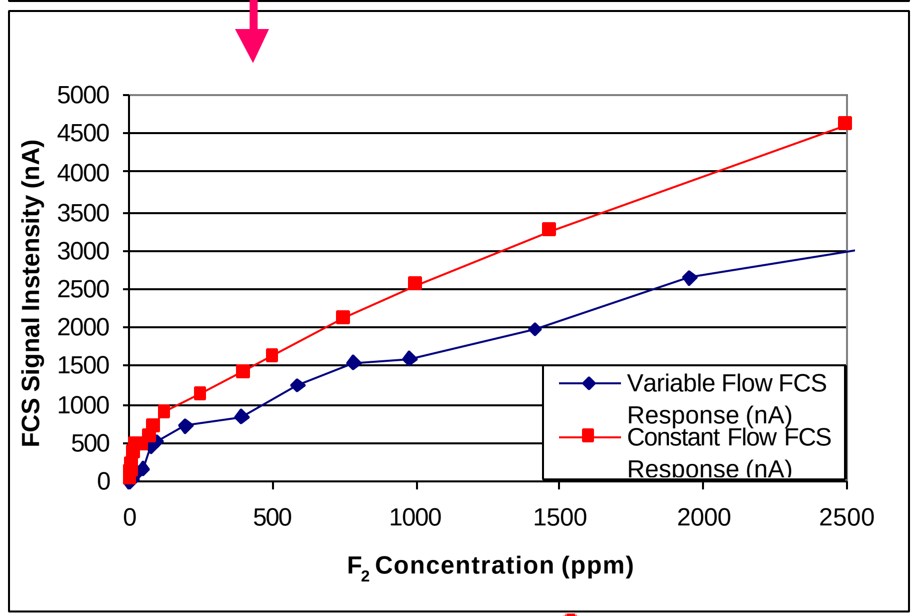
Conventional calibration--gas delivered directly to FCS; gas flow through FCS varies

F_2 Flow (sccm)	Nitrogen Flow (sccm)	Total Gas Flow (sccm)	Actual %	ppm
5	4995	5000	0.00195	19.5
10	4990	5000	0.0039	39.0
20	4980	5000	0.0078	78.0
25	4975	5000	0.00975	97.5
25	2475	2500	0.0195	195.0
50	2450	2500	0.039	390.0
60	1940	2000	0.0585	585.0
80	1920	2000	0.078	780.0
100	1900	2000	0.0975	975.0
75	925	1000	0.14625	1462.5
100	900	1000	0.195	1950.0
200	800	1000	0.39	3900.0
300	700	1000	0.585	5850.0
500	500	1000	0.975	9750.0
500	250.0	750	1.3	13000.0
500	0.0	500	1.95	19500.0

Calibration performed using mixing chamber at excess total gas flow; 5.0 slm constant flow through FCS

F_2 Flow (sccm)	Nitrogen Flow (sccm)	Total Gas Flow (sccm)	Actual %	ppm
10	30000	30010	0.000167	1.7
15	30000	30015	0.00025	2.5
20	30000	30020	0.000333	3.3
100	29900	30000	0.001667	16.7
100	19900	20000	0.0025	25.0
300	29700	30000	0.005	50.0
400	29600	30000	0.006667	66.7
500	29500	30000	0.008333	83.3
500	19500	20000	0.0125	125.0
1000	19000	20000	0.025	250.0
1600	18400	20000	0.04	400.0
2000	18000	20000	0.05	500.0
3000	17000	20000	0.075	750.0
4000	16000.0	20000	0.1	1000.0
5000	12000	17000	0.147059	1470.6
5000	5000.0	10000	0.25	2500.0





