Addressing the EHS Issues with Advanced Gate Stack Processes

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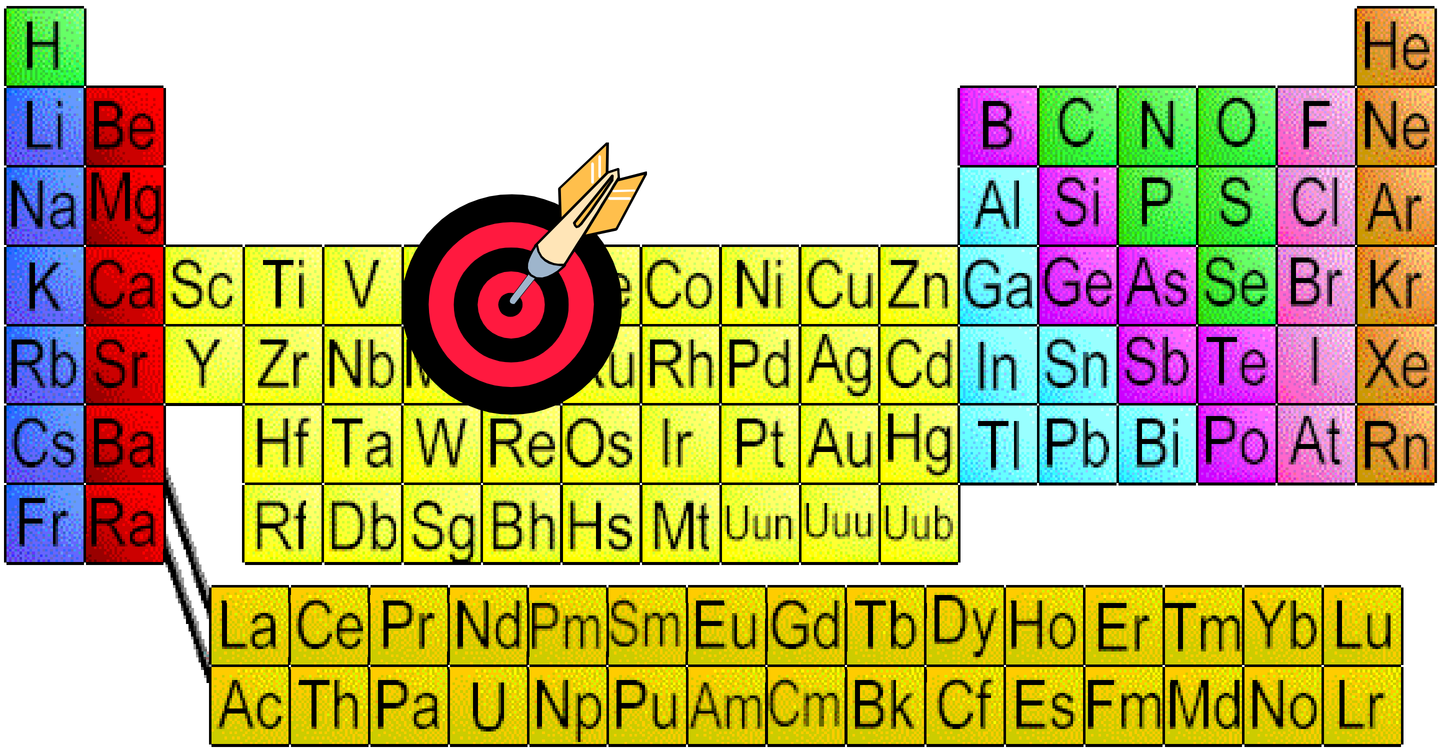
Overview

- R&D Areas of Focus
- EHS Strategy for R&D Processes
- Process Emissions Characterization
- Examples of CVD Processes Evaluated
- Point of Use Abatement
- Summary

New Materials Everywhere!

New materials & processes are being introduced at an unprecedented rate



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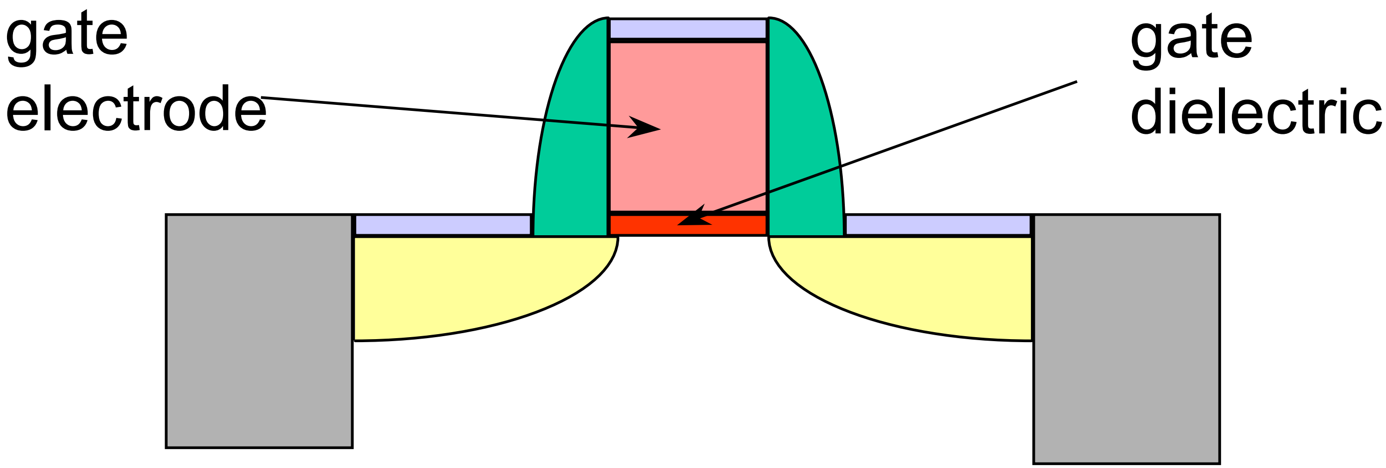
Advanced Gate Stack

- 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



EHS Concerns

- Employee exposure
  - chemical handling
  - accidental release/leak
  - chamber/exhaust maintenance
- Impacts to infrastructure
  - drain lines, exhaust lines
- Material compatibility
  - potential reaction with other components
  - materials of construction
- Environmental impact

EHS Strategy

- EHS review required for ALL new materials
- Specific tool, process, tool location, storage location, usage rate
- Specific point of contact
- Ensure compatibility with tool exhaust/drain and sufficient TGM
- EHS considers potential for exposure and associated hazards
- EHS can require tool/procedure modifications if necessary

EHS Strategy (cont)

- Thorough review of MSDS
  - chemical components - adducts, solvents, etc.
  - toxicity, flammability, reactivity (if known)
  - material incompatibilities
    - tool components, co-flow materials, etc.
  - predicted reaction products
  - special handling procedures
  - recommended PPE
  - component for TGM
- Available supplier data, other data sources
  - TOMES, “like” materials or chemical families, web surfing, etc.

EHS Strategy (cont.)

