# Sorbents for Desulfurization of Natural Gas, LPG and Transportation Fuels

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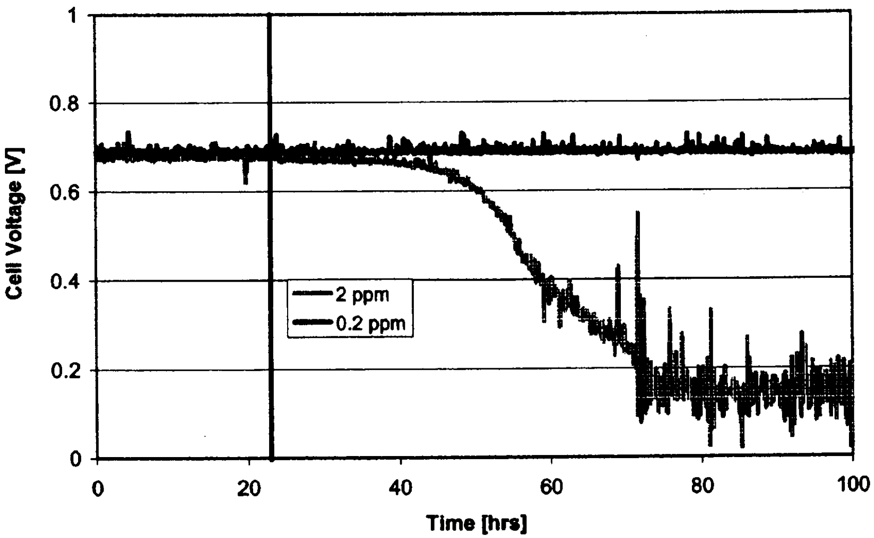
# Introduction

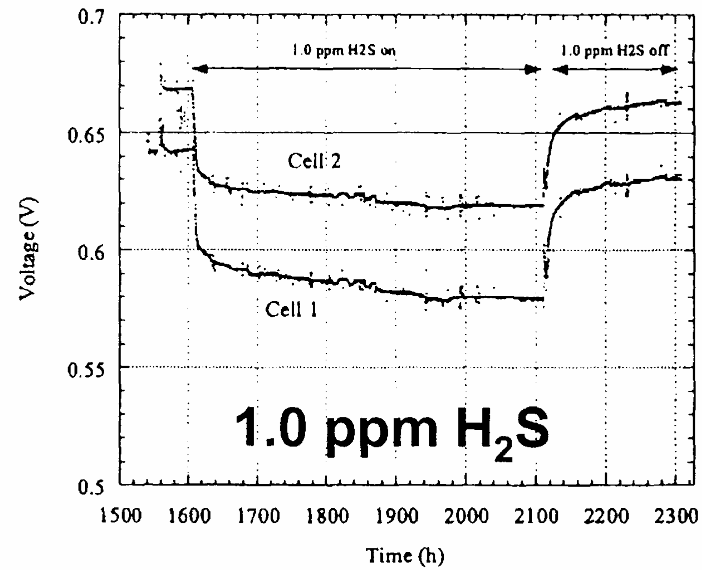
- **Advances in fuel cell technologies have the potential to revolutionize the way the power is generated and distributed**
- **Fuel cells require an ample supply of <u>high quality</u> fuel**
- **Pipeline natural gas is the fuel of choice because of its abundance and well-developed supply infrastructure**
- **In addition to naturally occurring $H_2S$, chemical odorants made with sulfur-containing compounds are added to natural gas for leak detection**
  - Common odorants include mercaptans, sulfides and thiols
  - The total sulfur content of the pipeline gas averages about 4 ppmv but can be as high as 10-12 ppmv

# Sulfur As an Electrocatalyst Poison

- **Sulfur compounds contaminate the catalysts used in fuel cell systems and degrade power generation performance**




Source: De Wild, "The removal of sulfur-containing odorants from natural gas for PEMFC", Proceedings of Fuel Cell Seminar, p227, 2002




Source: Israelson, " Results of Testing Various Natural Gas Desulfurization Sorbents", J. of Materials Engineering and Performance, Vol. 13 (3), June 2004

- **Traditionally sulfur removal is carried out with a two-step process:**
  - HDS of the organic sulfur compounds and subsequent $H_2S$ removal
  - It is not practical for small-scale residential units or for transportation systems

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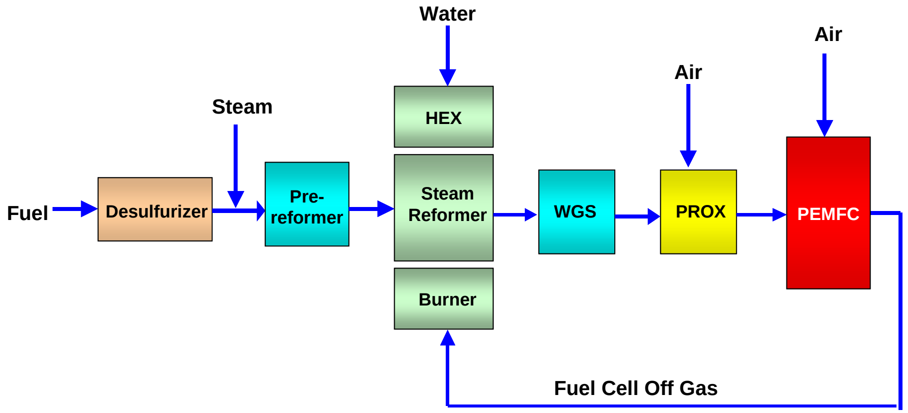
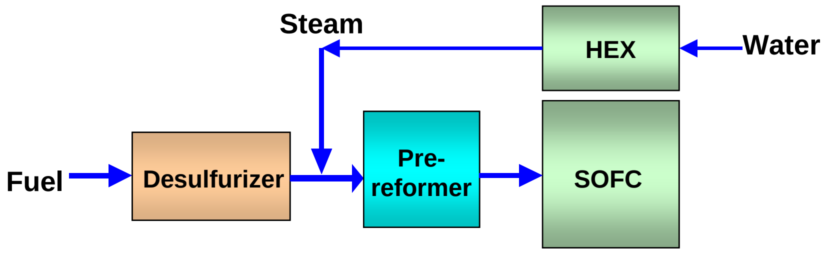
# Project Objective

- **TDA Research, Inc. is developing a passive adsorbent for ambient temperature natural gas desulfurization**




PEM System




SOFC System

- **Requirements of the sorbent**
  - High sulfur capacity (minimum replacement frequency, small size)
  - Low cost
  - Reducing total sulfur concentration to sub-ppm levels
  - Inertness (no side reactions or chemisorption of hydrocarbons)
  - Tolerance to possible natural gas contaminants (hydrocarbons, $CO_2$, $H_2O$)
  - Ease of disposal (no toxicity, flammability, pyrophorocity)

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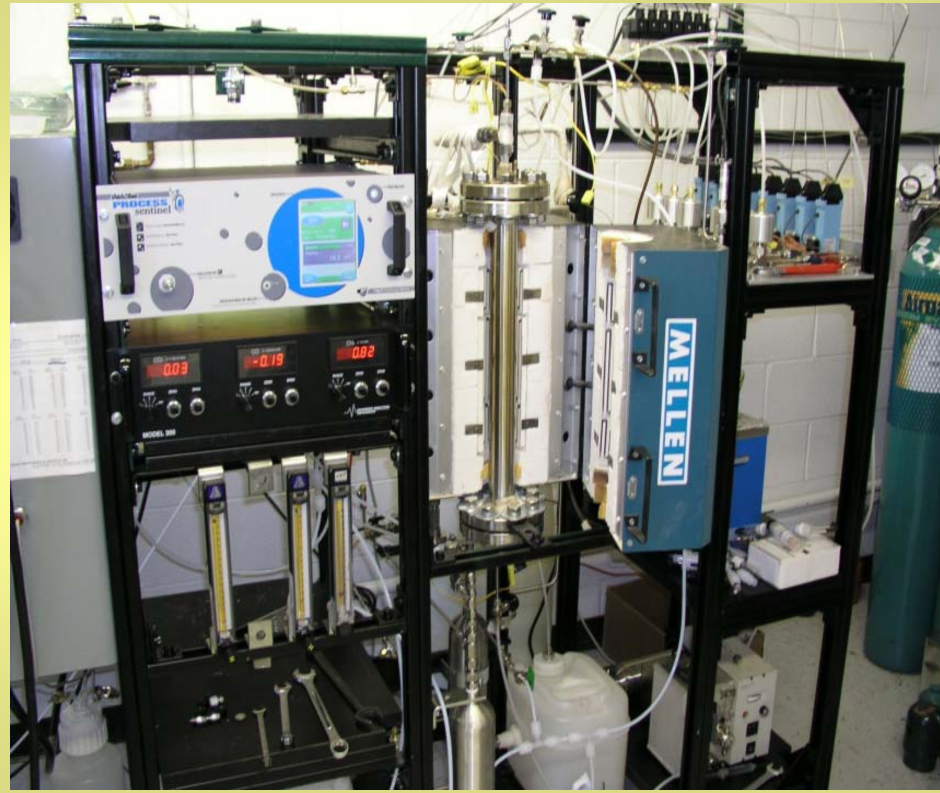
# Outline

