U.S. NAVAL RESEARCH LABORATORY

Nanosensor Testing

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Nanosensor Manufacturing Workshop
Nanosensor Manufacturing: Finding Better Paths to Products
June 13-14, 2017, National Science Foundation

This work was funded by the Department of Homeland Security, Science and Technology Directorate, Homeland Security Advanced Research Projects Agency (HSARPA), Explosives Division and First Responders Group

June 13, 2017

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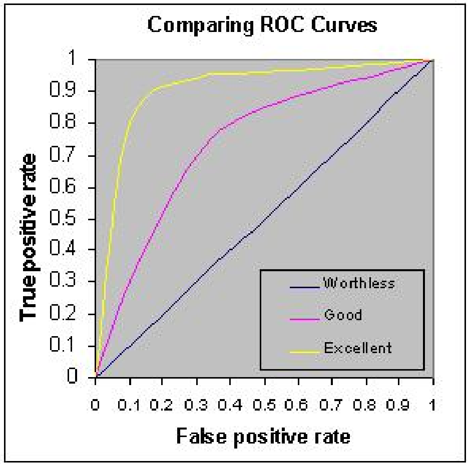
Outline

- Test Objectives
- Frequent mistakes
- TESTbed
  - -Design
  - -Limits of Quantitation
- TV-Gen
  - -Purpose
  - -Design
  - -Operation
- Conclusions/Acknowledgements

Test Objectives

Effectively evaluate the sensor performance under normal operating conditions

- Response and Recovery Times
  - 90% of full scale
  - 10% of full recovery to baseline
- Sensitivity
  - LoD vs LoQ
- Selectivity
  - Potential interferences
  - Mixtures
- Receiver Operating Characteristic Curve
- Sensor to Sensor Reproducibility
- Sensor Repeatability
- Relative Humidity Effects
- Temperature Effects
- Dynamic Range

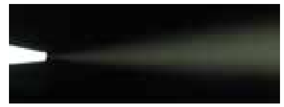


Frequent Mistakes

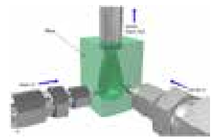
- Testing in dry nitrogen rather than humid air
- Lack of stability in vapor generation
- Lack of stability in temperature/relative humidity (RH) controls
- Failure to collect enough trials for statistical significance/reliability of measurement
- Carryover effects from previously utilized analytes
- Lack of rapid switching from analyte to clean
- Lack of independent validation of vapor/RH
- Not doing side by side testing
  - Calibration transfer is important
    - Fabrication must be reproducible
    - Sensor Stability/Robustness

Key Features for Testbed Design

- Vapor Generation
  - Reproducibility
  - Stability
- Effective Mixing
  - Different volumes
- Stable Delivery
  - Materials compatibility
  - Uniformity
- Validation
  - Verify concentration
  - Unexpected contamination



Nebulizer



Vortex Mixer

Electronic Impactor Chamber

Optical Impactor Chamber

TDS-GC/ECD

Online GC/MS

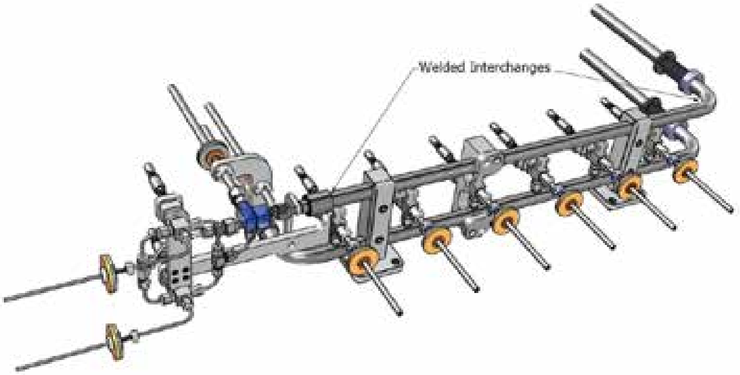
Trace Explosives Sensor Testbed (TESTbed)

