



## R2-B.1: Orthogonal Sensors for Trace Detection

# ***Orthogonal Sensors for Residue Vapors***

***Zach Caron, Vivek Patel, Dylan Meekins,  
Michael J. Platek and Otto J. Gregory***

***Sensors and Surface Technology Partnership  
Chemical Engineering Department  
University of Rhode Island  
Kingston, RI 02881***



Center for Sensors and  
Instrumentation Research

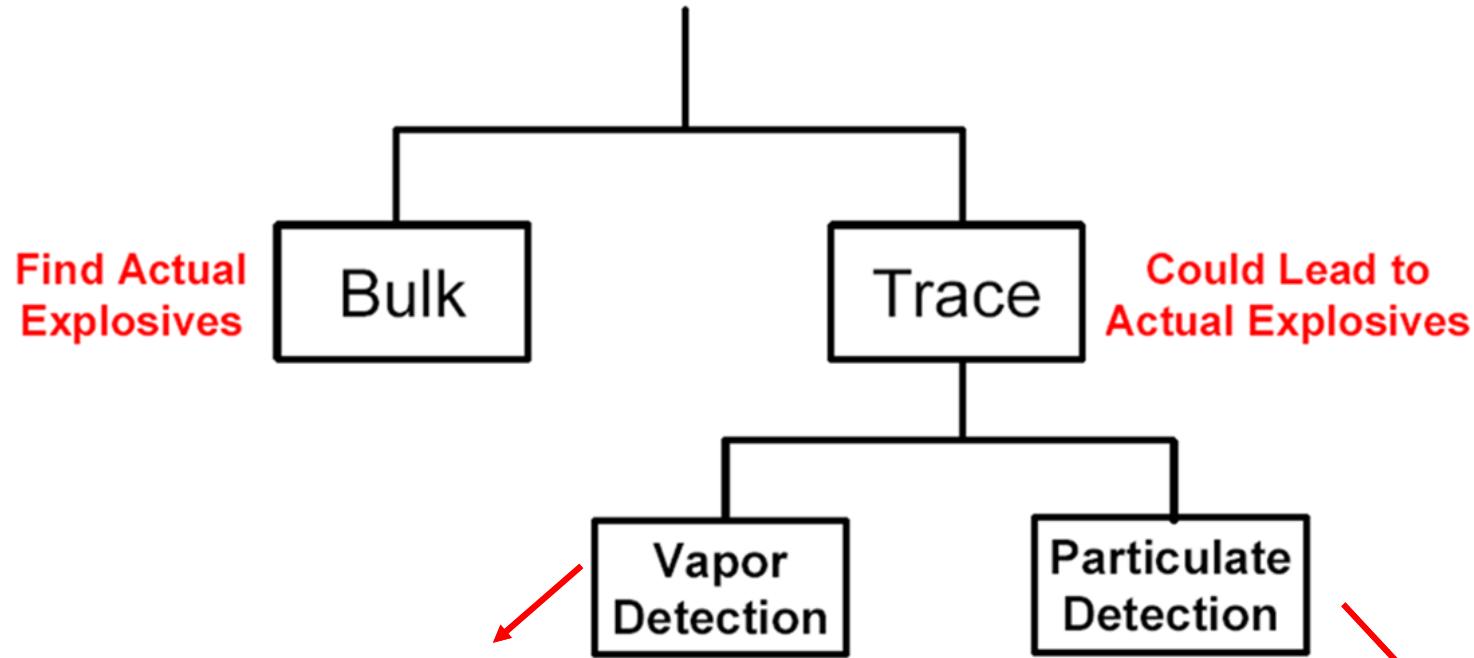
*August 5, 2015*





# Detection of Residue Vapors

## Explosives Detection\*



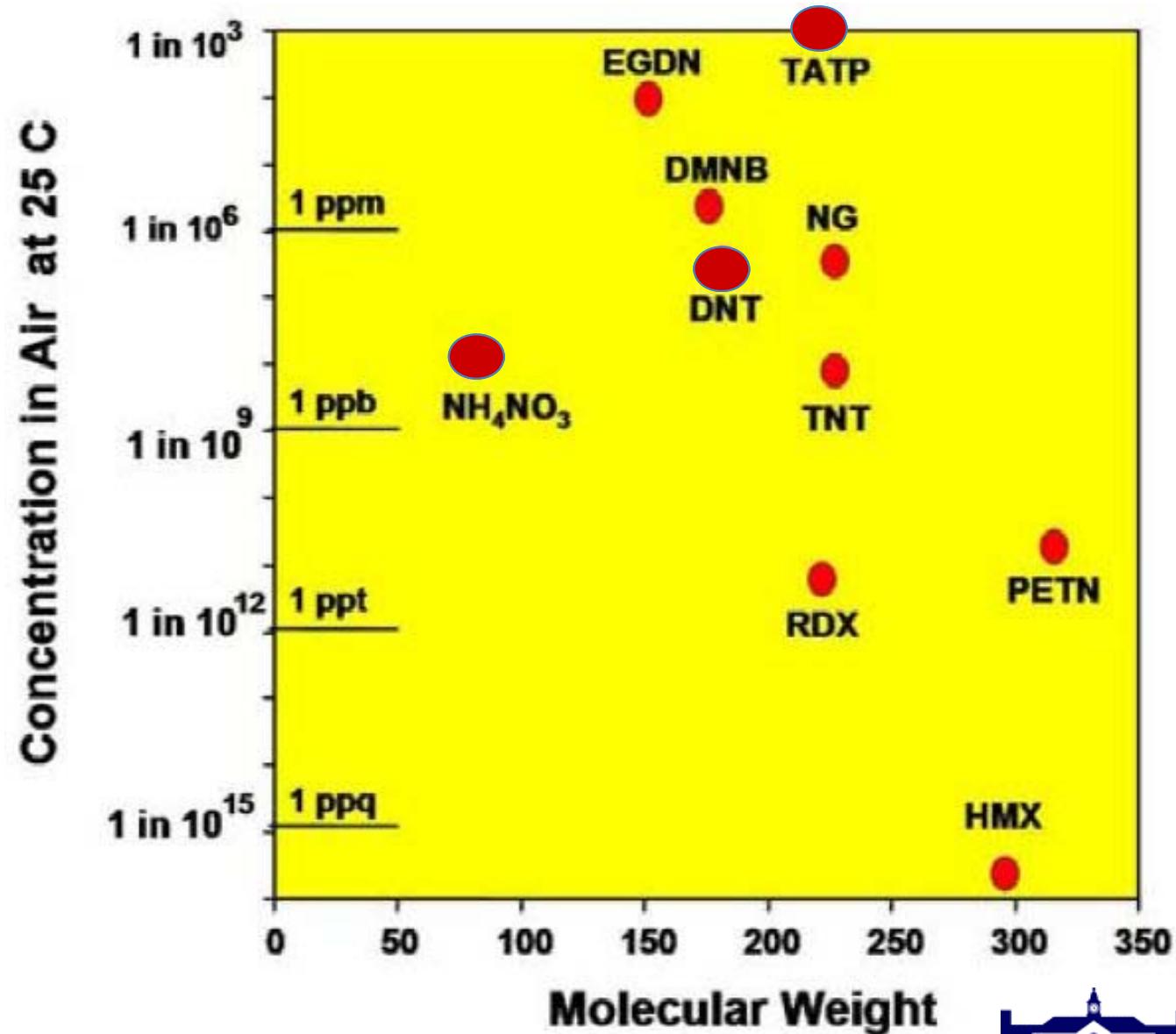
**Vapor Detection:** the concentration of explosives in the vapor phase is related to its vapor pressure and other factors such as, packaging, air circulation in the location, etc. all are critical for continuous monitoring of threats.

**Particle Detection:** techniques such as Ion Mobility Spectrometry (IMS) and colorimetric based detectors are typically used but require samples obtained by swabbing and thus cannot be used for continuous monitoring of threats.



# Residue Vapors.....Concentration in Air?

Vapor pressure determines residue concentration in vapor phase; TATP, DNT and ammonium nitrate can be detected in vapor phase .....conc. in the ppm to ppb range; PETN and RDX are not readily detected in vapor phase.....conc. in the ppt range



\*U.S. Department of Justice, November 2004





# Components Comprising Orthogonal Sensors (thermodynamic and conductometric)

(1) Metal Oxide Catalyst

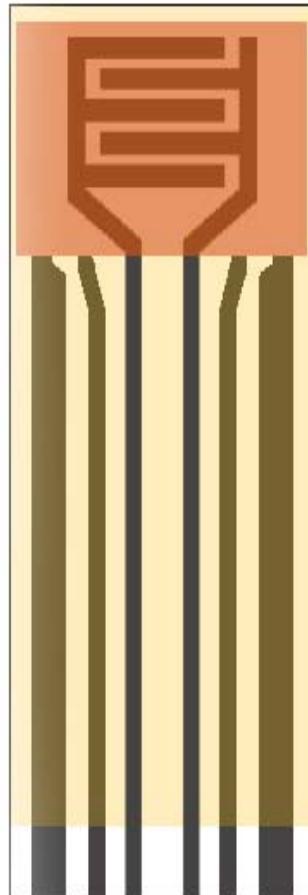
(2) Ni Conductometric Electrodes

(3) Alumina (porous)

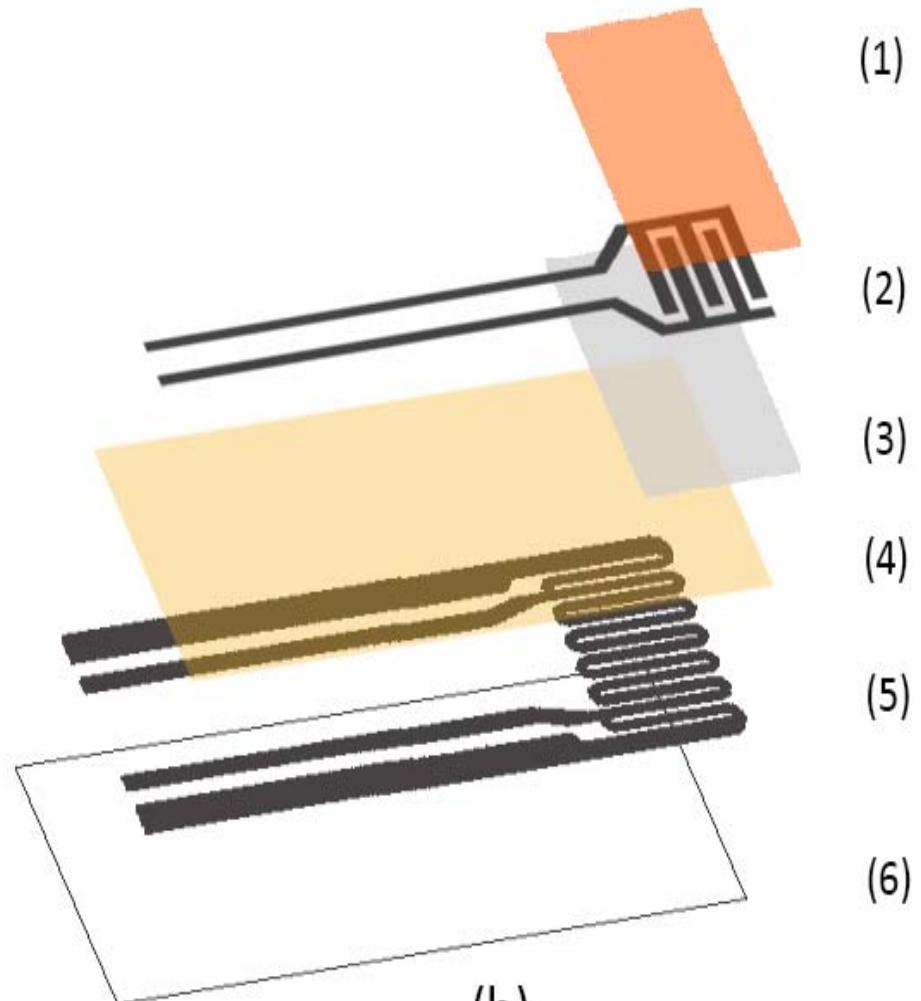
(4) Sputtered Alumina

(5) Ni Microheater

(6) Alumina Substrate



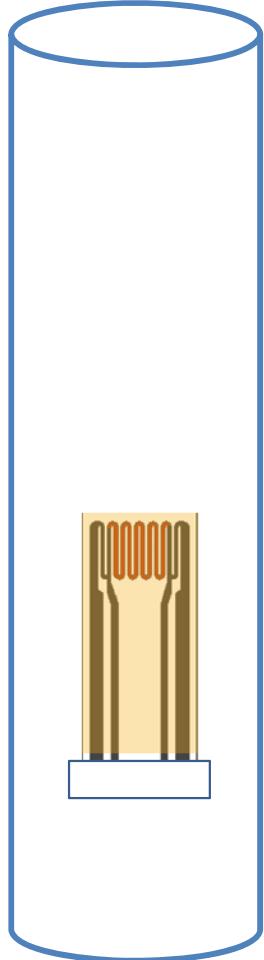
(a)



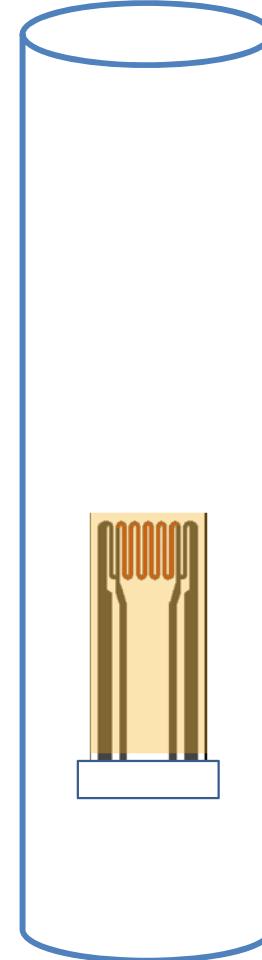
(b)



# *Dynamic Protocol for Trace Detection* *(thermodynamic platform)*

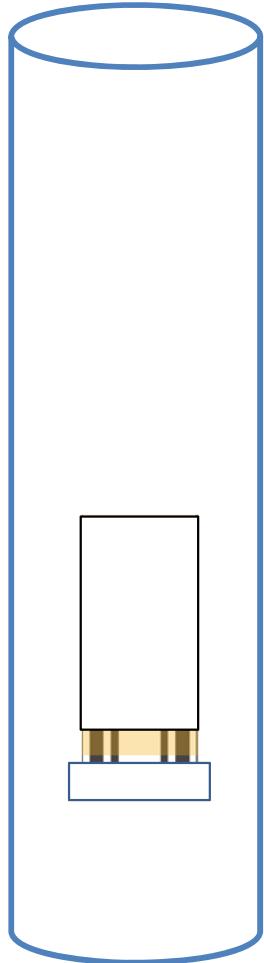


Two microheaters  
with identical  
electrical  
properties are  
thermally isolated  
in separate  
chambers.

