Gas Chromatographic Applications of the Dielectric Barrier Discharge Detector

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Outline

Challenges facing gas chromatography

Operating principle of Dielectric Barrier Discharge detector

Applications

Observations

Conclusions

Acknowledgements

Despite significant advances in GC since James and Martin, challenges remain:

Sampling discrimination

Challenging separations

Analysis speed

Sensitivity

Cost/Ease of use

Continued development work underway

Some new tools now available to address challenges:

Sample introduction: PTV, LVI, PLIS

Separations: new phases, high speed GC, multi-dimensional GC

Detection schemes: Not the “steady state”* once thought to be... DBD detectors offer one means of solving these challenges

***Chromatographic Detectors: Design, Function, and Operation, ed. Scott, R.P.W., Marcel Dekker, 1996, p 172**

DBD detectors can address:

Separations challenges

- Selectivity available in argon mode

Sensitivity

- Sensitive detector can eliminate pre-concentration for some applications
- High sensitivity to fixed gases

Cost

- Very low gas consumption/low wear on electrodes
- High sensitivity can mean less matrix on column/longer lifespan
- Low initial cost

Ease of Use

- Flame-less
- Low Maintenance/field repairable

Principle of Operation

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 Modified FID electrometers

- Collected electrons converted to signal

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

Chromatographic Conditions

GC 1: Agilent 6890N

Injection valve to Split/splitless injector, manual pressure control, split/splitless injector, FID, ¾ DBD, Detector at 250C

GC 2: Agilent 6890A

Injection valve to Split/splitless injector, manual pressure controlSplit/splitless injector, FID, Mini DBD, Detector at 250C

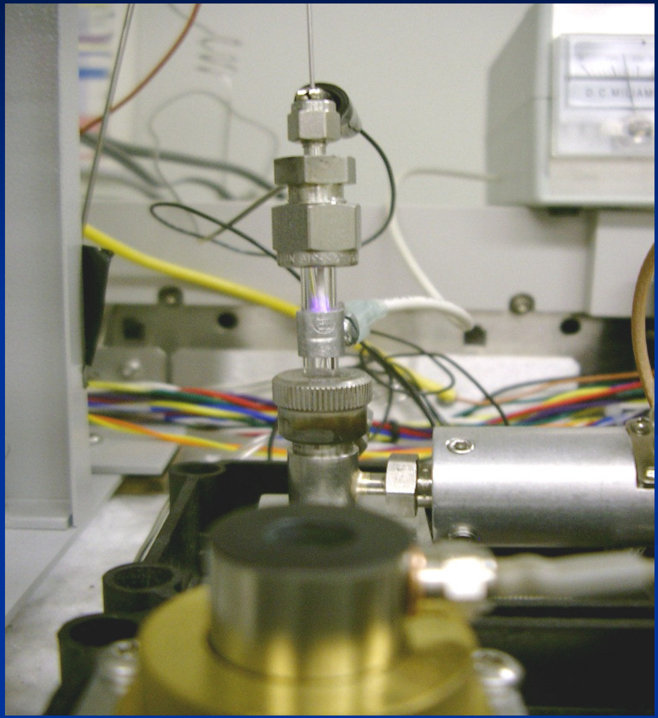
RVM LTMGC shared between GC's for several applications