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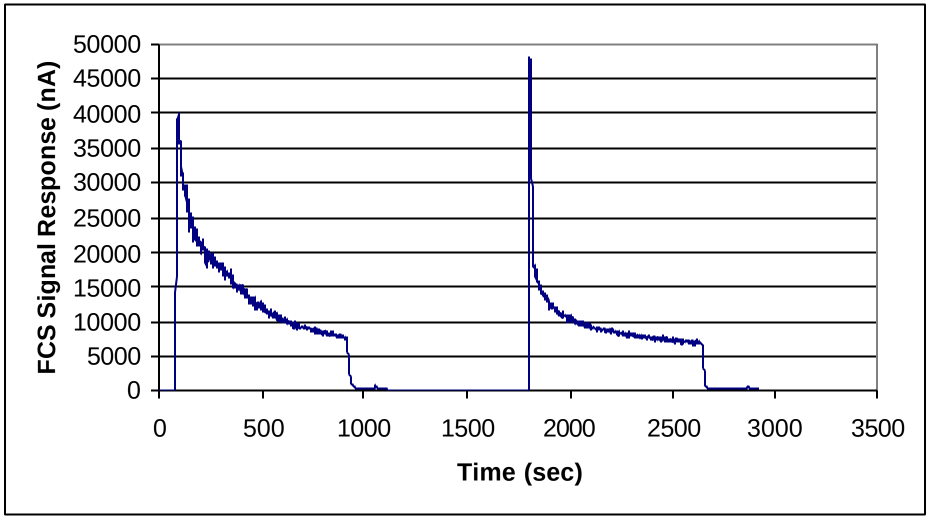
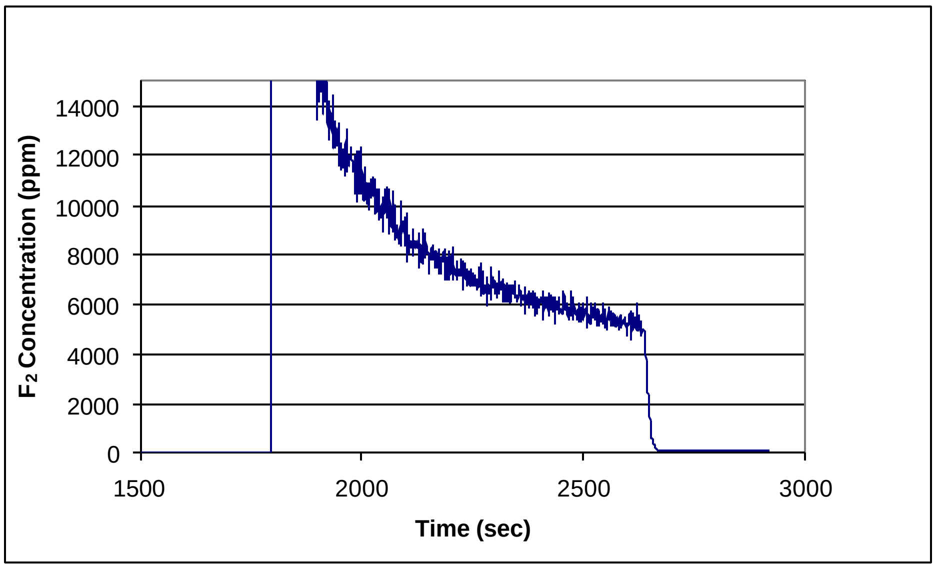
FCS Quantitation of F_2 Emissions in Stainless Duct