− Key Features

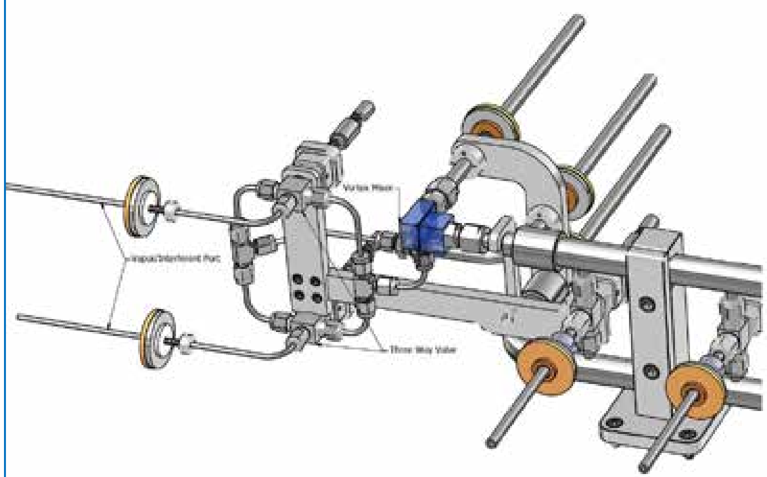
- Dedicated computer control, custom GUI, fully automated for standardized vapor delivery
- Six identical sample ports
- Zero air source
- Four vapor generation sources
- Housed in an oven for temperature control
- Humidity control 0-85% relative humidity
- Online validation system

TESTbed Dual-Manifold System

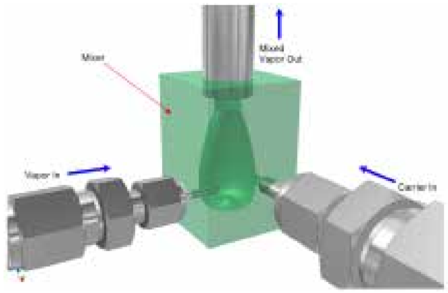
– Key Features



- Sulfinert™ treated stainless steel
- Dual distribution manifolds
- Rapid switching from clean to analyte vapor streams
- Multiple vapor inputs
- Custom mixer for vapor stream uniformity
- Three way inlet/bypass valve
- Easily removable and exchanged to eliminate cross contamination issues



Three way inlet/bypass valves



Vortex mixer

Conditioned Air

Environics and Miller-Nelson

Key features:

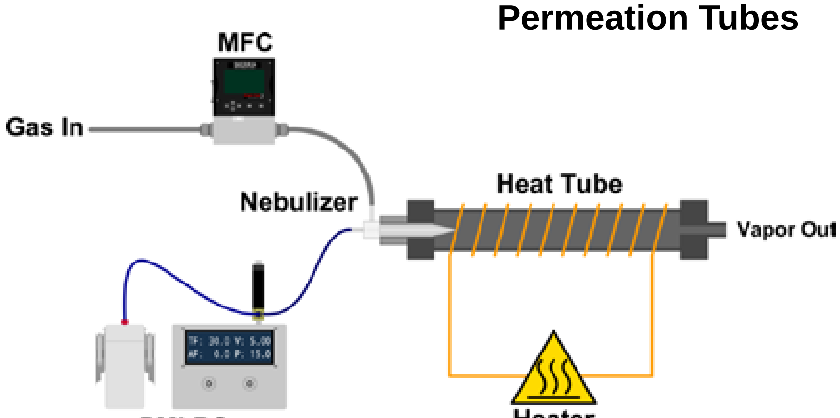
- Environics Series 7000 Zero Air Generator
  - Delivers up to 20 liters per minute, 30 psi of dry, contaminant-free air.
  - Free from
    - Water vapor
    - Particulates
    - <0.5 ppb Sulfur dioxide, hydrogen sulfide, oxides of nitrogen, nitrogen dioxide, ozone, carbon monoxide and hydrocarbons
- Miller-Nelson Test Atmosphere Generator controls and monitors the initial Flow Rate, Temperature, and Humidity level
    - Flow Rate : 2 - 20 L/min
    - Temperature : 20 - 35 °C
    - Humidity : 20 - 85 %RH