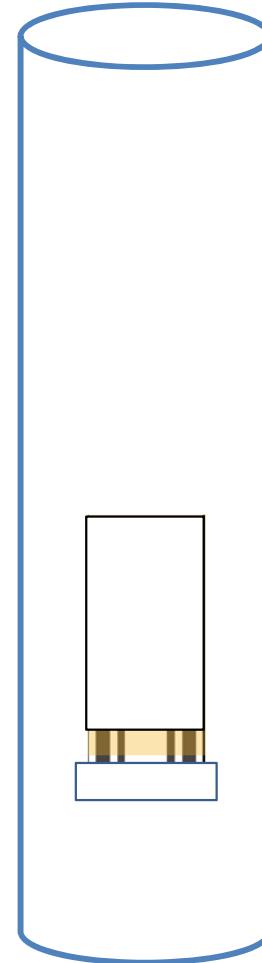




# *Dynamic Protocol for Trace Detection (thermodynamic platform)*

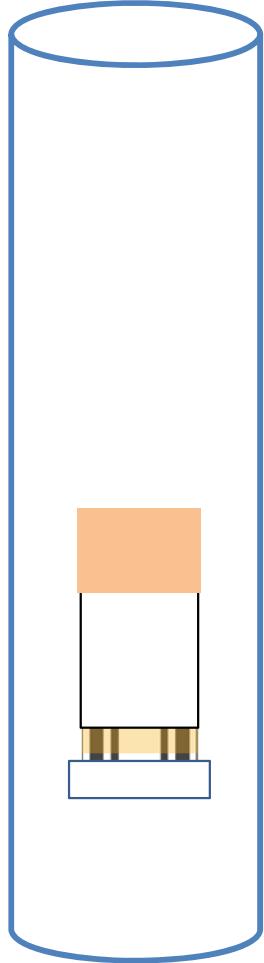


Both heaters are  
coated with an  
alumina dielectric.

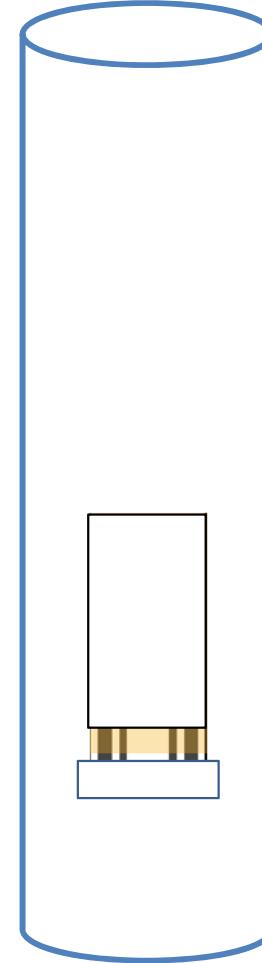




# *Dynamic Protocol for Trace Detection (thermodynamic platform)*

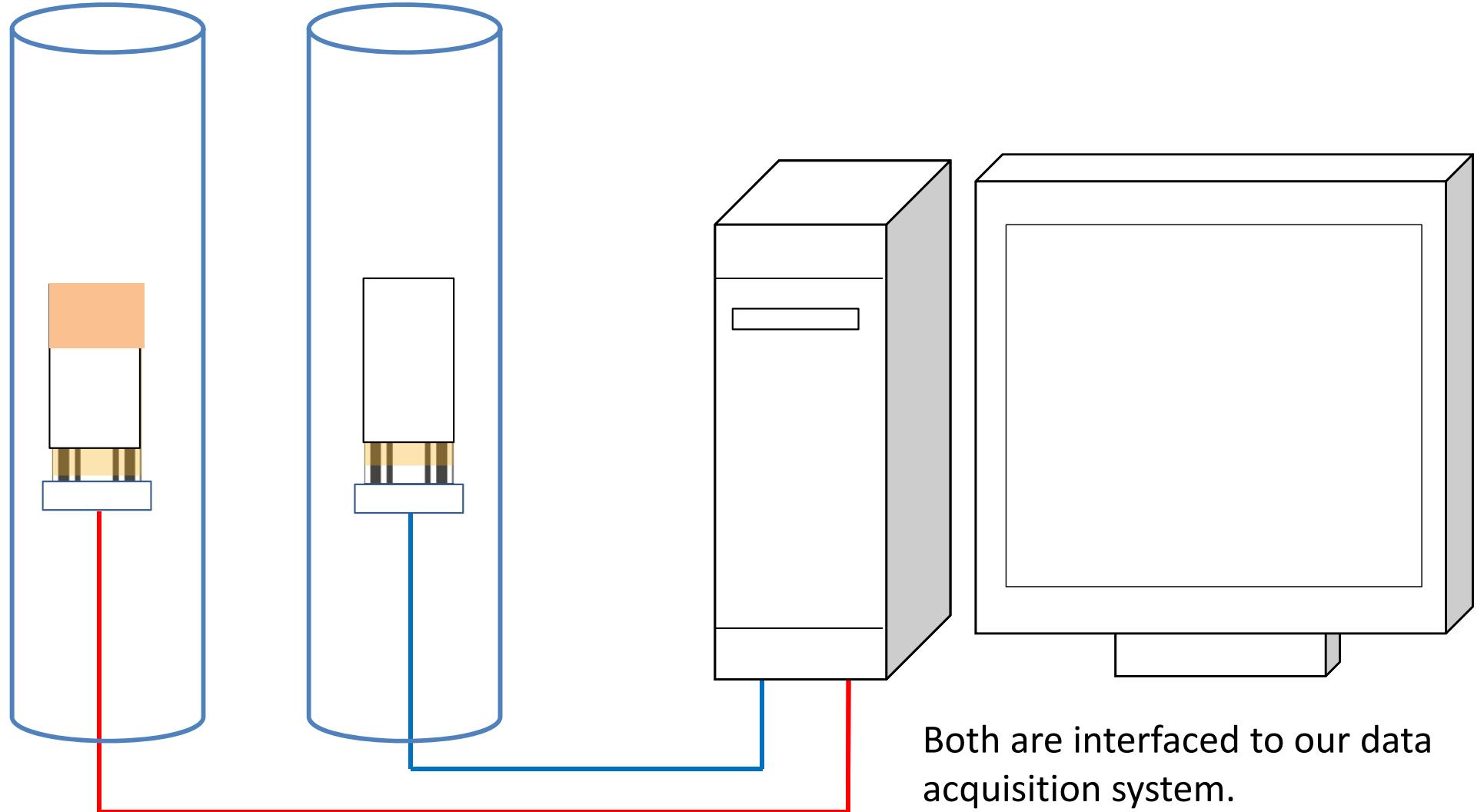


Only one is coated  
with a metal oxide  
catalyst.



