CVD Emissions - Analysis and Treatment

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Acknowledgments

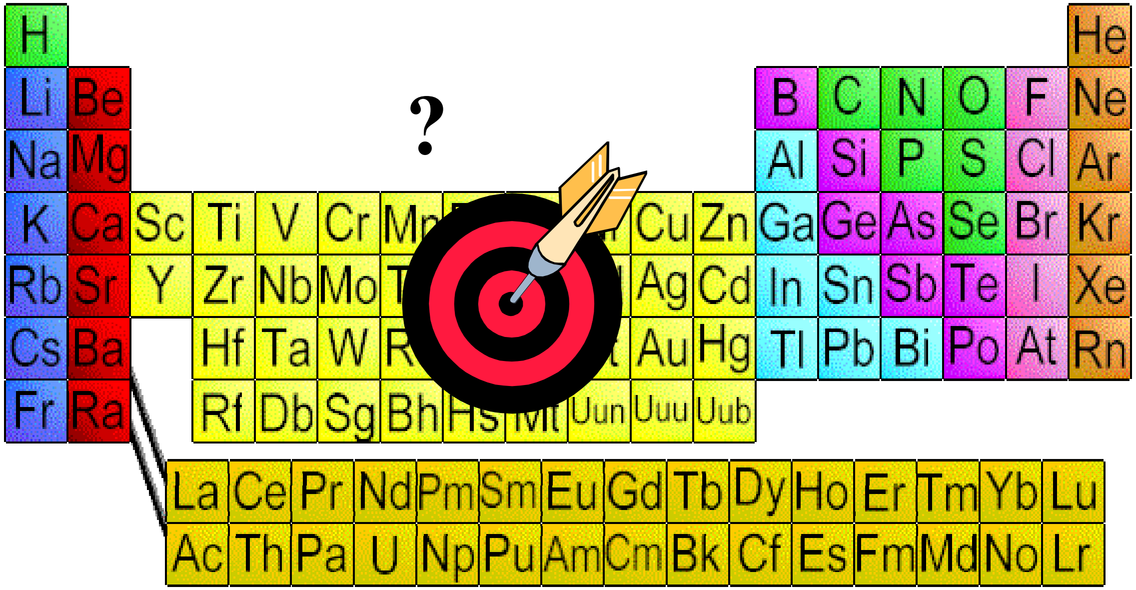
- Victor Vartanian – Motorola EPI
- Kim Reid – formerly of Motorola
- Joe VanGompel - BOCE

Overview

- CVD Trends Steering Characterization Needs
- Process Emissions Characterization
- Examples of CVD Processes Evaluated
- Point of Use Abatement
- Examples of CVD Emissions Abatement
- Conclusions

New Materials Everywhere!

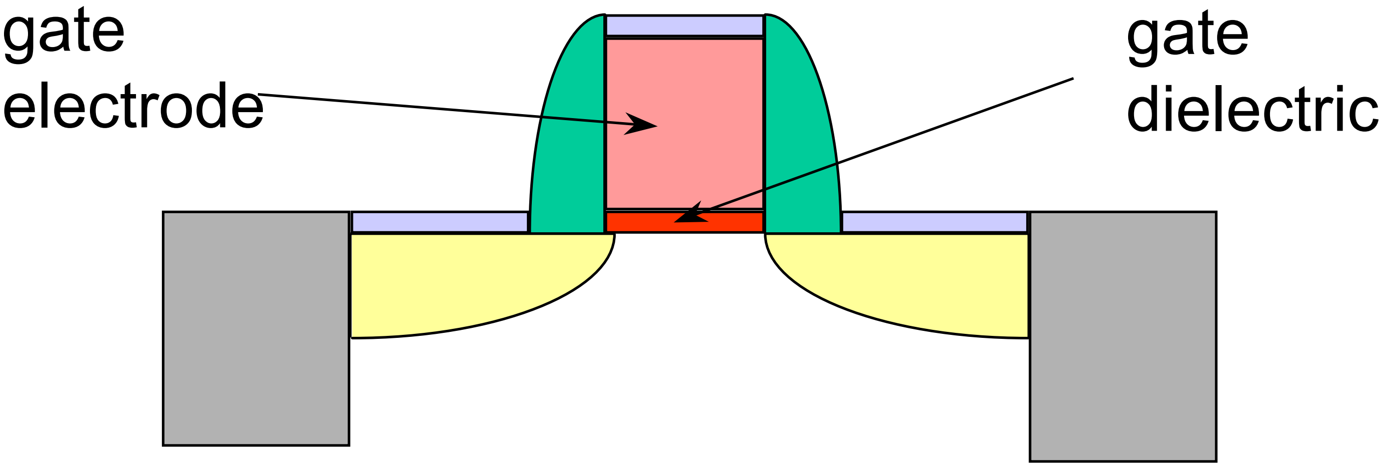
- New materials & processes are being introduced at an unprecedented rate



- Films are thinner
- Utilization should be improved

Advanced Gate Stack

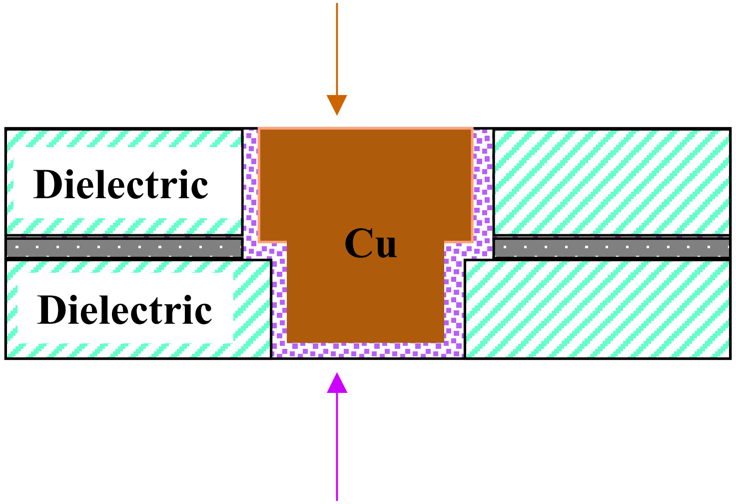
- Metal oxide gate dielectric (replaces SiO_2)
  - – oxides or silicates of Ti, Ta, Sr, Zr, Hf, Al, Y, Sn, La, etc.
- Metal gate electrode (replaces doped polysilicon)
  - – metals and nitrides of W, Ti, Ta, Mo, Al, Pt, etc.
- CVD process using metal-based precursors



Advanced Metallization

Copper Deposition

- Electroplating, CVD



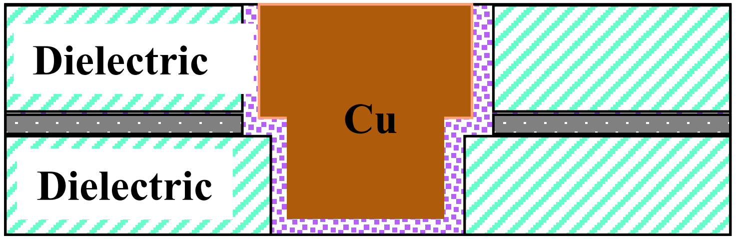
Barrier Deposition

- PVD, CVD
- TaN, TiN, TaSiN, TiSiN, etc.