- Process hazard analysis
  - how material will be used, potential for exposure, etc.
- TGM based on breakdown product(s)
  - often no specific sensor for precursor itself
- Handle with conservative PPE strategy
- Operate under engineering control only
- Monitor process emissions - QMS, FTIR, RGA, other
  - reaction by-products & unreacted precursor
  - residual precursor/by-product in chamber
- POU abatement for process emissions where needed
  - highly toxic/flammable material, by-product, or co-flow material (e.g., silane)
- Special chamber maintenance strategy

Monitoring Strategy

- Detect release/leak of hazardous gas/vapors before concentration reaches dangerous level
- For toxic gases, warn at 1/2 TLV (or less), alarm (with automatic source shut down) at TLV
- For flammable gases, warn at 10% of LEL and alarm at 20% LEL
- Can monitor in gas cabinet, valve box, tool (inside enclosure) and area (work, utility, subfab)
- Various types of monitors
  - specific compound
  - general class (flammable, mineral acid, hydride, etc.)
- May monitor breakdown product

Chamber Maintenance Strategy

- Conservative “worst case” procedure for first chamber opening after process has been run
- Clear area around chamber and sub-fab
- Response team on stand by
- Supplemental exhaust (elephant trunk) if available
- Maintenance personnel in full PPE, SCBA
- TGM sensor point in chamber/area if available
- IH personnel and area monitoring
- Monitor emissions during purge
  - ensure no signal for residual precursor, by-product
- Special wipes & spent wipe container if necessary
  - wipes may be analyzed

Regulatory Issues

- TSCA inventory status
  - must be listed or have low volume exemption to be used in manufacturing
  - low volume exemption = only 10,000 kg/yr can be manufactured by all suppliers collectively
  - Listing process is data intensive, lengthy and expensive
  - Promising materials can transfer to manufacturing quickly

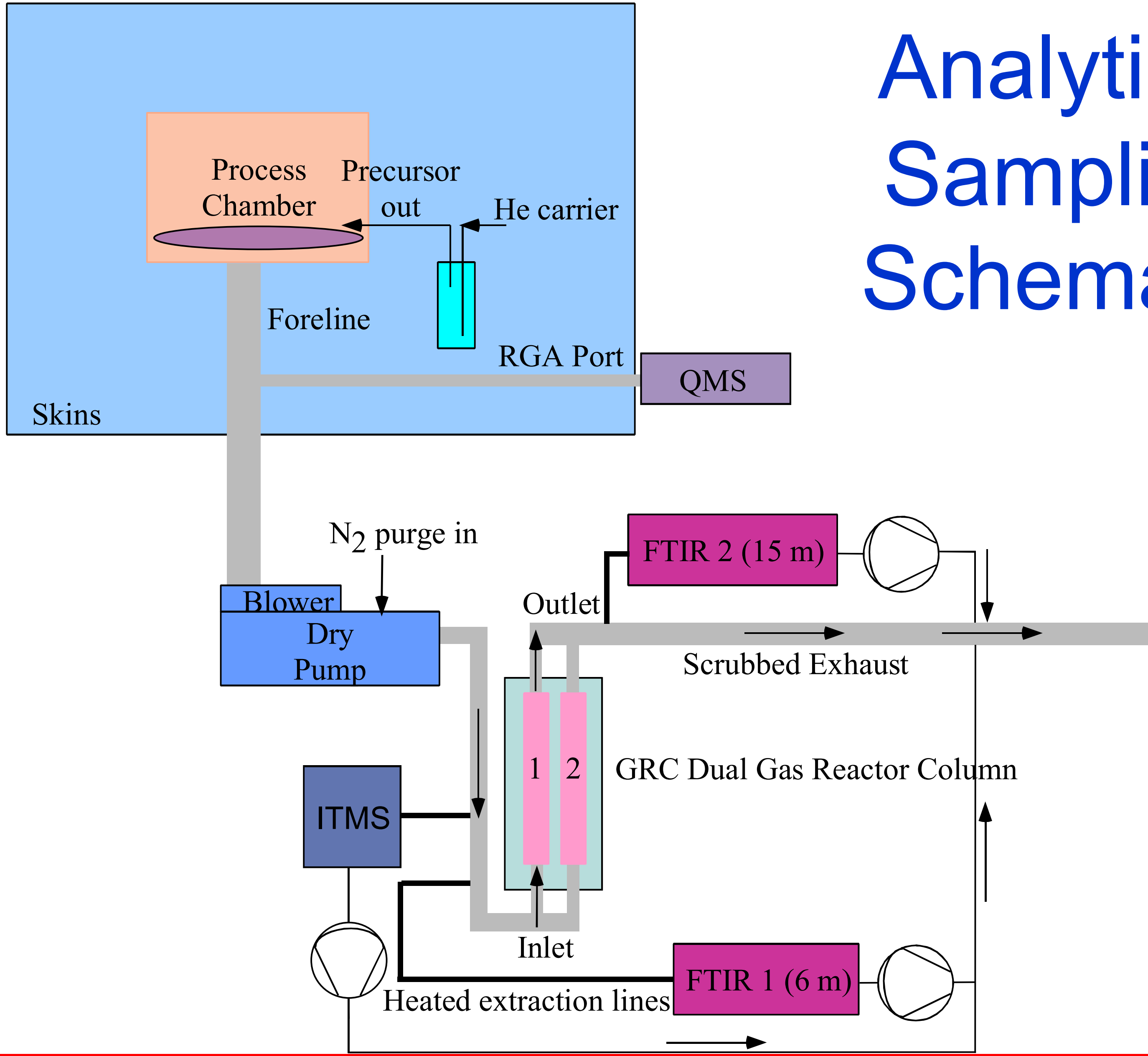
EHS Data Collection

- Evaluation CVD precursor candidates:
  - TN [Ti $(NO_3)_4$]
  - $TiCl_4$
  - TDMAT
  - Zr t-butoxide and Hf t-butoxide
  - TDEAH
- $TiCl_4$, TDMAT somewhat characterized, TSCA listed
- Zr t-butoxide and Hf t-butoxide, TDEAH not TSCA listed
- TN newly synthesized, not TSCA listed
  - worked with supplier to determine properties and potential hazards (e.g., upon exposure to air or water, solvents, thermal decomposition)

Process Emissions Characterization

- QMS
  - foreline monitoring, by-product identification
- ITMS
  - post pump, species identification & reaction pathway determination
- FTIR
  - species quantification, high mass precursor identification, abatement efficiency determination