Test Vapor Sources

Kin-Tek FlexStream Automated Permeation Tube Oven

Calibrated Gas Standards

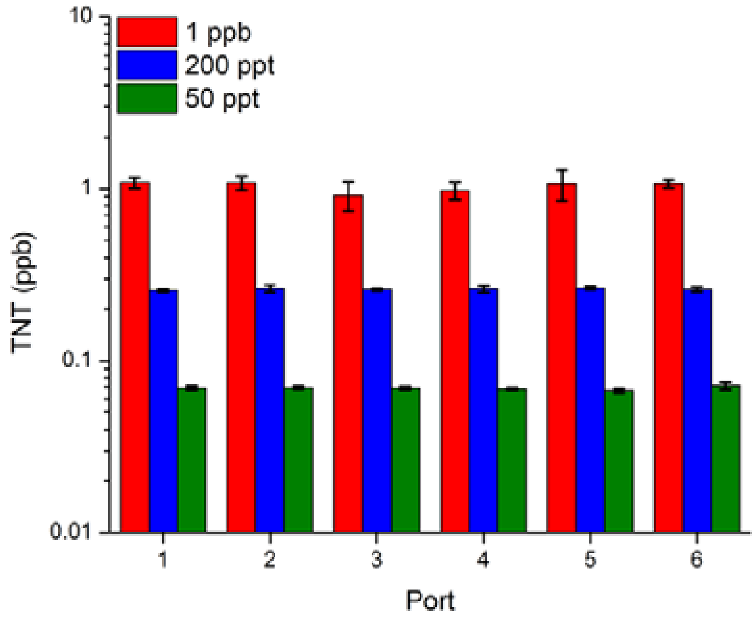
Permeation Tubes



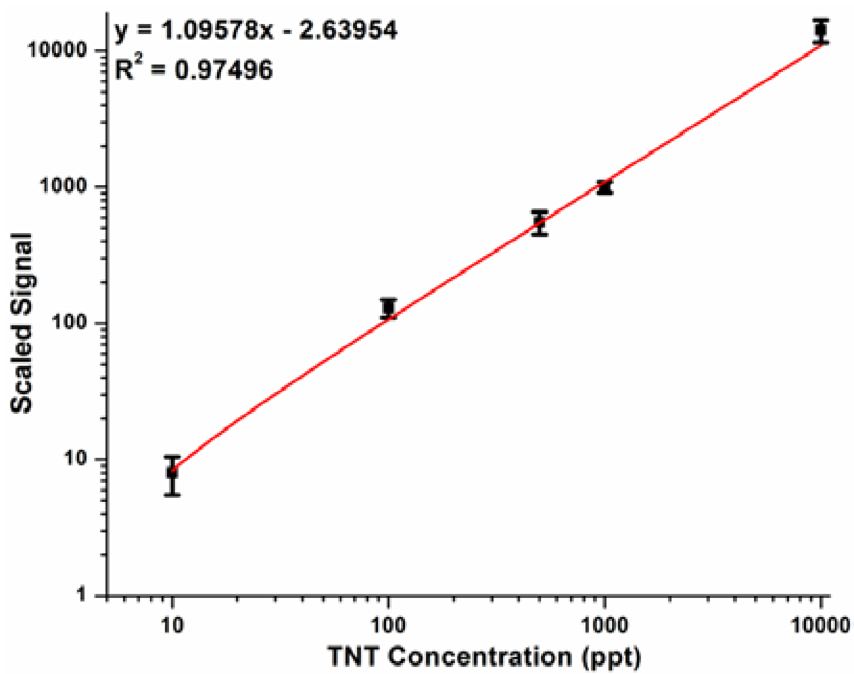
- The FlexStream Automated Permeation Tube System controls both its oven temperature as well as the carrier gas flow rate through the oven module
  - 500 permeation tubes available
    - NH_3
    - HNO_3
    - DNT
  - Custom tubes optional
- Auxiliary flow controller for calibrated gas standards (Flow Rate: 10 - 1000 mL/min)
- Custom Vapor Generators
  - **Pneumatically Modulated Liquid Delivery System (PMLDS)**

TESTbed Validation

Characterization of the sensor test system



Port to Port Reproducibility: Uniform Distribution Across All Sample Ports

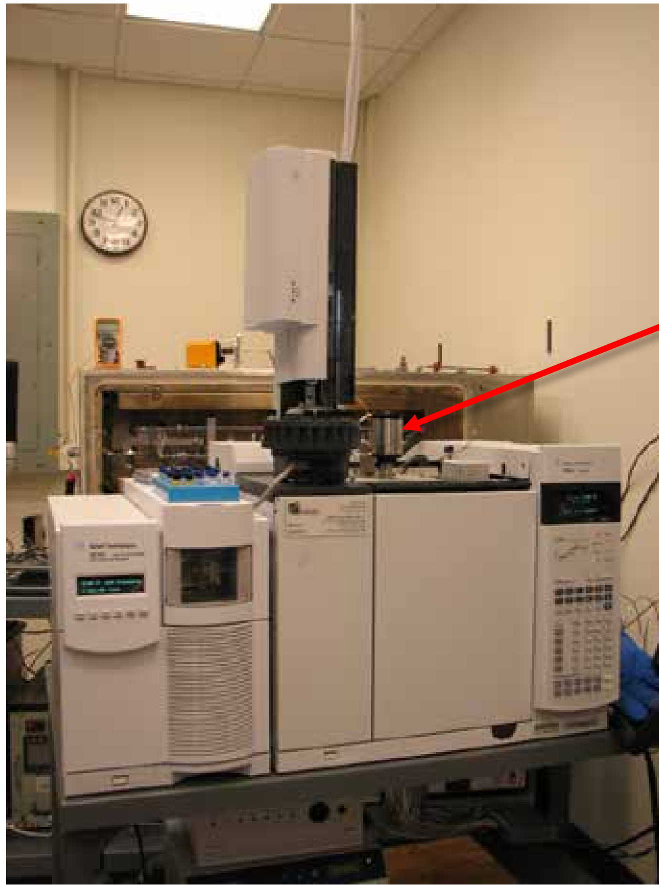


TNT from 10 ppt – 10 ppb

Online Verification

Agilent 5975C MSD

- Electron Impact
  - Rapid Identification of 1000 compounds
- Chemical Ionization
- Negative CI
  - Selectivity
  - Low Limits of Detection
    ØTNT = 40 fmole
    ØRDX = 100 fmole