Low k Dielectrics

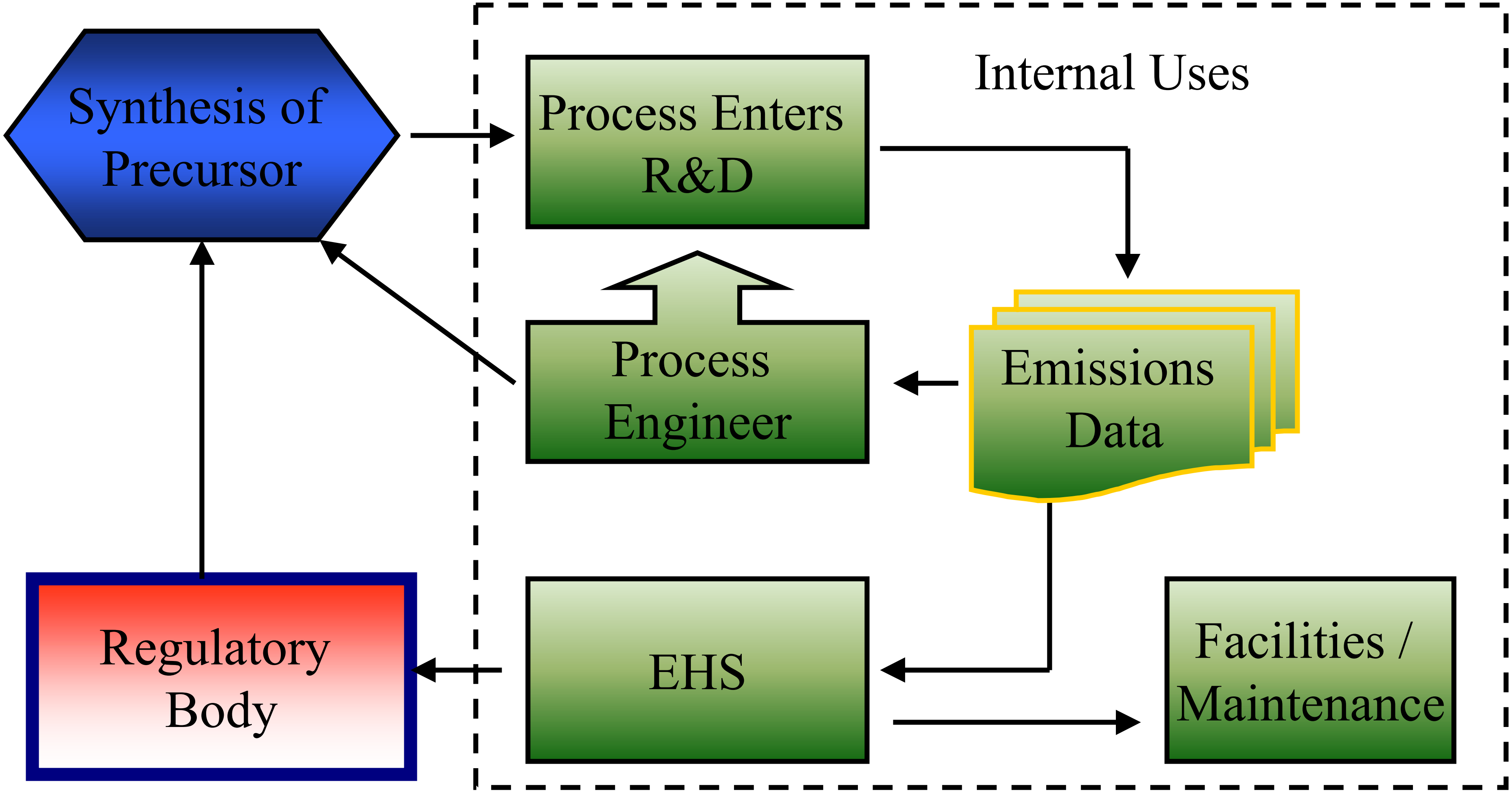
- Carbon-doped, porous organosilicates, porous polymers
- Spin-on
- CVD
  - organosilanes, siloxanes, halosiloxanes, silicones, etc.

$$RC = \rho\varepsilon\frac{l^2}{td}$$



ρ = metal resistivity
ε = dielectric permitivity
l = line length
t = dielectric thickness
d = line thickness

The Need for Analytical Data



Synthesis of Precursor

Process Enters R&D

Internal Uses

Process Engineer

Emissions Data

Regulatory Body

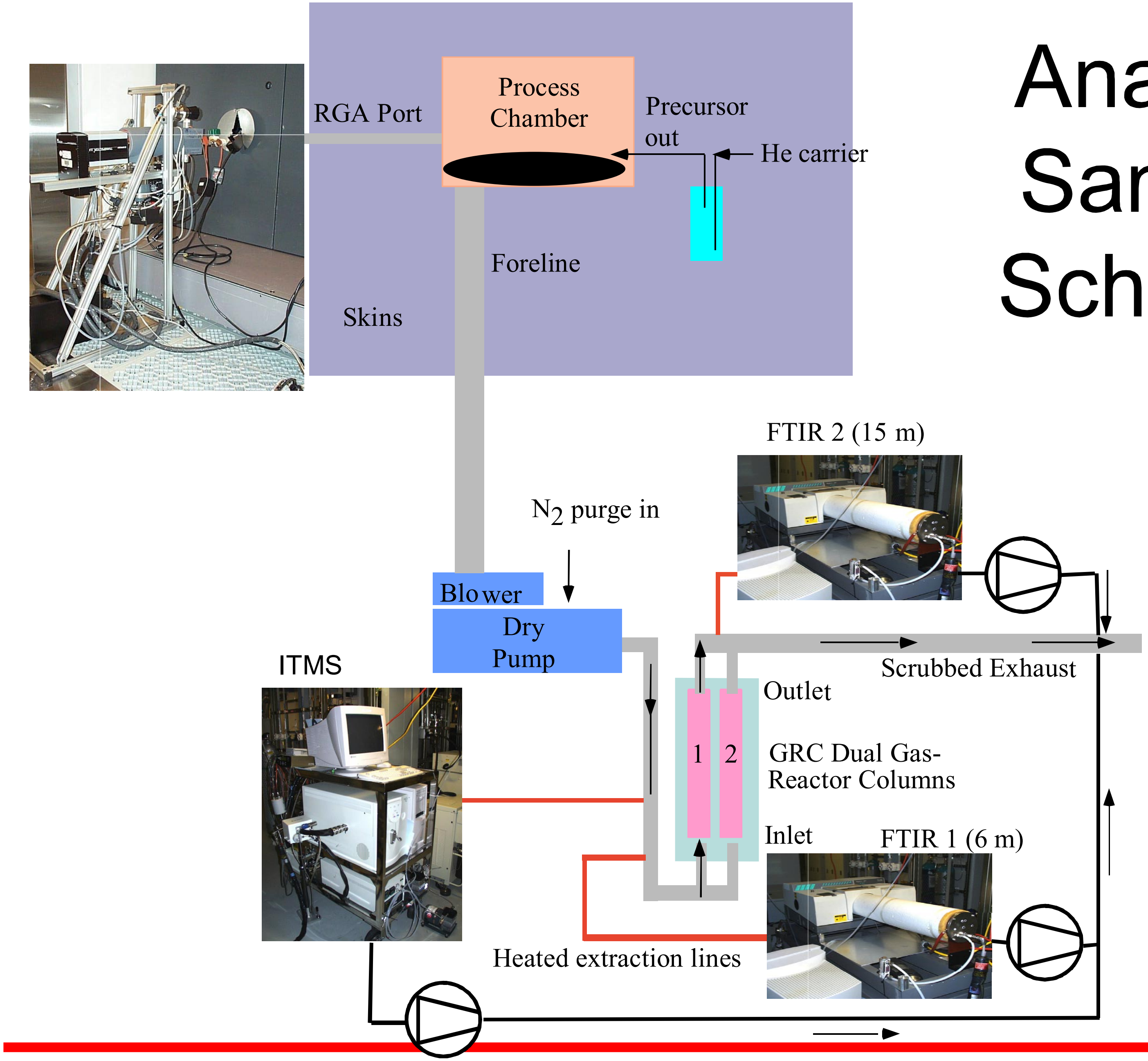
EHS

Facilities / Maintenance

Process Emissions Characterization

- Mass Spectrometry
  - Chamber monitoring, by-product identification
  - Emerging methods
    - high pressure sampling
    - trapping instruments
    - activated dissociation
- FTIR
  - Species quantification, high mass precursor identification, abatement efficiency determination
- Chemical-Specific
  - Limited in scope and availability, very sensitive

Analytical Sampling Schematic



Process Chamber

RGA Port

Precursor out

He carrier

Foreline

Skins

N_2 purge in

Blower

Dry Pump

ITMS

FTIR 2 (15 m)