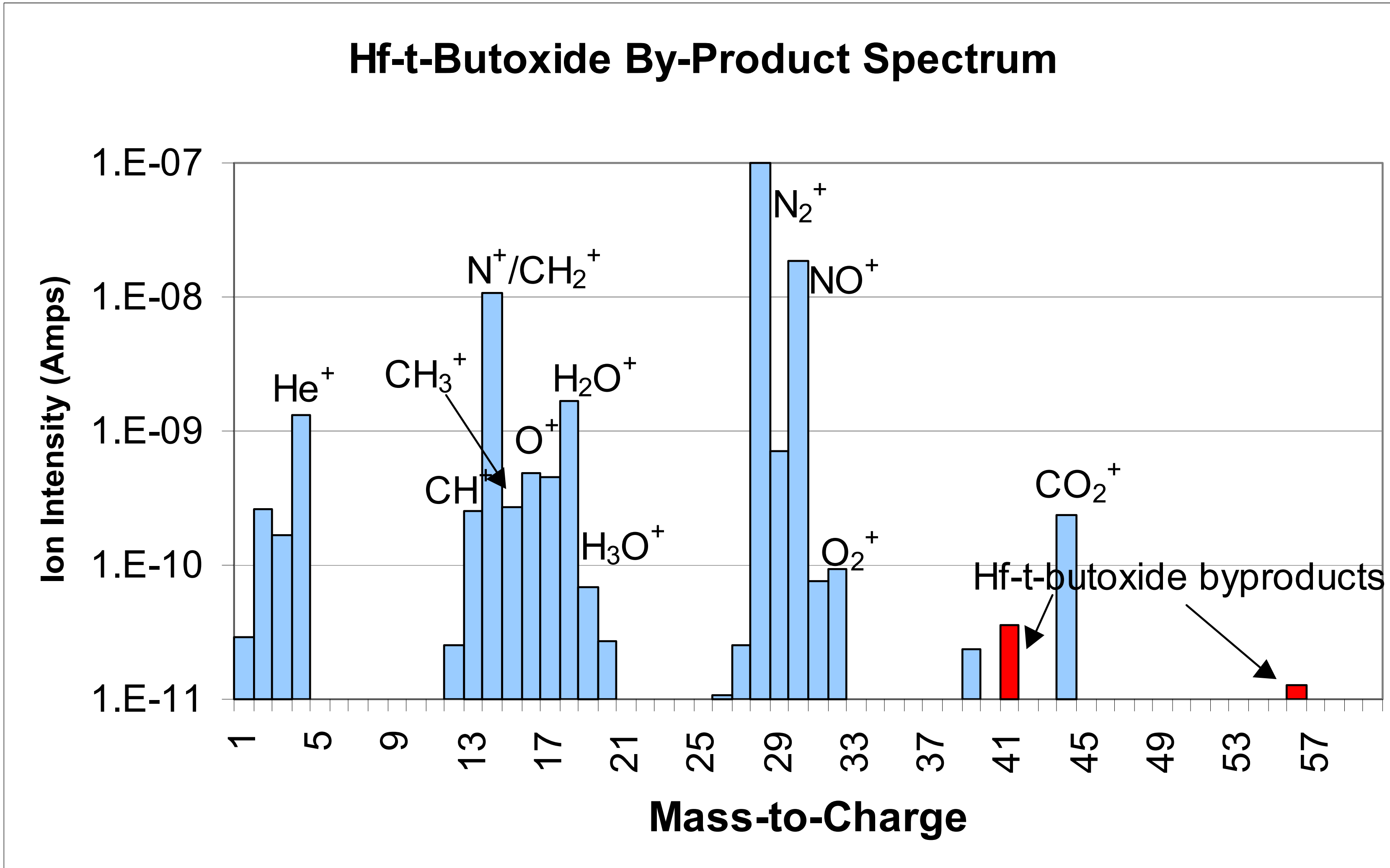
Analytical Sampling Schematic



Metal-based CVD Precursors and Process By-Products Detected

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

Mass Spectrum of Hf-t-Butoxide Process



$TiCl_4$

- 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

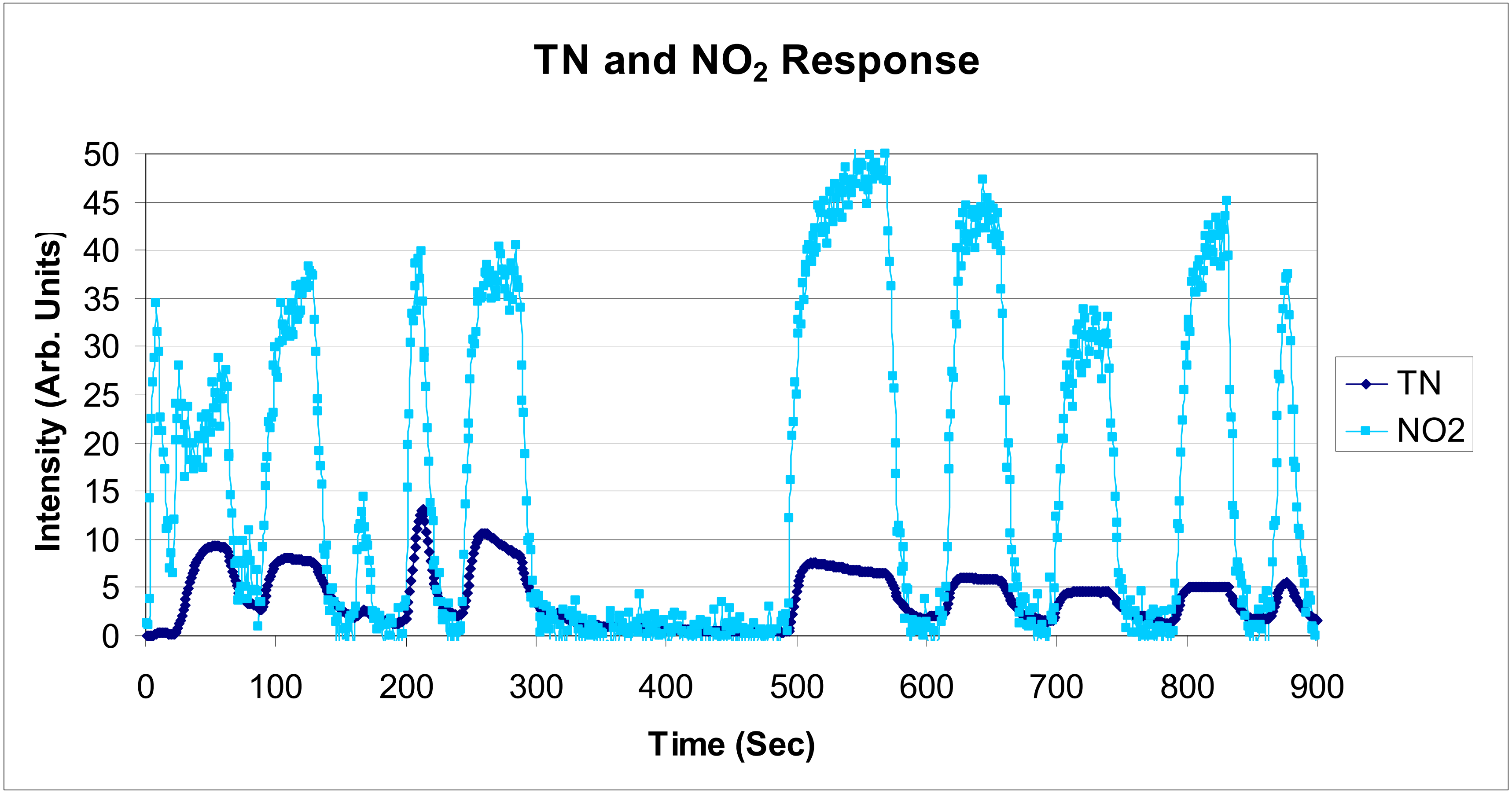
$TiCl_4$ Chamber Maintenance

- Purged system prior to opening
  - no HCl or $TiCl_4$ signal detected
- HCl detected in “elephant trunk” when chamber first opened
  - indicates residual HCl or $TiCl_4$ in chamber or lines that reacted upon exposure to air
  - further studies to determine adequate purging