Gerstel Online Cooled Inlet

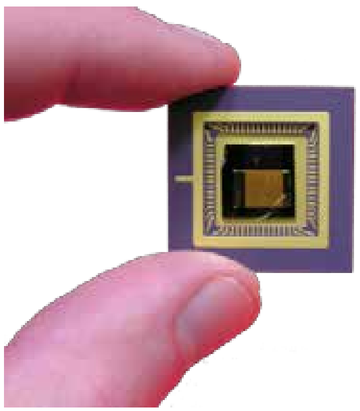
- Adsorbs at 250 mL min^{-1}
  - 10 mL-10 L adsorption Vol.
- Cyro-cooled sorbent bed
- Rapid desorption (12^{o}C sec^{-1})
- Variety of sorbents
  - Tenax TA™
  - CarboTrap C
  - CarboTrap B
  - Silanized Glass

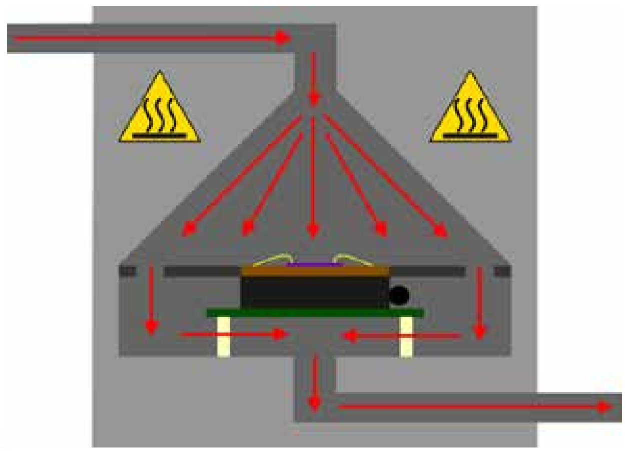
Agilent mECD

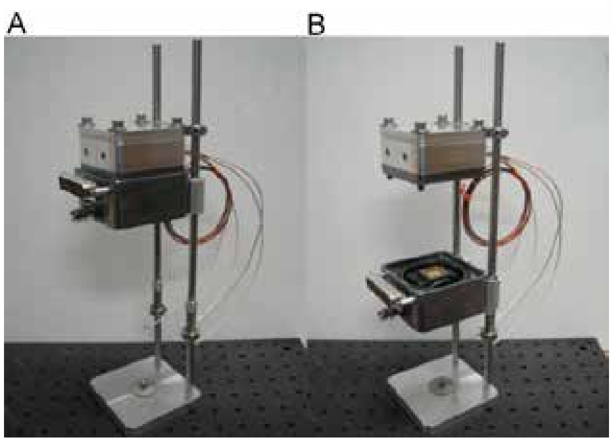
- Selectivity
- Low Limits of Detection
  ØTNT = 440 fmole
  ØRDX = 1.1 pmole
  ØPETN = 1.5 pmole

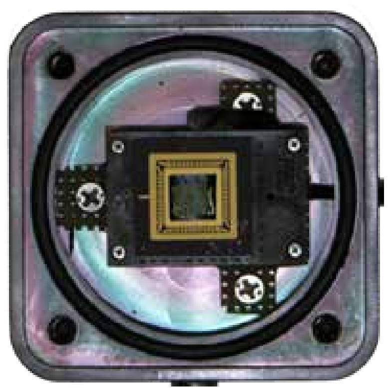
Sensor Chambers

- Chamber for electronic sensors
- Temperature controlled
- Sulfinert™ coated sample chamber









- Optical Chamber
- Chemiluminescence/fluorescence
- Temperature controlled
- Sulfinert™ coated chamber

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Limits of Quantitation

Summary of the vapor concentrations detected in our laboratory. Realize that lower vapor concentrations are achievable with longer sample times.