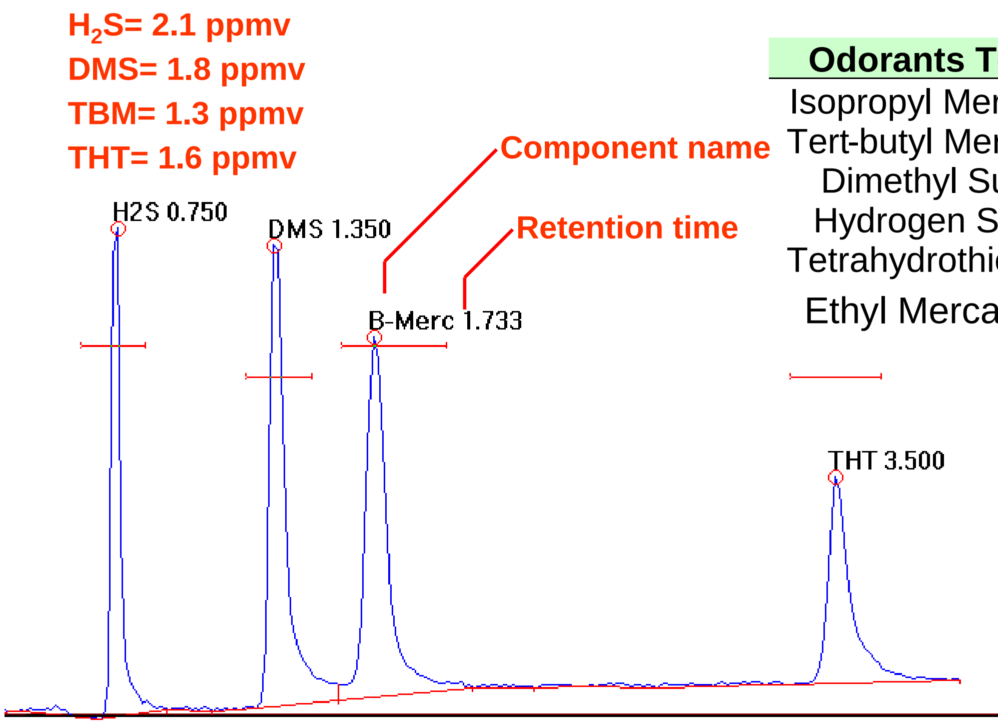
- **Introduction**
- **Outline**
- **Natural Gas Desulfurization**
  - Experimental Setup
  - Performance Comparison with Other Sorbents
  - Parametric Tests
  - Sorbent Regeneration
  - Demonstrations
- **LPG Desulfurization**
  - Sorbent Performance
- **Desulfurization of Transportation Fuels**
  - Experiments with Model Fuels
  - Battlefield Fuels (i.e., JP-8)
- **Conclusions**

# Experimental Setup


- **A high pressure quartz reactor (with internal pressure stabilization) was used for bench-scale testing**
  - All lines and system components were either quartz, Teflon or Silcosteel
    - to minimize sulfur interaction with system components

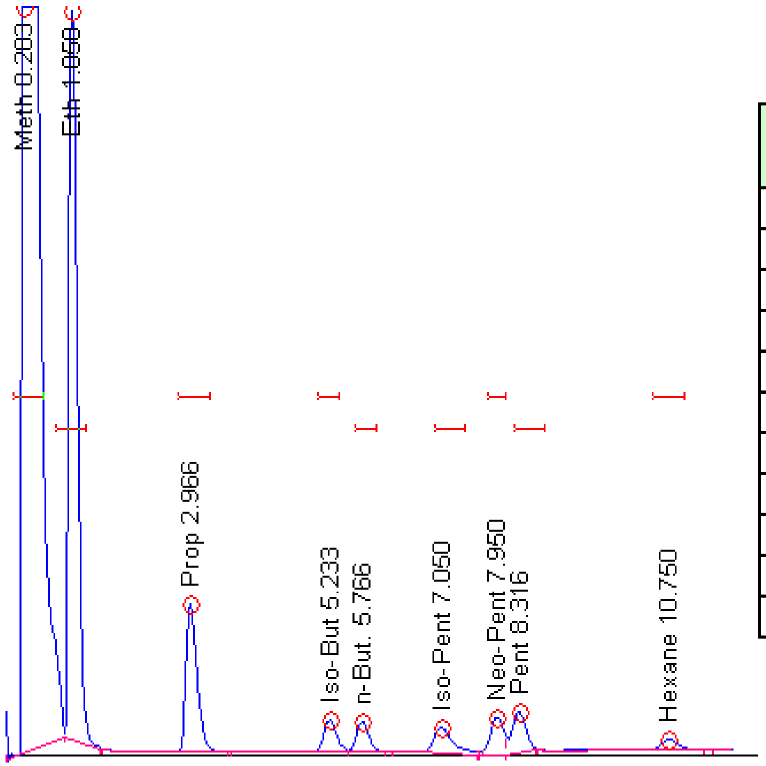
# Sulfur Analysis




| Odorants Tested | Formula | Acronym |
|---|---|---|
| Isopropyl Mercaptan | $(CH_3)_2CHSH$ | IPM |
| Tert-butyl Mercaptan | $(CH_3)_3CSH$ | TBM |
| Dimethyl Sulfide | $CH_3SCH_3$ | DMS |
| Hydrogen Sulfide | $H_2S$ | H2S |
| Tetrahydrothiophene | $CH_2CH_2CH_2CHS$ | THT |
| Ethyl Mercaptan | $C_2H_5SH$ | EM |

- **Two gas chromatographs with sulfur chemiluminescence detector (SCD) and flame photoionization detector FPD) were used to analyze organic sulfur species**
- **The detection limit of the SCD and FPD were 1 and 50 ppbv, respectively**
  - signal/noise ratio greater than 10
- **Restek RTX-1 column was used for separation of the sulfur species**

# Natural Gas Analysis




**Natural gas composition during sorbent testing**

| Component | Volume % Sample Jan. 2004 | Volume % Sample June 2004 |
|---|---|---|
| Methane | 92.83 | 92.39 |
| Ethane | 3.30 | 3.42 |
| Propane | 0.61 | 0.56 |
| Butane | 0.13 | 0.11 |
| Isobutane | 0.12 | 0.12 |
| Pentane | 0.10 | 0.11 |
| Isopentane | 0.10 | 0.10 |
| Neopentane | 0.10 | 0.10 |
| Hexane | 250 ppm | 280 ppm |
| Carbon Dioxide | 0.70 | 0.81 |
| Nitrogen | 2.01 | 2.08 |

**In selected tests, the natural gas contained up to 200 ppmv water vapor**

- **Two gas chromatographs with a TCD and FID detectors were used to analyze natural gas components**
- **The FID detector could measure as low as 1 ppmv hexane in natural gas**

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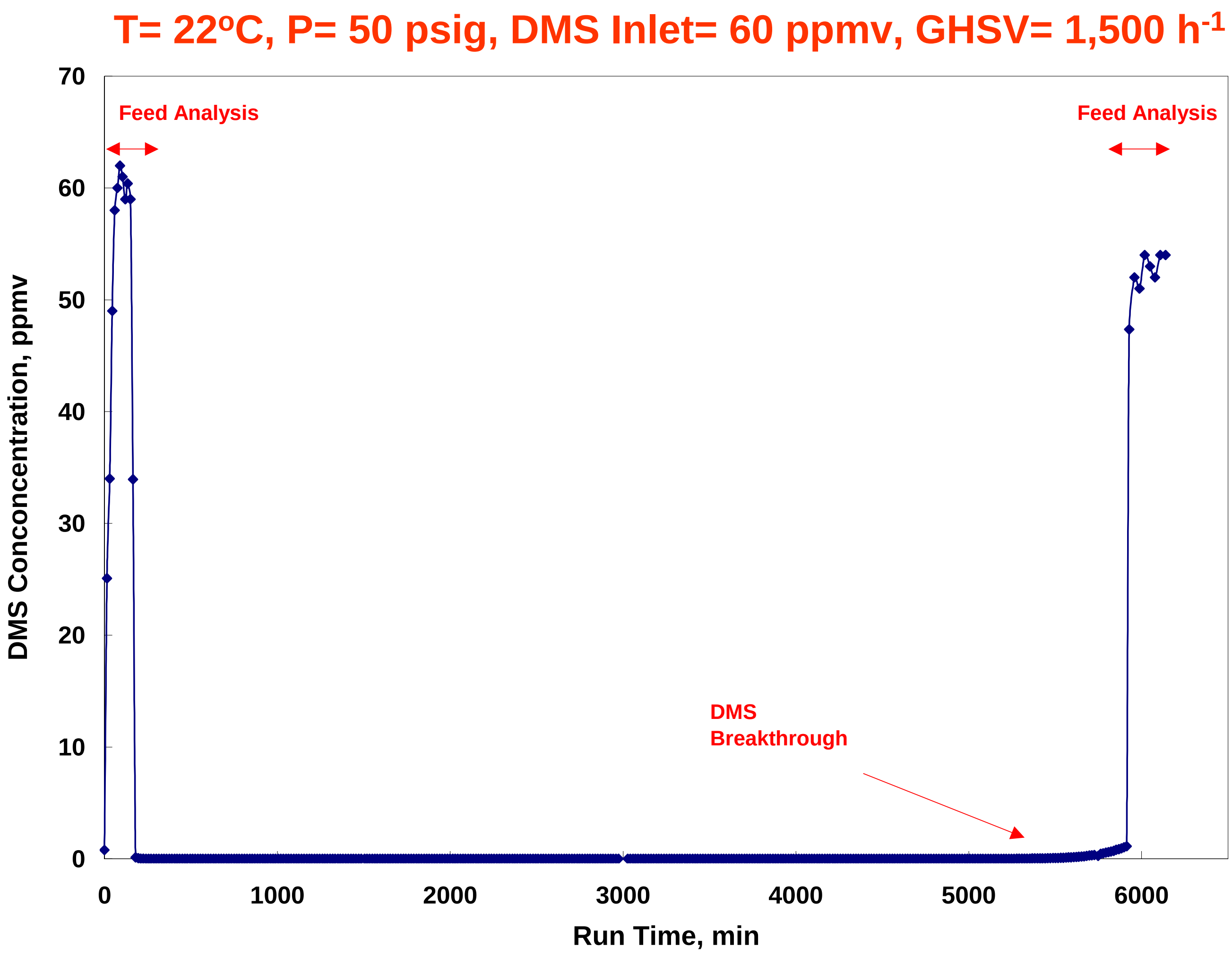
# Typical Test Profile