Scrubbed Exhaust

Outlet

1

2

GRC Dual Gas-Reactor Columns

Inlet

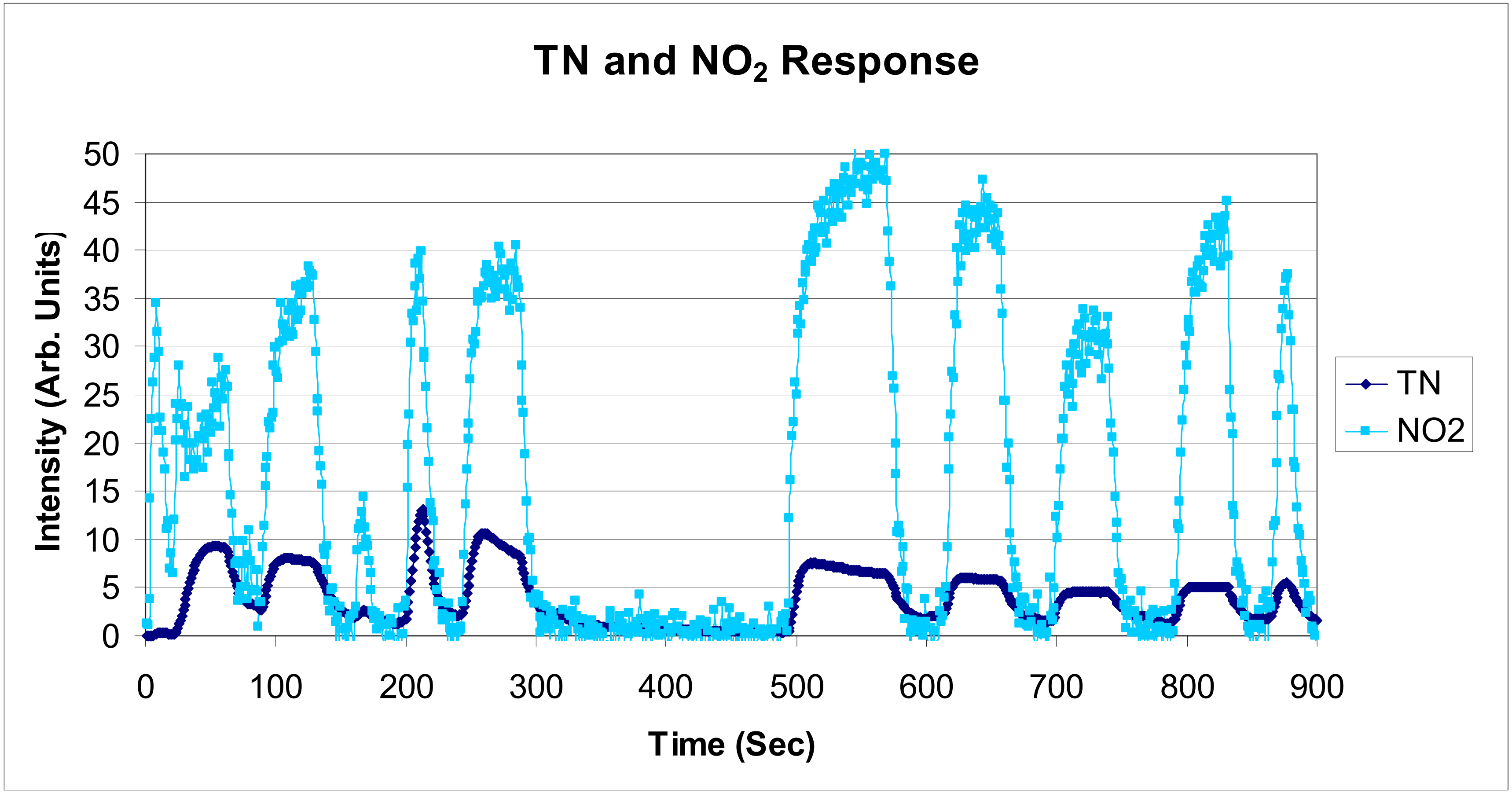
FTIR 1 (6 m)

Heated extraction lines

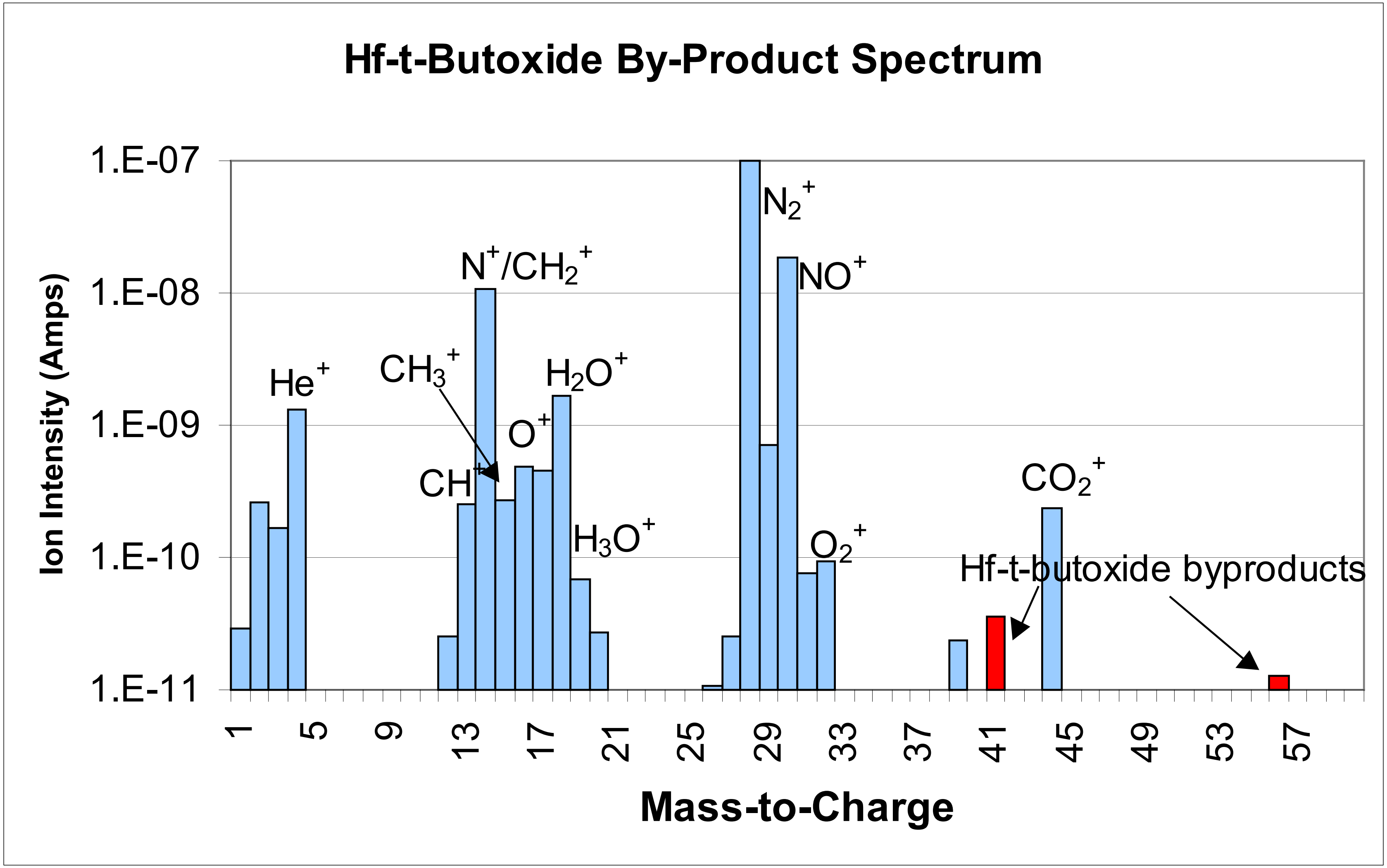
Metal-based CVD Precursors and Process By-Products Detected

- Tetranitrato titanium (TN)
  - NO, NO_2, HNO_3
- Titanium tetrachloride ($TiCl_4$)
  - HCl
- TDMAT
  - Dimethylamine, ammonia
- Zirconium t-butoxide
  - t-butanol, isobutylene, propylene
- Hafnium t-butoxide
  - t-butanol, isobutylene , propylene