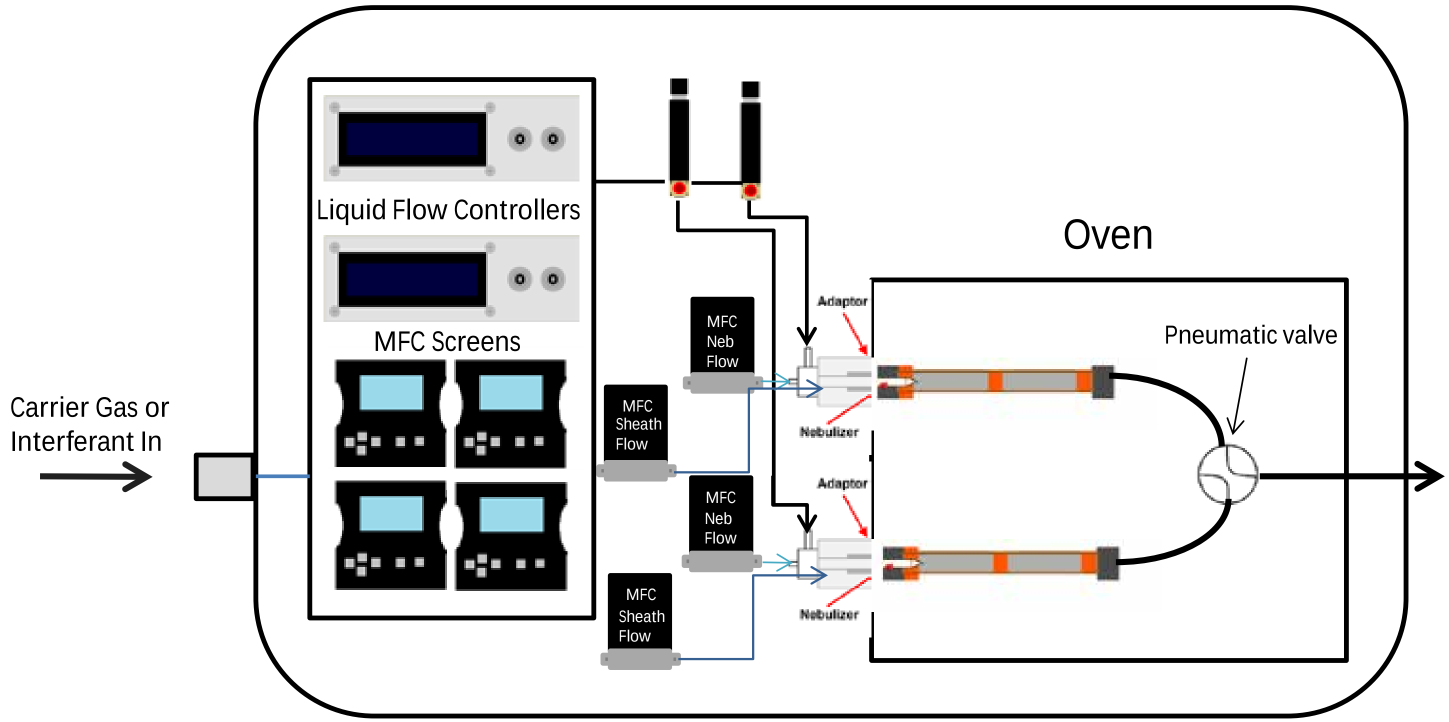
Explosive	Sat. Vapor Conc.*	TDS-CIS-GC		On-line CIS-GC	
		Sample Time (Vol.)	LCQ	Sample Time (Vol.)	LCQ
TNT	~9 ppb_v	60 min (6 L)[a]	3.4 ppt	4 min (0.66 L)[b]	100 ppq
RDX	~5 ppt_v	60 min (6 L)[a]	4.3 ppt	4 min (0.66 L)[b]	500 ppq
PETN	~11 ppt_v	30 min (3 L)[a]	12 ppt		
TATP	~63 ppm_v			1 min (0.025 L)[a]	5.5 ppb
NM	~46,800 ppm_v			0.5 min (0.0125 L)[a]	*3000 ppb*
EGDN	~102 ppm_v			1 min (0.1 L)[a]	*3.0 ppb*
NG	~645 ppb_v			1 min (0.1 L)[a]	*3.0 ppb*

[a] Sample was collected on Tenax-TA sorbent at 25°C
[b] Sample was collected on a Silconert coated glass tube at 10°C

* From "The Vapor Pressure of Explosives," Ewing *et al.* Trends in Analytical Chemistry, Vol. 42, 2013, 35-48