Chromatographic Conditions/Columns given with each application

Agilent 6890 with ¾ DBD

Mini DBD

Uninstalled View

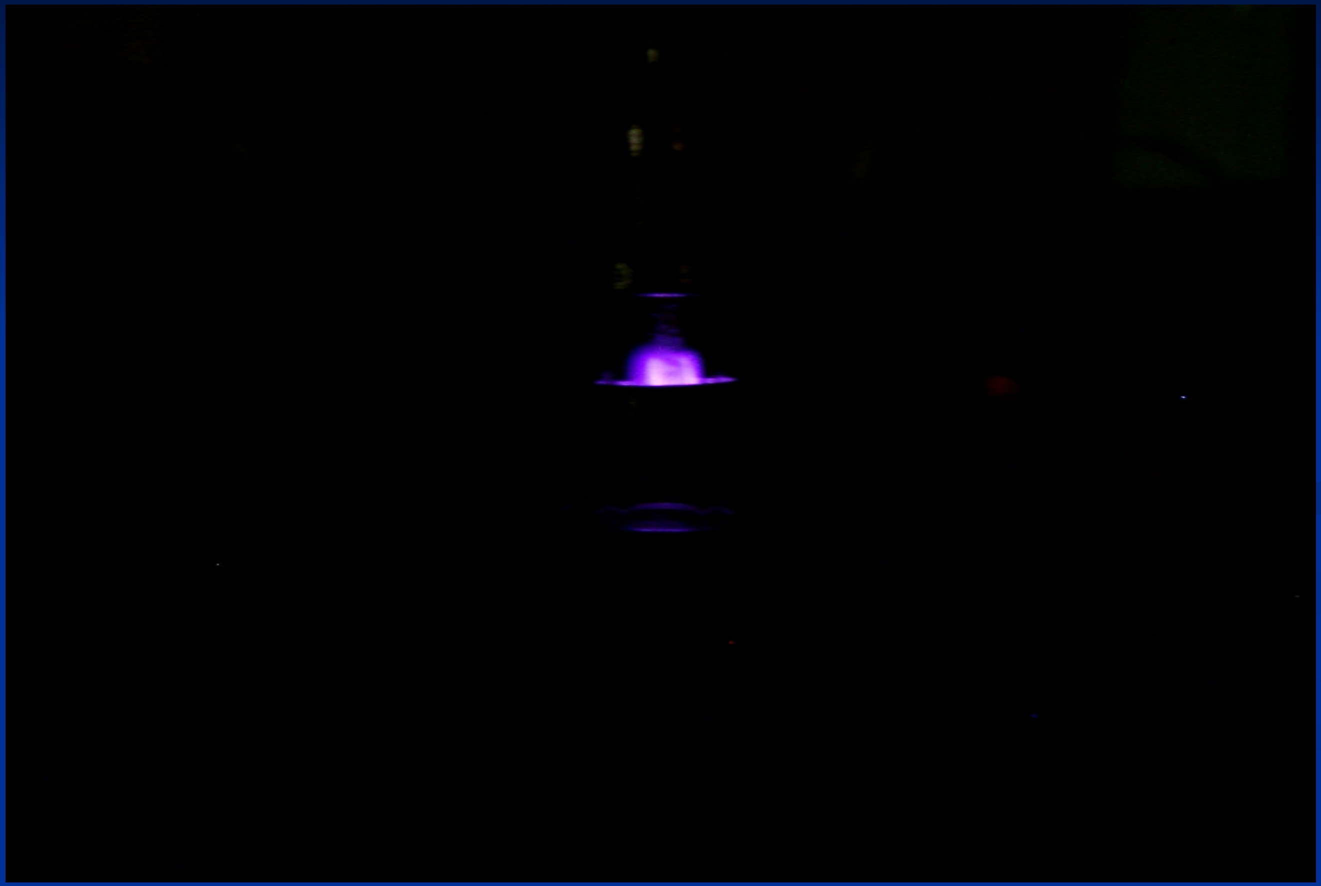


Installed on 6890

DBD Plasma in Argon Mode

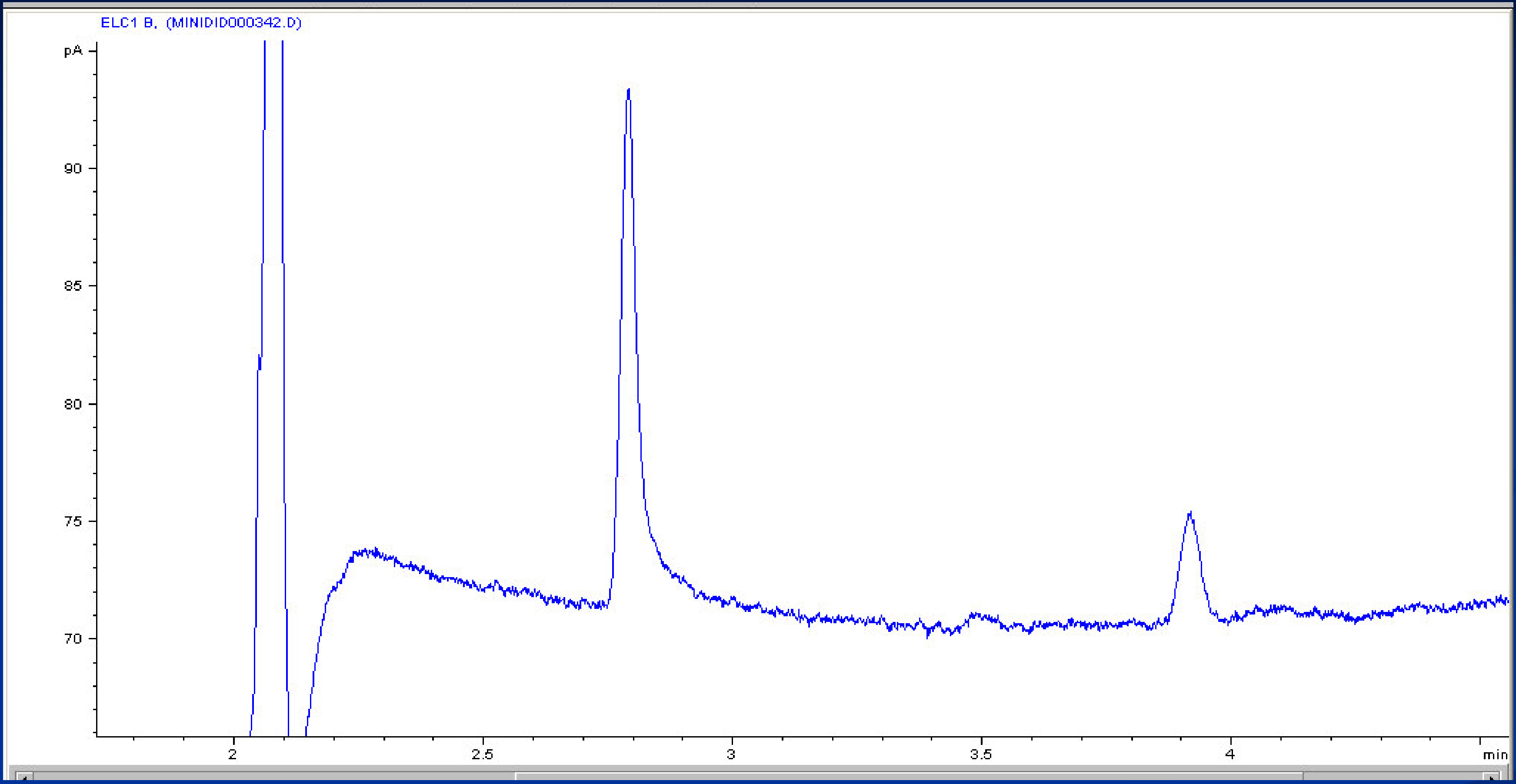
Note almost white appearance of plasma in Argon Mode