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# Prior Work

| Manufacturer | Active Component | Product Name | DMS (ppmv) | Sulfur (ppmv) | DMS Index |
|---|---|---|---|---|---|
| United Catalysts, Inc. (Süd-Chemie) | ZnO @ 350°C (No preceding CoMo catalyst bed or hydrogen addition) | G-72E | 1.5 | 6.7 | 668 |
| Norit | Carbon w. chromium & copper salts | RGM-3 | 0.8 | 5.1 | 24000 |
| Calgon Carbon | Carbon | PCB | 1.5 | 6.2 | 26550 |
| United Catalysts, Inc. (Süd-Chemie) | Carbon w. copper oxide | C8-7-01 | 1.8 | 6.7 | 27900 |
| Süd-Chemie | Nickel, Nickel Oxide (Unheated) | C28 | 1.1 | 4.2 | 44992 |
| Grace Davison | Molecular Sieve; 13X (10 Å pore) zeolite-X | 544HP | 0.8 | 4.4 | 110376 |
| Supplier C | Unknown | Proprietary Adsorbent S | 1.2 | 5.1 | 182573 |
| Pacific Northwest National Lab (PNNL) | Copper impregnated zeolite-Y substrate | Unnamed | 0.8 | 4.1 | 2416800 |
| Synetix | Copper Oxide & Zinc Oxide 100°C top, 170°C bottom | Puraspec 2084 | 3.4 | 8.4 | 3661800 |
| Supplier E | Unknown | Proprietary Adsorbent T | 2.3 | 8.2 | 3814300 |

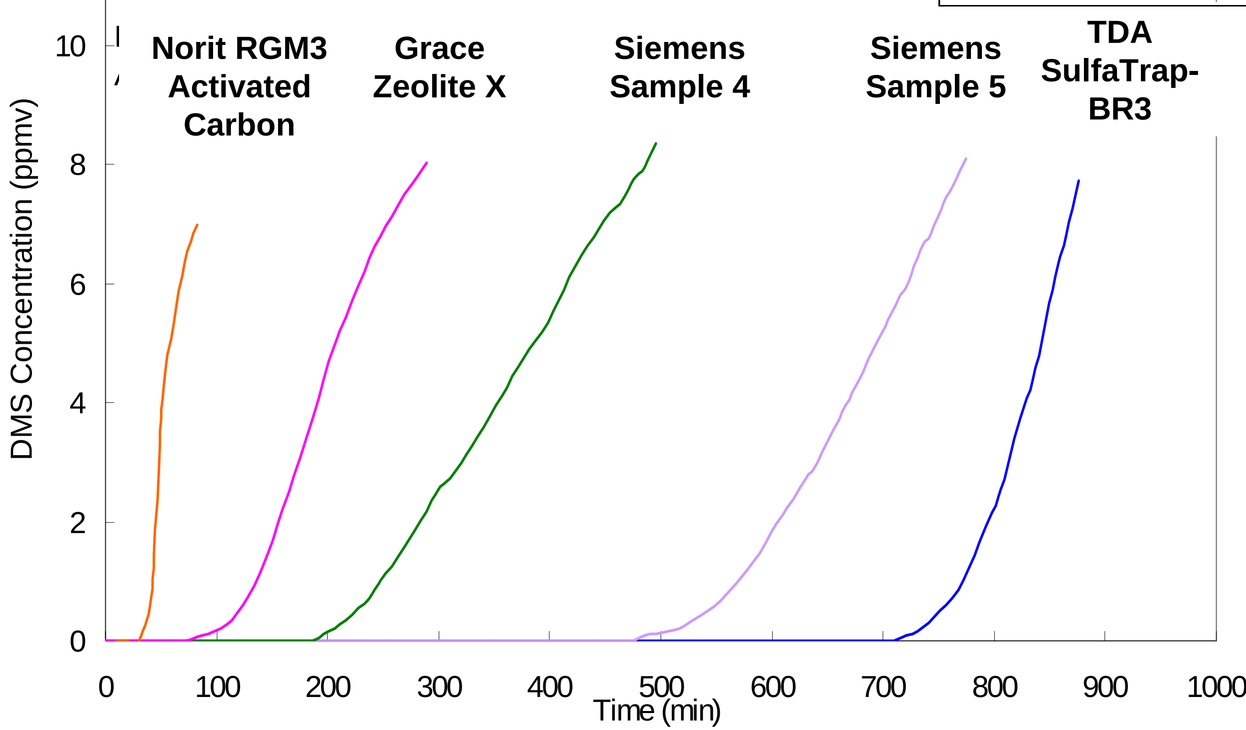
**Source: Israelson, " Results of Testing Various Natural Gas Desulfurization Sorbents", J. of Materials Engineering and Performance, Vol. 13 (3), June 2004**

- **DMS Index = average ppm DMS x cubic feet of natural gas/cubic feet of adsorbent**

# Performance Comparison at Bench-scale

| Sample | Pre-Breakthrough Capacity (% wt.) |
|---|---|
| TDA's SulfaTrap™ | 3.12% |
| Siemens Sample 5 | 1.96% |
| Siemens Sample 4 | 0.85% |
| Grace X Zeolite | 0.36% |
| Norit RGM3 Activated Carbon | 0.18% |

**T= 20°C, P= 3 psig, DMS = 12.3 ppmv, TBM = 9 ppmv, THT= 9 ppmv in Nat. Gas GHSV= 60,000 h$^{-1}$**




- **TDA's sorbent showed the highest sulfur adsorption capacity**
  - 60% higher sulfur capacity than Siemens Sample #5

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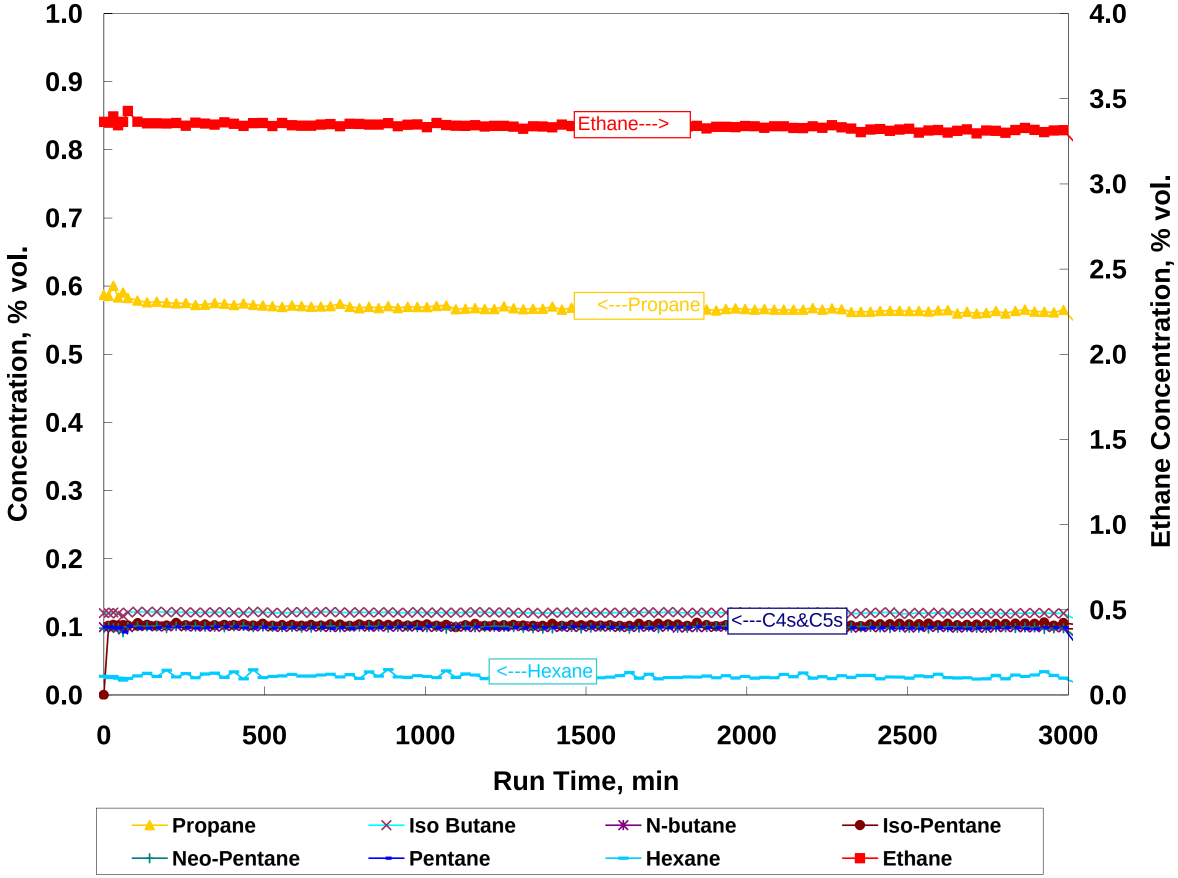
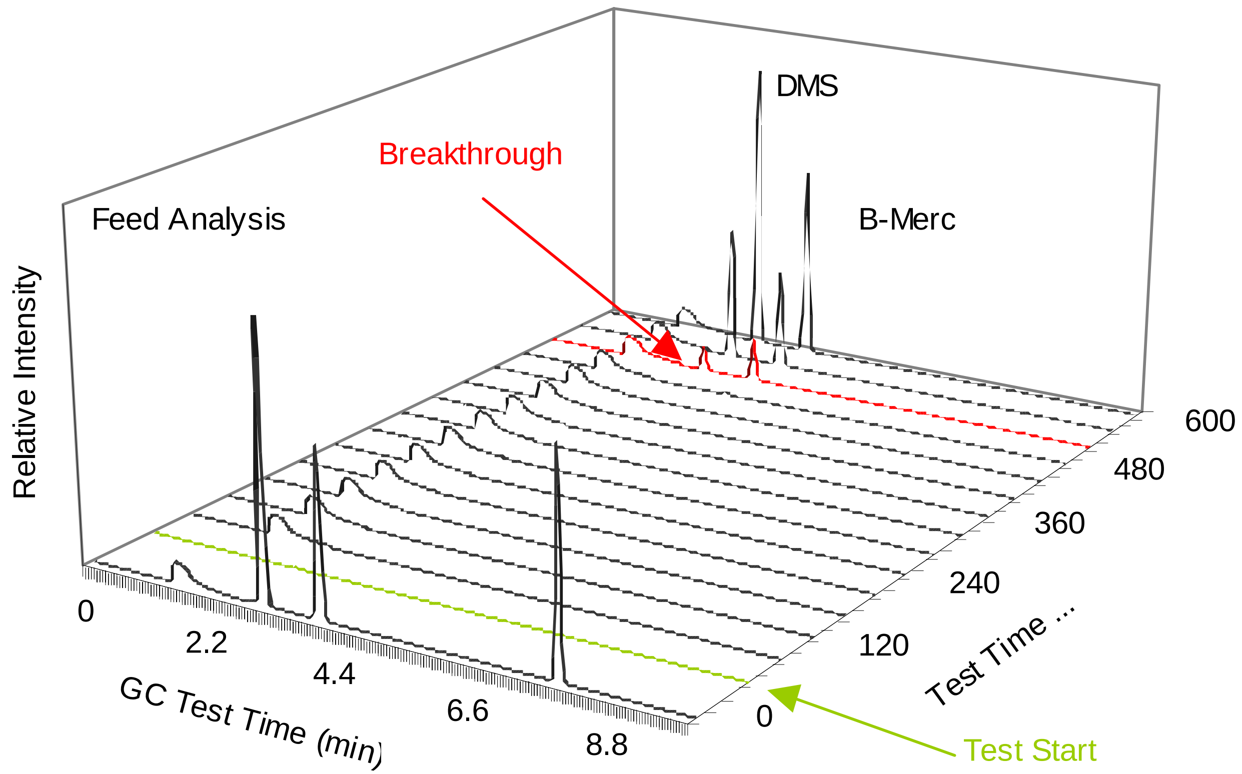
# Hydrocarbon Adsorption