Two consecutive cleans

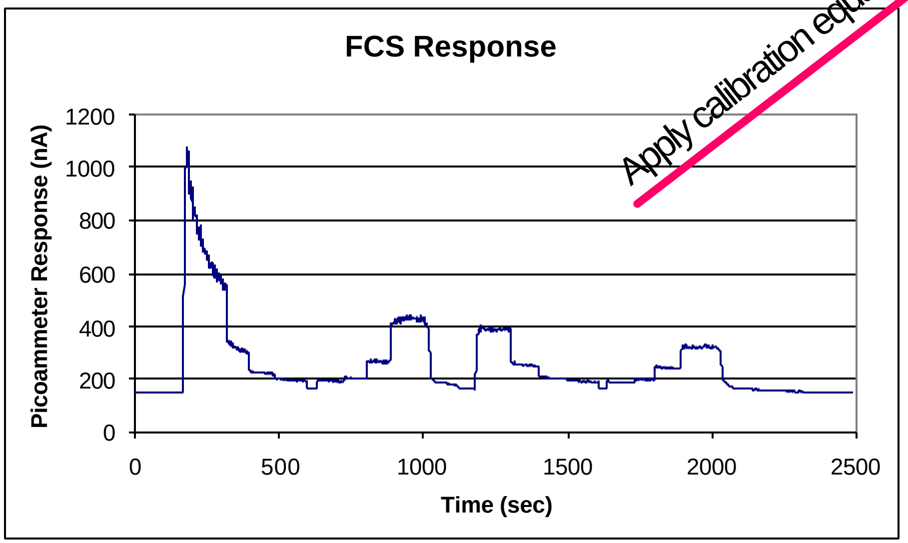


Calibration equation converts nA to ppm

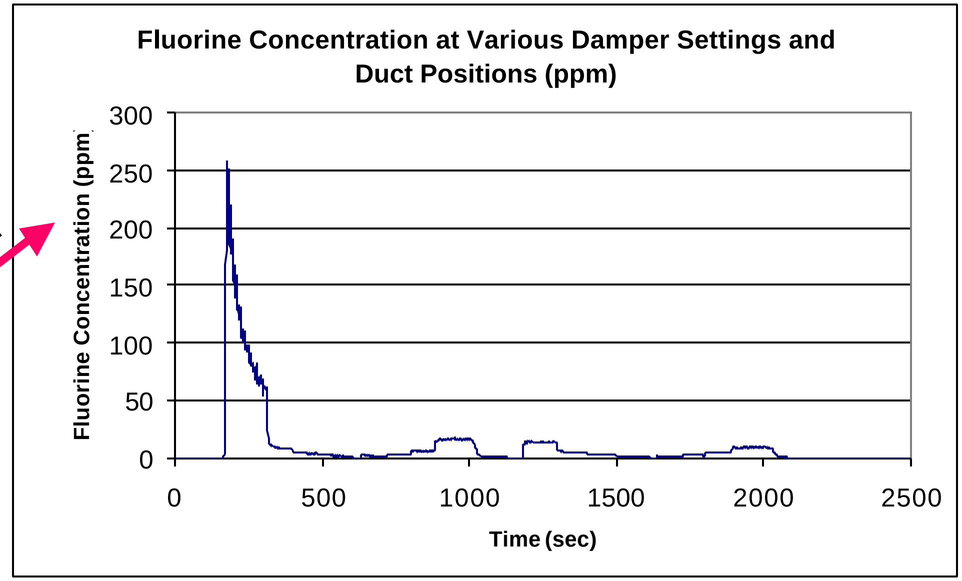


7500 ppm (avg.) = ~700 sccm F_2 from a 700 sccm NF_3 process

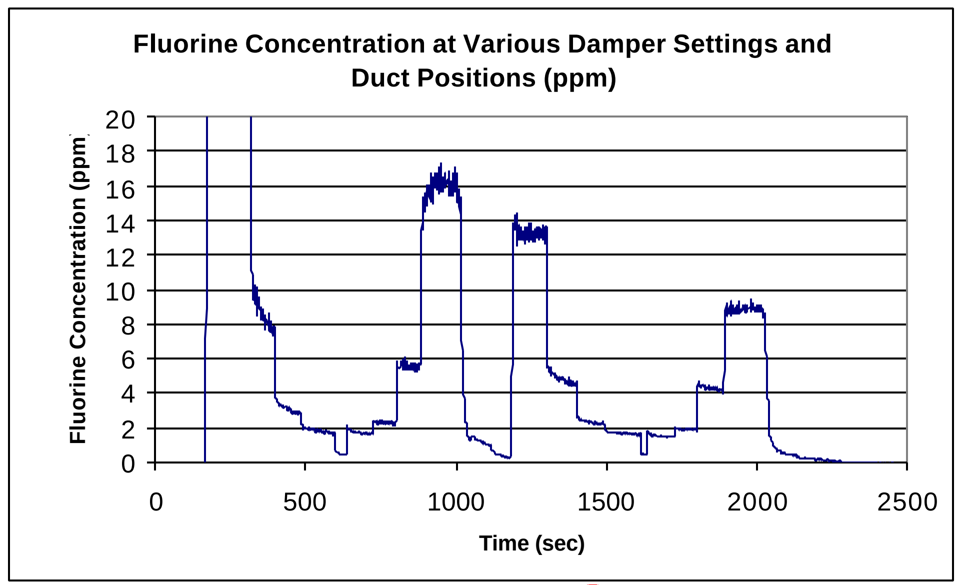
FCS Quantitation of F_2 Emissions in FRP Duct