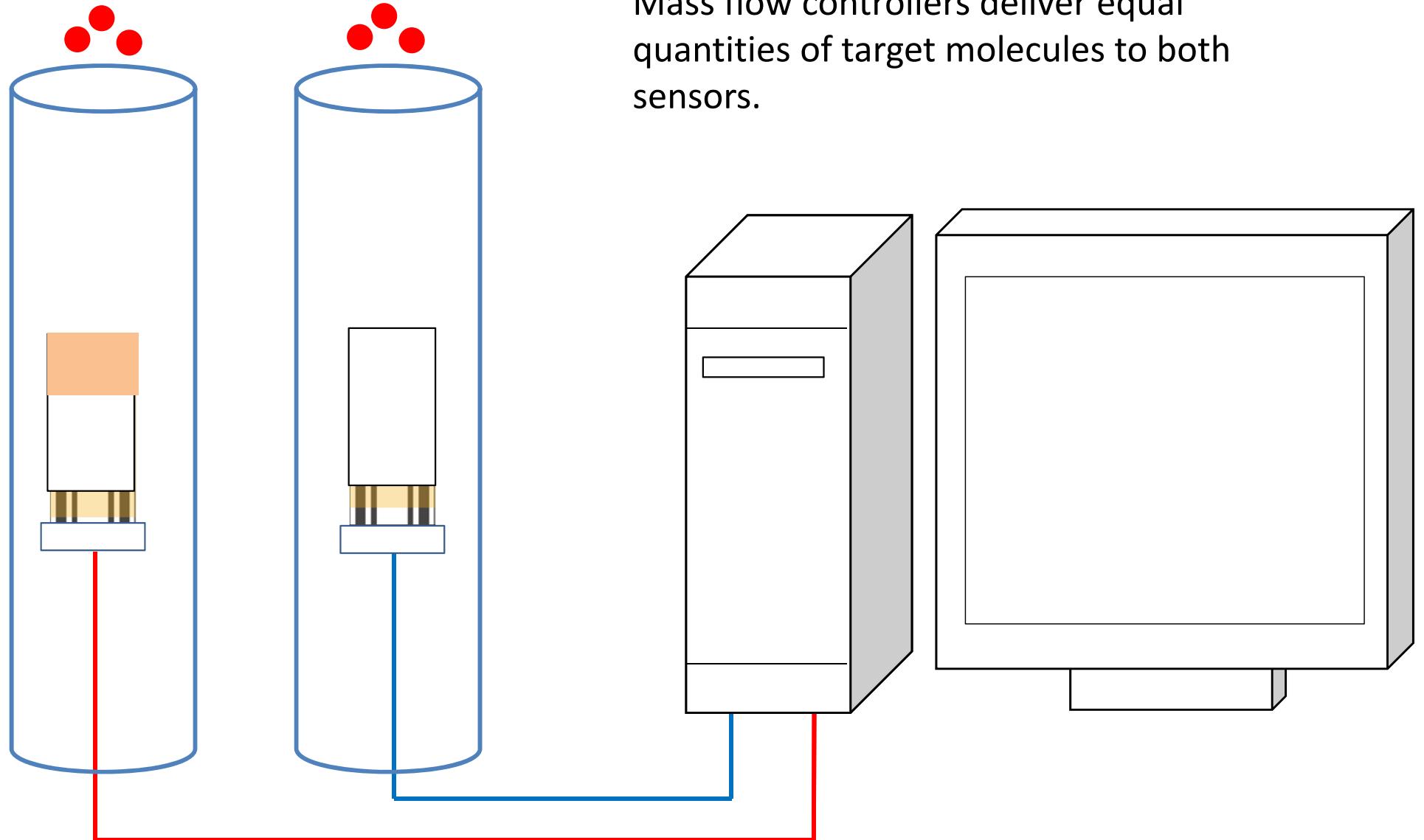


# *Dynamic Protocol for Trace Detection (thermodynamic platform)*



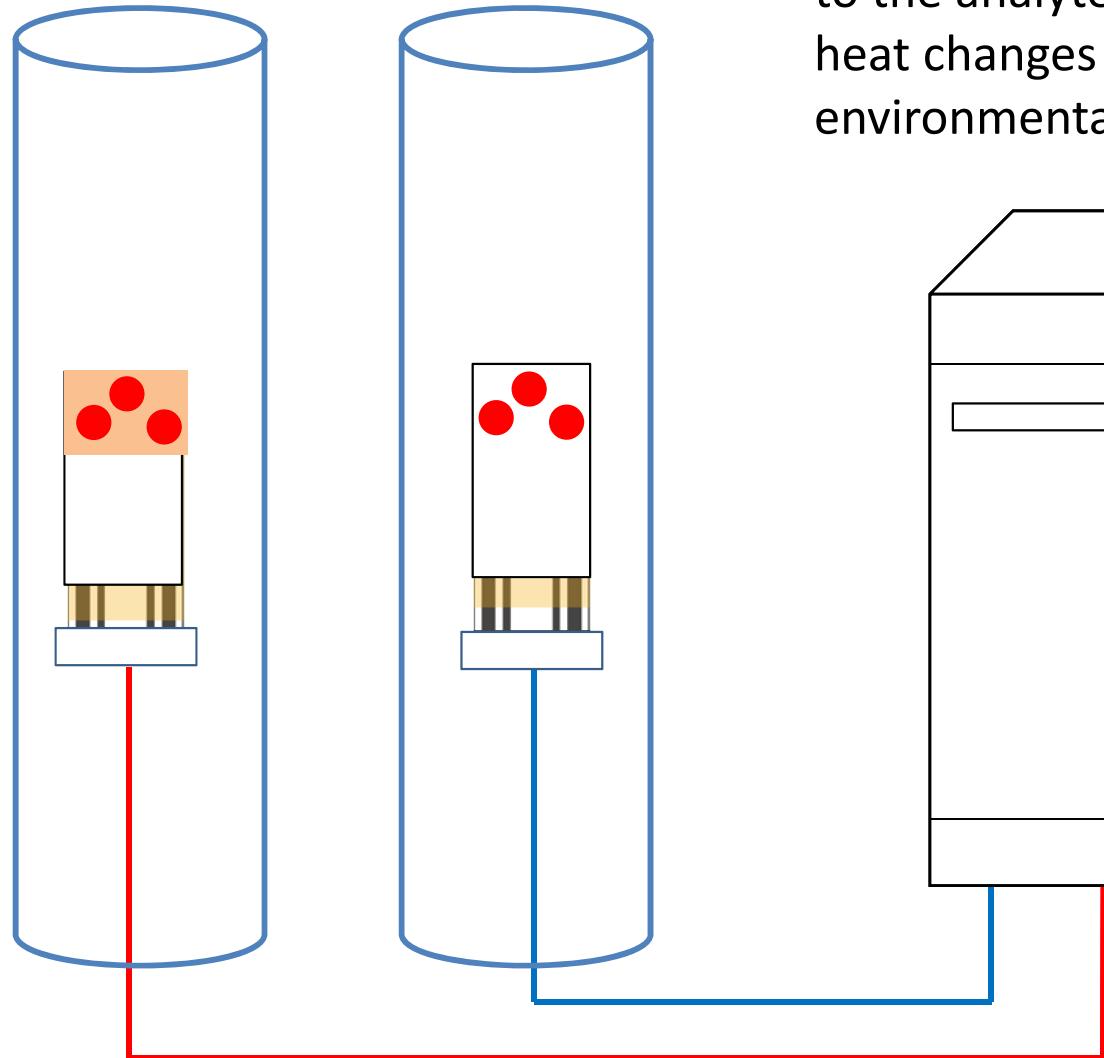


# *Dynamic Protocol for Trace Detection (thermodynamic platform)*

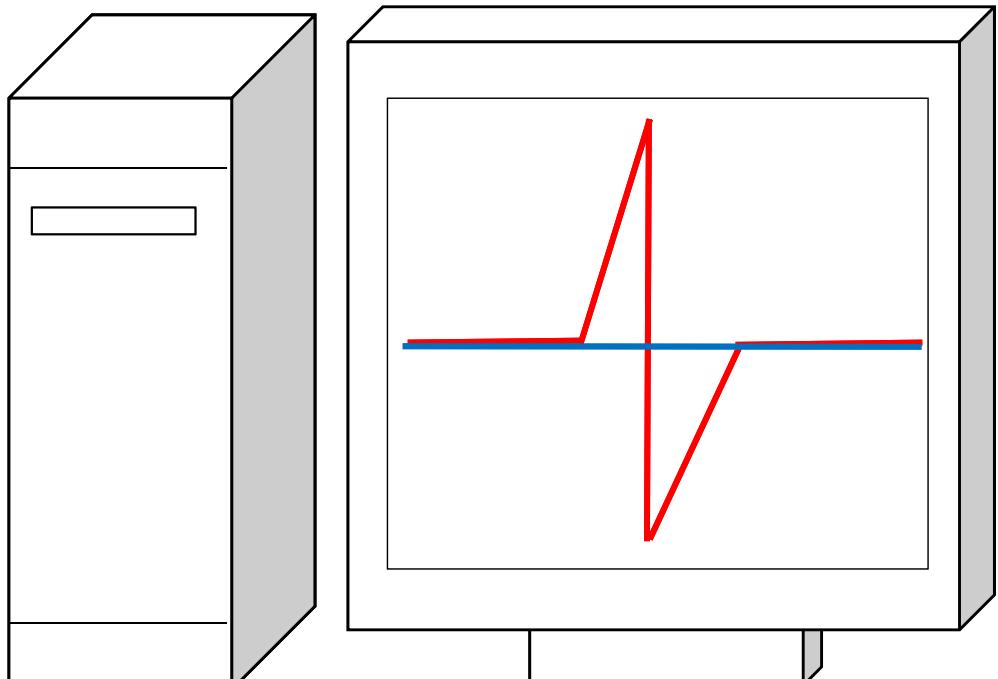




# Dynamic Protocol for Trace Detection (thermodynamic platform)



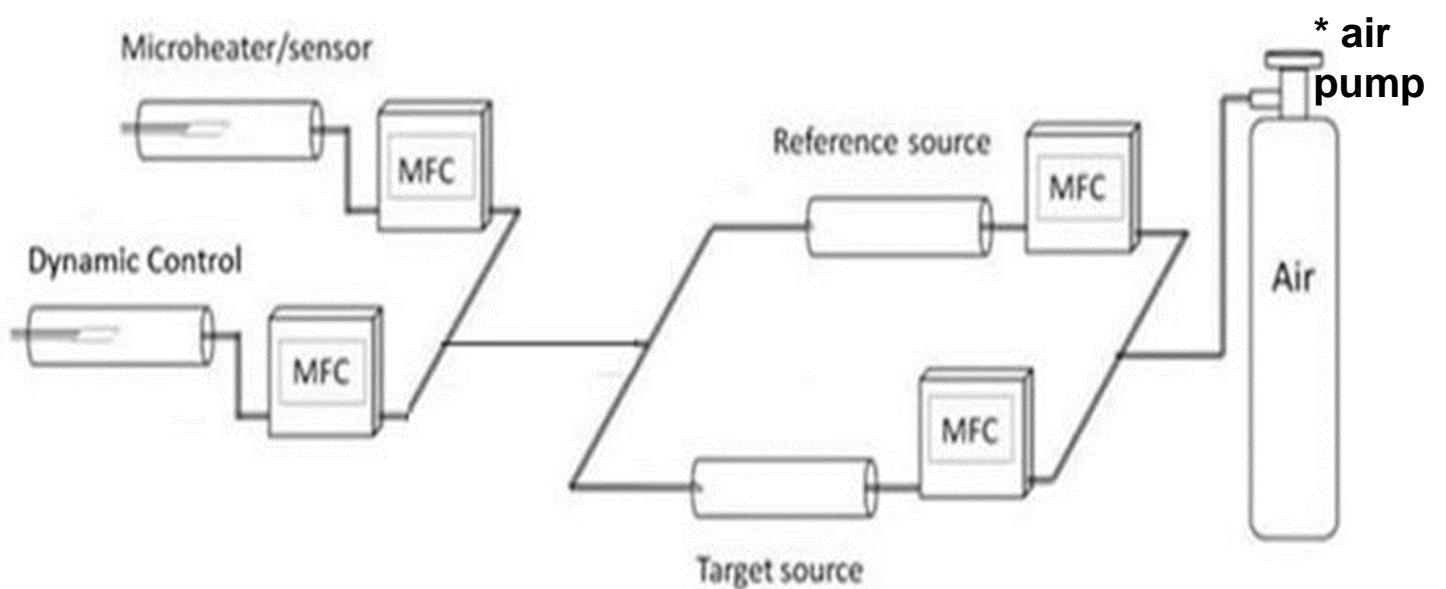
Only the catalyst coated microheater will respond to the analyte, and the bare sensor will record heat changes due to flow differences and environmental stimuli.





# Dynamic Protocol for Trace Detection\* (thermodynamic platform)

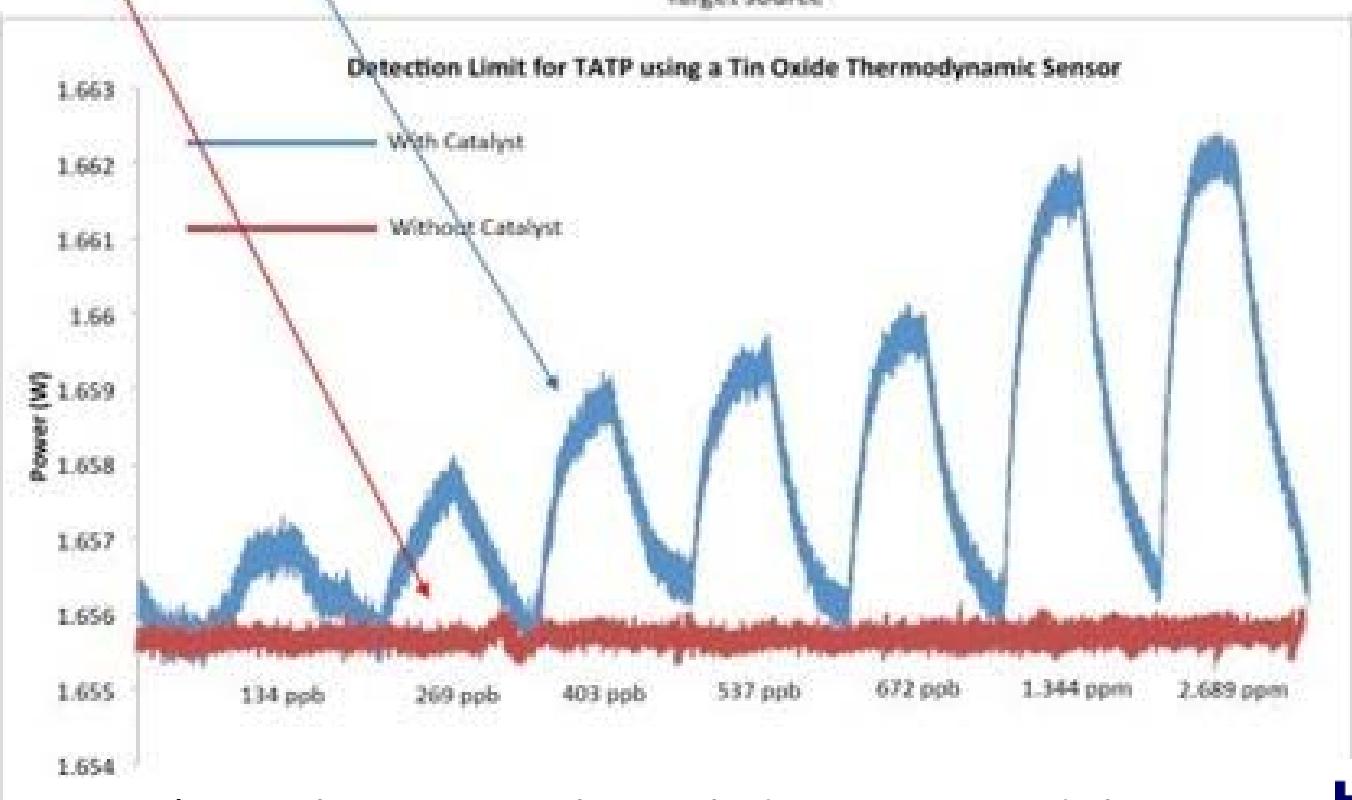
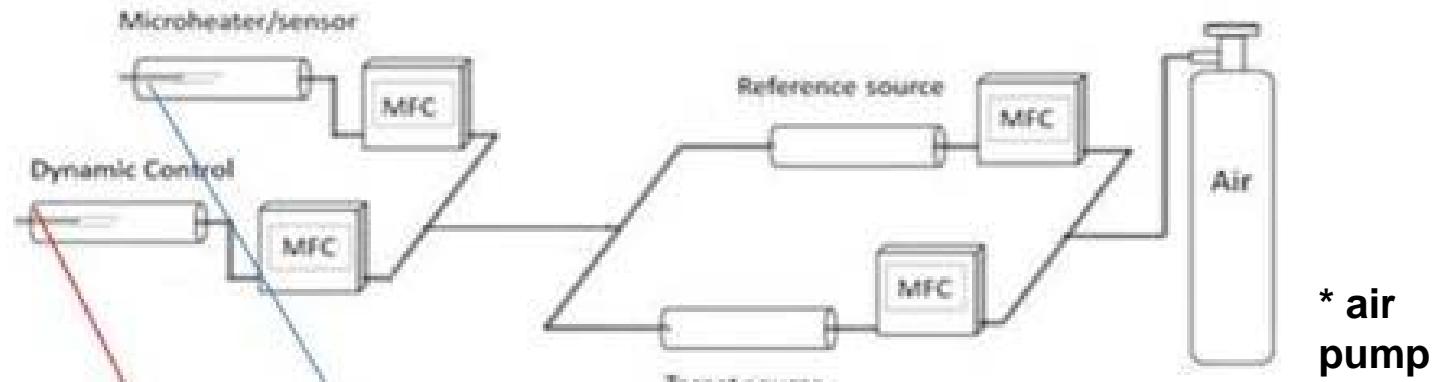
Dynamic (2 sensor) approach employs sensors with and without catalysts to eliminate sensible heat effects.....



\*microheaters can be cycled to 1000C and thus, can decompose almost any organic molecule



# Dynamic Protocol for Trace Detection\* (thermodynamic platform)



\*microheaters can be cycled to 1000C and thus,  
can decompose almost any organic molecule



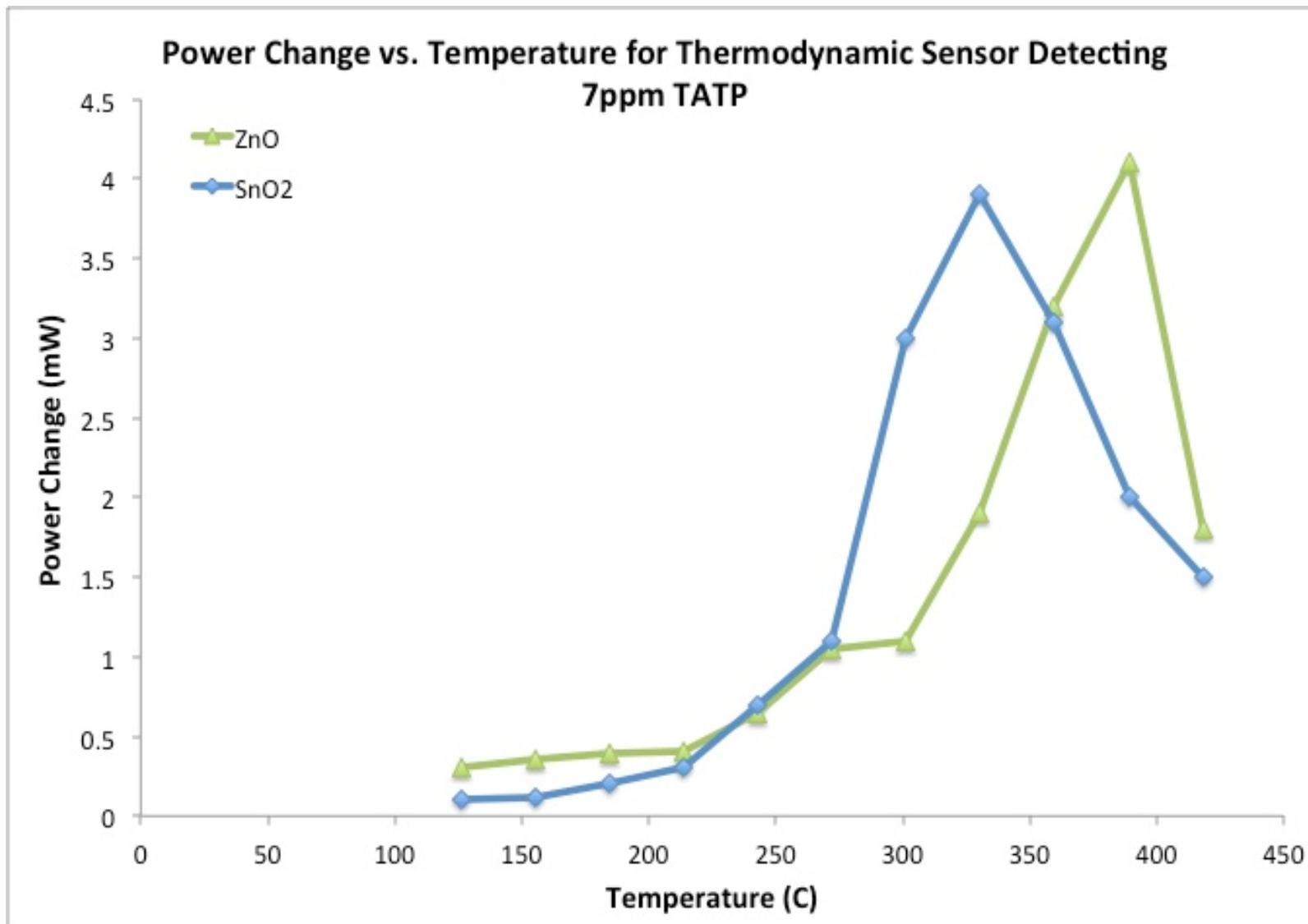
# Data Collection/Compilation (7 sec)

