

**Dielectric Barrier Discharge Detector  
with  
Multi-Dimensional Gas Chromatography Using  
Capillary Flow Technology**

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# Outline

- Dielectric Barrier Discharge Detector
- Multi-Dimensional Gas Chromatography with Capillary Flow Technology
- Illustrations of Performance
- Conclusions
- Acknowledgements

# DBD detectors has the potential of addressing:

- **Separations challenges**
  - Selectivity available in argon mode
- **Sensitivity**
  - Contemporary detector has to be sensitive to keep pace with advancement of science
  - Addressing the unmet needs in chromatography: fixed gases, carbon monoxide, carbon dioxide, formaldehyde applications
- **Cost and Ease of Use**
- **Tuneable complementary selective detector for use in conventional multi-dimensional gas chromatography**

# Principle of Operation of DBD

## ■ AC discharge across dielectric barrier

- Each discharge capacitance limited; self terminating, non-thermal discharge eliminates electrode wear
- Number of discharges function of operating frequency
- Creates metastables and photons

## ■ Counter Current Flow Scheme

- Separate plasma and ionization chamber reduces plasma upset
- Metastables and photons interact with analytes

## ■ Two bias/collector configurations

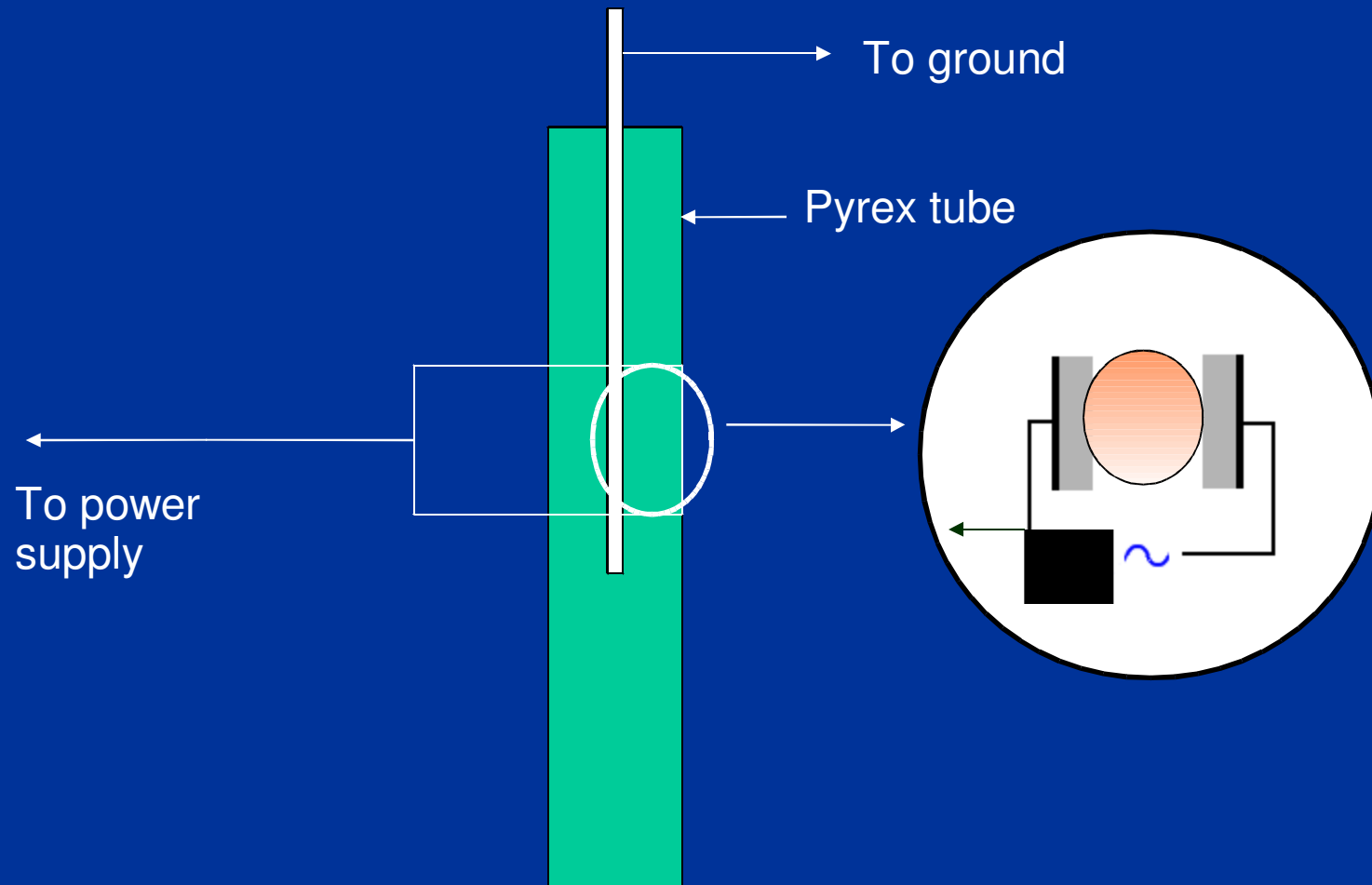
- Concentric electrodes; over/under electrodes
- Analytes ionized and electrons collected

## ■ Uses standard FID electrometers

- Collected electrons converted to signal

# Principle of Operation

## Side View Cross Section



# Two Modes of Operation

## ■ Helium Mode

- Sensitive to everything below 19.7 eV (all but neon)
- Considered to rely on He metastable
- Requires high purity reaction and carrier gas (nitrogen quench)

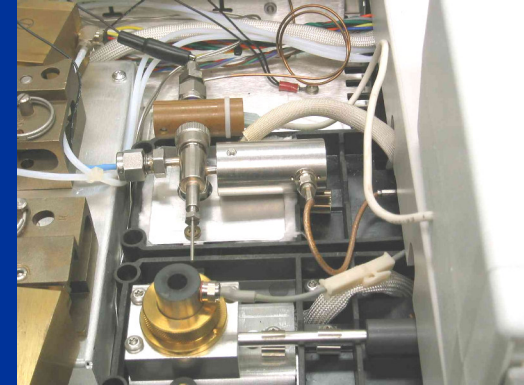
## ■ Argon Mode

- More selective mode of operation (below 11.7 eV)
- Considered to rely on photoionization
- Fewer constraints on gas purity
- Able to operate with pure argon at low flow (<5 mL/min)

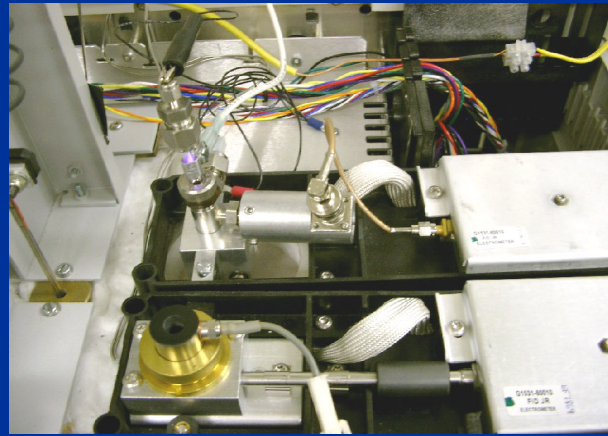
**Easy to switch between two modes**

# Chronology of DBD Development

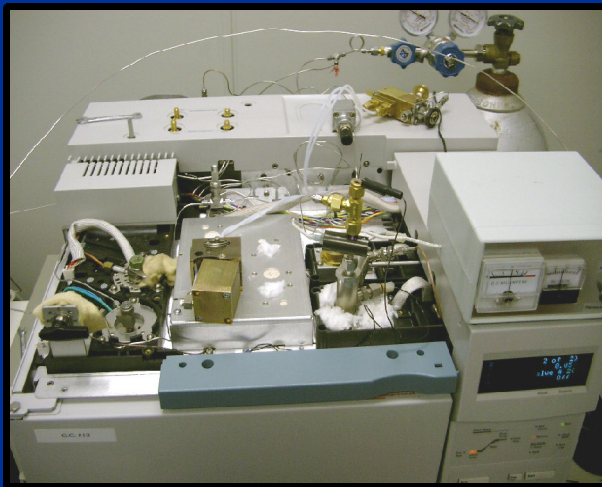
MiniDBD-PF – May 2006



MiniDBD - 2005



Conventional DBD - 2003



Gras R., J. Luong, M. Monagle, B. Winniford, "Journal of Chromatographic Science", ISSN 0021-9665 Volume 44, Number 2, February 2006, pp.