TN [$Ti(NO_3)_2$]

- TN (solid) is corrosive, strong oxidizer, reacts with moisture to form HNO_3 (exothermic)
- NO_x is CVD reaction by-product
- Reacts with IPA to form NO_x
  – Standard chamber wipe down solution of 10% IPA in water NOT recommended -- water only
- No degradation with standard o-ring materials

Simultaneous Unutilized Precursor and Reaction Byproduct Monitoring for TN



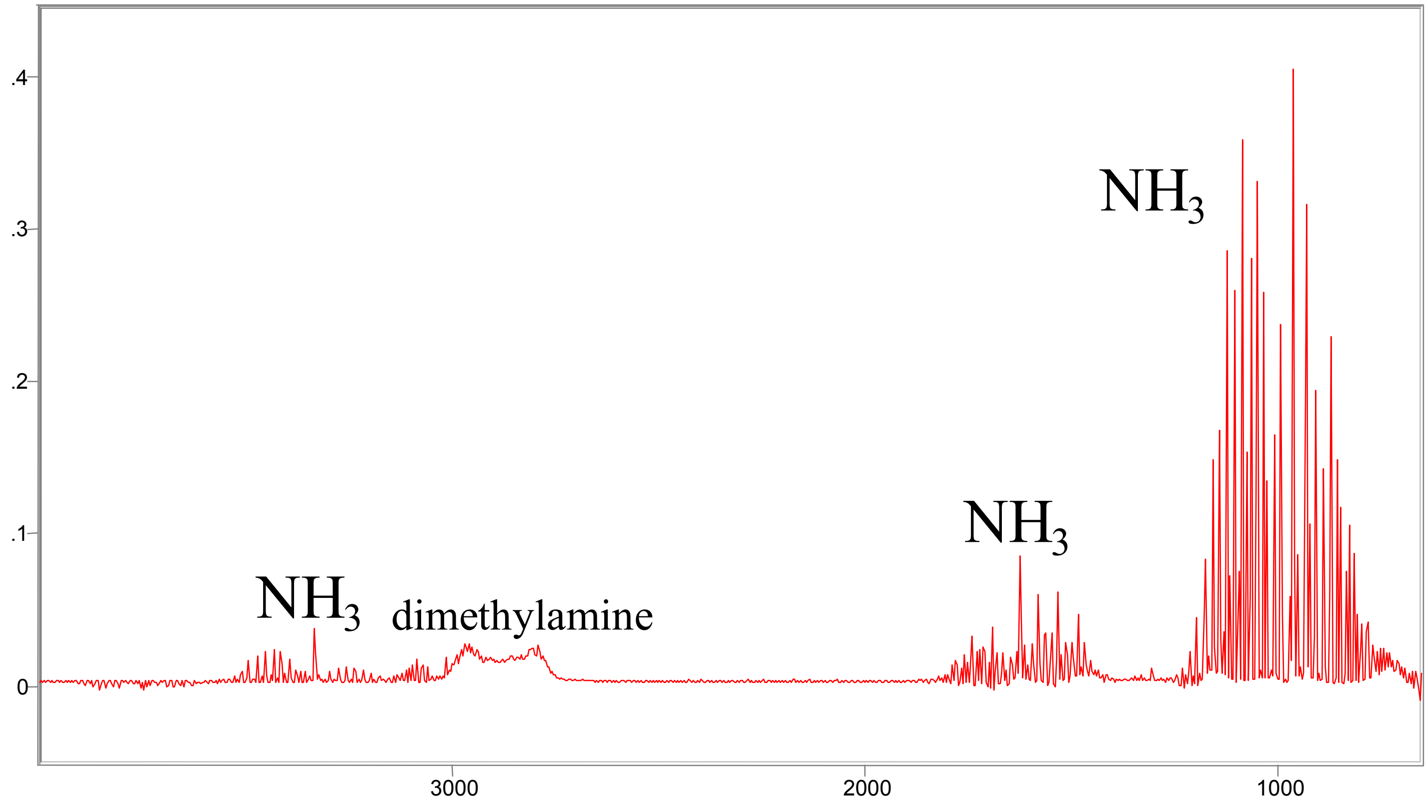
TN Chamber Maintenance

- Purged thoroughly
  - no NO_x or TN signal noted
- No issues with chamber opening (no detections)
- No issue with water wipe down (minimal temperature rise)

TDMAT

- Tetrakis (dimethylamino) titanium
- Highly flammable, corrosive,odorous liquid
- Reacts violently with water
  - forms dimethylamine (toxic, extremely flammable) and NH_3 by-product
- Require amine sensor (TGM) in ampoule cabinet, tool, area
- Require point of use abatement for process emissions

FTIR Spectra from TDMAT Process



Absorbance / Wavenumber (cm-1) Y-Zoom CURSOR

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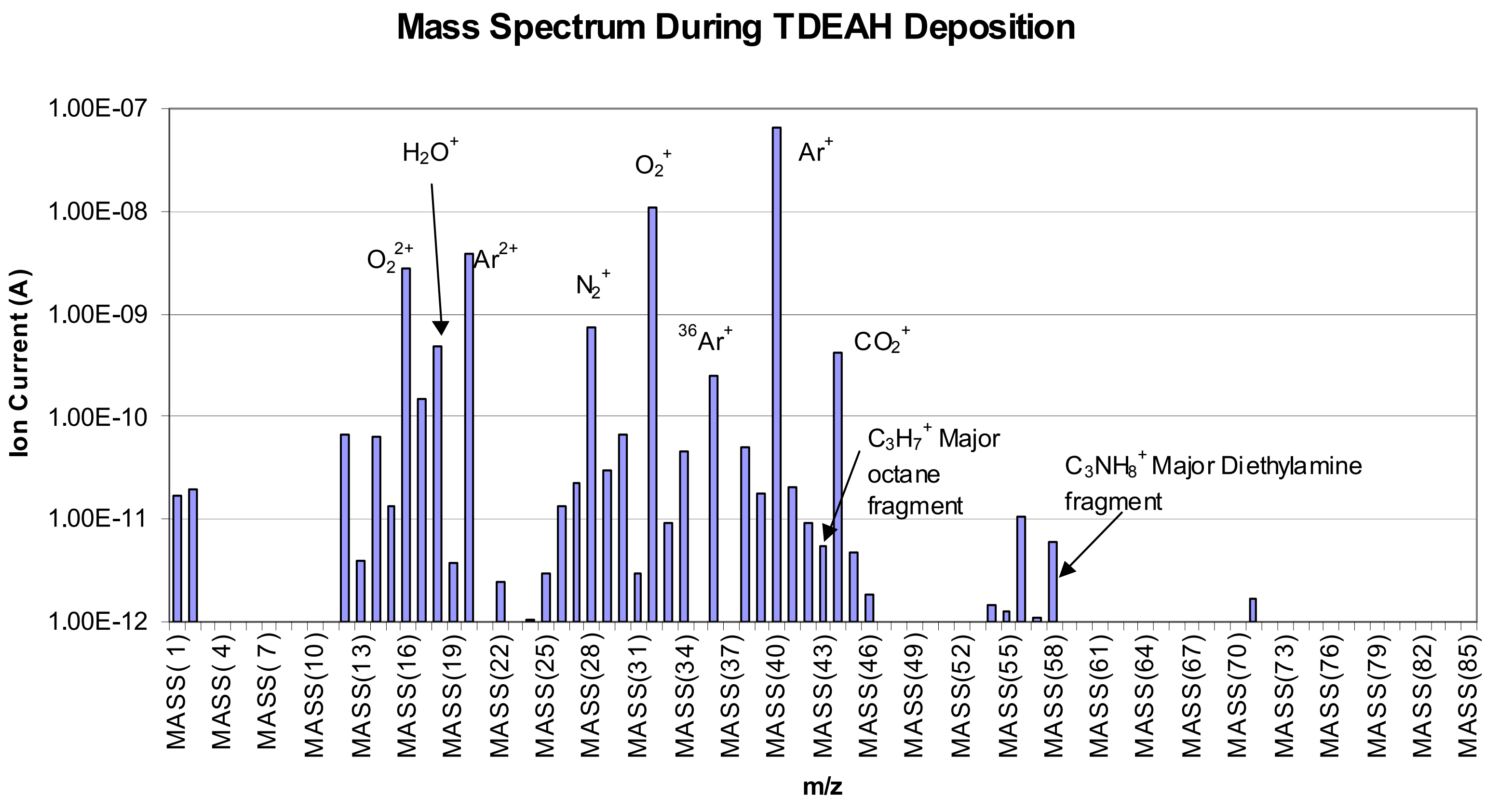
TDMAT Chamber Maintenance