Time	Ch1_Va	Ch1_Ra	Ch1_Ia	Ch1_Pa	Ch1_Temp	Ch1_Vb	Ch1_Rb	Ch1_1b	Ch1_Pb	Ch1_Temp	Ch1_Vamp	Ch1_Vamp	Ch1_Tref	Ch1_SPa	Ch1_SPb	Ch1
10:57.1	2.320004	9.000592	0.257761	0.598007	-104023	3.60185	17774.91	0.000203	0.00073	-16212.4	3.708564	0.458428	80.07792	9.001	9.001	
10:57.1	2.320009	9.001723	0.257729	0.597935	-104203	3.631596	20376.74	0.000178	0.000647	-16178.1	3.708564	0.458428	80.07792	9.001	9.001	
10:57.1	2.320044	8.999898	0.257786	0.598074	-103983	3.644916	19389.06	0.000188	0.000685	-16231.5	3.708564	0.458428	80.07792	9.001	9.001	
10:57.1	2.320033	9.000705	0.257761	0.598014	-103166	3.633594	20387.94	0.000178	0.000648	-16285	3.708564	0.458428	80.07792	9.001	9.001	
10:57.1	2.319998	9.001251	0.257742	0.59796	-102868	3.625616	19039.13	0.00019	0.00069	-16132.5	3.708564	0.458428	80.07792	9.001	9.001	
10:57.2	2.320027	9.000597	0.257764	0.598019	-104604	3.624094	20907.45	0.000173	0.000628	-16235.3	3.708564	0.458428	80.07792	9.001	9.001	
10:57.2	2.320006	9.0012	0.257744	0.597968	-102928	3.595312	20741.41	0.000173	0.000623	-16381	3.708564	0.458428	80.07792	9.001	9.001	
10:57.2	2.320074	9.001716	0.257737	0.597968	-103305	3.63385	19082.37	0.00019	0.000692	-16246.7	3.708564	0.458428	80.07792	9.001	9.001	
10:57.2	2.320015	9.001063	0.257749	0.597982	-104356	3.557684	18445.92	0.000193	0.000686	-16298.8	3.708564	0.458428	80.13896	9.001	9.001	
10:57.3	2.319986	9.001462	0.257734	0.59794	-103723	3.589204	21619.68	0.000166	0.000596	-16377.1	3.708564	0.452551	80.07792	9.001	9.001	
10:57.3	2.320074	9.001289	0.257749	0.597997	-104003	3.628342	18812.27	0.000193	0.0007	-16361.7	3.708564	0.458428	80.07792	9.001	9.001	
10:57.3	2.320036	9.001654	0.257734	0.597953	-104055	3.614912	17839.37	0.000203	0.000733	-16287.3	3.708564	0.458428	80.13896	9.001	9.001	
10:57.3	2.320085	9.000738	0.257766	0.598039	-104303	3.592732	20438.65	0.000176	0.000632	-16415.7	3.708564	0.458428	80.07792	9.001	9.001	
10:57.3	2.320001	8.999643	0.257788	0.598069	-103603	3.632214	21253.64	0.000171	0.000621	-16300.3	3.708564	0.458428	80.07792	9.001	9.001	
10:57.3	2.320024	8.999733	0.257788	0.598075	-104155	3.647449	22984.54	0.000159	0.000579	-16360.3	3.708564	0.458428	80.13896	9.001	9.001	
10:57.4	2.320004	9.000933	0.257751	0.597984	-102150	3.63911	20702.49	0.000176	0.00064	-16364.1	3.708564	0.458428	80.13896	9.001	9.001	
10:57.4	2.320001	9.001603	0.257732	0.597938	-103504	3.626406	20072.65	0.000181	0.000655	-16365.6	3.708564	0.458428	80.07792	9.001	9.001	
10:57.4	2.320044	9.001432	0.257742	0.597972	-103903	3.592006	19882.24	0.000181	0.000649	-16331	3.696809	0.458428	80.07792	9.001	9.001	
10:57.4	2.320024	9.000927	0.257754	0.597995	-103325	3.584667	19577.06	0.000183	0.000656	-16392.5	3.714441	0.458428	80.07792	9.001	9.001	
10:57.5	2.32005	9.00154	0.257739	0.597968	-103863	3.611107	18037.92	0.0002	0.000723	-16319.5	3.708564	0.458428	80.07792	9.001	9.001	
10:57.5	2.320039	9.001324	0.257744	0.597976	-103883	3.617764	18294.27	0.000198	0.000715	-16300.3	3.708564	0.458428	80.07792	9.001	9.001	
10:57.5	2.320033	9.001984	0.257725	0.59793	-103066	3.559836	18693.7	0.00019	0.000678	-16124.9	3.708564	0.458428	80.07792	9.001	9.001	
10:57.5	2.320044	9.002114	0.257722	0.597927	-103404	3.549299	21379.3	0.000166	0.000589	-16427.2	3.702686	0.464305	80.07792	9.001	9.001	
10:57.5	2.320018	9.001586	0.257734	0.597948	-102118	3.570619	17620.79	0.000203	0.000724	-16408	3.702686	0.458428	80.07792	9.001	9.001	
10:57.5	2.32005	8.99975	0.257791	0.598087	-103205	3.585174	20978.39	0.000171	0.000613	-16304.1	3.708564	0.458428	80.07792	9.001	9.001	
10:57.6	2.32005	8.99975	0.257791	0.598087	-103205	3.585174	20978.39	0.000171	0.000613	-16304.1	3.708564	0.458428	80.07792	9.001	9.001	
10:57.6	2.320021	9.001597	0.257734	0.597949	-103563	3.653322	17814.29	0.000205	0.000749	-16269.7	3.708564	0.458428	80.07792	9.001	9.001	
10:57.6	2.320021	9.001597	0.257734	0.597949	-103563	3.653322	17814.29	0.000205	0.000749	-16269.7	3.708564	0.458428	80.07792	9.001	9.001	
10:57.6	2.320003	9.001461	0.257739	0.597963	-102987	3.605722	18934.66	0.00019	0.000687	-16143.8	3.708564	0.458428	80.07792	9.001	9.001	
10:57.6	2.320056	9.001733	0.257734	0.597958	-103923	3.626295	23576.68	0.000154	0.000558	-16022.7	3.708564	0.458428	80.07792	9.001	9.001	
10:57.7	2.320044	9.001603	0.257737	0.597961	-103106	3.612865	20553.19	0.000176	0.000635	-16071.8	3.708564	0.458428	80.07792	9.001	9.001	
10:57.7	2.320056	9.000539	0.257769	0.598037	-102631	3.63325	20960.27	0.000173	0.00063	-16128.7	3.708564	0.458428	80.07792	9.001	9.001	
10:57.7	2.320033	9.001898	0.257727	0.597935	-101725	3.5897	21004.87	0.000171	0.000613	-16204.7	3.708564	0.458428	80.07792	9.001	9.001	
10:57.7	2.320015	9.000722	0.257759	0.598004	-104243	3.590277	21626.14	0.000166	0.000596	-16162.8	3.708564	0.458428	80.07792	9.001	9.001	
10:57.8	2.320068	9.001778	0.257734	0.597961	-103643	3.621102	20600.05	0.000176	0.000637	-16174.3	3.708564	0.458428	80.07792	9.001	9.001	
10:57.8	2.320062	9.001074	0.257754	0.598005	-102453	3.616178	17425.72	0.000208	0.00075	-16185.7	3.708564	0.458428	80.07792	9.001	9.001	
10:57.8	2.319986	8.999842	0.257781	0.598048	-103763	3.589735	21622.87	0.000166	0.000596	-16079.4	3.708564	0.458428	80.07792	9.001	9.001	
10:57.8	2.320001	9.001092	0.257747	0.597972	-102564	3.545304	18617.39	0.00019	0.000675	-16172.8	3.702686	0.458428	80.13896	9.001	9.001	



# Catalyst Selectivity for Residue Vapors (thermodynamic platform)

Response of orthogonal sensor to TATP using different metal oxide catalysts..... different peak temperatures for each oxide catalyst are observed..... translates into cat selectivity