Simultaneous Unutilized Precursor and Reaction Byproduct Monitoring for TN



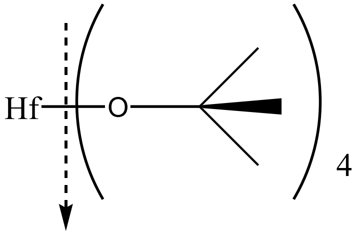
Mass Spectrum of Hf-t-Butoxide Process



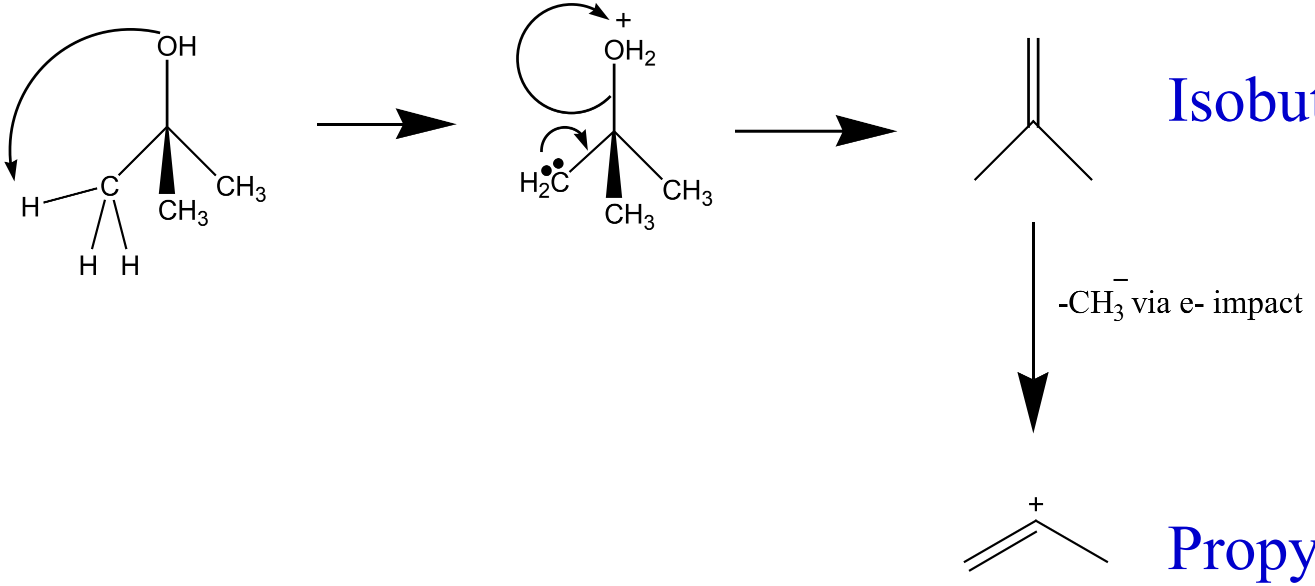
Ligand By-product Reactions

Proposed reaction for:

Hf-t-butoxide



Cleavage during deposition
(surface reaction)

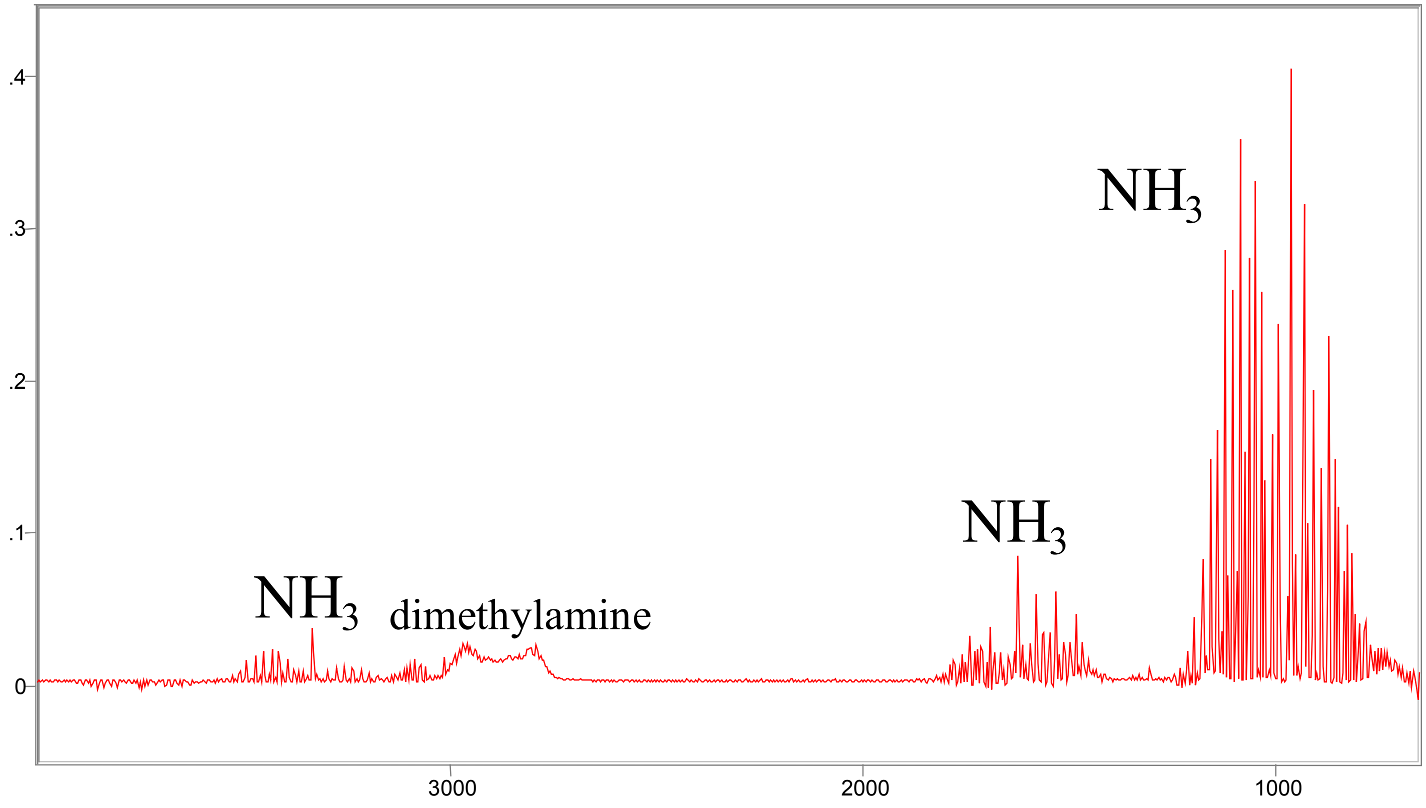


-CH_3^- via e- impact

Isobutylene

Propylene

FTIR Spectra from TDMAT Process



Absorbance / Wavenumber (cm-1)