- **The sorbent does not adsorb any hydrocarbon species from the natural gas**
    - Even the heavy hydrocarbons such as hexane were not removed

# Potential Side Reactions

**T= 20$^{o}$C, P= 17 psia, DMS = 17.0 ppmv, TBM= 7 ppmv, THT= 5 ppmv, GHSV= 60,000 h$^{-1}$**




- **The organosulfur species do not undergo any side reactions that cause formation of complex sulfur species**

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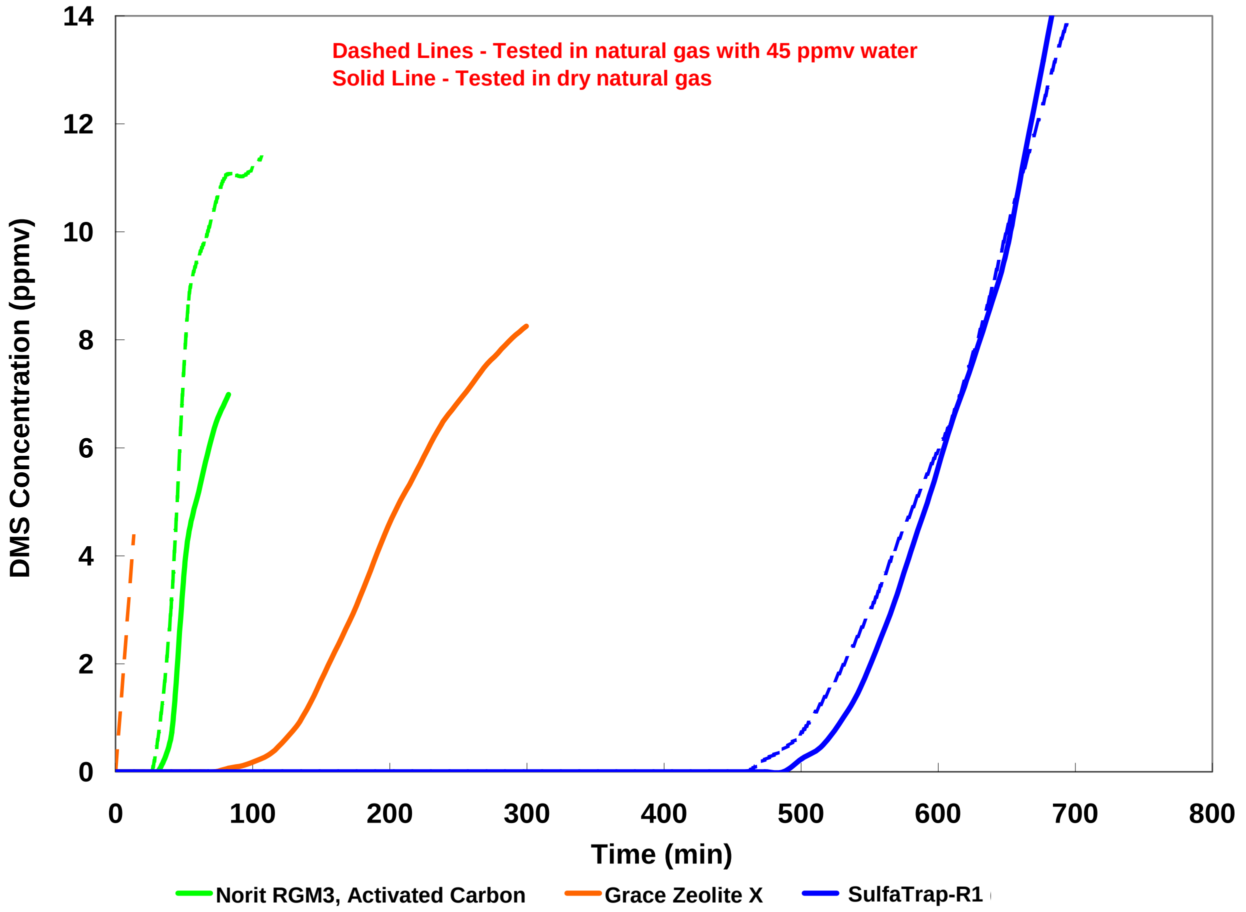
# Effect of Water Content in Natural Gas

T= 20°C, P= 3 psig, DMS Inlet= 12.4 ppm, TBM= 9 ppm, THT= 9 ppm in Natural Gas, GHSV= 60,000 $h^{-1}$




- Pipeline gas may contain up to 155 ppmv of water vapor
- SulfaTrap$^{TM}$-R1 sorbent was impacted the least by presence of water

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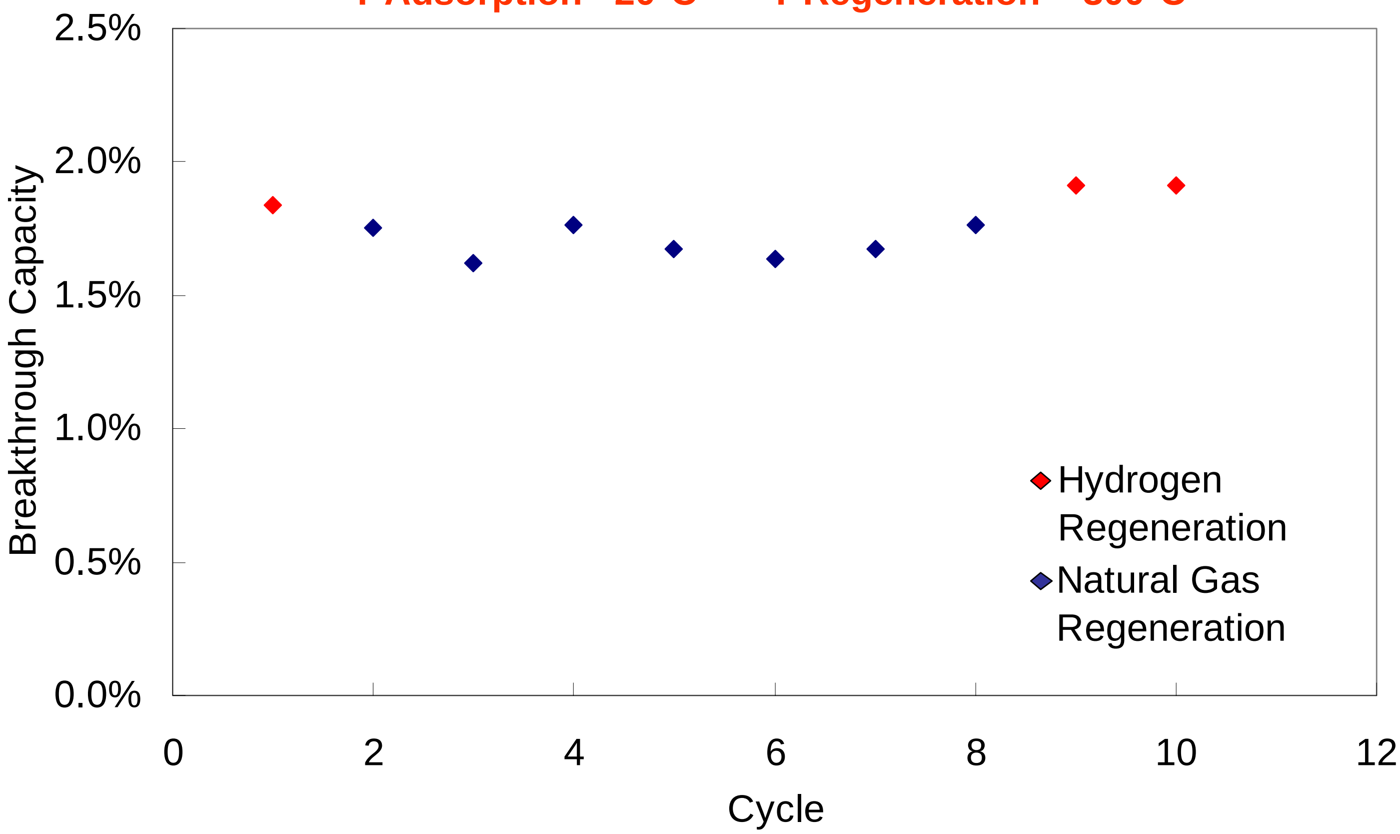
# Cyclic Capacity