Center for Sensors and  
Instrumentation Research

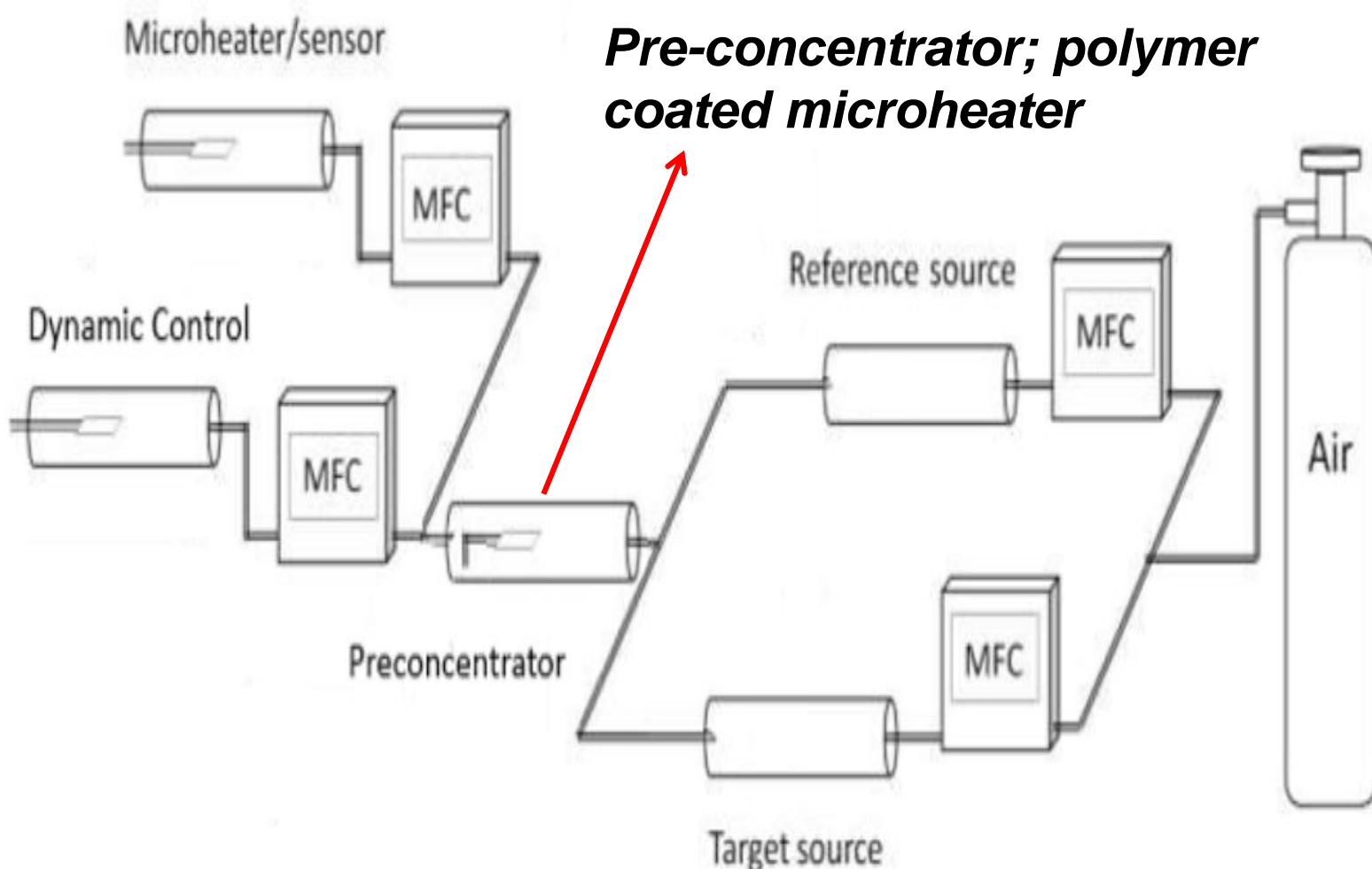
August 5, 2015





# Pre-concentration of Residue Vapors

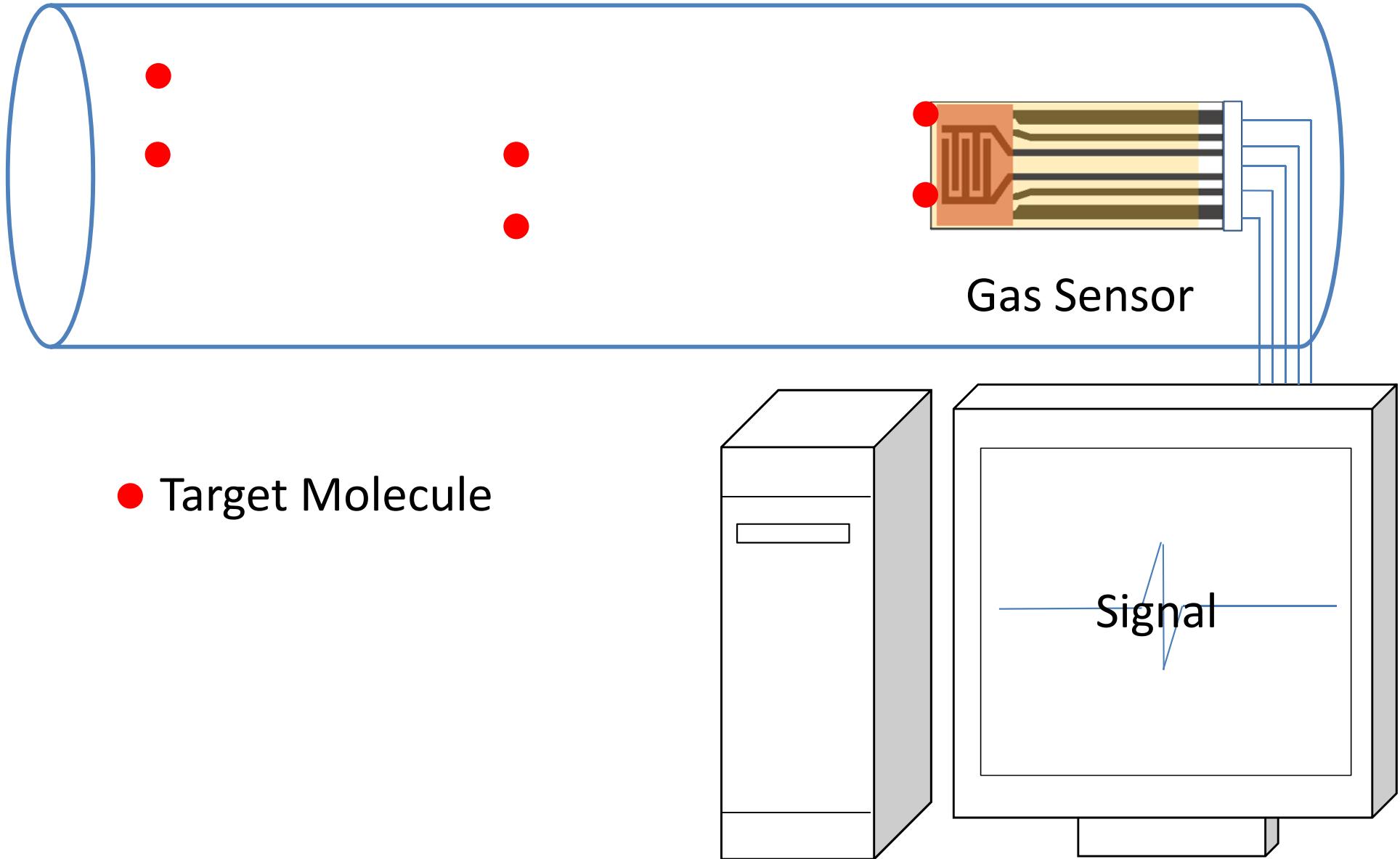
Pre-concentration employs an additional microheater upstream from active sensor that is coated with a polymer..... polystyrene possesses the desired adsorption/desorption characteristics for concentrating analyte in the vapor phase



August 5, 2015

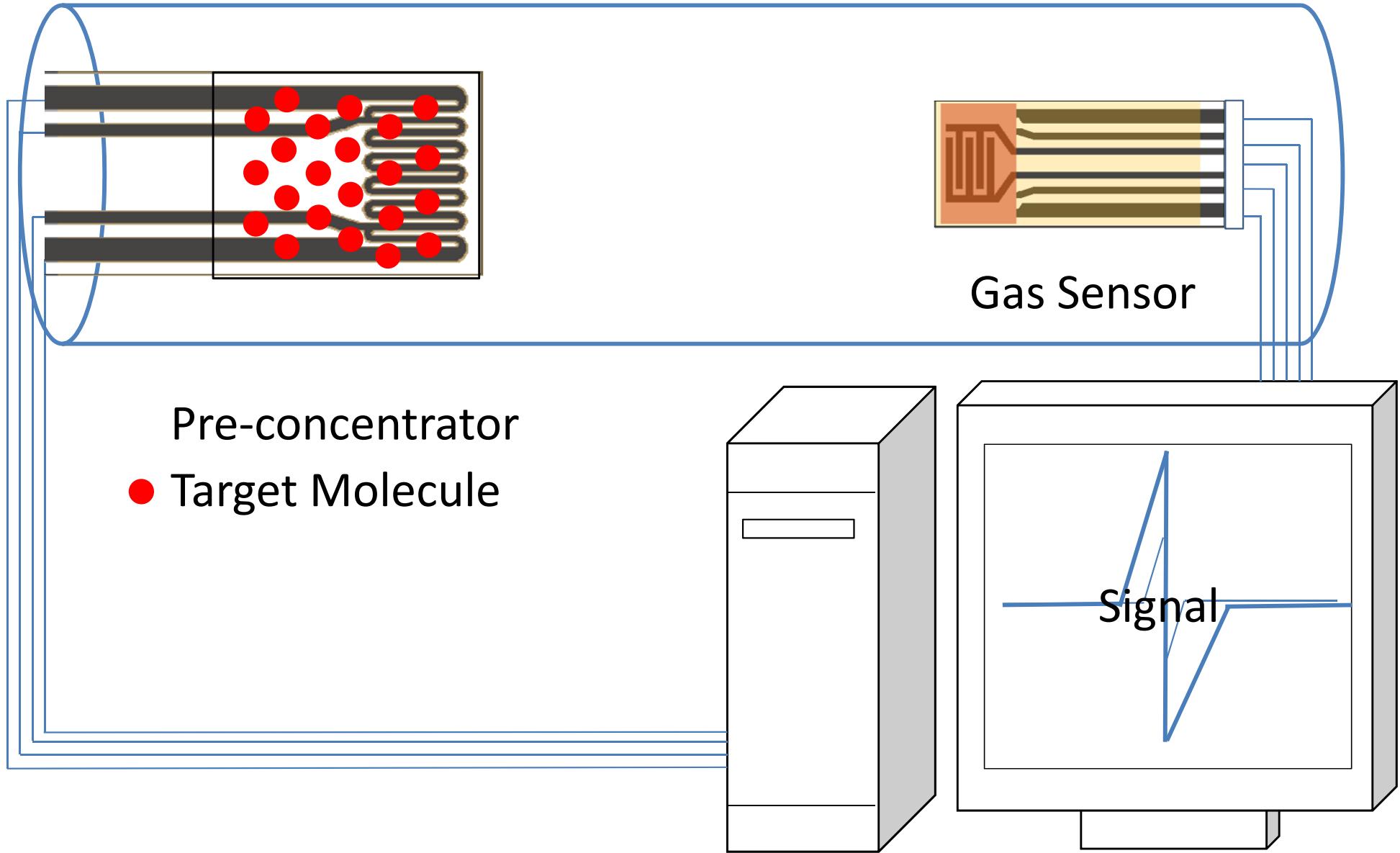


# Pre-concentration methodology



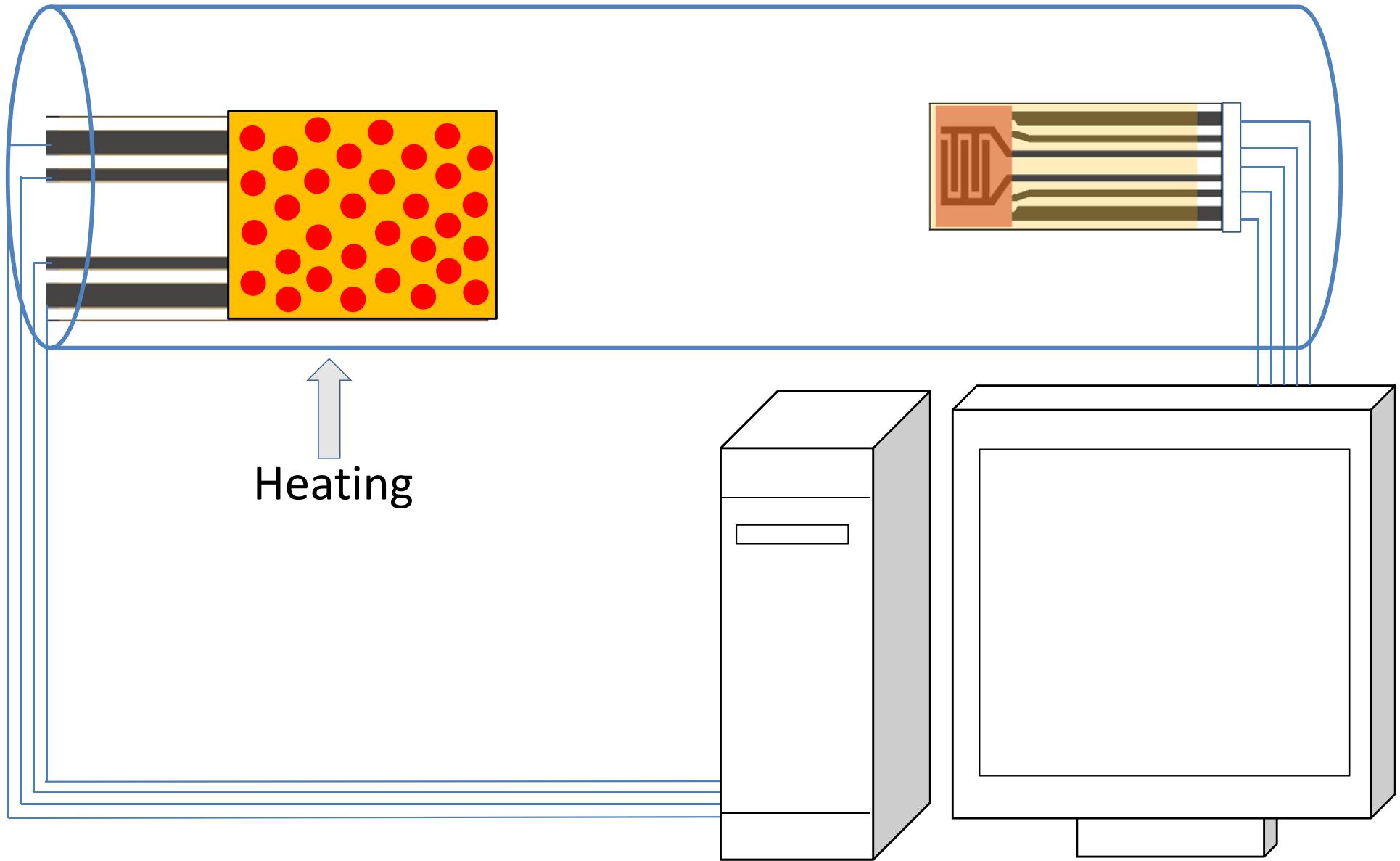


# Pre-concentration methodology



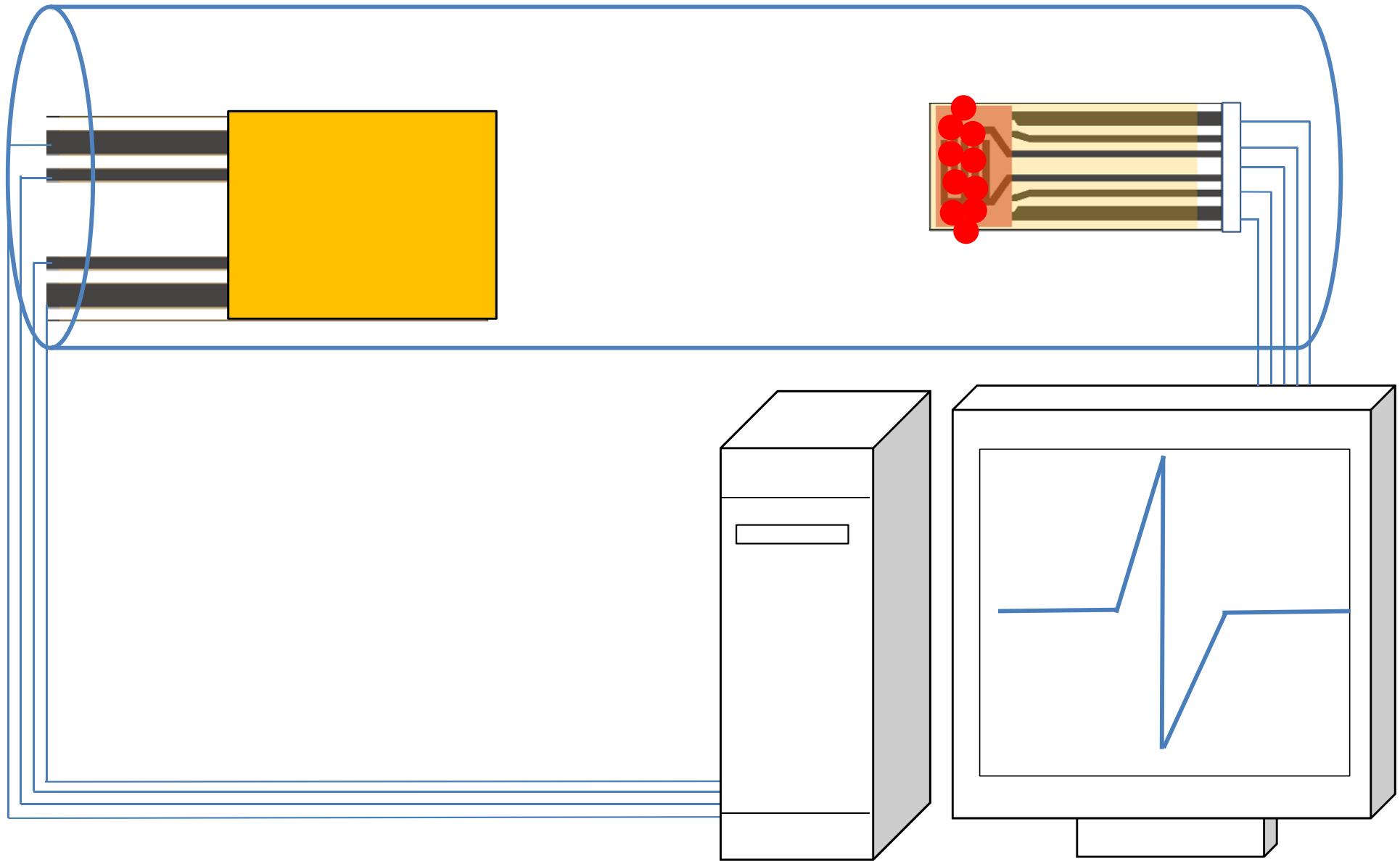


# Pre-concentration methodology





# Pre-concentration methodology





# Pre-concentration of Residue Vapors

## Desorption Efficiency of TNT at 120C°

Sample	Total Amount Adsorbed	Total Amount Desorbed	% Desorbed
Tenax	12	0.13	1%
Poly(2,6-dimethyl-1,4-phenylene oxide)	4.7	0.16	3%
Polystyrene	6.3	0.70	11%
Nomex	2.4	2.0	83%