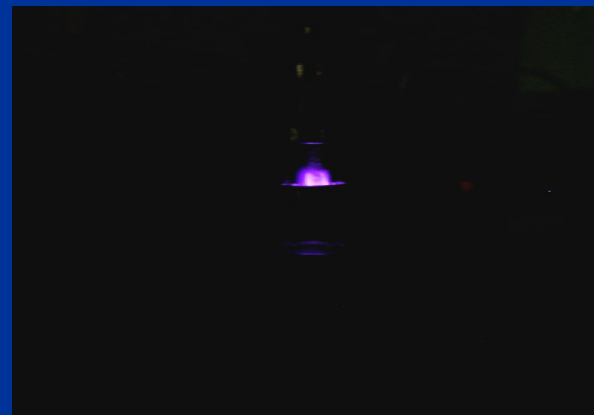
101-107

# Current Analytical Apparatus Used

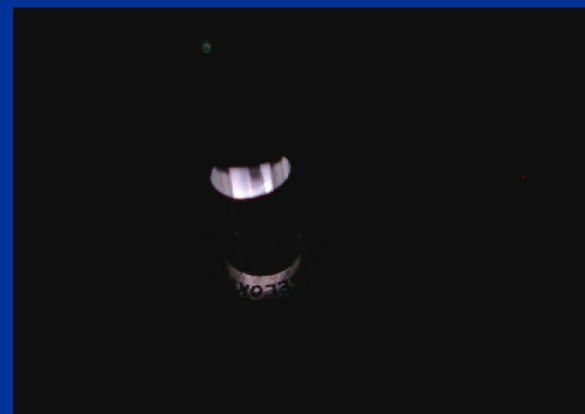
Dow Chemical Canada, Western Canada Operations, Analytical Sciences