Y-Zoom CURSOR

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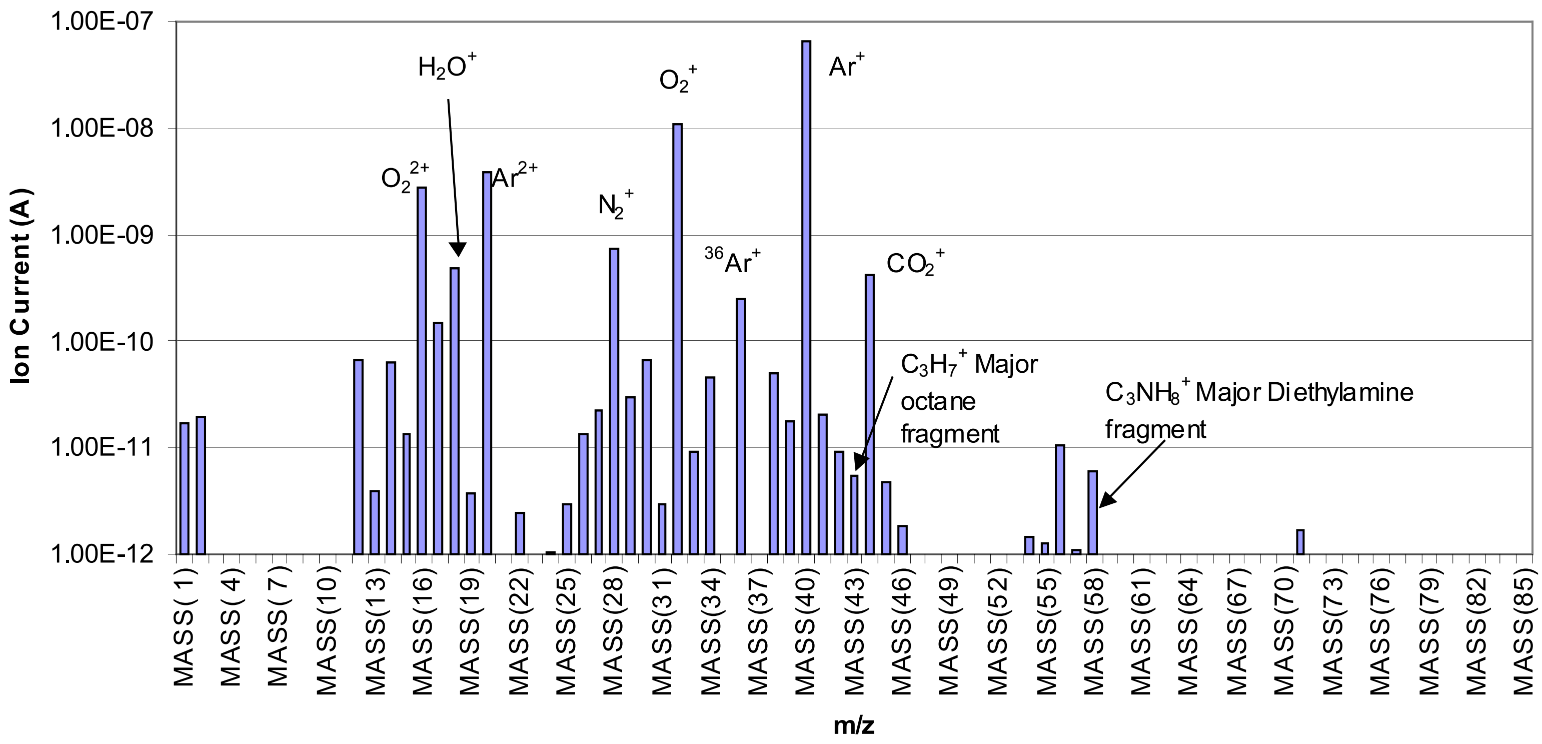
TDEAH

- Tetrakis diethylamino Hafnium
- Highly flammable, toxic, corrosive
- Reacts violently with water
  - forms diethylamine (toxic, extremely flammable)
- Require amine sensor (TGM) in ampoule cabinet, tool, area

Mass Spectrum from TDEAH



Mass Spectrum During TDEAH Deposition

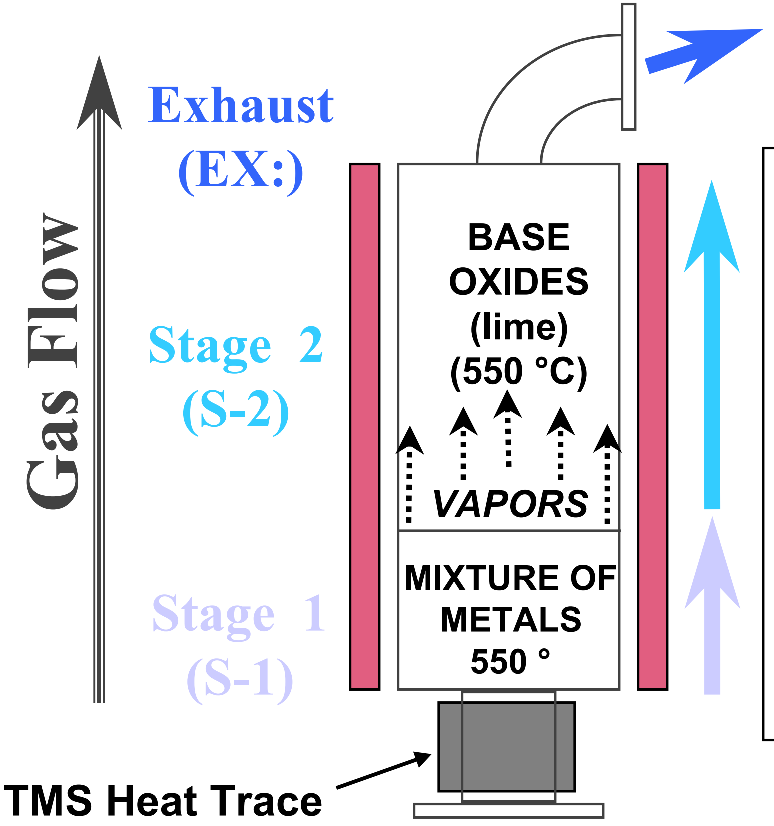
Shows diethylamine by-product

Handling Process Emissions

- Point of Use Abatement Devices
  - Minimize overall EHS impacts of precursors and by-products
  - Minimize personnel exposure during maintenance
  - Remove acid gases
  - Remove unreacted precursor to prevent deposition in exhaust ducts or release to environment

DESTRUCTION OR CONVERSION	ENTRAINMENT
-Resistive heating -Flame -Catalytic	-Chemical canister -Water scrubbing