## Desorption Efficiency of TNT at 170C°

Sample	Total Amount Adsorbed	Total Amount Desorbed	% Desorbed
Poly(ethylene terephthalate)	2.40	0.11	5%
Tenax	7.88	0.50	6%
Poly(2,6-dimethyl-1,4-phenylene oxide)	6.60	0.46	7%
Poly(4-vinyl phenol)	10	0.80	8%
Polystyrene	6.22	3.61	58%
Teflon	2.32	2.48	107%

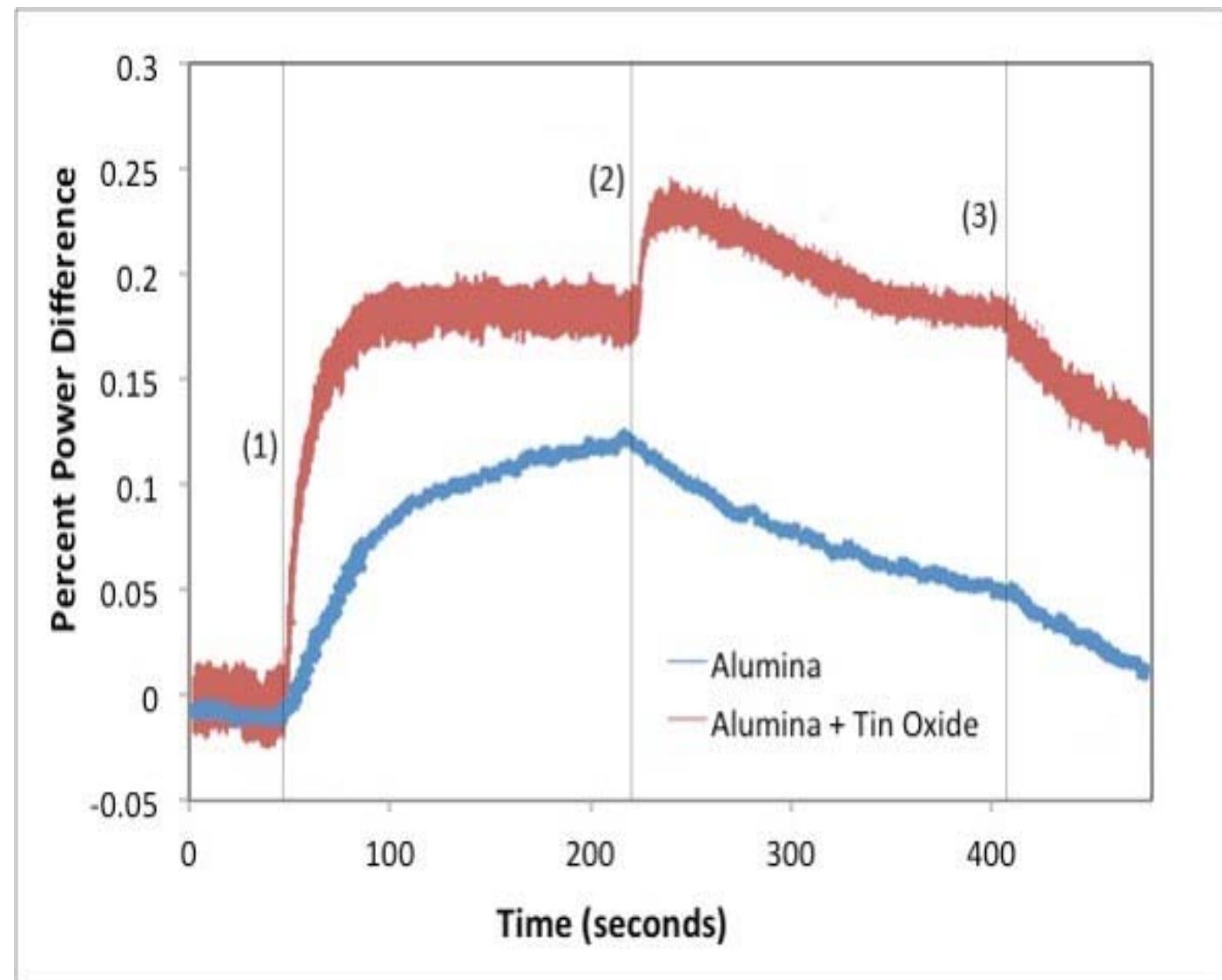
\*Data courtesy of Dr. Jimmy Oxley *et al*, Dept of Chemistry, University of Rhode Island



# Pre-concentration of Residue Vapors

Duty cycle used for pre-concentration: (1) introduction of DNT target gas. (2) thermal desorption of pre-concentrator (3) reference gas is re-introduced to the system

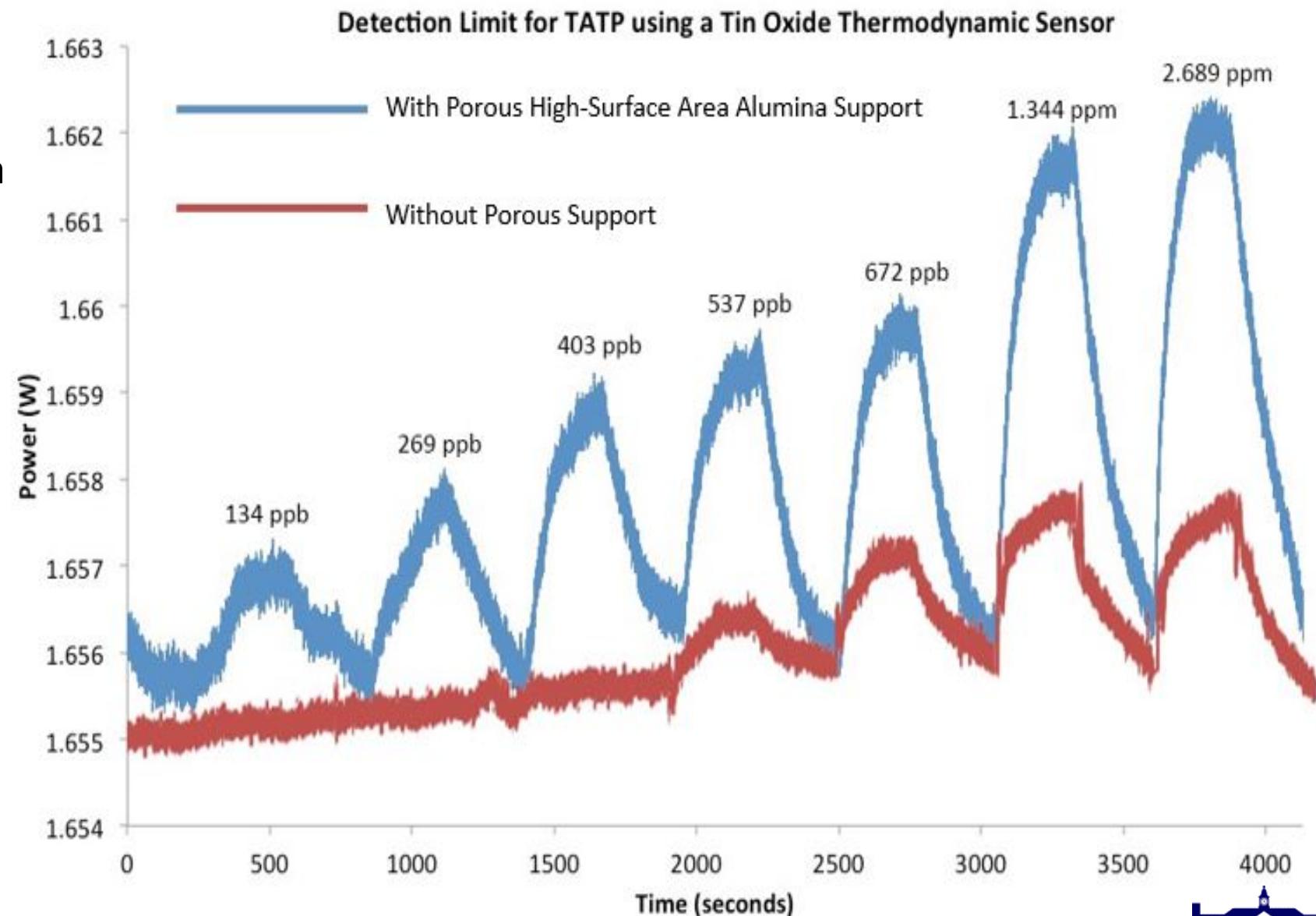
The pre-concentrator yields a 47% increase in sensor response with only minimal surface area for contact. With further surface modifications to increase surface area, a more concentrated burst of analyte is anticipated





# Effect of Catalyst Surface Area on Response

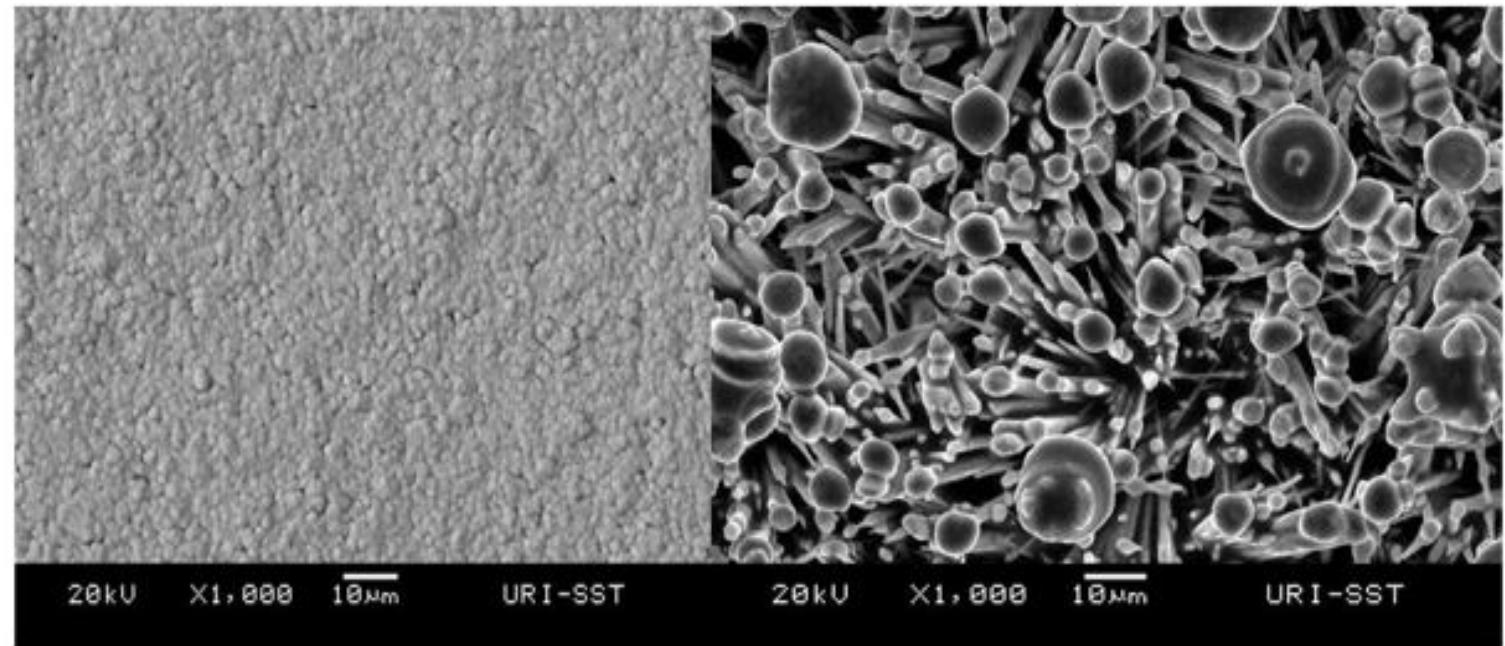
Porous catalyst and/or catalyst support yields a much larger signal than a sensor without porous catalyst and/or catalyst support