Plasma in Helium Mode



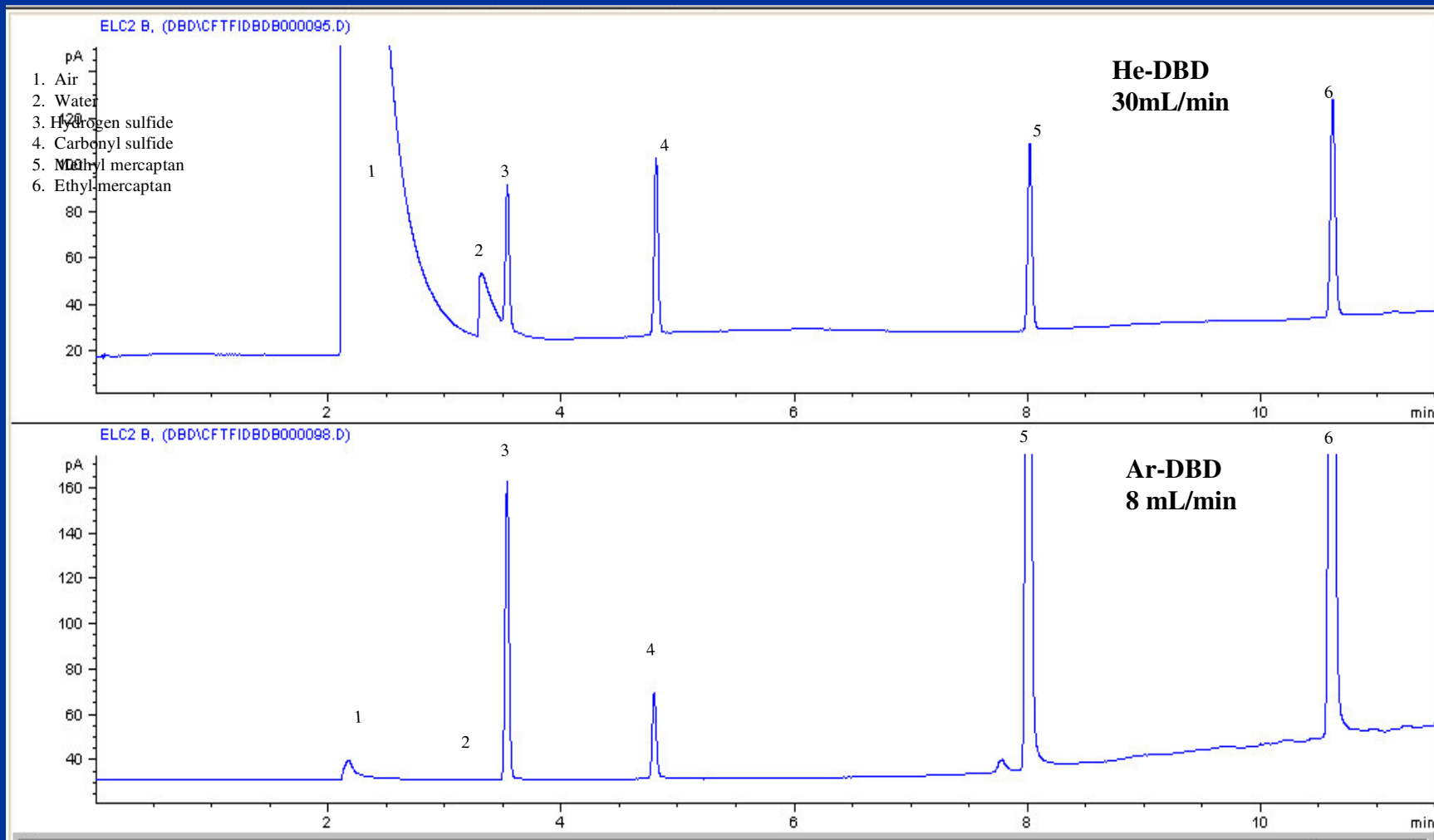
Plasma in Argon Mode





# Selectivity between He-DBD and Ar-DBD

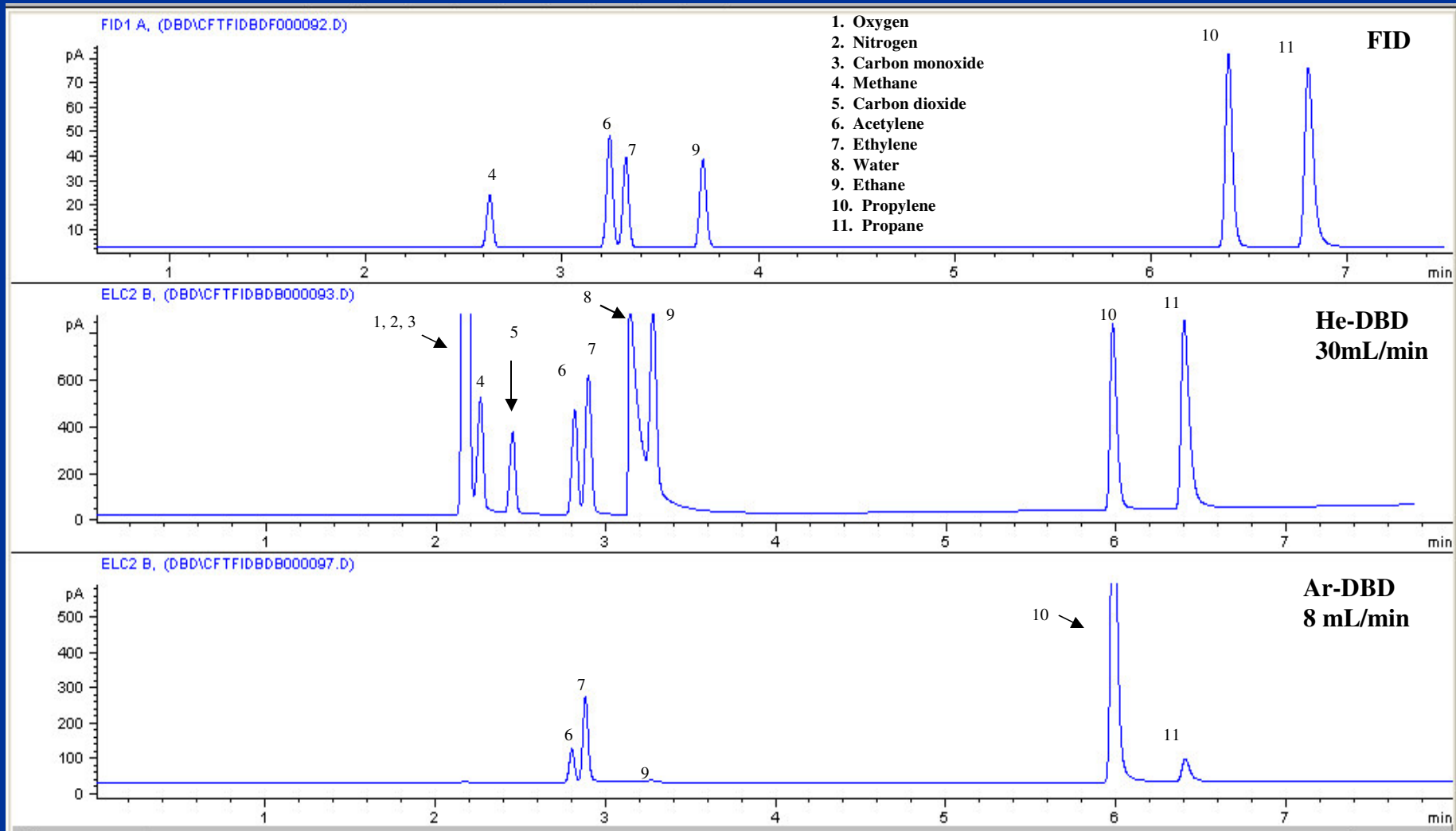
25 metre, 0.32 mm id, divinyl benzene type column  
50C – 3 min – 15C/min – 250C



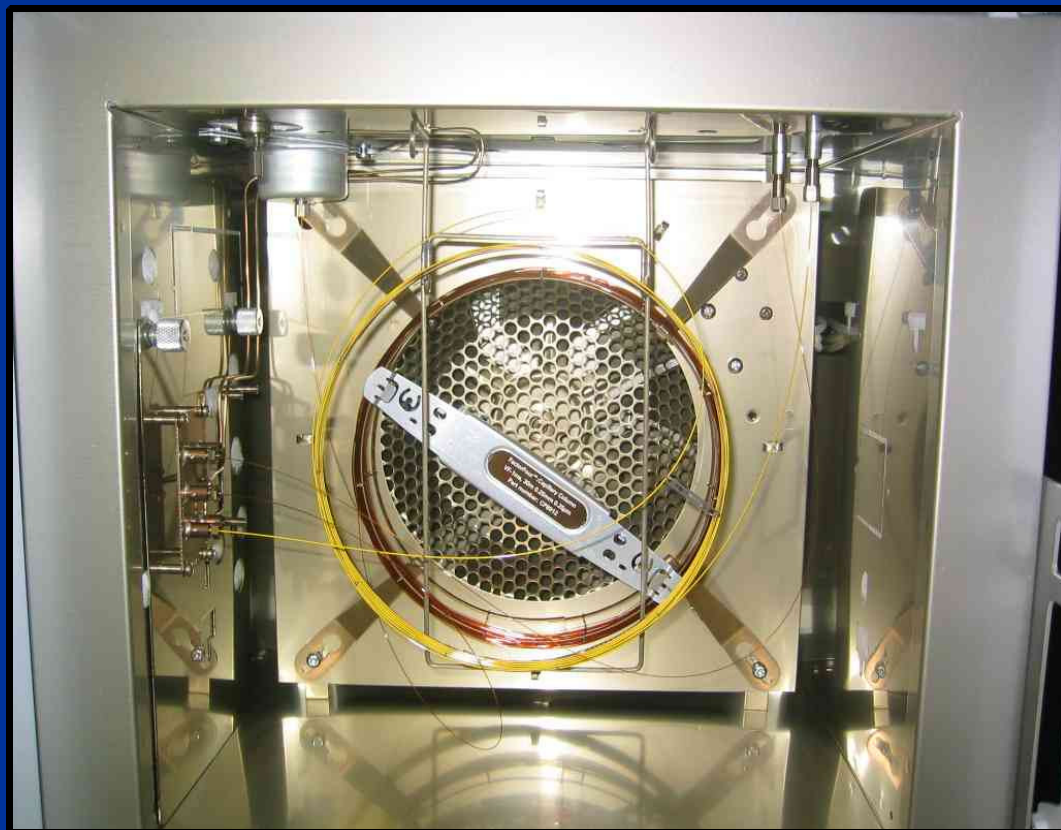
# Selectivity between FID, He-DBD and Ar-DBD