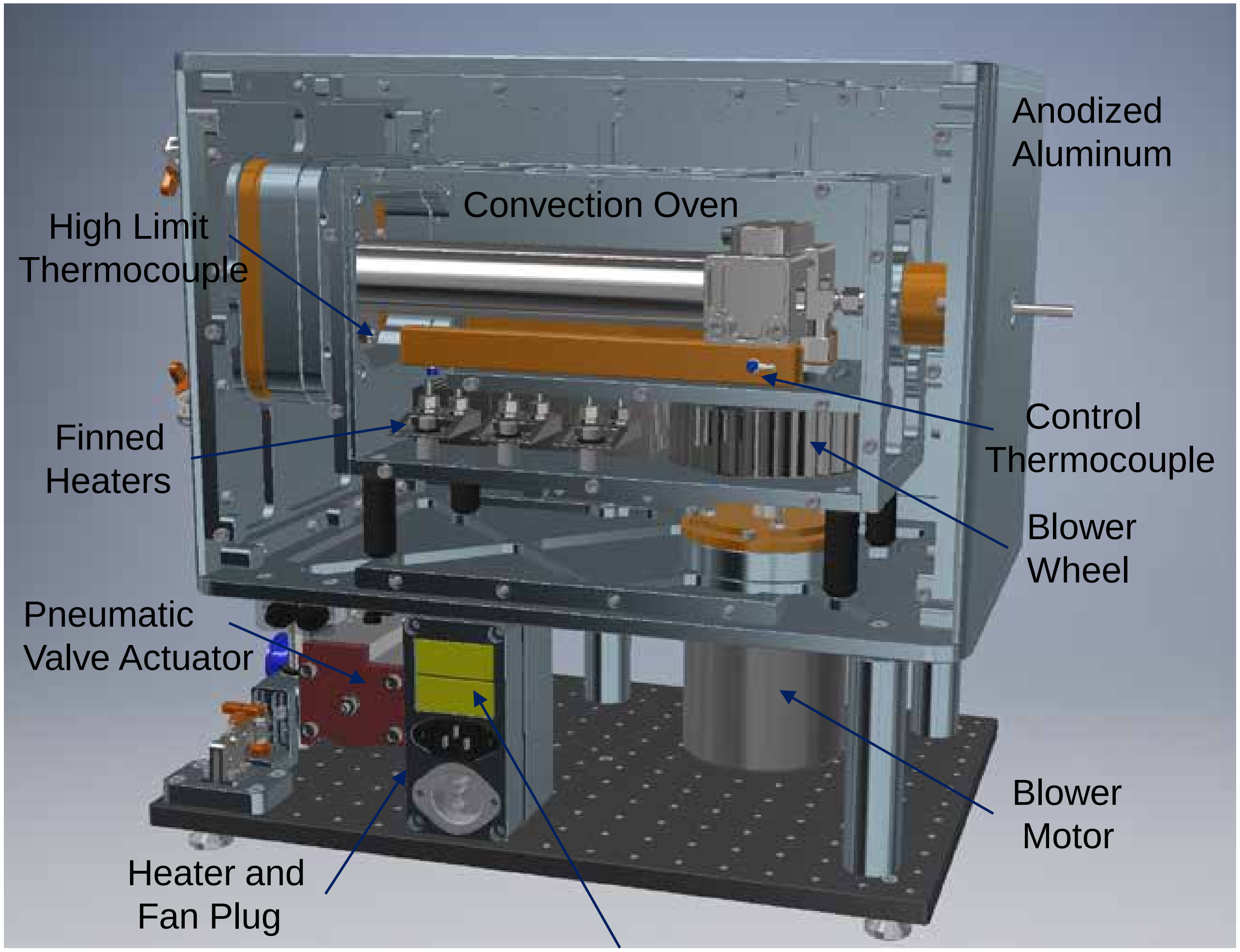
TV-Gen Design

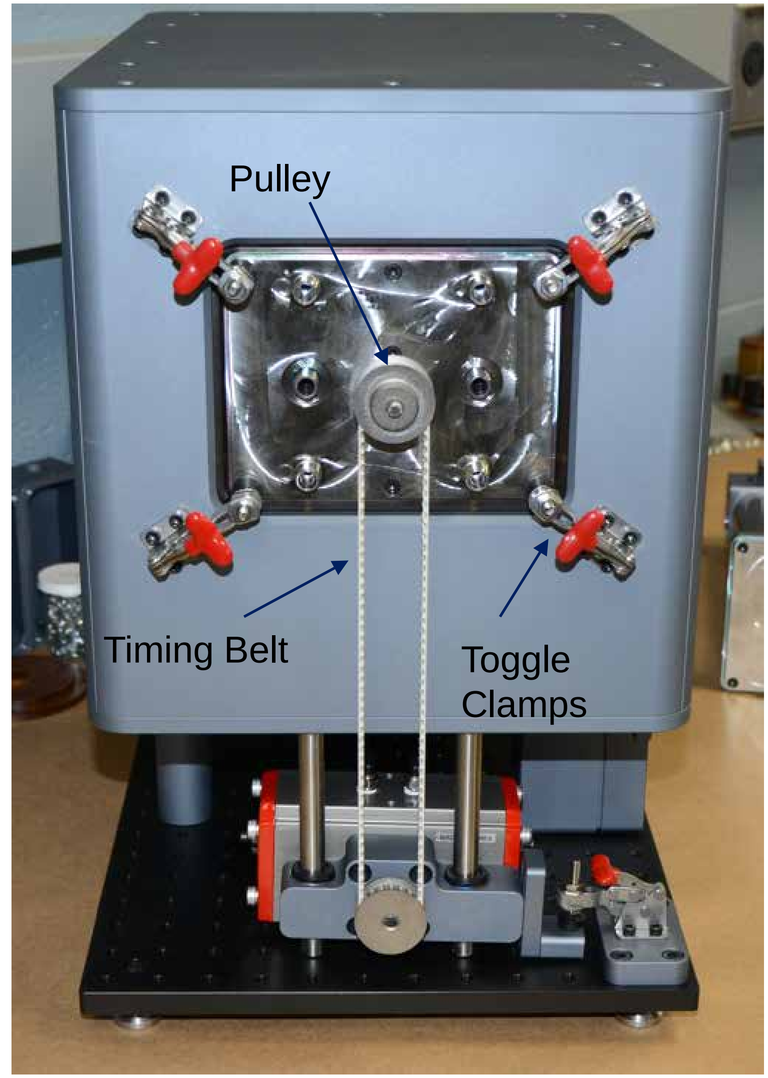
TV-Gen Control Screen and Flow Controller Box