# Oxide Nanowires as Catalyst Support for Detection of Residue Vapor

High surface area catalyst and catalyst support achieved with ZnO nanowires

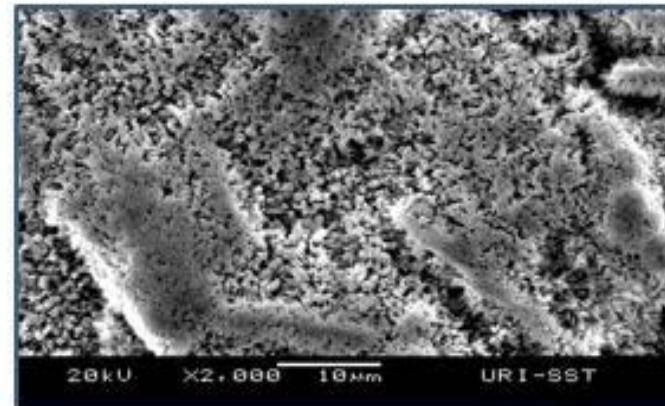




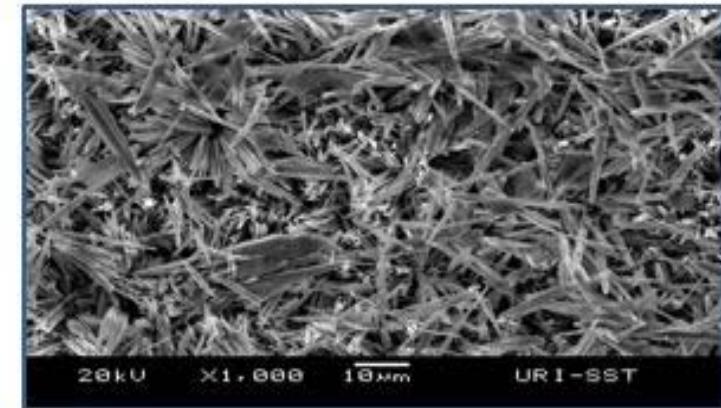
# Oxide Nanowires as Catalyst Support for Detection of Residue Vapor

High surface area catalyst and catalyst support achieved with ZnO nanowires

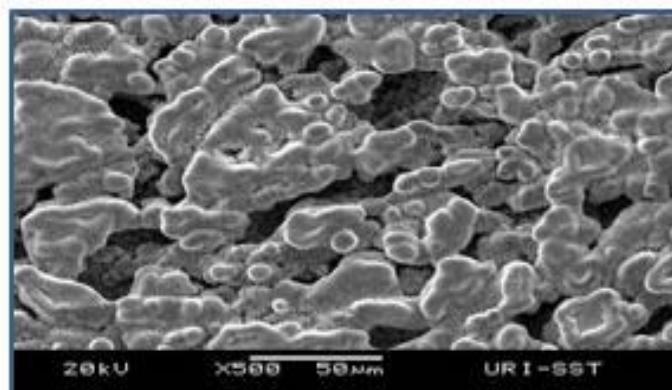
ZnO nanowires grown using a hydrothermal process