25 metre, 0.32 mm id, divinyl benzene type column

50C – 3 min – 15C/min – 250C

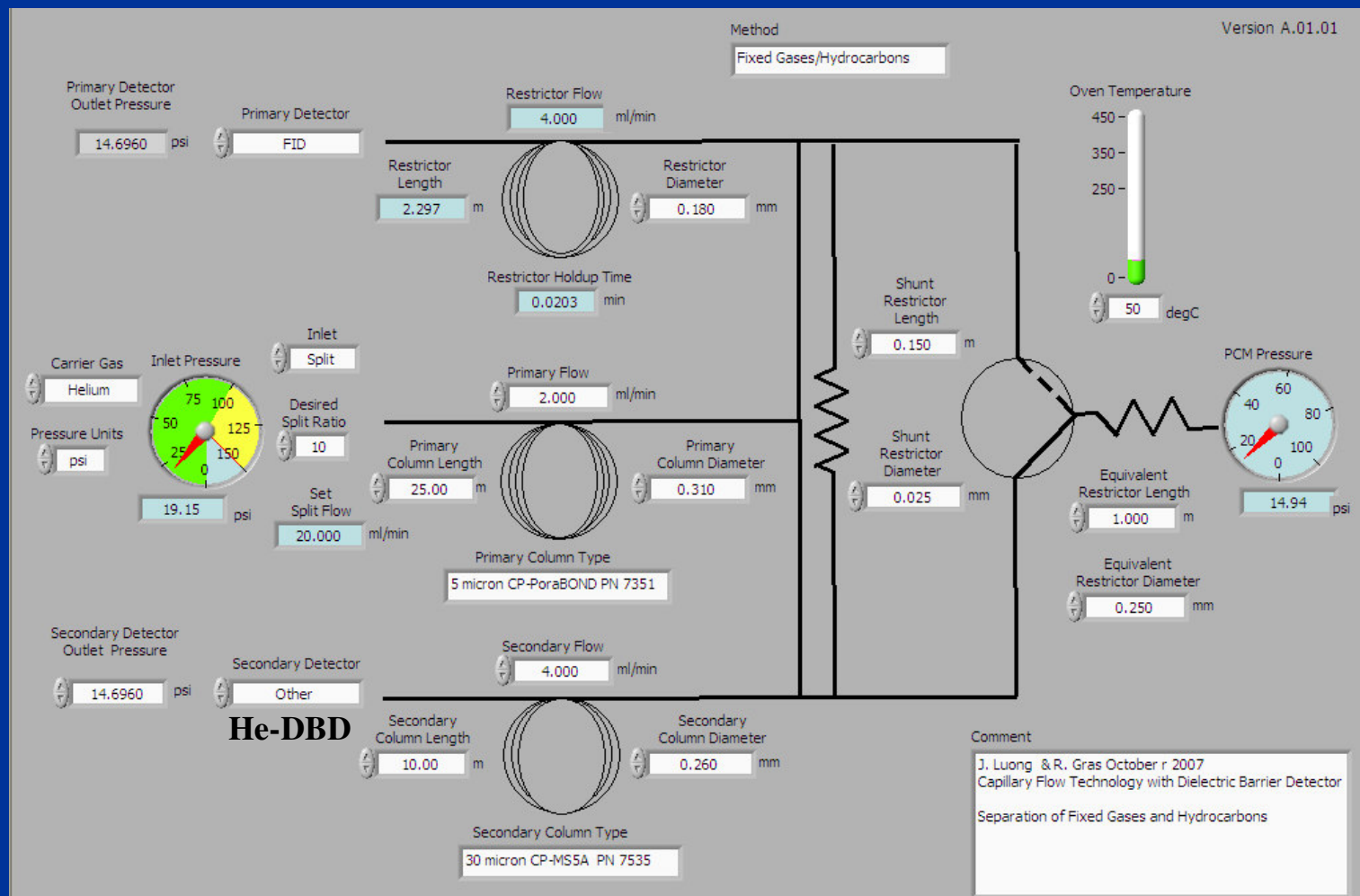


# Conventional Multi-Dimensional Gas Chromatography with Capillary Flow Technology (CFT) and DBD



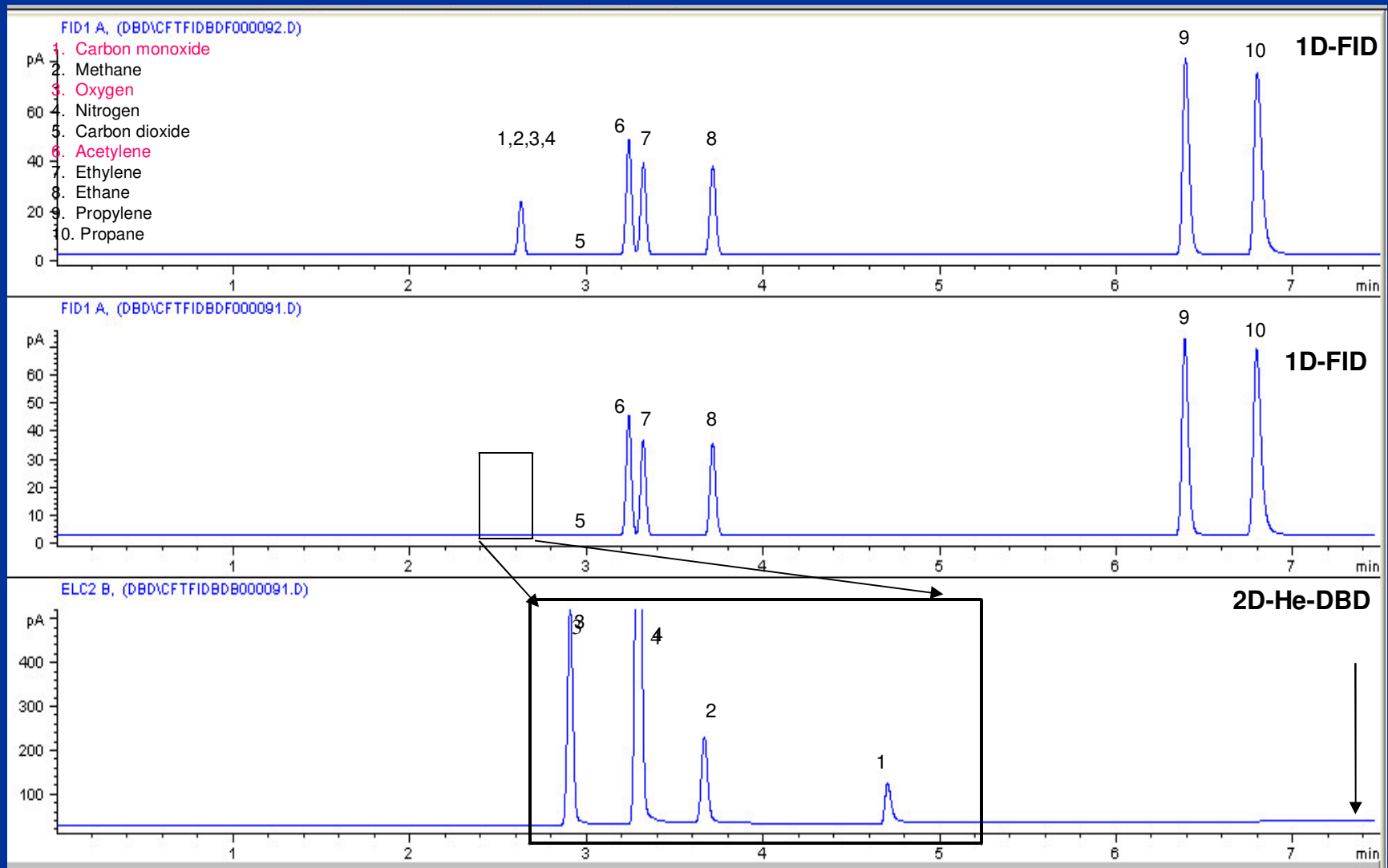
*Improved peak capacity, speed of analysis, analytical capability*