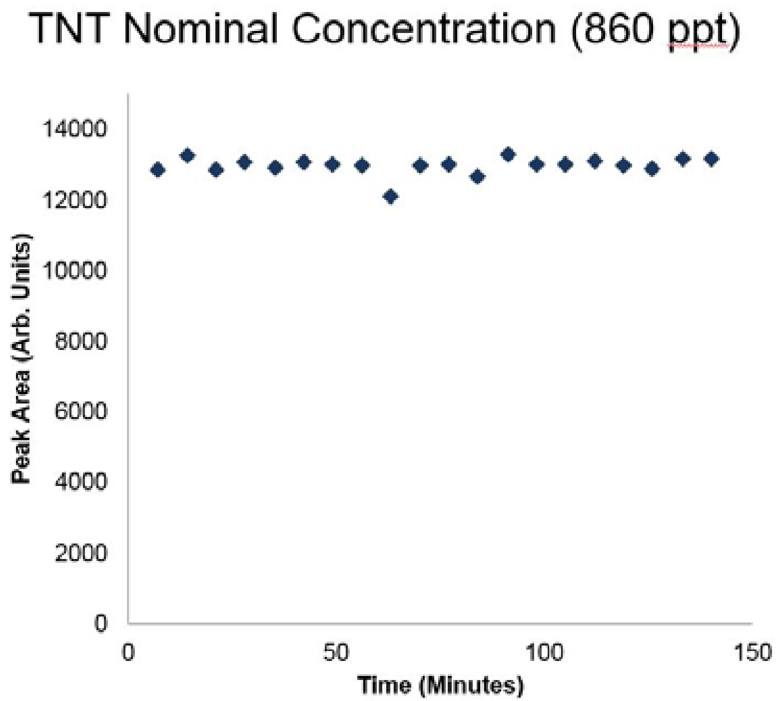
- Two manifolds- Clean and Analyte
- Nebulizer utilized to generate explosives/narcotics vapor from aqueous solution
- Vapor system contained within oven, 130°C, to prevent adsorption
- Manifolds are easily exchangeable for different analytes
- Single sensor/detector sampling port