Apply calibration equation



Expanded



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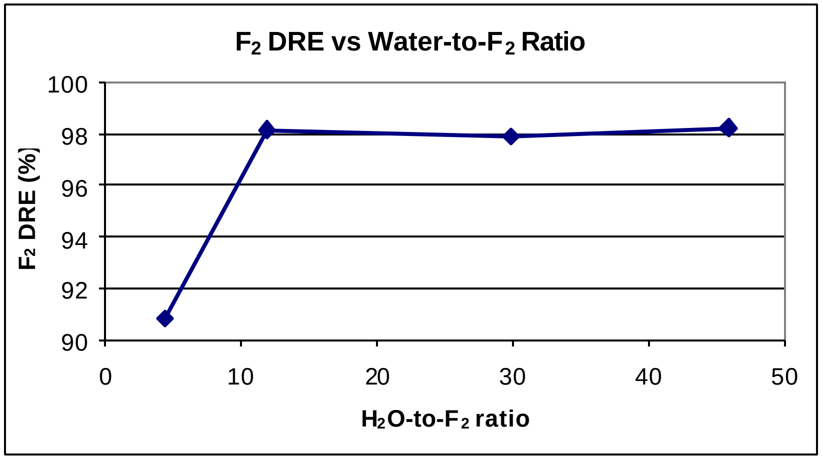
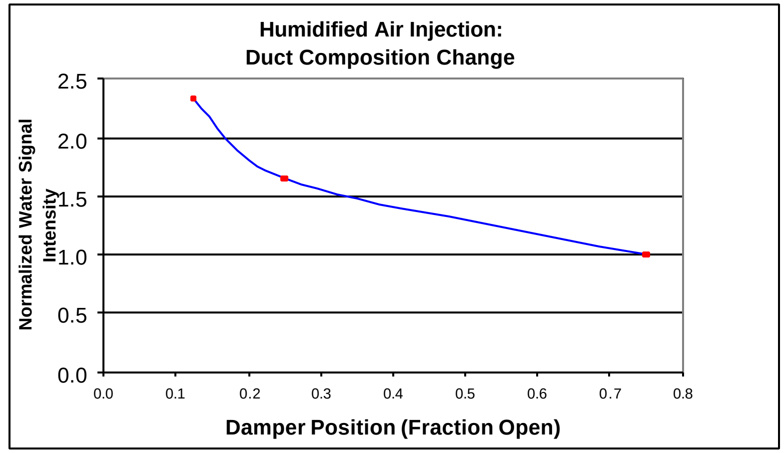
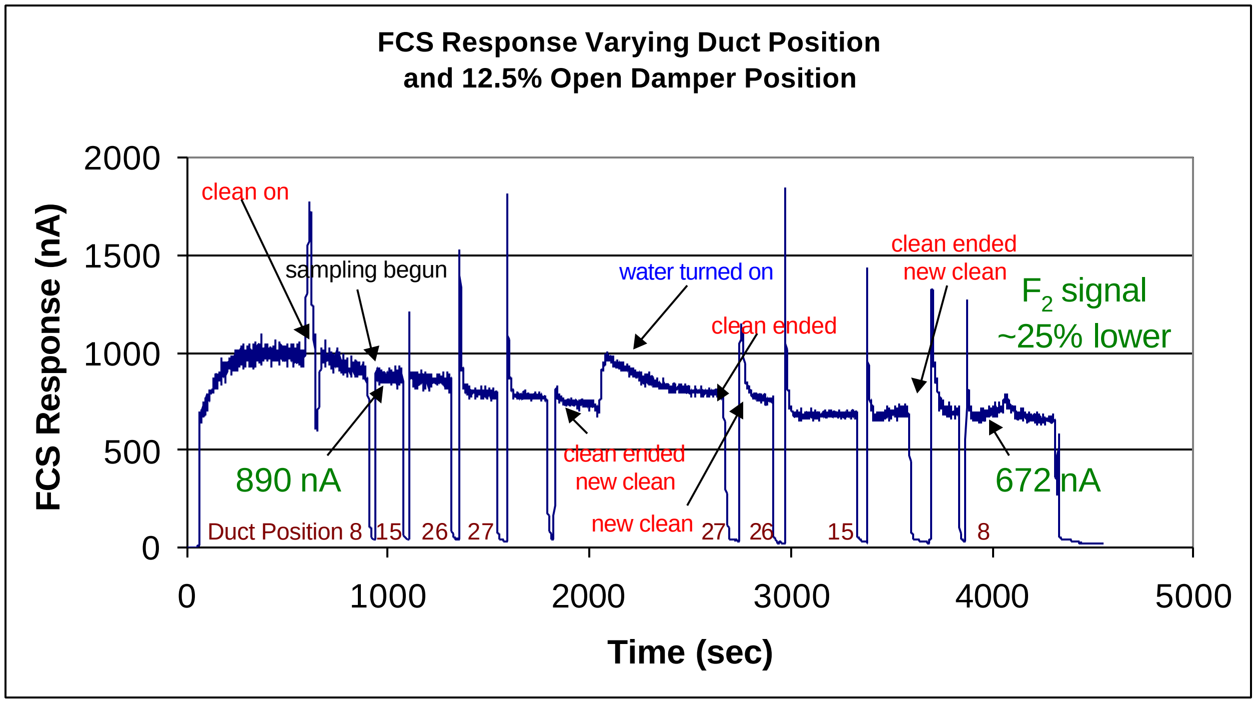
Effect of Water Concentration on F_2 DRE