# Fixed Gases and Light Hydrocarbons



# MDGC/CFT/FID/He-DBD

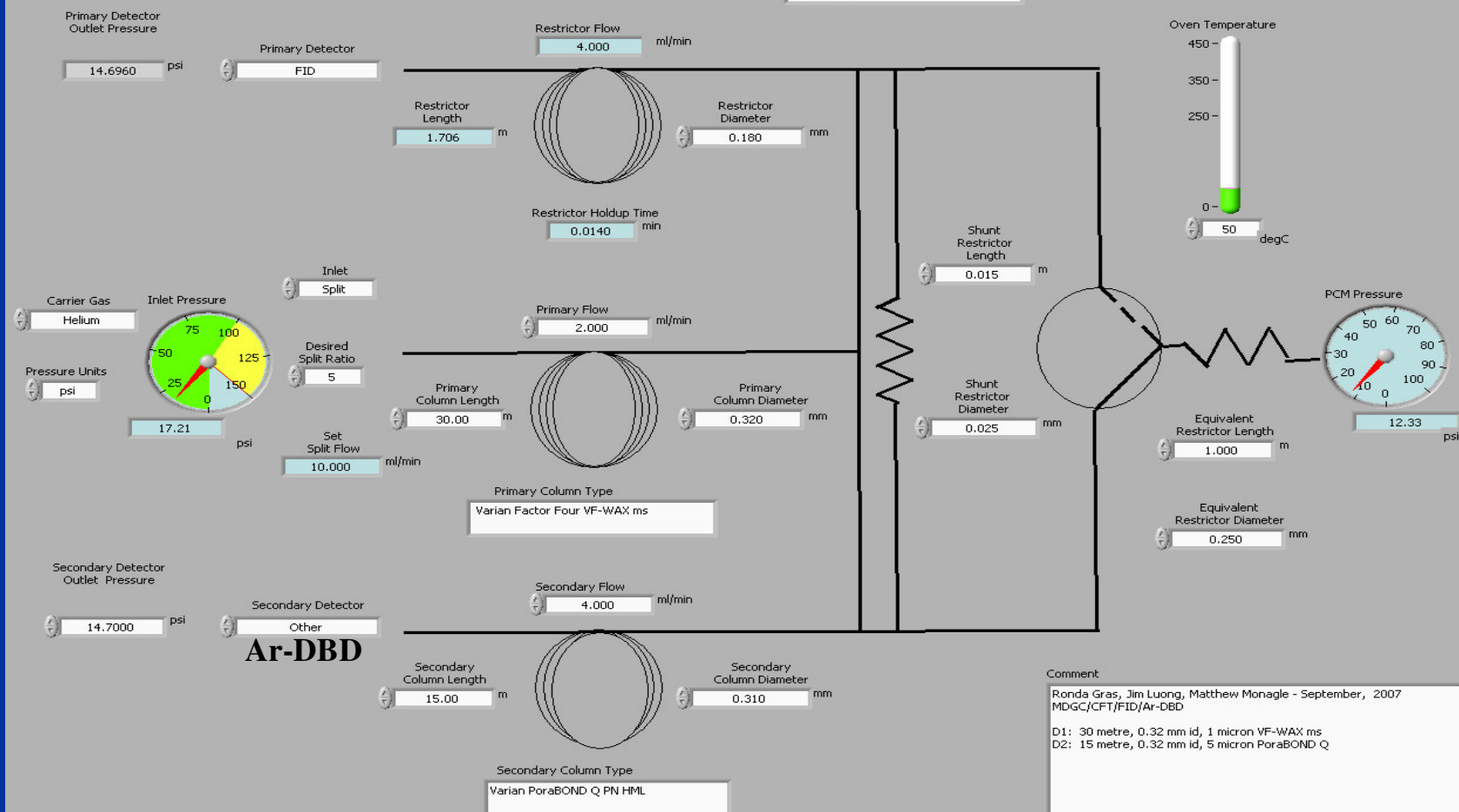
1D – Divinyl benzene (FID), 2D – MS-5A (DBD)