- TGM sensor point in chamber detected dimethylamine at 7.5 ppm or greater
  - > than TLV (5 ppm), possibly greater than PEL (10 ppm)
- Special wipes for chamber wet clean
  - cleanroom polypropylene
  - use 100% IPA - NO WATER
- Supplemental exhaust to be installed

TDEAH

- Tetrakis dimethylamido 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

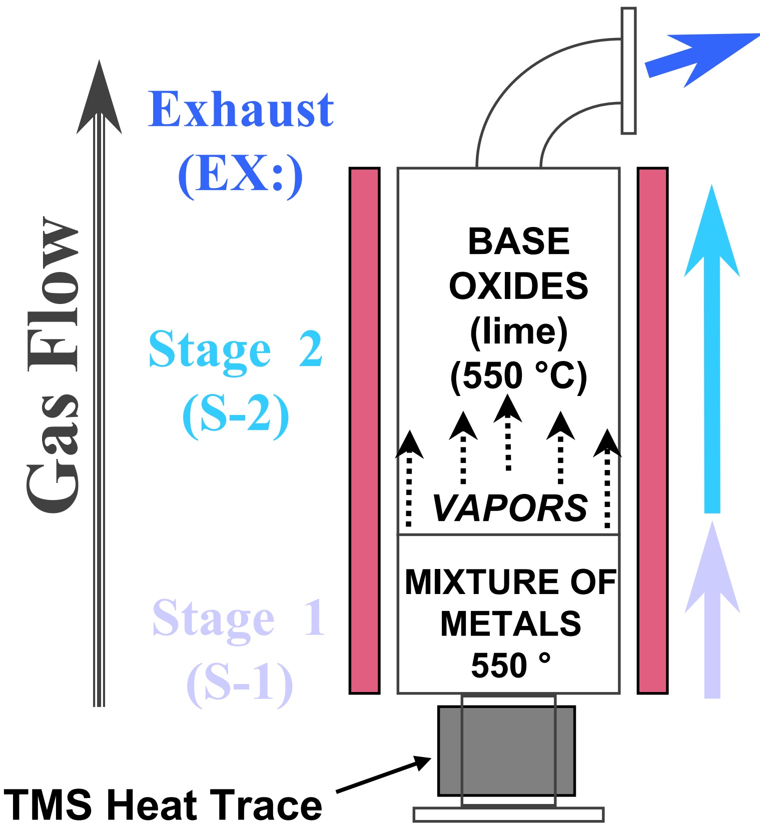


Shows diethylamine by-product

Handling Process Emissions

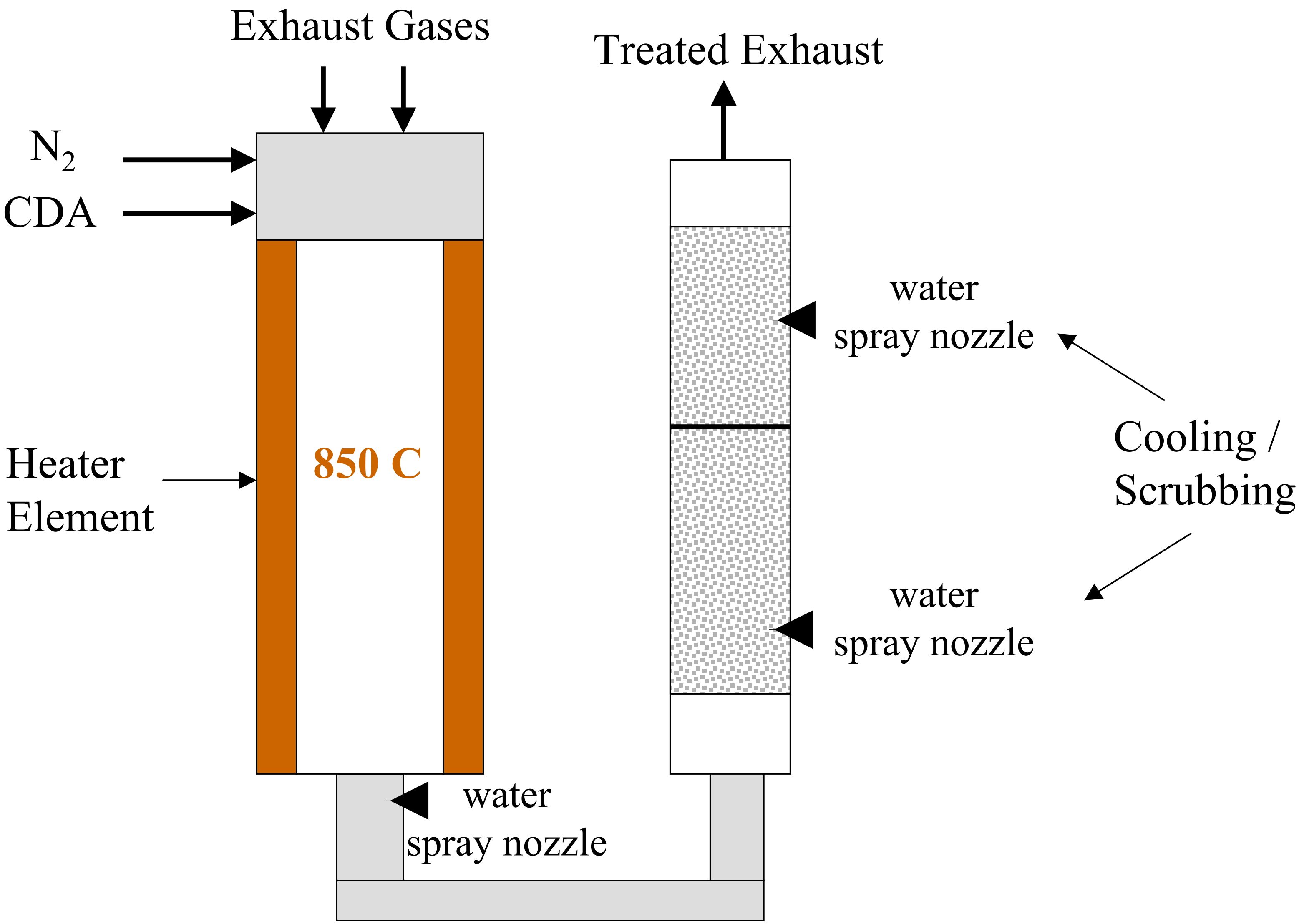
- Point of Use Abatement Device
  - Minimize overall EHS impacts of precursors and by-products
  - Minimize personnel exposure during maintenance
  - Remove unreacted precursor to prevent deposition in exhaust ducts or release to environment
  - Remove/destroy hazardous by-products or co-flow materials