**T= 20$^o$C, P= 3 psig, DMS = 7 ppmv, TBM= 7 ppmv, THT= 15 ppmv, GHSV= 75,000 h$^{-1}$**

**T Adsorption= 20$^o$C T Regeneration = 300$^o$C**




- **Sorbent maintains its capacity for 10 adsorption/regeneration cycles**
- **Sorbent regenerates using clean natural gas as well as hydrogen**

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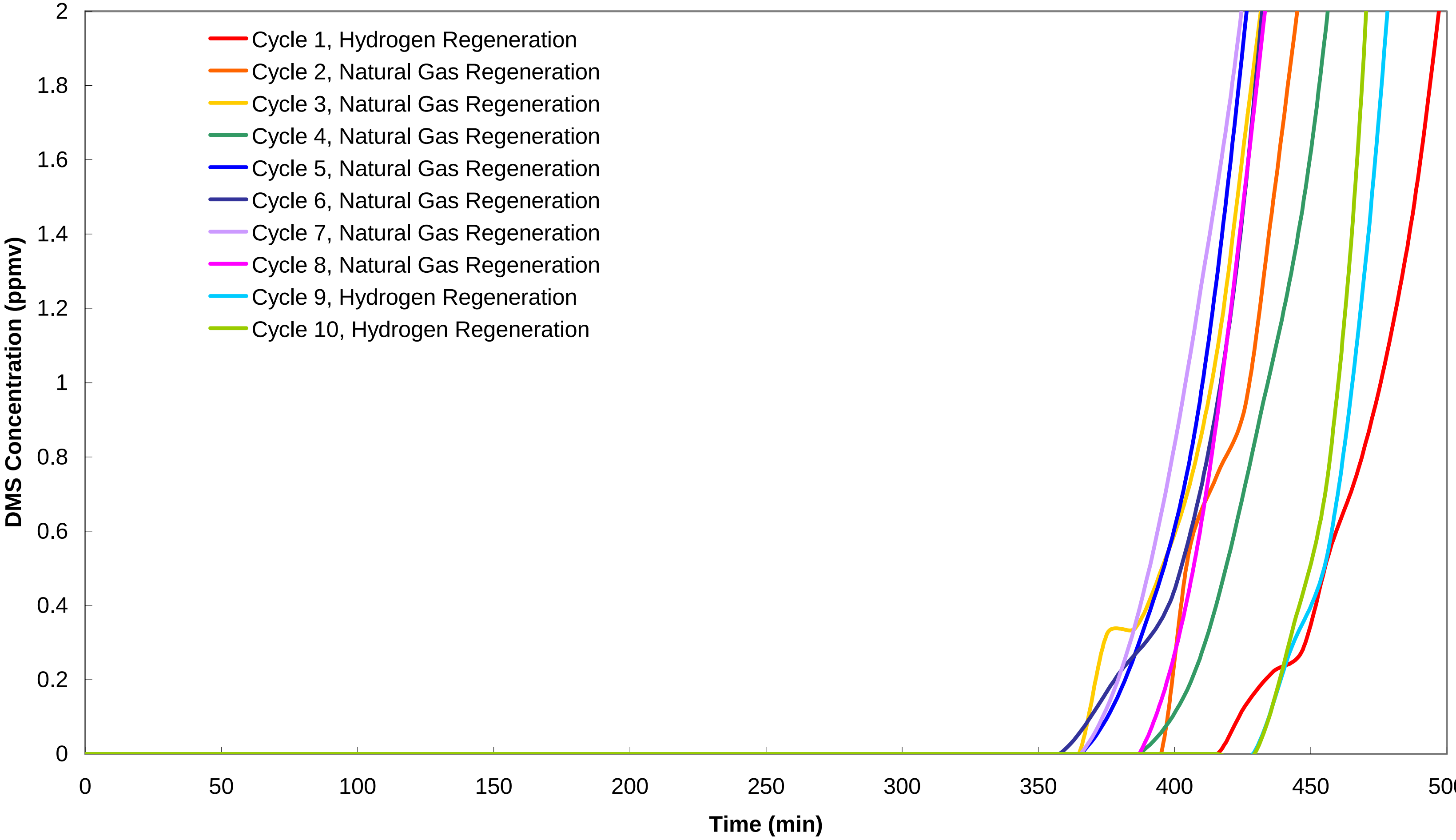
# DMS Breakthrough Profiles in the 10-Cycle Test

## T= 20ºC, P= 3 psig, DMS = 7 ppmv, TBM= 7 ppmv, THT= 15 ppmv, GHSV= 75,000 h$^{-1}$

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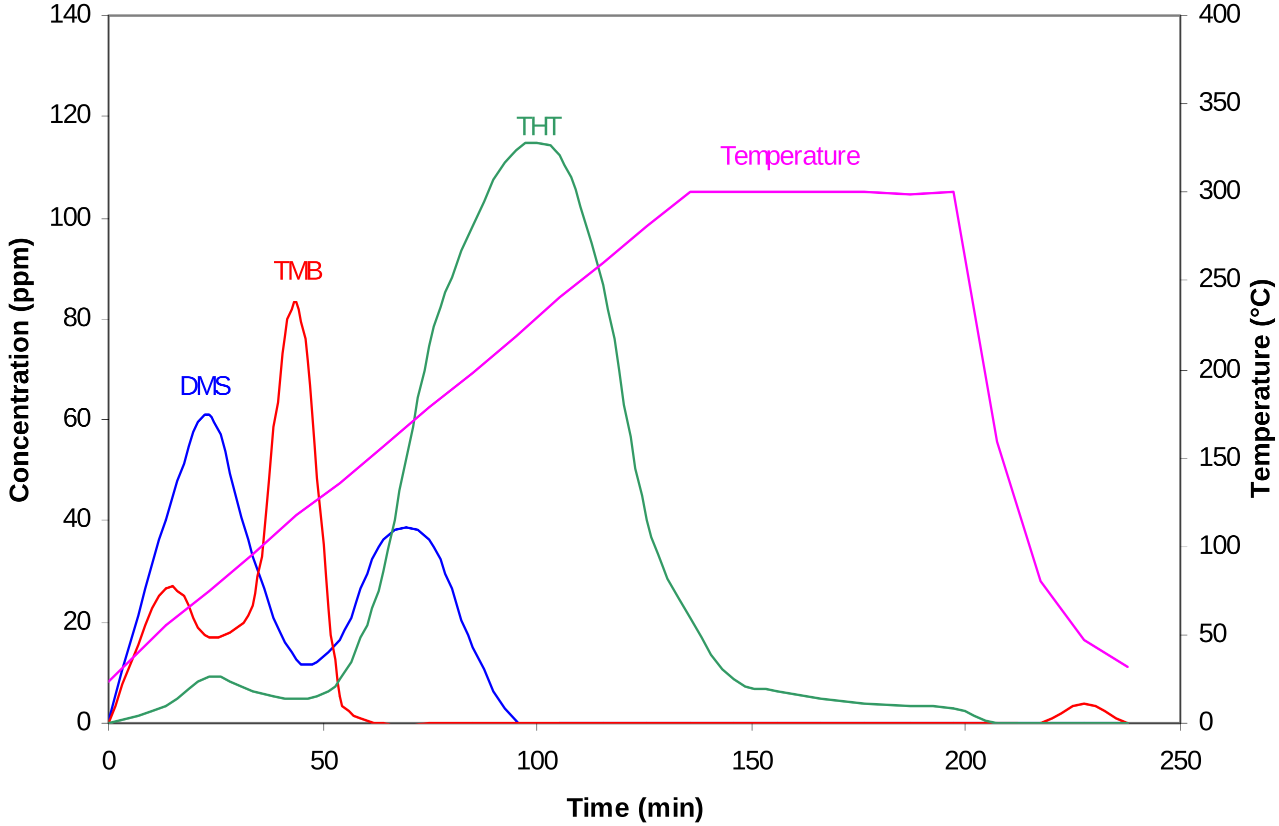
# Temperature-Programmed Desorption




- The sorbent DMS interaction is the weakest as evident by low desorption temperature
- Close sulfur balance between the adsorption and regeneration indicates full regeneration potential for the sorbent