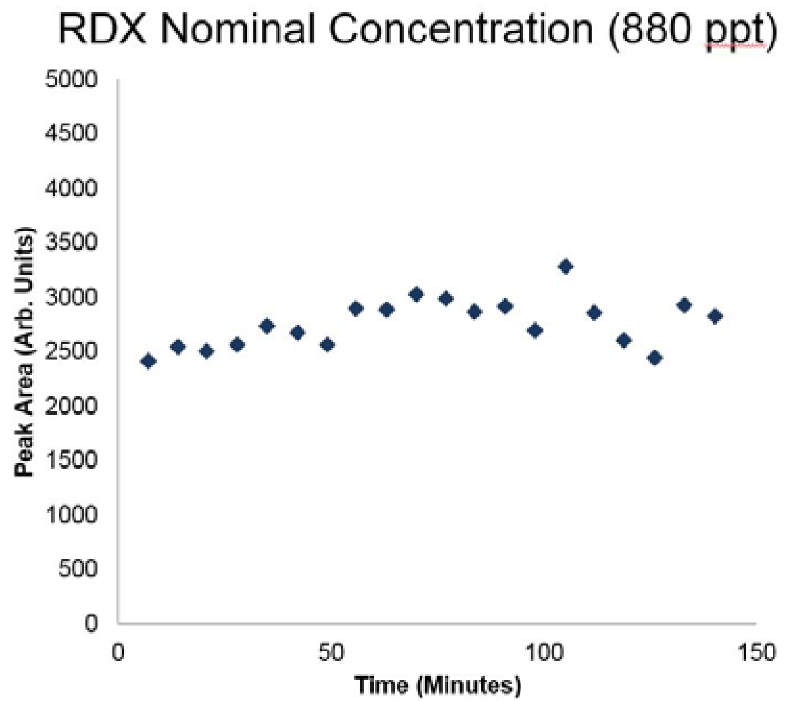
TV-Gen Components





TV-Gen Analytical Evaluation





Average %RSD= 1.9 ◆ Peak Area Average %RSD= 8.1

Environmental Chambers

Sensor Lab Facilities

- Walk-in environmental chamber
  - 10’ X 15’
  - Temp: -30-50ºC, Humidity: 10-95% RH
  - Walls that can be washed down
- CSZ Temperature/Humidity /Altitude Chamber
- Aerosol Lab with wind tunnel

Other Facilities

- Desert High Bay
- Littoral High Bay
- Tropical High Bay
- Reconfigurable Prototyping High Bay
- Power and Energy Lab
- Human-System Interaction Labs

N5 Sensors Evaluation

Sensor Testing

- Level 1 – Characterization of Sensor Response

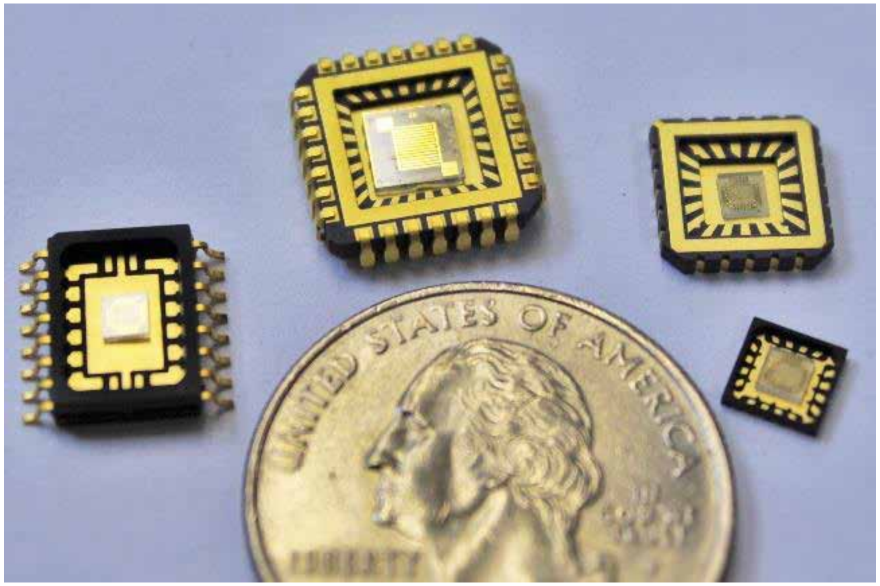
Determine magnitude, the time required to achieve 90% of full scale and the time required to recover to 10% of full scale for each test gas at one concentration using the procedure below. Generate an air stream with target analyte at a single concentration at one relative humidity

- Level 2 – Characterization of Sensor Dynamic Range

Determine sensor performance for analytes at multiple concentrations. Test at 3 target gas concentrations. Concentrations span the specifications from Minimum to Maximum Detection Limit.

- Level 3 – Characterization of sensor performance at multiple concentrations, in presence of varying humidity and interferents.

Perform test at 3 separate target RH levels 20%, 40%, 60%. At each RH level, evaluate the sensors for varying concentrations of the target gas. Repeat the test and introduce interferents in the background.



	ACGIH/NIOSH			Recommended Concentrations		
	TWA/TLV	STEL	IDLH	low	med	high
H_2				1000	10000	40000
CO_2	5000	30000	40000	5000	10000	40000
HCN	4.7	10	50	5	10	20
NH_3	25	35	300	15	35	70
SO_2	2	5	100	2	5	10
CO	35	200	1200	25	200	400
Cl_2	0.5	1	10	0.5	1	2
HCl	2	5	50	2	5	10
H_2S	5	10	100	5	10	20
CH_4				5000	25000	50000

Test Challenges/Considerations:

What configuration is best for testing these very small devices

Active sampling: fan/push or pull sample or Passive sampling: No fan/Static/Face velocity

Optimal Flow rate/Dwell time. *What are the expected conops for the technology?*

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Acknowledgements

- This work is funded by the Department of Homeland Security, Science and Technology Directorate, Homeland Security Advanced Research Projects Agency (HSARPA), Explosives Division and First Responders Group

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