Hot Bed Dry Scrubber

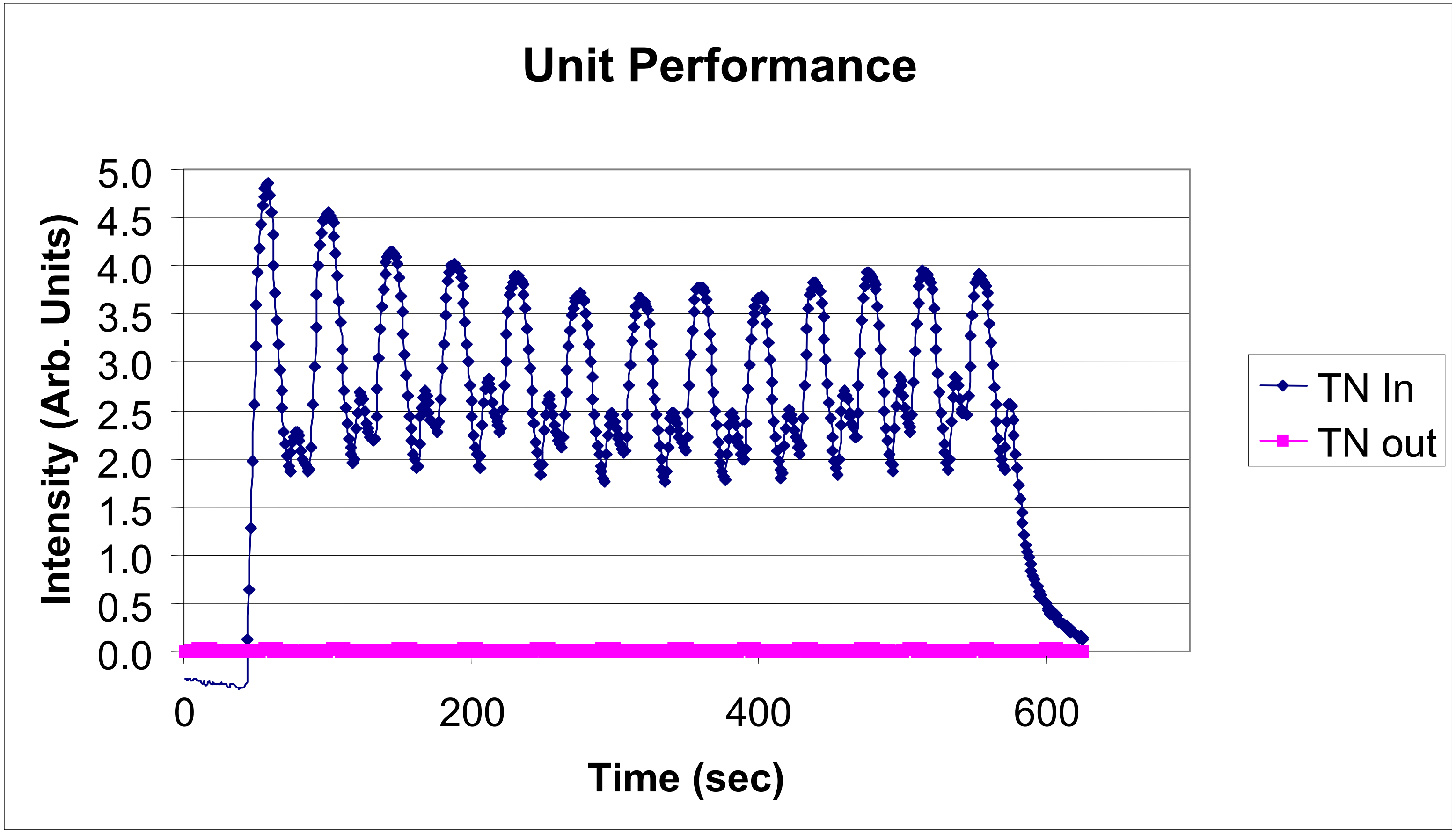


- S-1 Transfer heat into gas to reach reaction temperature
- S-1 Reacts with strong oxidizing agents (Cl_2, ClF_3) to form volatile metal halide species.
- S-1 Thermally decomposes Hydrides (SiH_4)
- S-2 Acid gases and volatile metal halides react to form <u>harmless inorganic salts</u>
- EX: Nonhazardous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