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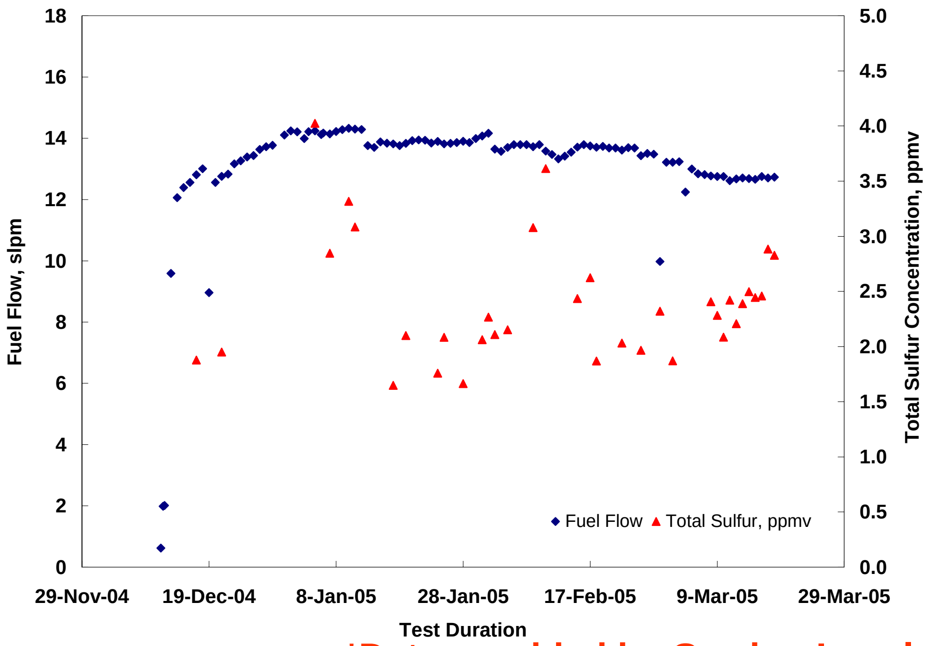
# 5 $kW_e$ SOFC Alpha Testing at SWPC

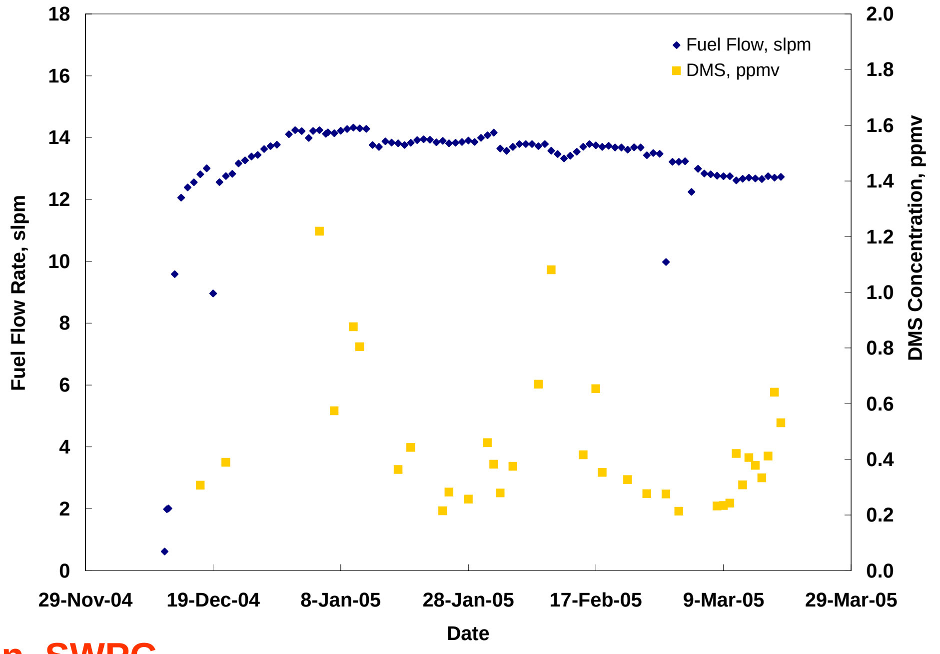
- TDA supplied its sorbent to Siemens Westinghouse to provide natural gas desulfurization during alpha testing of their SOFCs
- Sorbent bed was sized to provide 1 year continuous operation
  - 2.2 L sorbent (assuming 10 ppmv sulfur content for the gas all of which is DMS)
  - 1/16” cylindrical pellets
- 2,700 hrs testing was completed in March 2005
- The same canister will be used for additional tests

# Alpha Testing Results

## Variation in sulfur concentration




## Variation in DMS concentration




*Data provided by Gordon Israelson, SWPC

- **TDA's SulfaTrap$^{TM}$-R1 sorbent removed all sulfur for over 2,700 hrs**
- **The average concentration of the sulfur species in Pittsburgh pipeline gas were as follows:**

| H2S ppmv | EM ppmv | DMS ppmv | TBM ppmv | THT ppmv | NPM ppmv | Total S ppmv |
|---|---|---|---|---|---|---|
| 0.10 | 0.07 | 0.45 | 0.59 | 0.61 | 0.52 | 2.39 |

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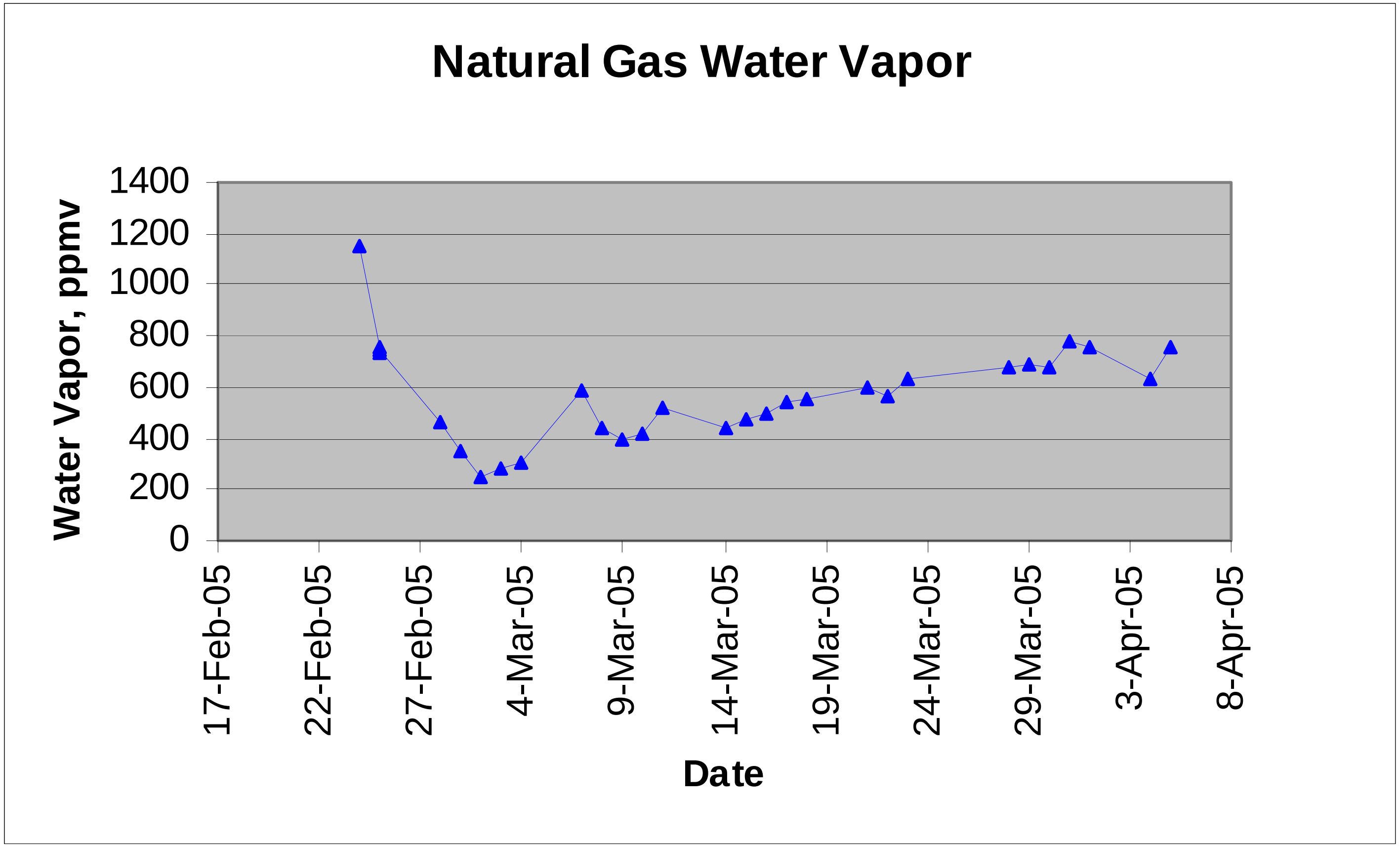
# Water Vapor in Natural Gas




*Data provided by Gordon Israelson, SWPC

- **SWPC measurements showed that natural gas used during the testing contained ~500 ppmv water vapor**