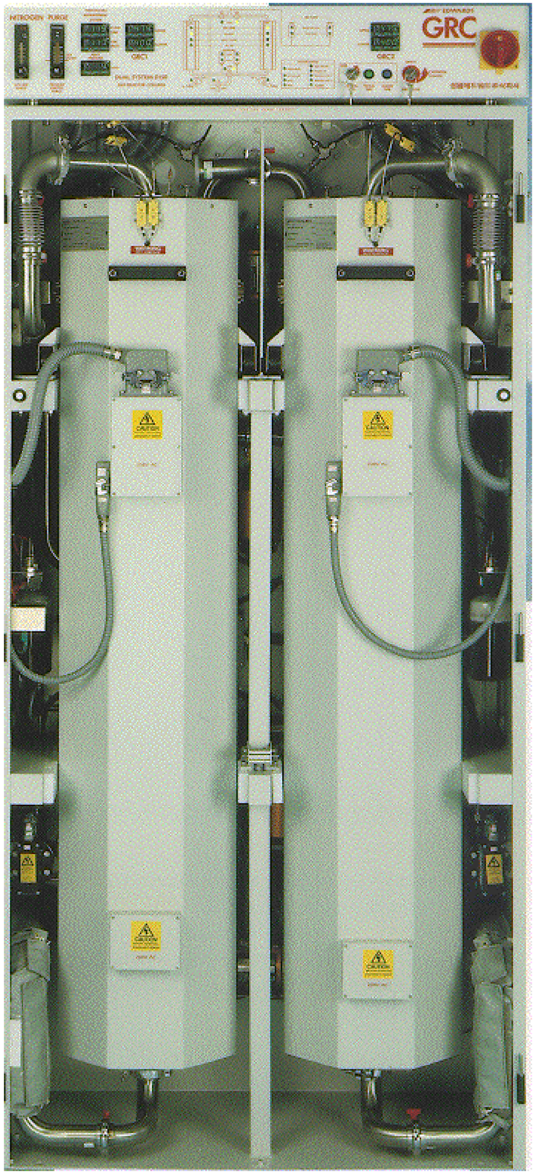
Edwards GRC



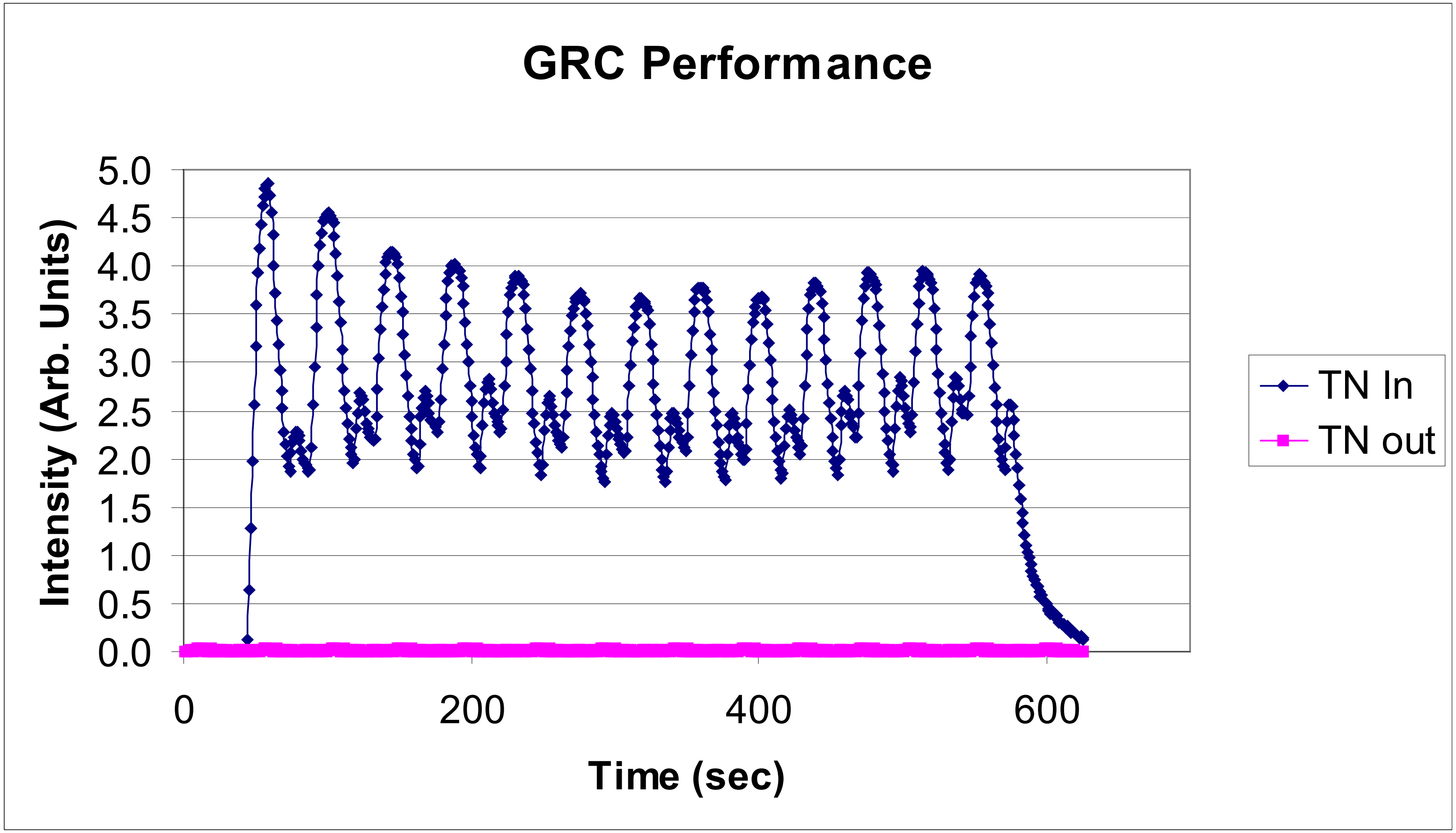
- S-1 Transfer heat into gas to reach reaction temperature
- S-1 Reacts with strong oxidizing agents (Cl_2, ClF_3) to form volatile metal halide species.
- S-1 Thermally decomposes Hydrides (SiH_4)
- S-2 Acid gases and volatile metal halides react to form harmless inorganic salts
- EX: Non-hazardous (N_2, Ar, inert gases) to duct. No acid gases.