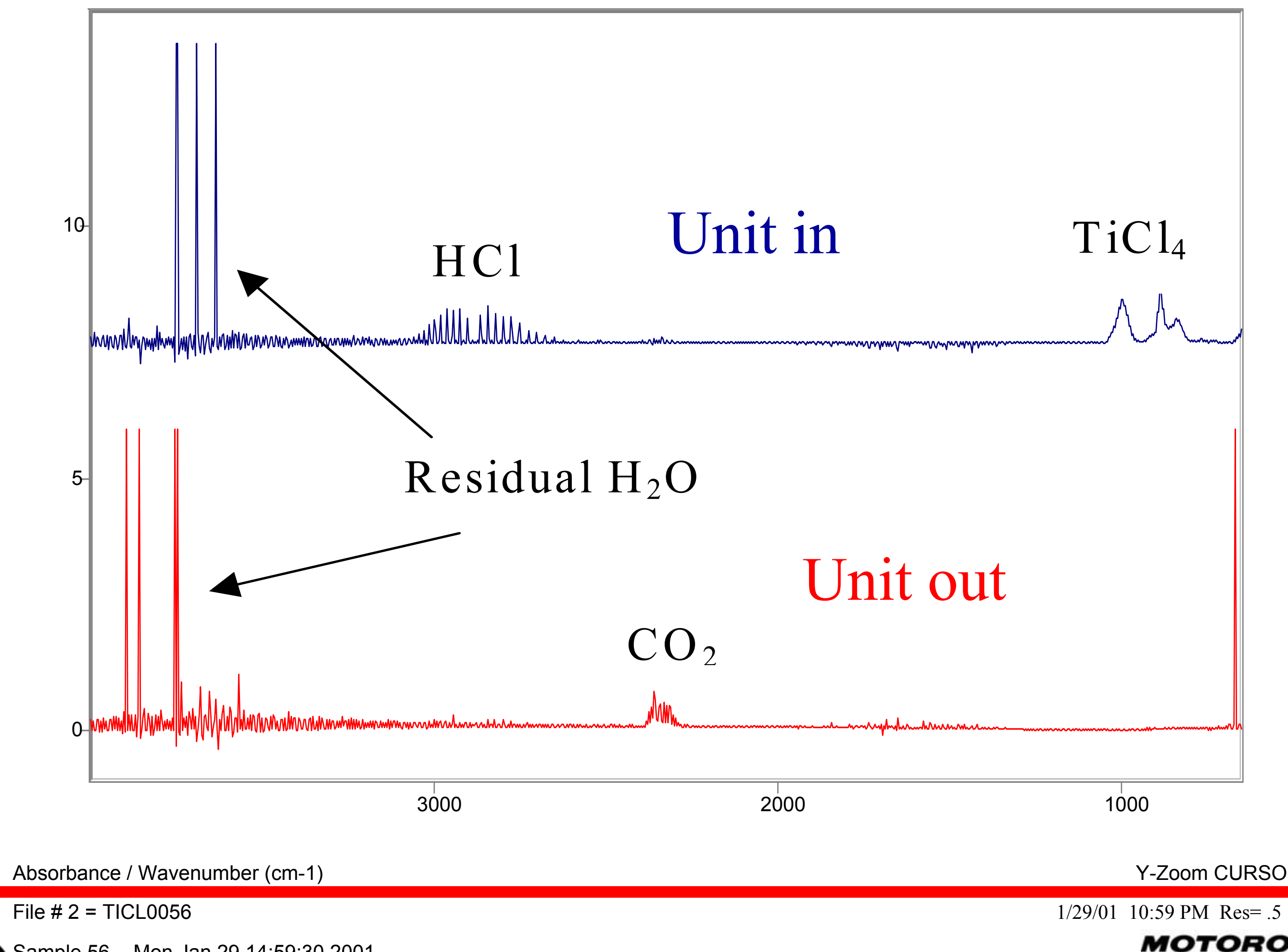
Thermal Destruction Unit



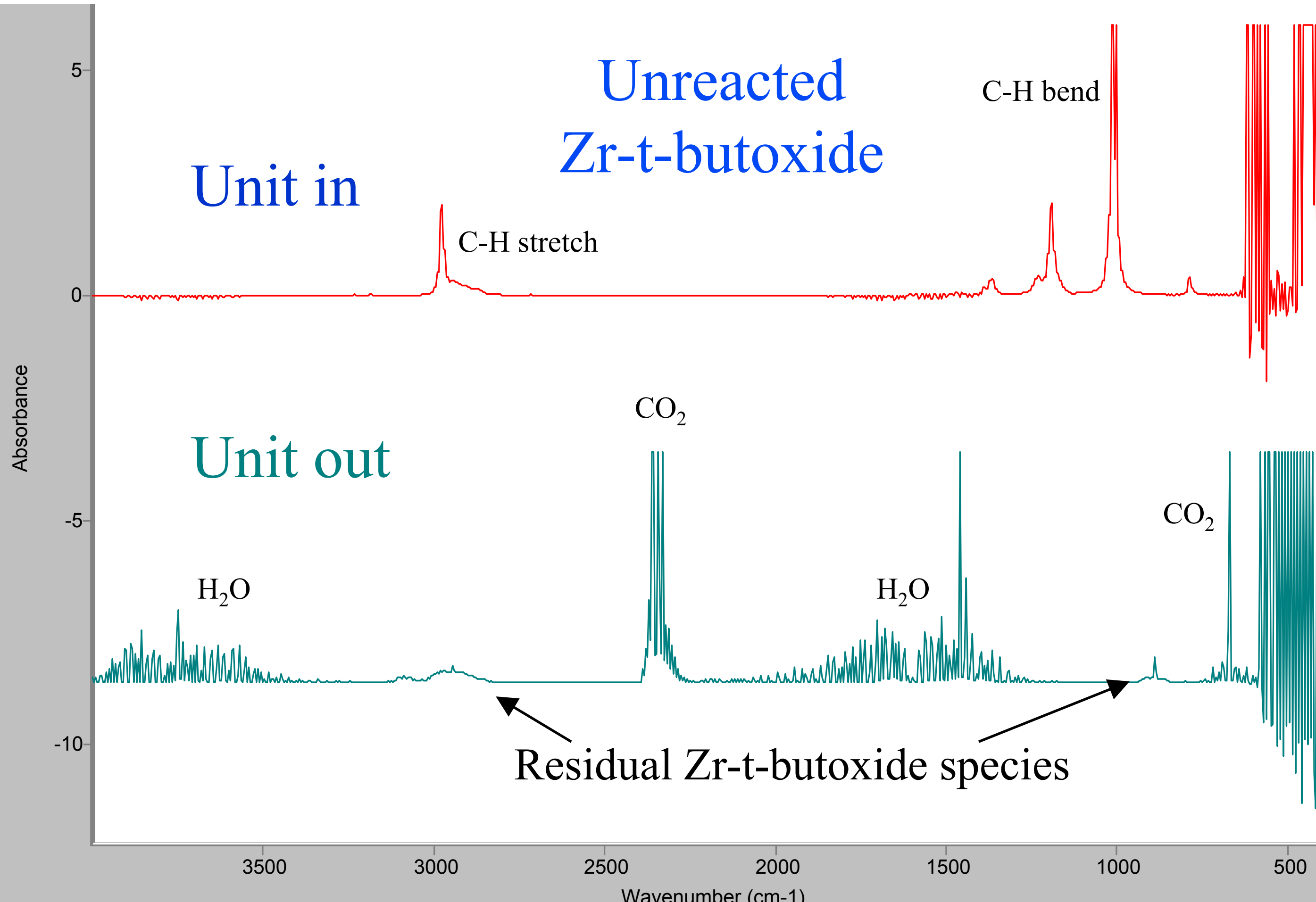
Hot Bed Dry Scrubber Performance for TN



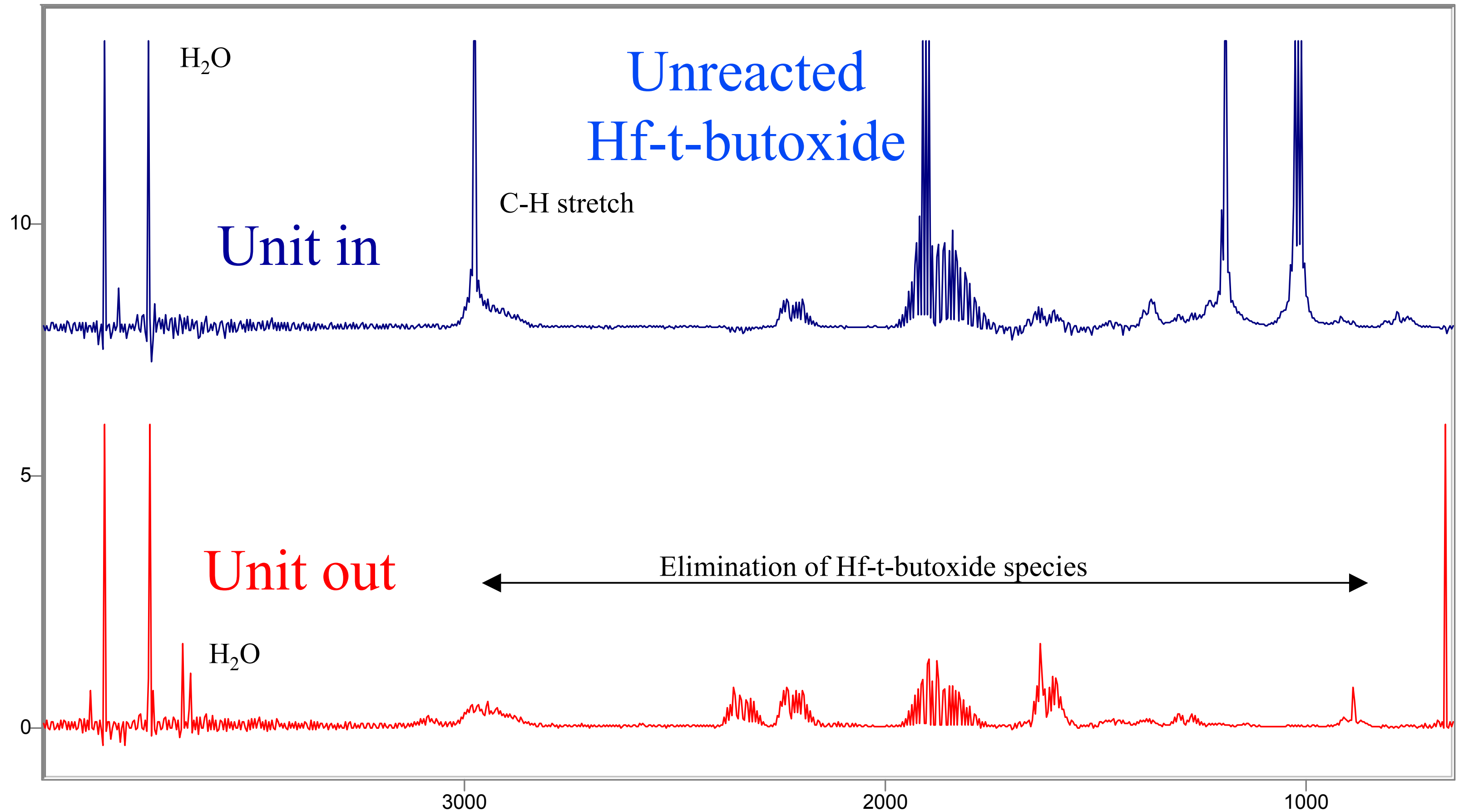
Hot Bed Dry Scrubber Performance for $TiCl_4$



Hot Bed Dry Scrubber Performance with Zr t-butoxide



Hot Bed Dry Scrubber Performance for Hf t-butoxide



Absorbance / Wavenumber (cm-1)

Y-Zoom CURSOR

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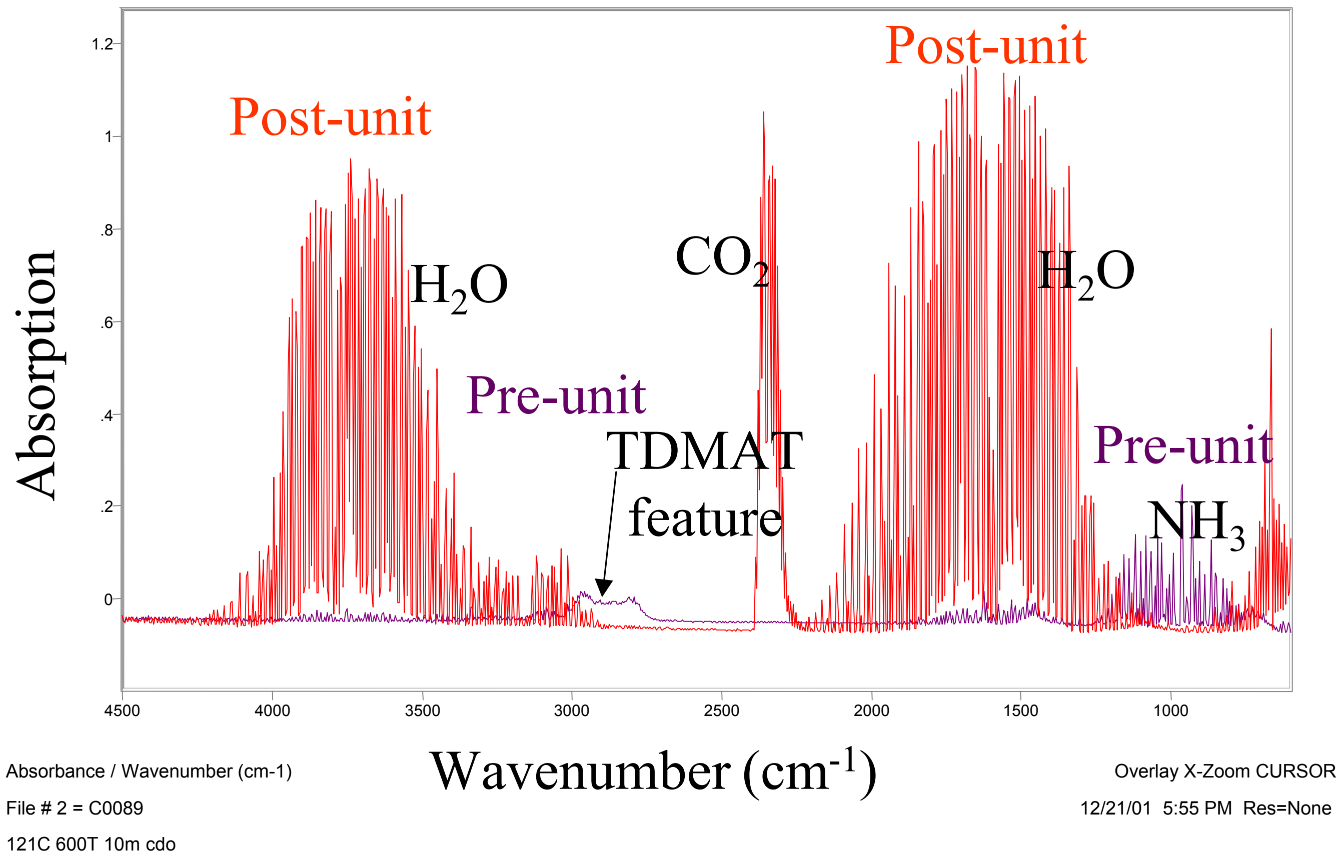
Thermal Destruction Unit Performance for TDMAT

FTIR spectra of TDMATTiN Deposition Process



Summary

- EHS Strategy must focus on entire process, not just the new material itself
- Must employ very conservative procedures until process is thoroughly characterized
- Collect as much data as possible in R&D phase
- Work with suppliers to collect additional data as needed to transfer to manufacturing