# Field Demonstration with a 5 $kW_e$ SOFC

- **A 5 $kW_e$ SWPC SOFC combined with TDA's desulfurizer will be delivered to CTC Fuel Cell Test Facility in Johnstown, Pennsylvania**
  - Desulfurizer dimensions 3" x 21"
- **The fuel cell will be delivered to US Army base at Fort Meade, MD**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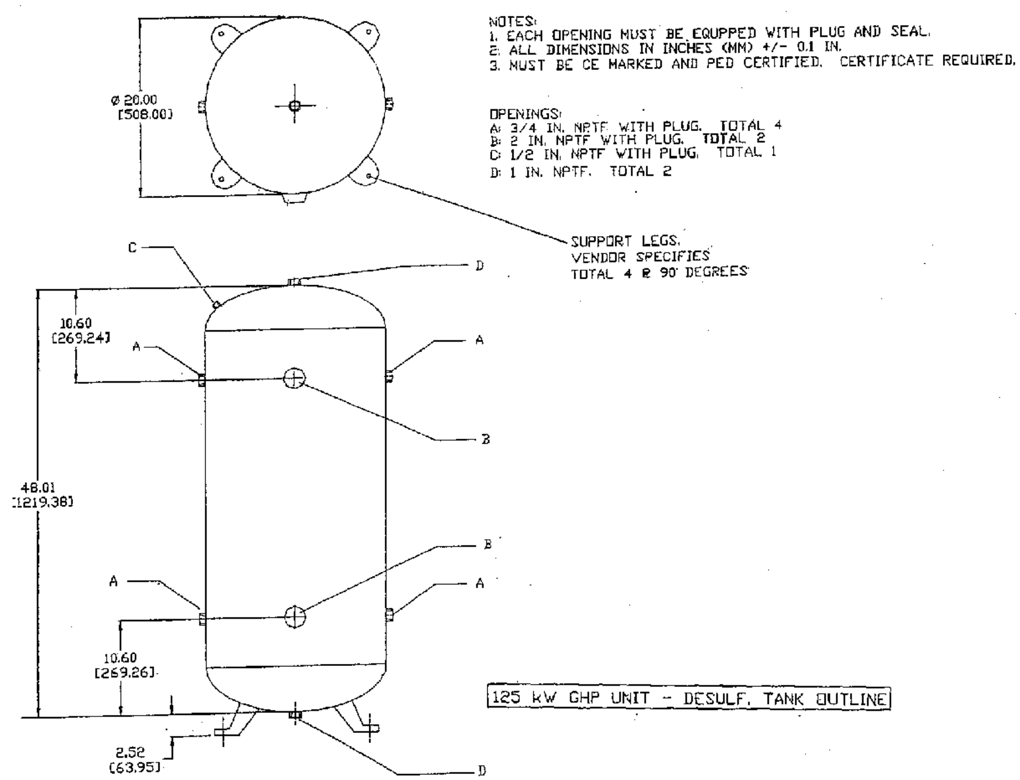
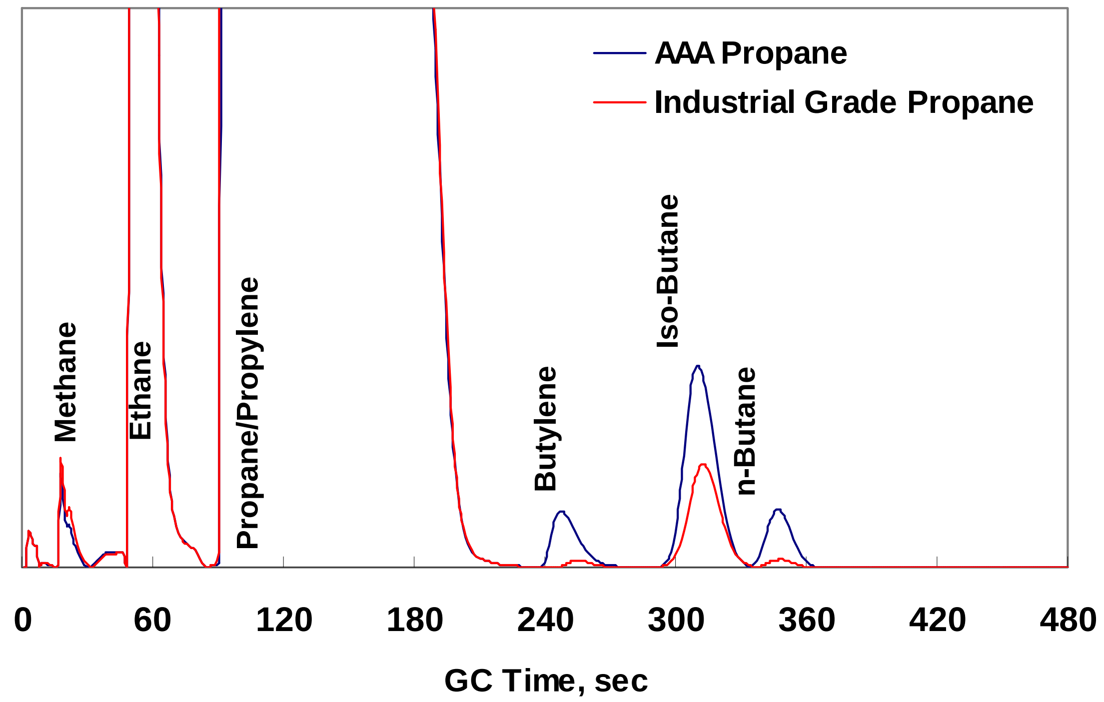
# Field Demonstration with a 125 kW$_e$ SOFC

- **TDA is also preparing a desulfurizer unit for a 125 kW$_e$ CHP SOFC system**
  - **Sorbent size = 150 L**
  - **1/8"cylindrical pellets**
- **TDA scaled-up the production capacity two-folds**
  - **The sorbent produced with high throughput equipment (e.g., spray dryer, screw extruder) exhibited good performance**
- **The unit will be shipped to Hanover, Germany**



# Desulfurization of LPG

- Liquified petroleum gas (LPG) has higher power density than natural gas on volume basis
- LPG-fed systems are suitable fuel for portable systems and applications in remote locations
- Mercaptans (mostly ethyl, n-propyl and isopropyl mercaptans) are the primary sulfur species in LPG




- The presence of unsaturated hydrocarbons affects the performance of the desulfurization sorbents

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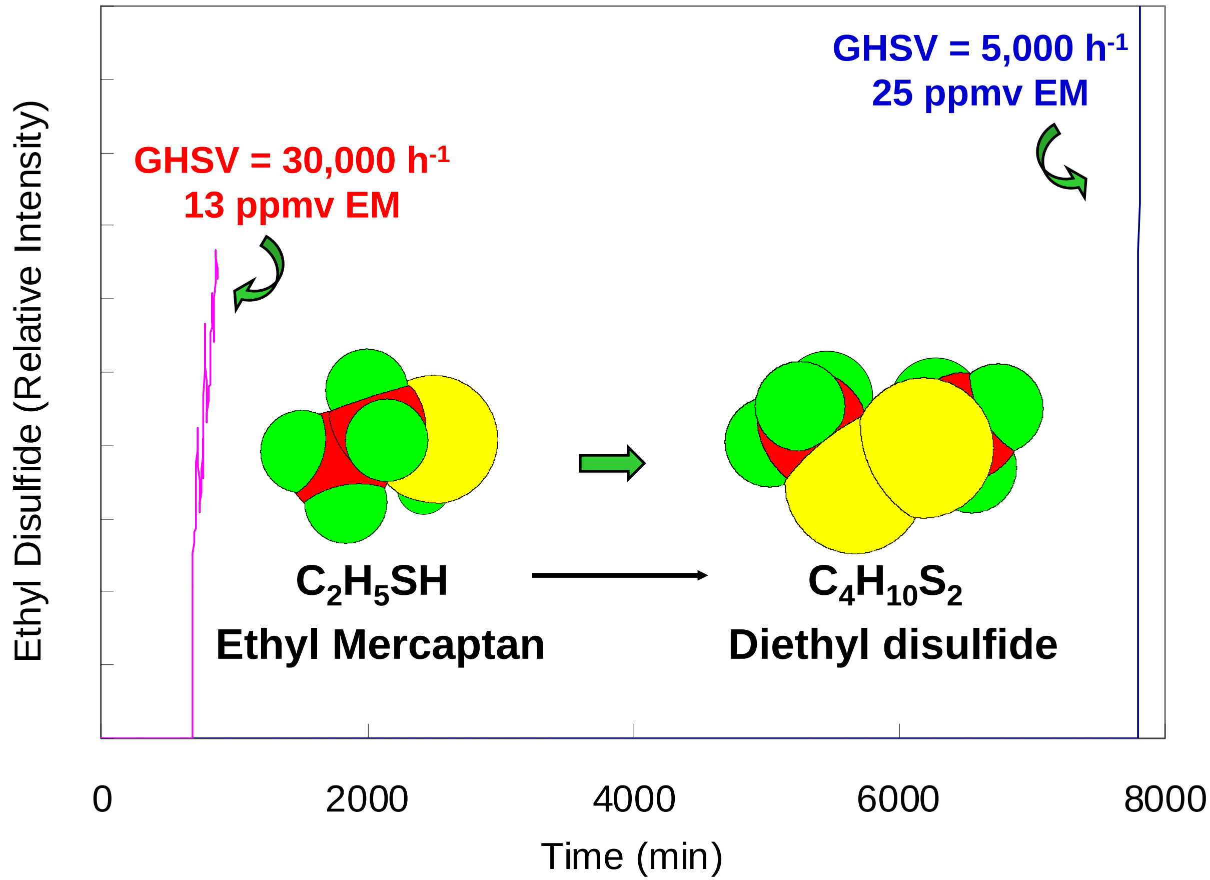
# Sorbent Performance for LPG Desulfurization

T=20°C, P=5 psig, GHSV= 5,000-30,000 $h^{-1}$, Ethyl Mercaptan Inlet = 13 ppmv–25 ppmv




- **TDA's SulfaTrap™-P sorbent achieved sulfur capacity of 0.63% and 2.35% wt. at GHSV of 30,000$h^{-1}$ and 5,000$h^{-1}$, respectively (based on diethyl disulfide breakthrough)**