H_2O concentration increased 15 to 168% depending on damper position



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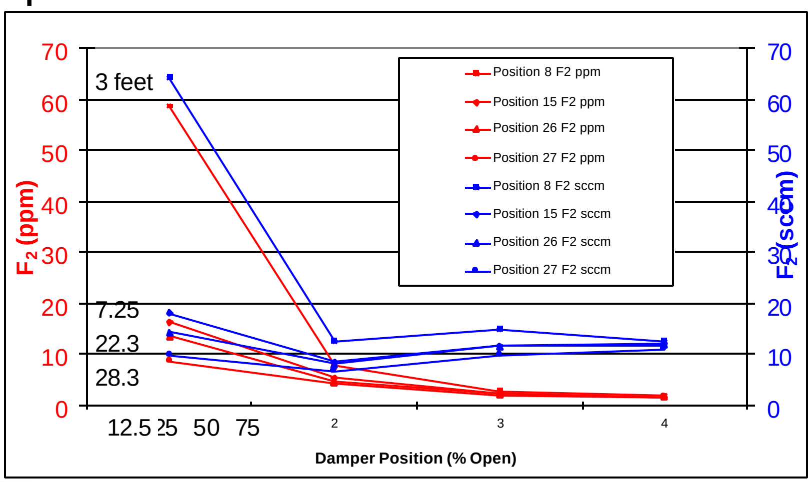
Fluorine DRE Summary

Damper Setting (% Open)	3.0 feet Downstream				7.25 feet Downstream				22.3 feet Downstream				28.3 feet Downstream			
	Average Flow (slm)	Maximum expected F_2 Concentration by Dilution (ppmv)	Average F_2 Measured (ppmv)	ΔF_2 (%)	Average Flow (slm)	Maximum expected F_2 Concentration by Dilution (ppmv)	Average F_2 Measured (ppmv)	ΔF_2 (%)	Average Flow (slm)	Maximum expected F_2 Concentration by Dilution (ppmv)	Average F_2 Measured (ppmv)	ΔF_2 (%)	Average Flow (slm)	Maximum expected F_2 Concentration by Dilution (ppmv)	Average F_2 Measured (ppmv)	ΔF_2 (%)
12.5	1096	639	58.51	-91	1098	638	16.33	-97	1058	662	13.50	-98	1125	622	8.73	-99
25	1617	433	7.79	-98	1559	449	5.51	-99	1782	393	4.57	-99	1586	441	4.22	-99
50	5275	133	2.81	-98	5116	137	2.25	-98	5254	133	2.21	-98	5267	133	1.86	-99
75	7539	93	1.66	-98	7625	92	1.61	-98	7565	93	1.56	-98	7600	92	1.45	-98

*700 sccm F_2 injected into FRP

Fluorine as a Function of Damper Position and Downstream Distance



Fluorine Mass Balance at First Test Point

3.0 Feet Downstream

Damper Position (% Open)	Mass Balance (F_{in}/F_{out})
12.5	21.4
25	17.4
50	35.3
75	37.8

*90-95% of F detected as HF

Duct Material Evaluation Results

Coupon #	Material	Other Identifier (Tradename etc.)	Initial Coupon Mass (g)	After F_2 Exposure (g)	After 10% HF Exposure (g)
1	PTFE	Teflon	8.74	8.74	8.74
2	FRP	Fiberglass reinforced plastic	5.13	5.13	5.29
3	FRPP	Flame retardant polypropylene Endura/Empee/Polyflam	7.92	7.92	7.92
4	PVC	Polyvinylchloride	12.38	12.36	12.36
5	PP	Polypropylene	8.04	8.02	8.02
6	ATS	ATS is a manufacturer of FRP using vinyl ester and phenolic resins	4.60	4.58	4.65
7	PVDF	polyvinylidenefluoride/Kynar	22.24	22.24	22.25
8	Flametec	Kytec-PVDF	17.88	17.88	17.89
9	Corzan	Corzan 4910 or CPVC	19.31	19.31	19.32
10	Halar	Halar ECTFE	15.92	15.94	15.92

Project Summary

- Industry trend toward NF_3-based chamber cleans
- Measuring F_2 in an ambient air exhaust system is challenging
- F_2 conversion to HF is thermodynamically favored
  - >90% F_2 converted to HF—humidity is critical factor
  - Increased reaction time did not increase F_2 to HF conversion
- F_2 DRE increased above 98% with H_2O-to-F_2 ratio >5-to-1
- Fluorine mass balance poor
  - Reaction on stainless steel and FRP wall surfaces may account for significant F_2 degradation
- FCS is a viable analytical technique for F_2 detection
  - more studies needed
- No OF_2 detected

Future Work

- Publish International SEMATECH report
- Continue analytical testing of FCS
  - Perform surface analysis of substrates
- Use FCS to evaluate F_2 emissions from other processes