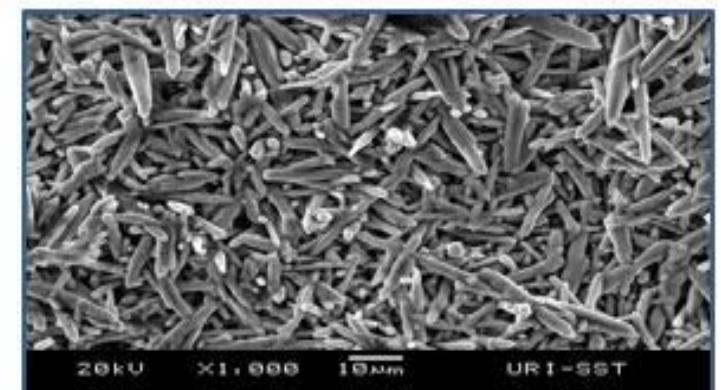
2 HOURS



10 HOURS



6 HOURS



8 HOURS

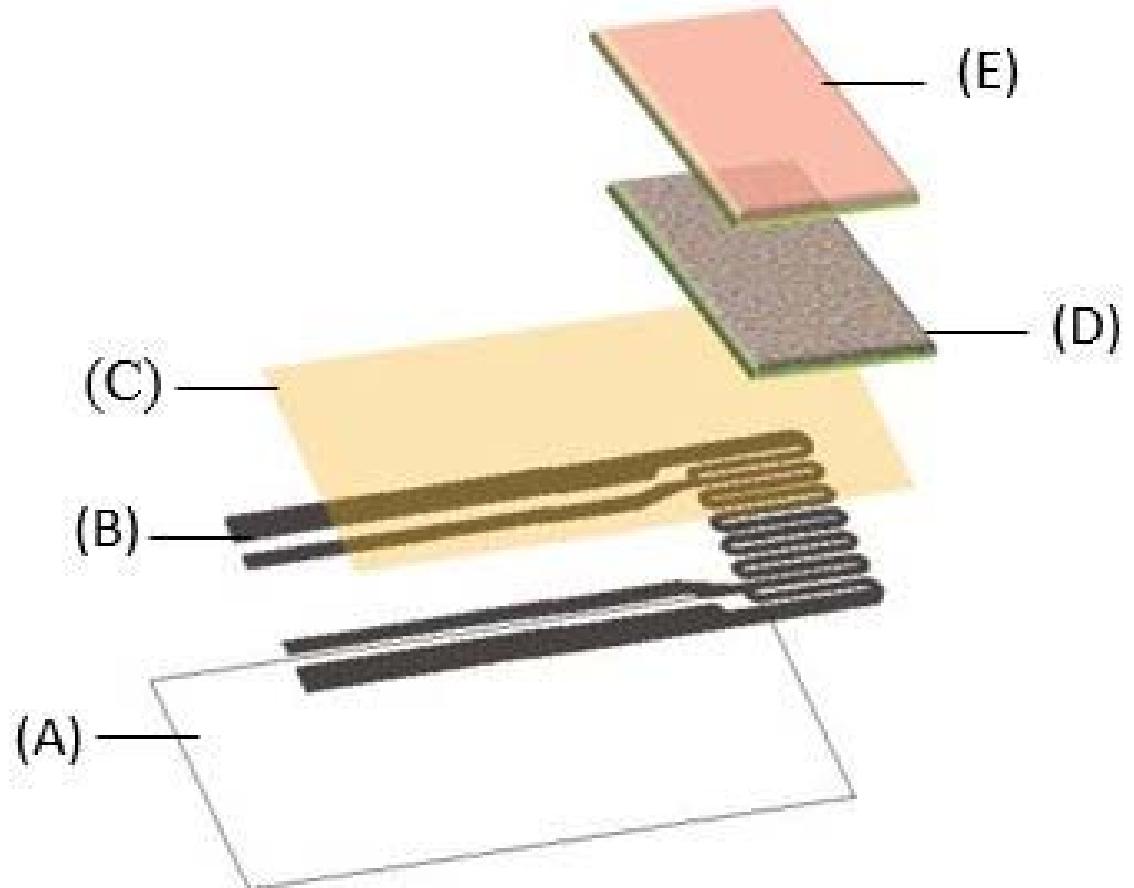


# Oxide Nanowires as Catalyst Support for Detection of Residue Vapor

High surface area catalyst and catalyst support achieved with ZnO nanowires

ZnO nanowires grown using a hydrothermal process

Sputtered oxide catalyst were deposited over ZnO nanowires

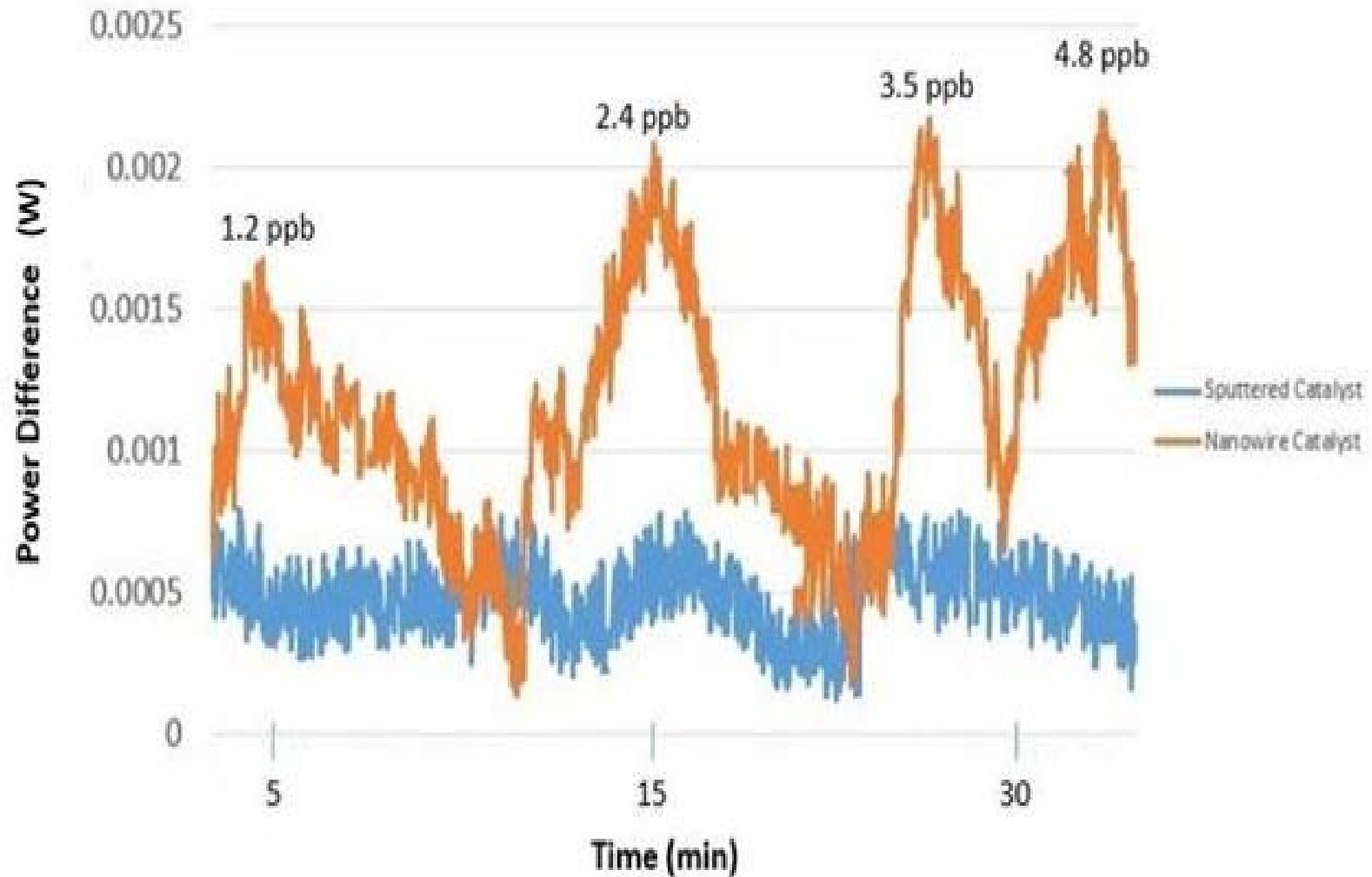




# Effect of Catalyst Surface Area on Sensor Response

Nearly a 300% increase in sensor response to DNT using ZnO nanowires

Single PPB range can now be detected for DNT

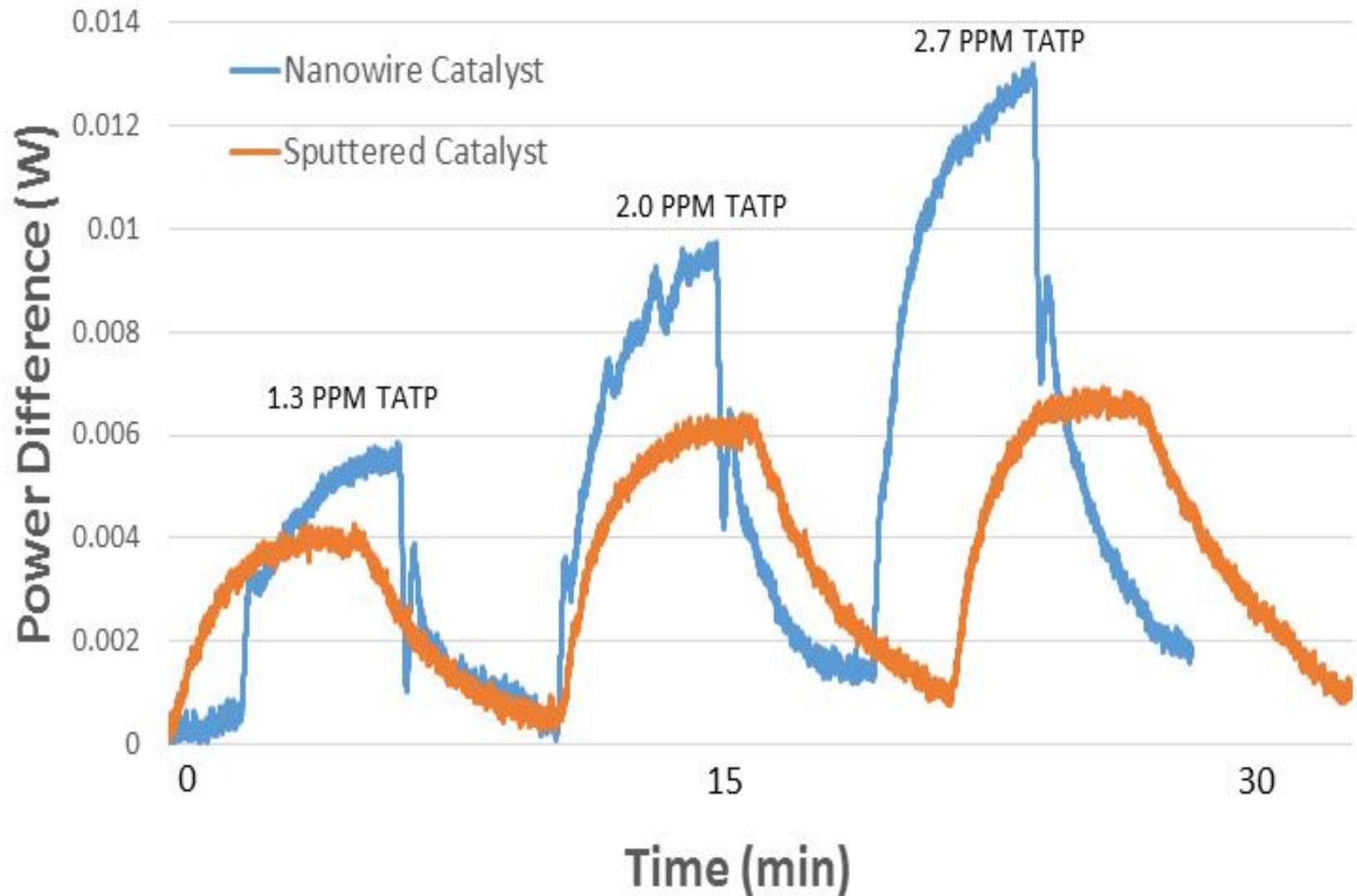




# Effect of Catalyst Surface Area on Sensor Response

Comparison of sensor response to TATP using ZnO catalyst

At the highest level, nanowires increased the response by nearly 100%



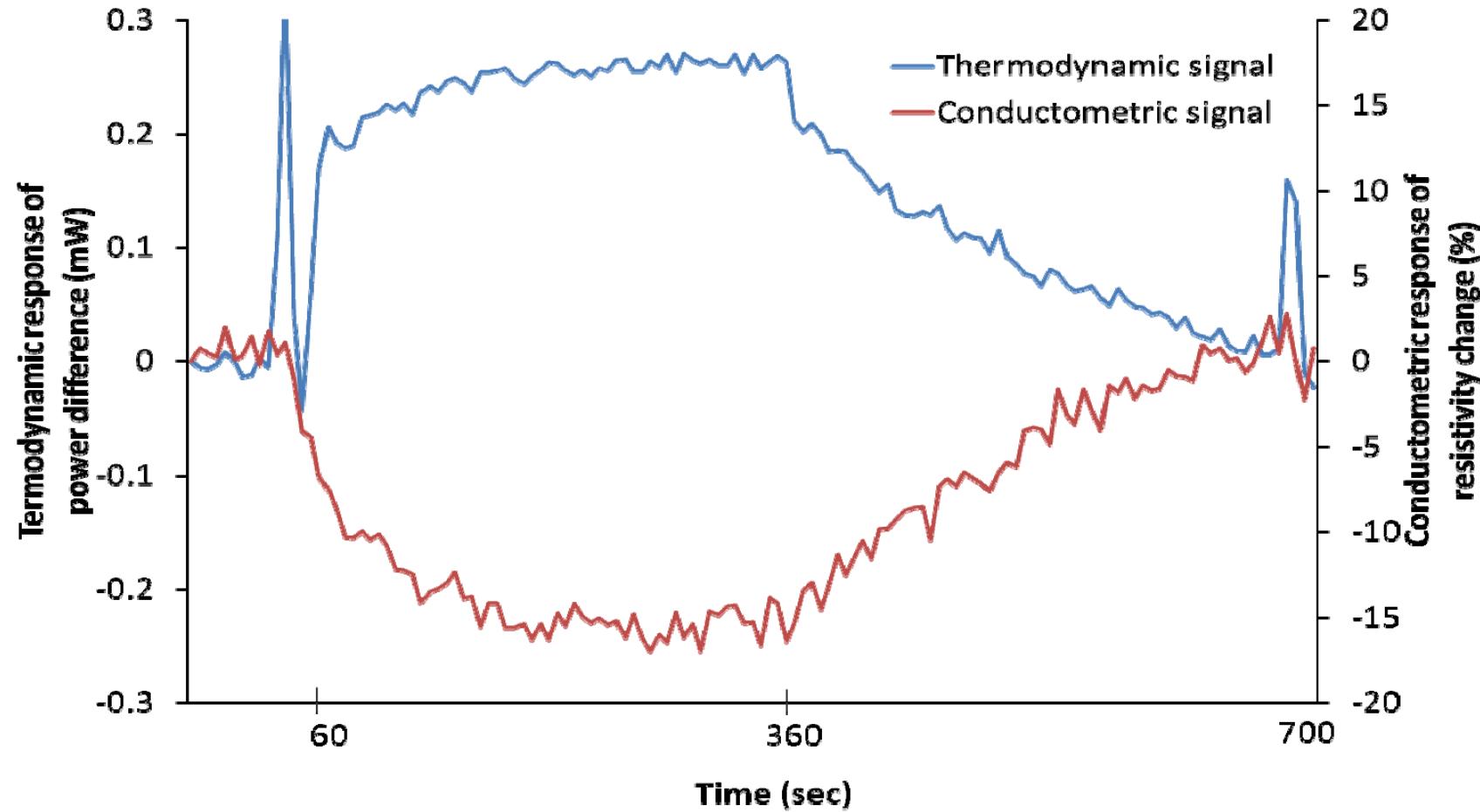
Center for Sensors and  
Instrumentation Research

August 5, 2015



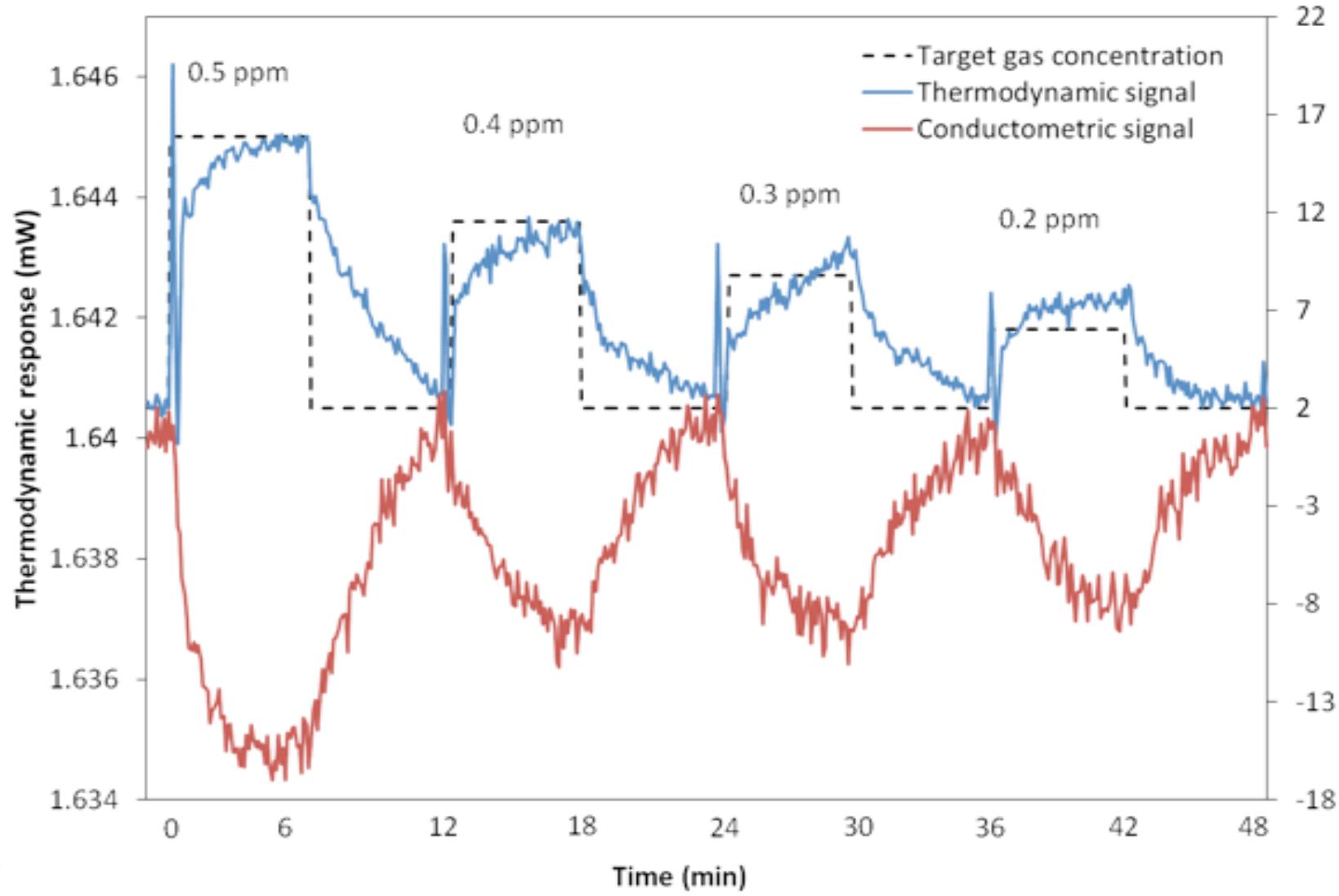


# Thermodynamic and conductometric sensor response to 2, 6-DNT at 410 °C (SnO catalyst)





# *Thermodynamic and conductometric sensor response to 2, 6-DNT at 410 °C (SnO catalyst)*

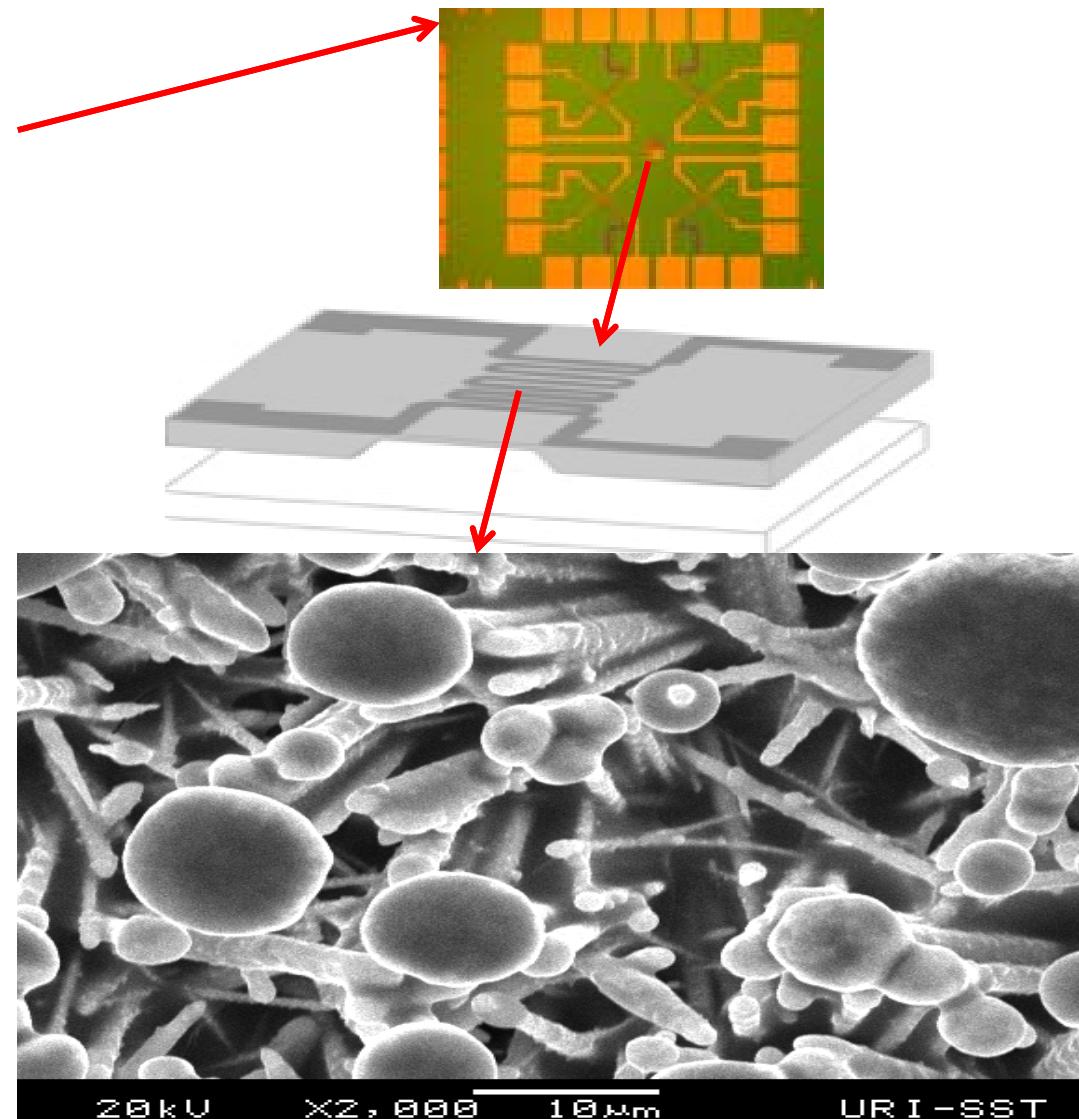




# *A small footprint, handheld sensor for residue vapor.....based on a MEMS platform*

MEMS quadrant sensor (diaphragm 0.5mmx0.5 mm) was fabricated that has all of the attributes of our orthogonal solid state sensor. We envision multiple catalysts on a single MEMS device for the continuous monitoring and identification of a wide range of unknown threats.

ZnO nanowires were prepared on the microheater surface to enhance the catalytic activity for the MEMS based vapor detection system.





# Summary

Dynamic (two sensor) approach was used to measure the heat effect due to analyte-catalyst interactions.....can detect TATP, AN and 2-6 DNT at the “single” ppb level

Using orthogonal sensor modalities, the metal oxide catalyst is simultaneously interrogated using two different sensing protocols; thermodynamic and conductometric protocols are combined to mitigate false positives and false negatives

Pre-concentration techniques produce a highly concentrated burst of analyte that is efficiently delivered to the sensor in an optimized duty cycle that lowers the detection limit by an order of magnitude

Metal oxide nanowire catalysts and/or catalyst support lowered the detection limit for residue vapors to the “single” ppb level



# Acknowledgements



*These materials are based upon work supported by the U.S. Department of Homeland Security, Science and Technology Directorate, Office of University Programs, under Grant Award 2013-ST-061-ED0001. The views and conclusions contained in this document are those of the authors and should not be interpreted as necessarily representing the official policies, either expressed or implied, of the U.S. Department of Homeland Security.*