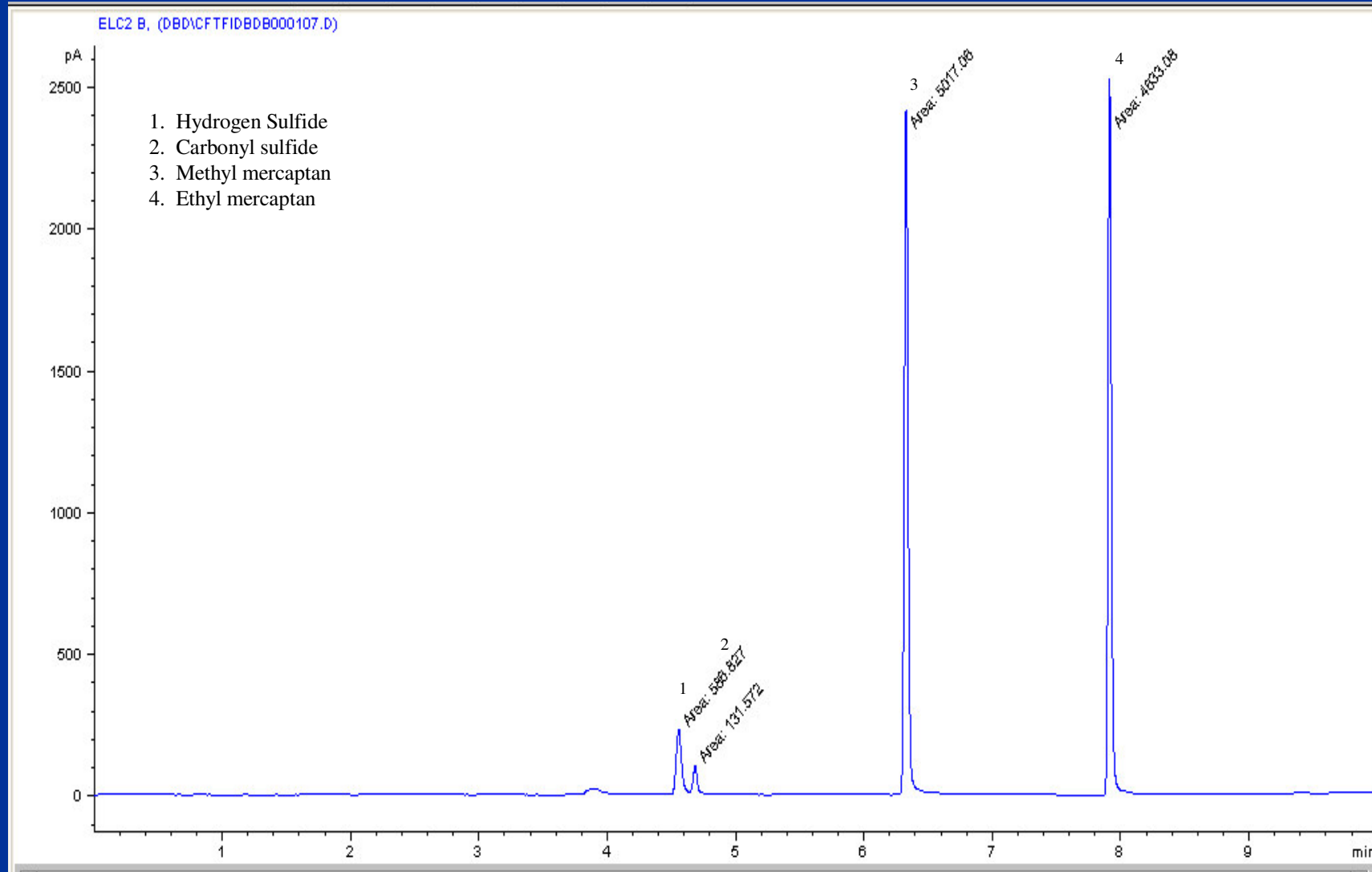
# Mercaptans in Natural Gas

Method  
VFWAX/PoraBONDQ for Mercaptans in Natural Gas

Version A.01.01



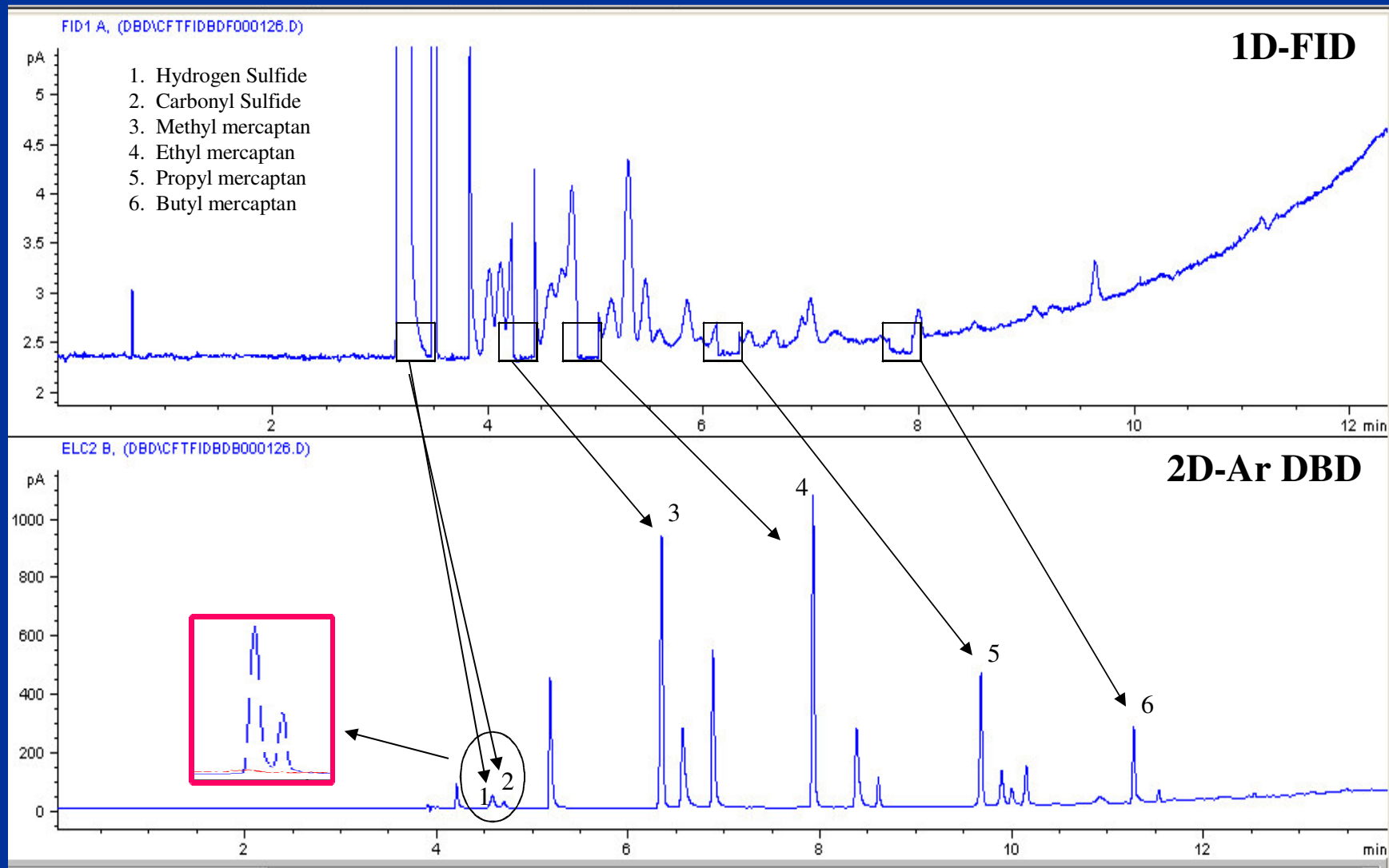
# 100 ppm v/v of hydrogen sulfide, carbonyl sulfide, methyl mercaptan and ethyl mercaptan in nitrogen by GC/Ar-DBD 25 metre, 0.32 mm id, divinyl benzene type column



# MDGC/CFT/FID/Ar-DBD

1D – Polyethylene glycol (FID), 2D – Divinyl benzene (DBD)

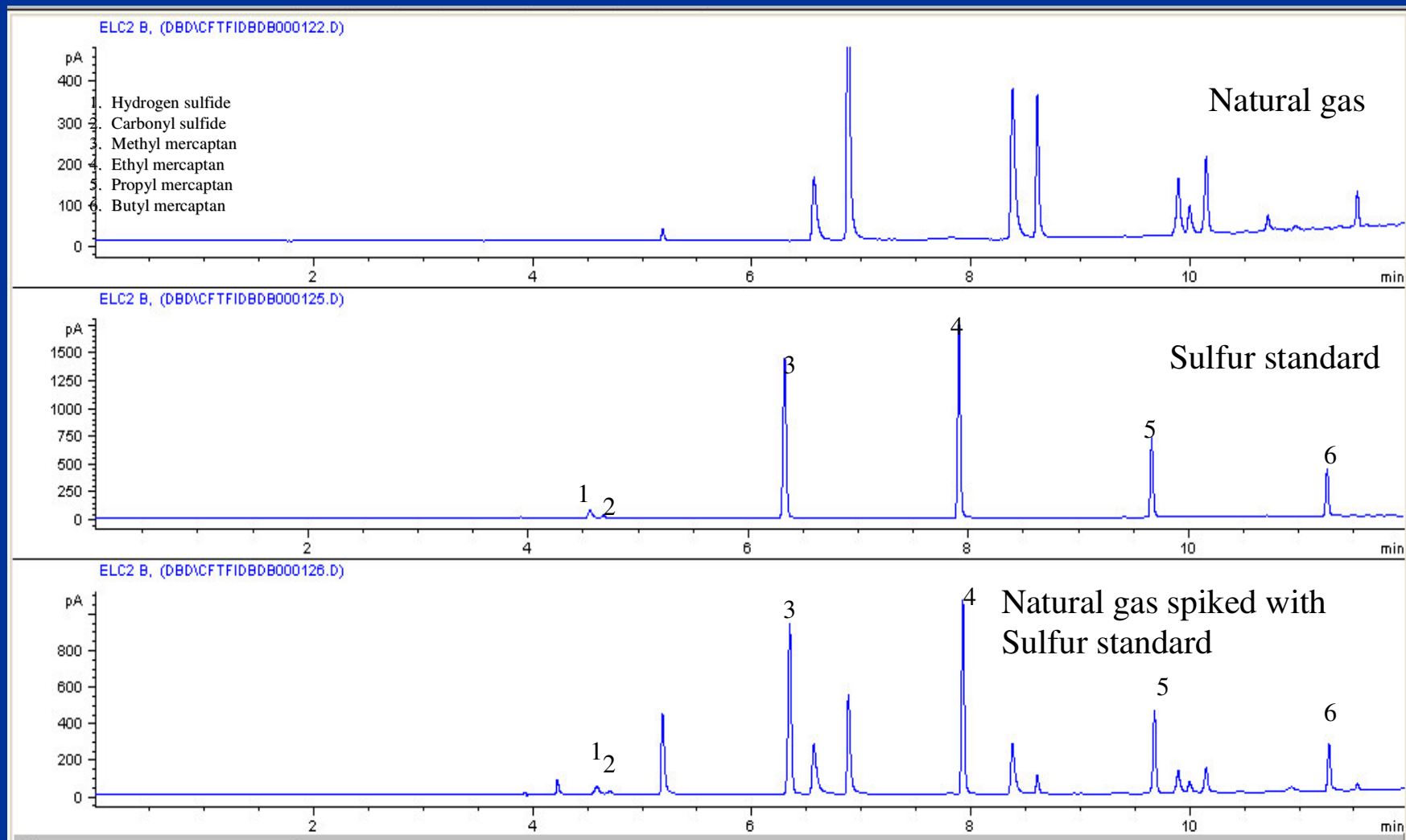
Natural Gas spiked with volatile sulfur compounds