Courtesy BOC Edwards, Joe Van Gompel

D150 GRC
Dual system



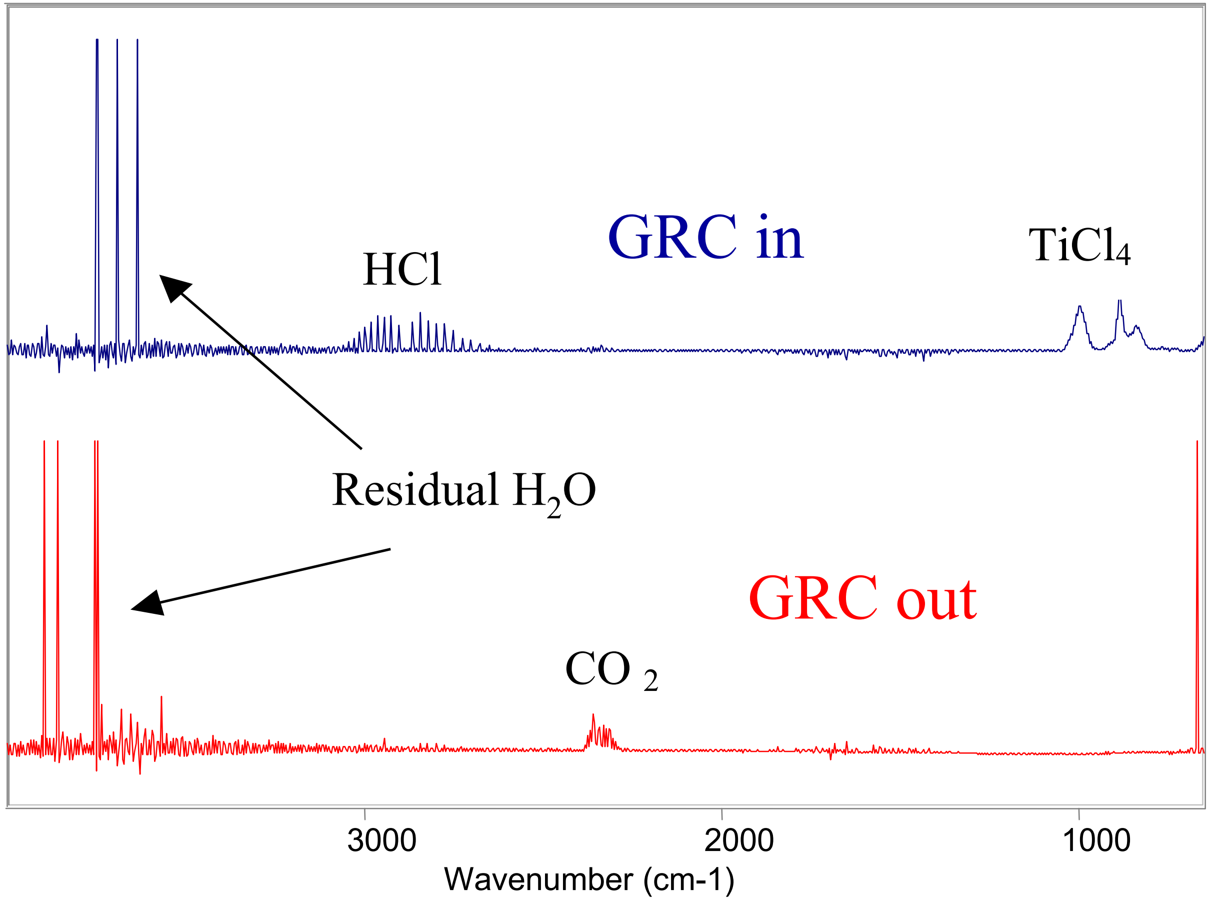
GRC Performance for TN



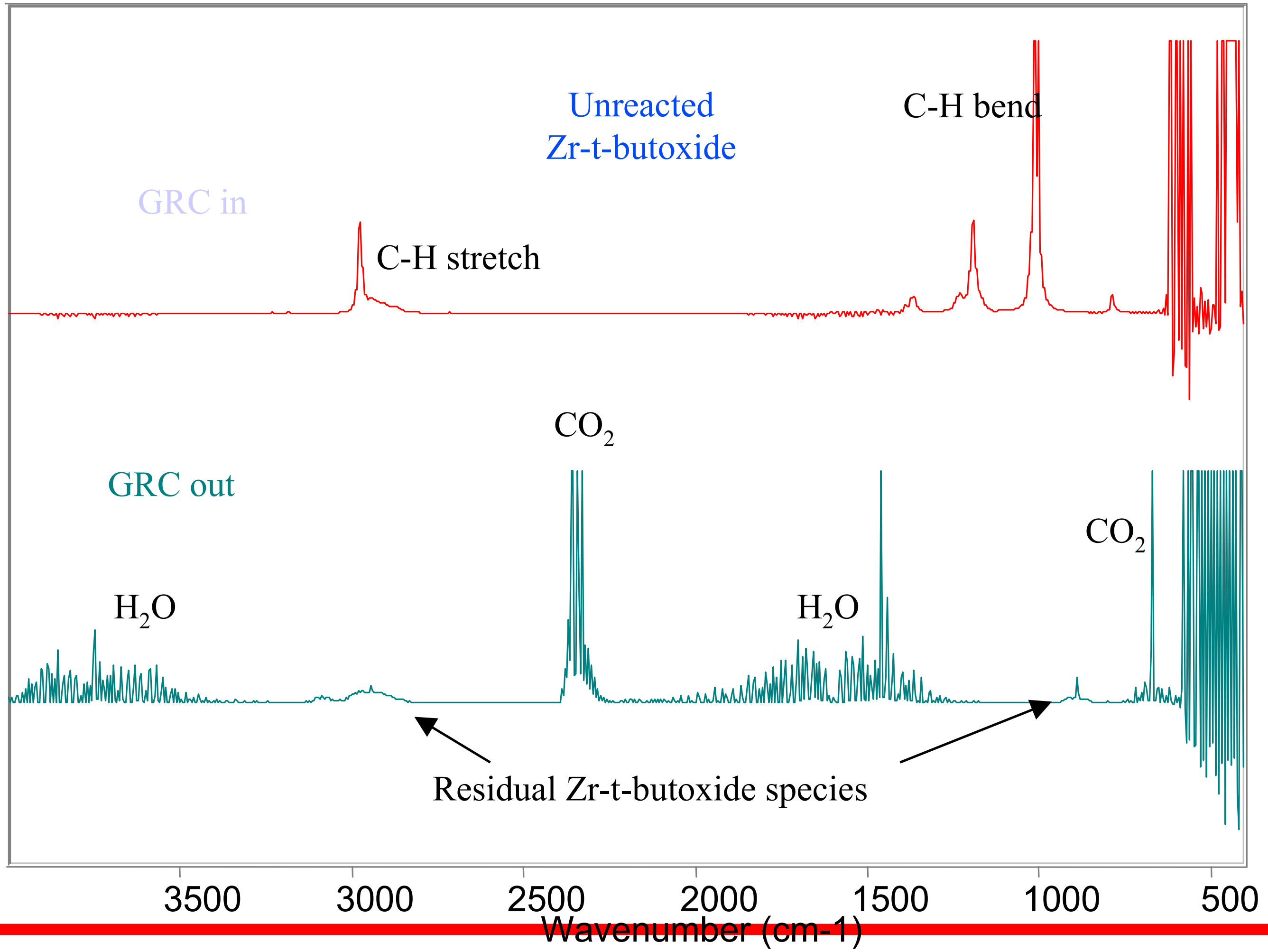
$TiCl_4$

- Material itself is corrosive, poisonous
- HCl is hazardous decomposition product (upon exposure to air/water)
  - monitor for HCl as TGM
- In closed CVD system, $TiCl_4$ and reaction by-products contained
  - HCl formed from unreacted $TiCl_4$ in exhaust
  - chamber maintenance becomes an issue