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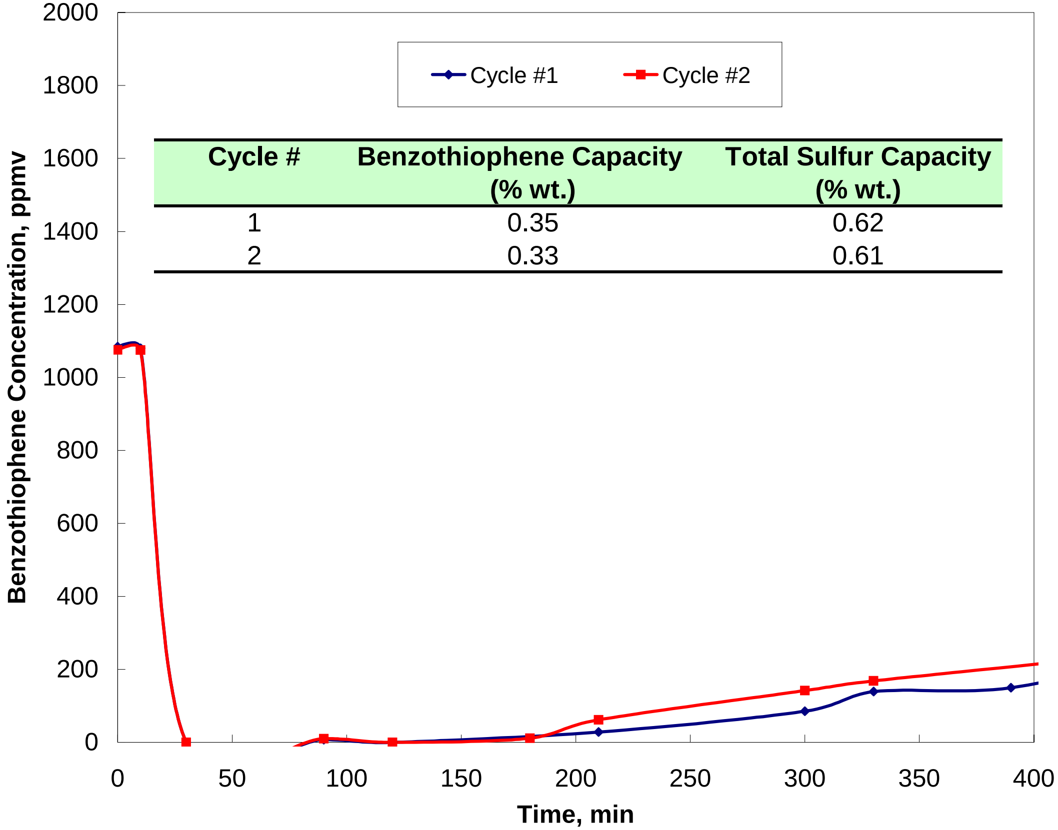
# Field Demonstration with a 100 $W_e$ SOFC

- **TDA will supply Mesoscopic Devices with its LPG desulfurization sorbent**
- **75-100 $W_e$ portable devices with up to 10 day continuous operation**
- **6 units will be developed for propane-fed SOFC by June 2005 and shipped to the Army for field testing**
- **Ultimate goal is to develop an effective sorbent for transportation fuels (gasoline and diesel) and logistics fuels (e.g. JP-8 fuel)**

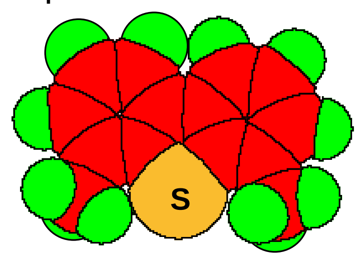
# A Regenerable Sulfur Sorbent for Liquid Fuels

**T= 60ºC, LHSV= 1 $h^{-1}$, 1,100 ppmw Benzothiophene, 900 ppmw 2-methyl Benzothiophene in a model fuel (70% aliphatic HCs, 30% aromatics)**




| Cycle # | Benzothiophene Capacity (% wt.) | Total Sulfur Capacity (% wt.) |
|---|---|---|
| 1 | 0.35 | 0.62 |
| 2 | 0.33 | 0.61 |

4,6-dimethyl dibenzothiophene




- **In the refractory sulfur molecules, the sulfur atom is sterically hindered and difficult to activate**

- **Benzothiophene breakthrough earlier than 2-methyl benzothiophene**
- **The sorbent was regenerated in hydrogen with a mild temperature swing**

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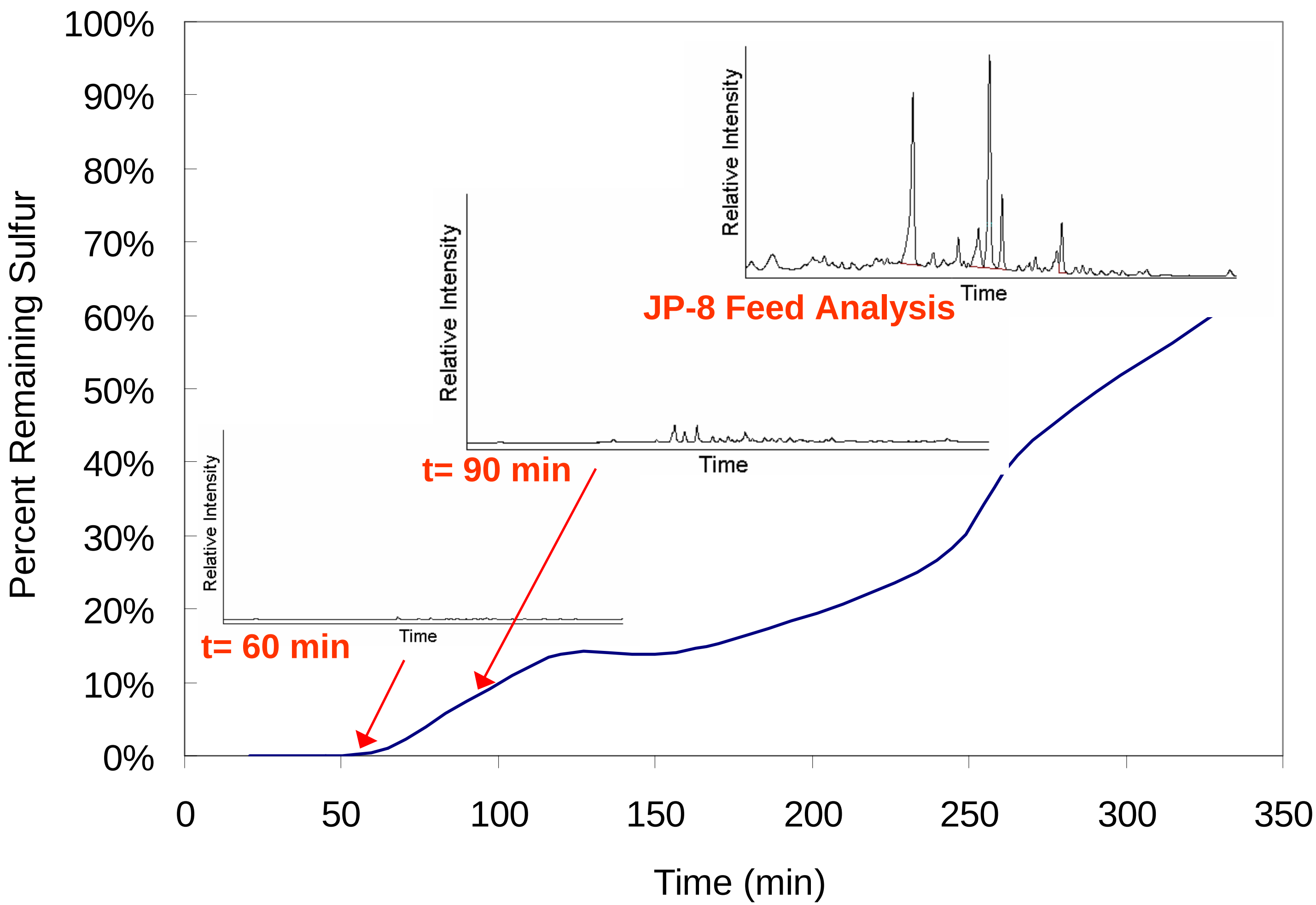
# Sulfur Removal From JP-8

**T=60°C, Sulfur Content= ~3,000 ppmw, LHSV= 1 $h^{-1}$ (Flow = 0.12 ml/min, 3.0 g sample)**




- **TDA's sorbent can remove all the sulfur in the JP-8 fuel**
- **Sulfur speciation and capacity calculations are underway**

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# Conclusions

- **TDA's sorbent can be effectively and economically used for natural gas desulfurization**

| | TDA's SulfaTrap™ Sorbent | Activated Carbon |
|---|---|---|
| Operating Temperature | Ambient | Ambient |
| Bed Volume | 1-2 L | 30-50 L |
| Hydrocarbon Adsorption | Minimal | Substantial |
| End-of-Life Indication | Yes | No |
| Regenerability | Yes | No |
| Flamability | No | Yes |
| Disposability | Easy<br>small volume | Difficult<br>toxic, pyrophoric |

- **Sorbent cost is estimated ~$10-25/lb (depending on production scale)**
- **Based on the conditions of the alpha test (~14 slpm fuel flow, 2.4 ppmv sulfur), sorbent cost is estimated as $4.71/1,000 m³ natural gas or $16 to $40/year ($3-$8/kW)**
- **TDA's SulfaTrap™-P sorbent can achieve 2.35% wt. capacity for desulfurization of LPG**
- **TDA's sorbent also shows promise for JP-8 desulfurization**

# Acknowledgements

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