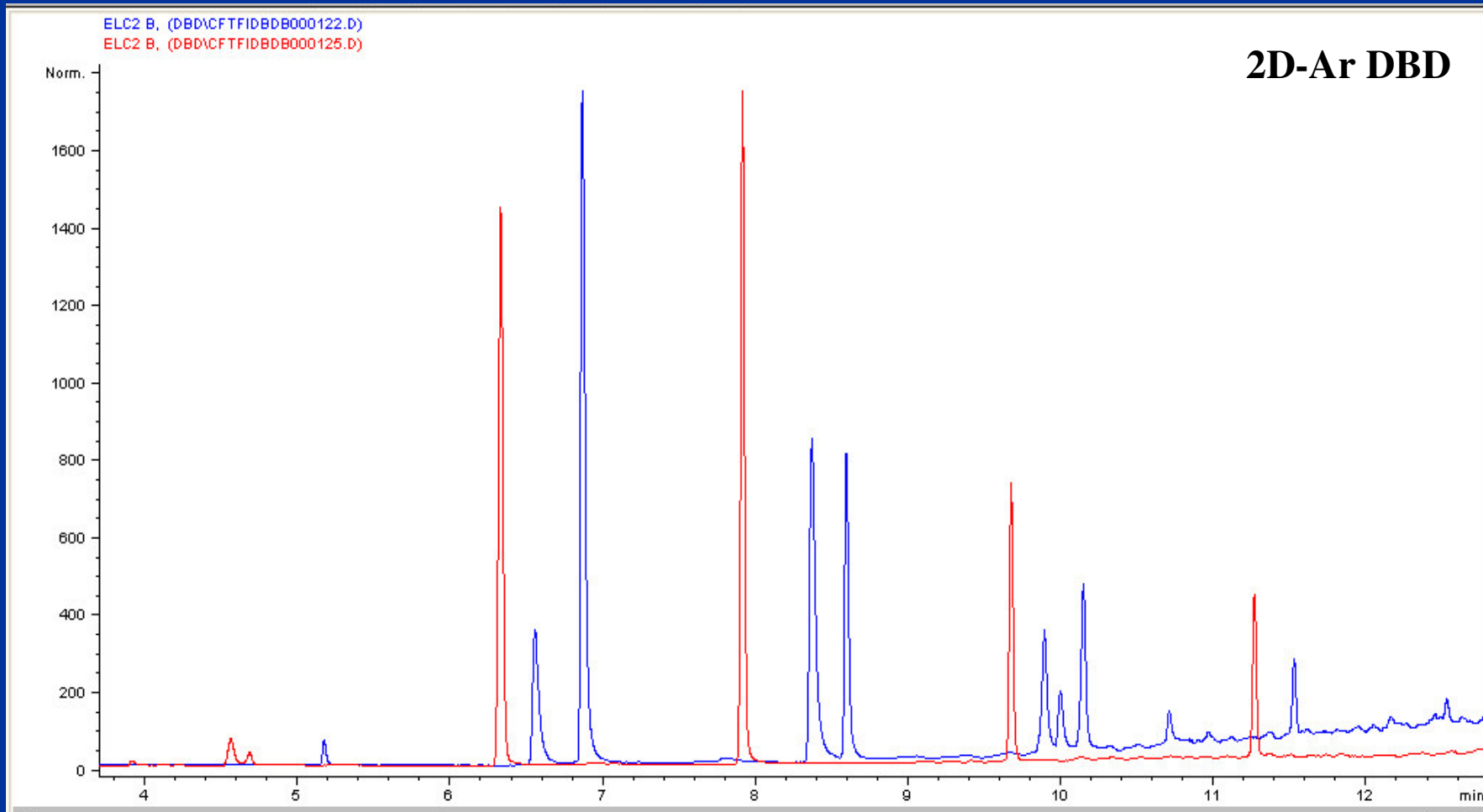
# MDGC/CFT/FID/Ar-DBD

1D – Polyethylene glycol (FID), 2D – Divinyl benzene (DBD)



# MDGC/CFT/FID/Ar-DBD

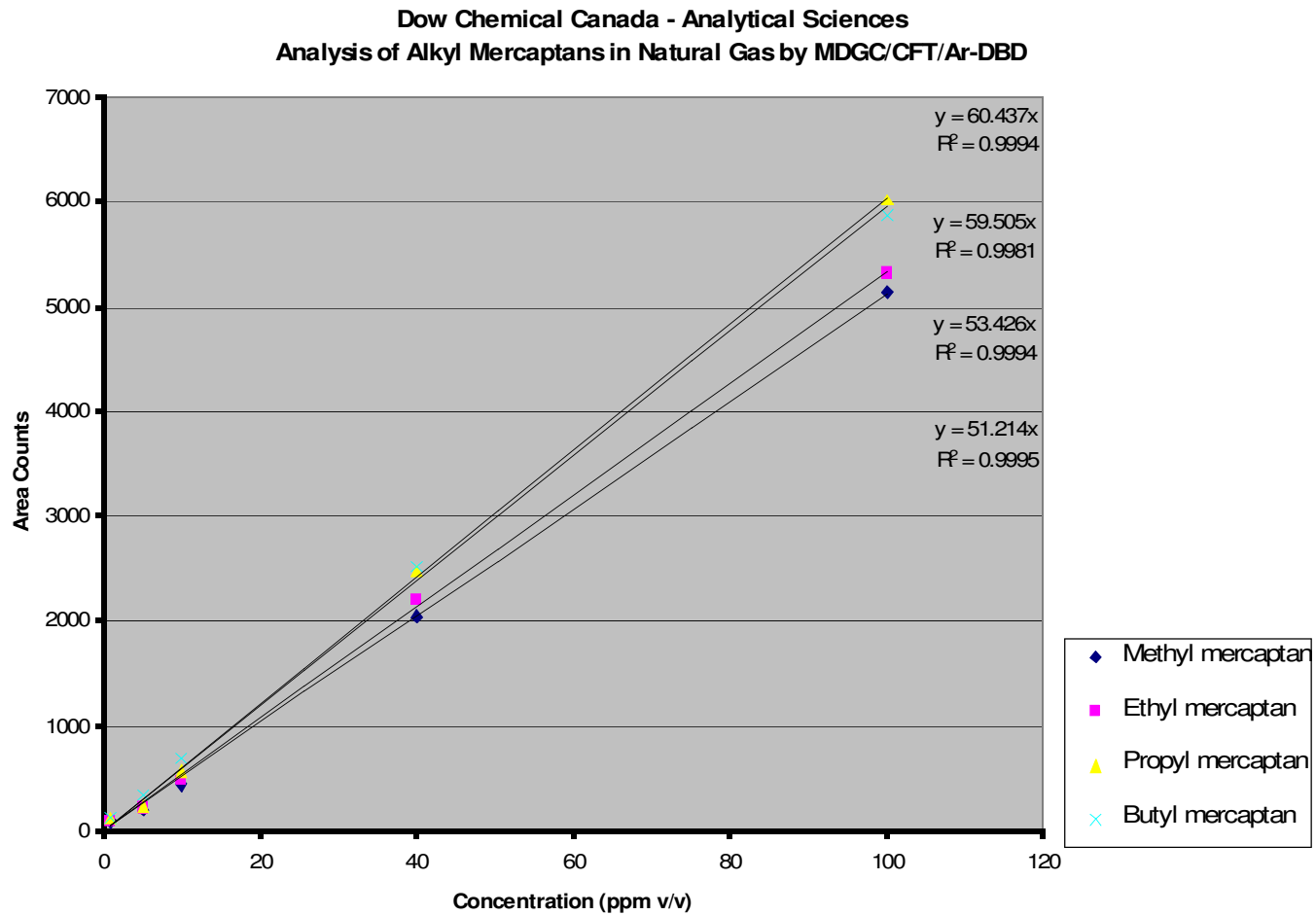
1D – Polyethylene glycol (FID), 2D – Divinyl benzene (DBD)