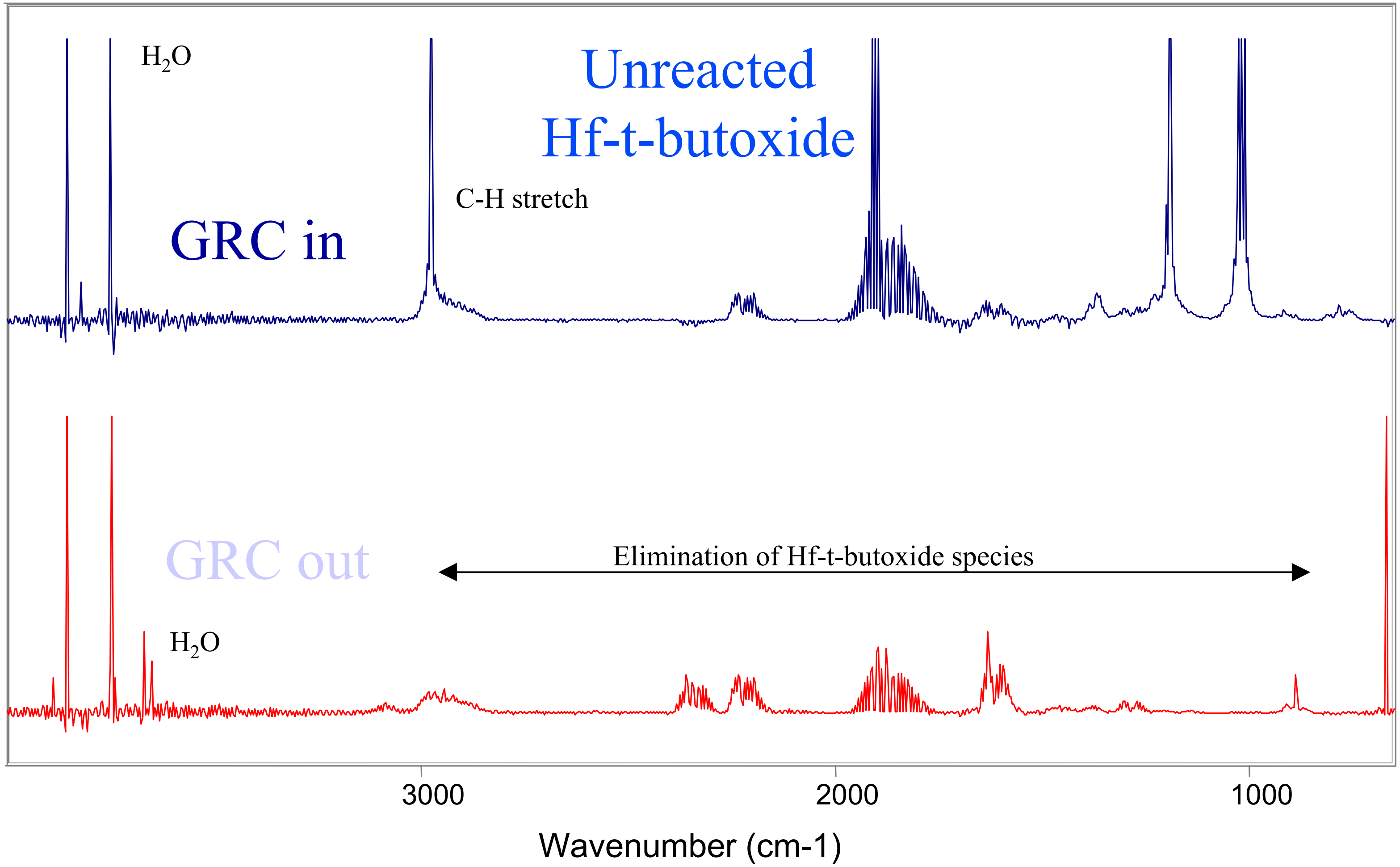
GRC Performance for $TiCl_4$



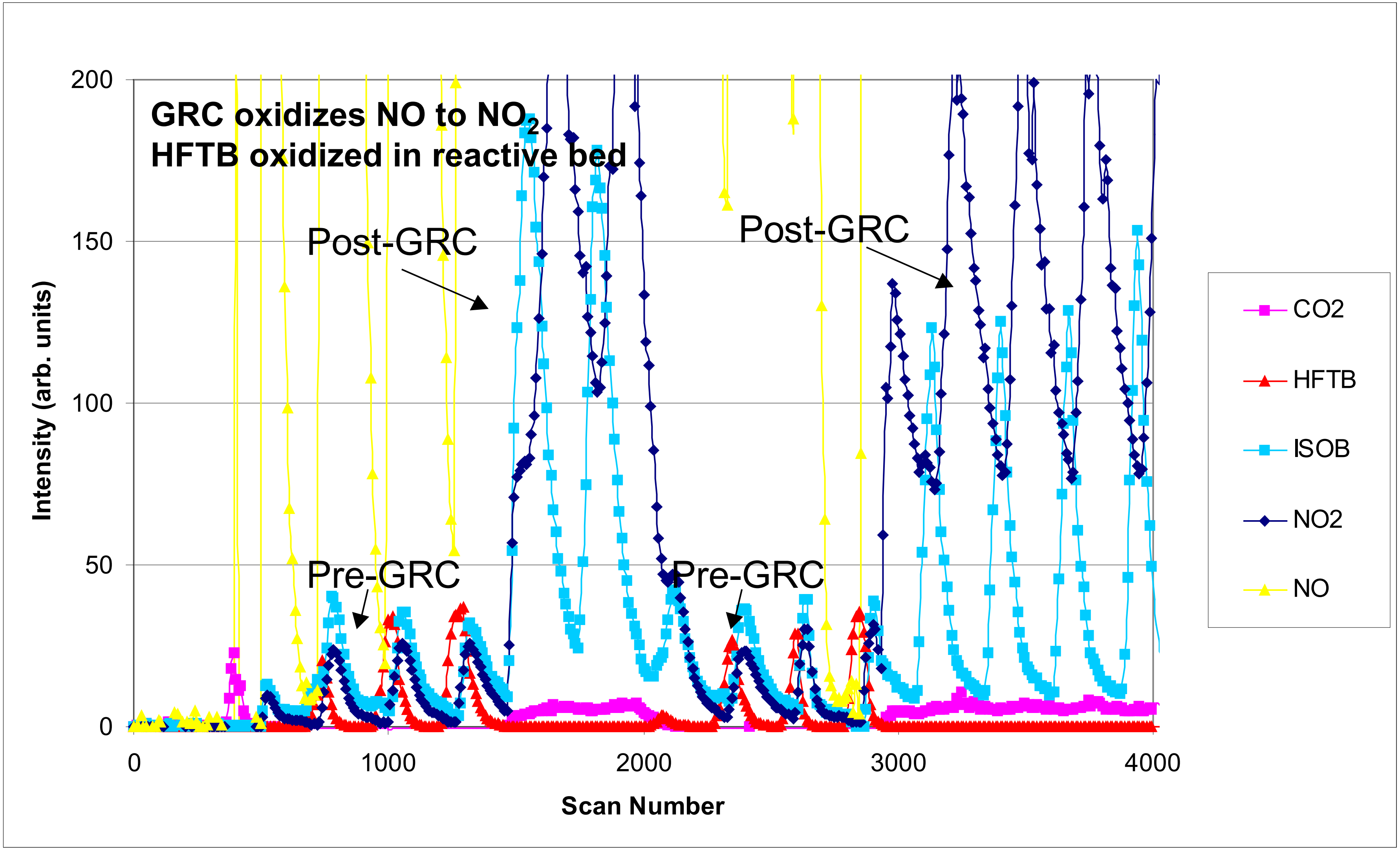
GRC Performance with Zr t-butoxide



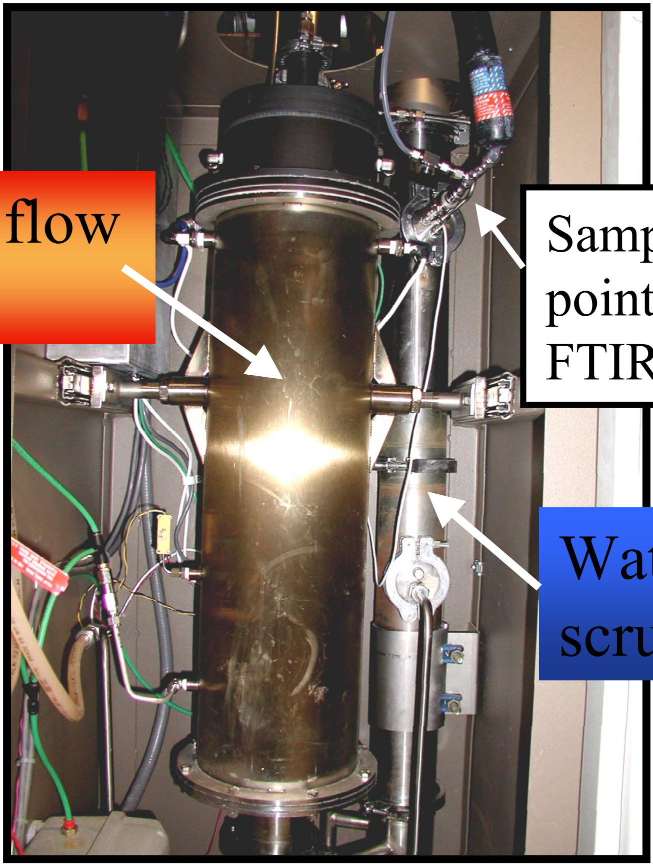
GRC Performance for Hf t-butoxide



Effect of GRC on Hf-t-Butoxide



CDO

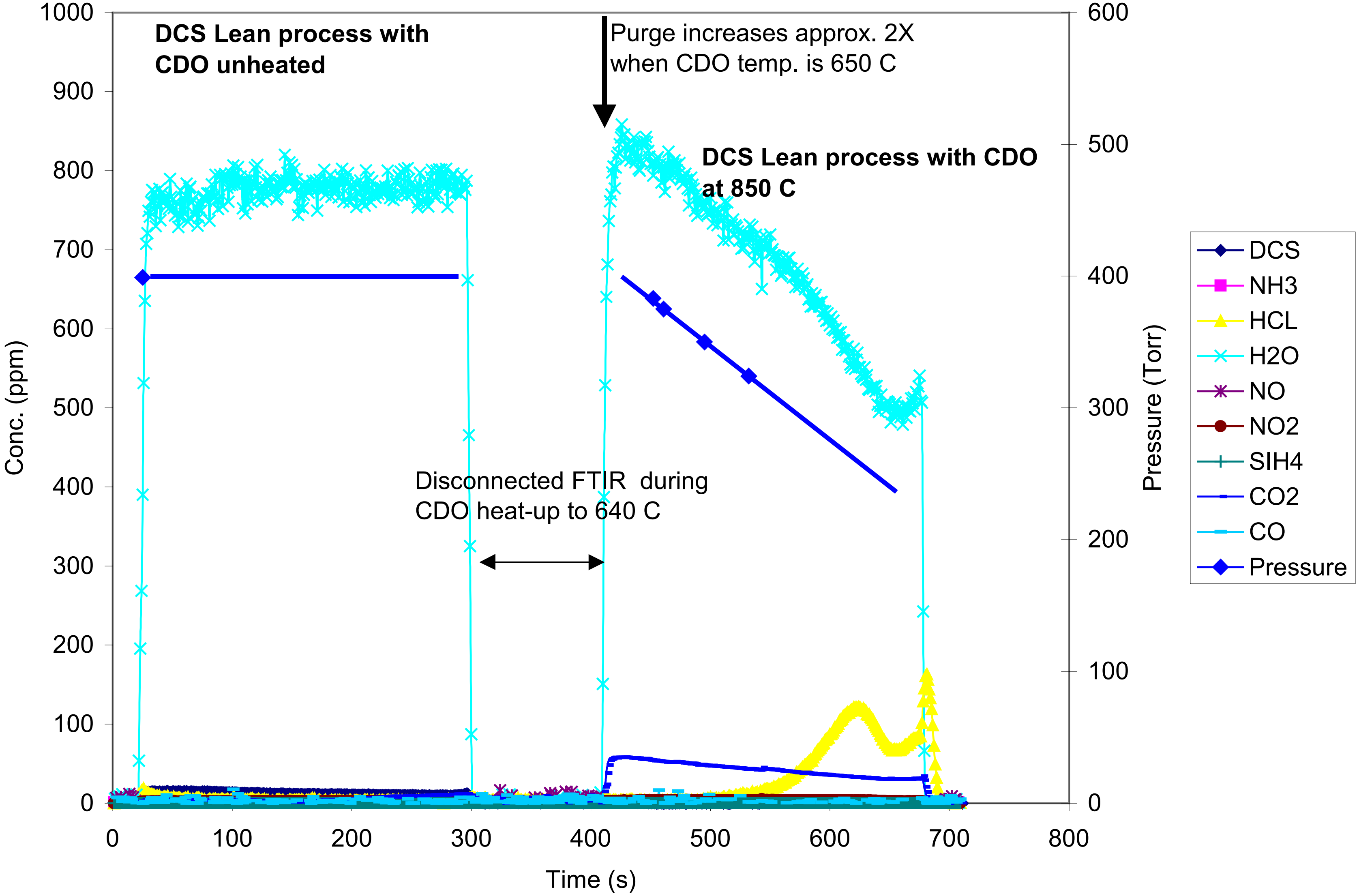


Heated flow tube

Sampling point - to FTIR

Water scrubber

Nitride Deposition - CDO Performance



Summary

- CVD emissions typically consist of unreacted precursor and ligand materials
  - determine process efficiency
  - evaluate abatement
- Collect predictive data during R&D phase
- Work with suppliers and engineers to aid design of appropriate molecules
- Abatement solution needs to fit job
- Abatement devices can be tweaked