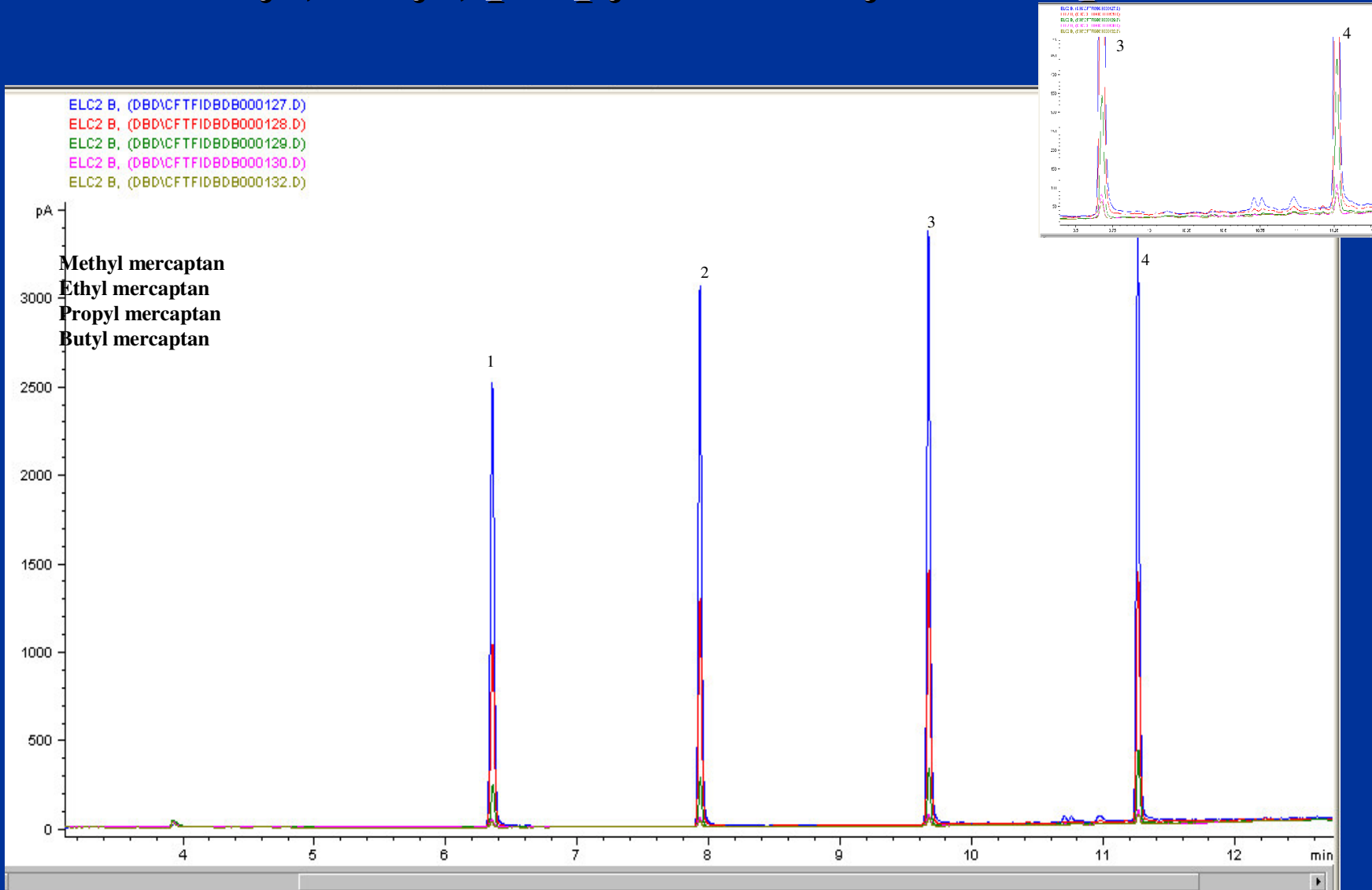
Red trace: Standard on 2D

Blue trace: Natural Gas on 2D

# Figure of Merit

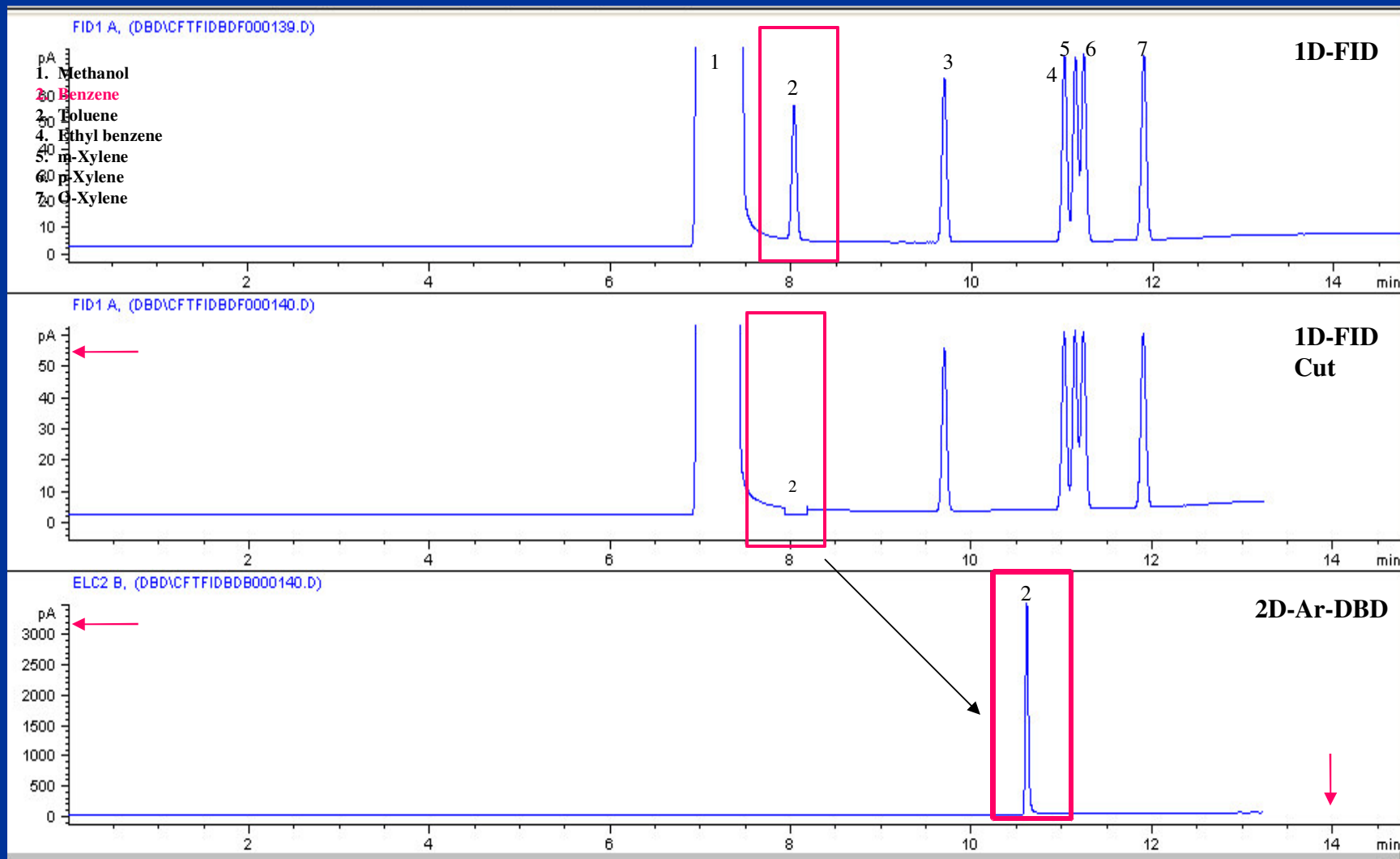


# 100, 40, 10, 1, 0.7 ppm (v/v) each of methyl, ethyl, propyl and butyl mercaptans



# Multi-dimensional Gas Chromatography

## Dual Retention Table & Dual Selectivity



# Observations & Constraints

- DBD shows minimal electrode wear even after two years
- Generally low reactivity: H<sub>2</sub>S, methanol, AA, EO and formaldehyde have excellent peak symmetry
- High level analytes or matrix tend to tail on MiniDBD
- Care must be taken in helium mode to minimize impurities in gas system
- Argon mode offers improved selectivity and sensitivity with low reaction gas flow rate (less than 10 mL/min)
- Using Agilent's capillary flow technology Deans Switch Configuration, first and second dimension shared the same oven

# Conclusions

- DBD Detectors are a new commercially available gas phase detector which utilize a robust plasma for analyte ionization
- DBD addressed unmet and unarticulated needs such as analysis of ultra trace fixed gases, water, carbon monoxide, carbon dioxide.
- DBD in argon mode provides improved selectivity and sensitivity for some solutes
- Low cost to operate and easy to service – ideal for areas where technical support and service can be a challenge
- Ideal complementary tuneable selective detector for use with conventional multi-dimensional gas chromatography

# Acknowledgements

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