DBD Plasma in HeliumMode



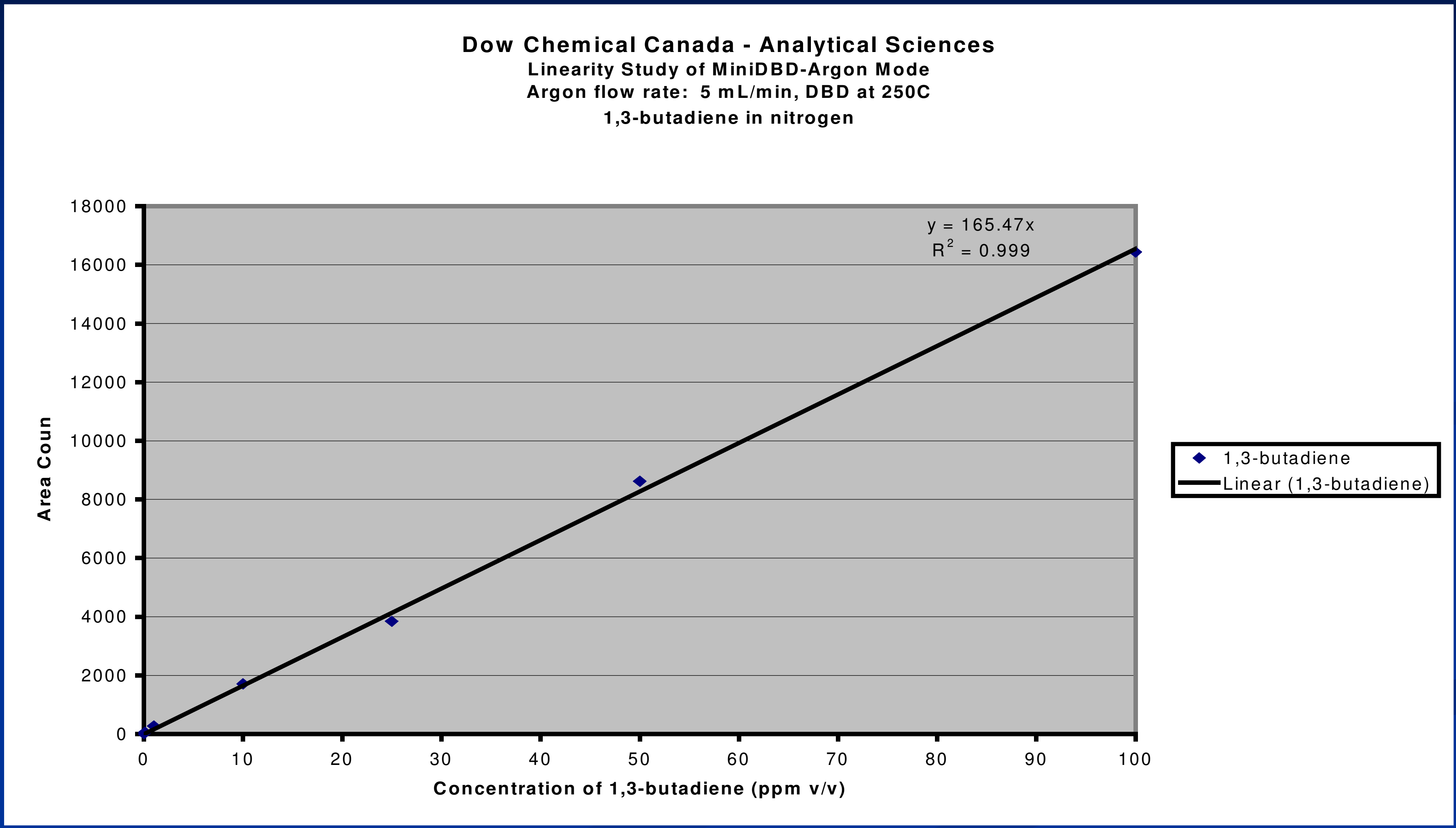
Note more red appearance of plasma in Helium Mode (gettered)

1,3-Butadiene (RT = 3.9 min) in Air, 10 ppb Split 10:1

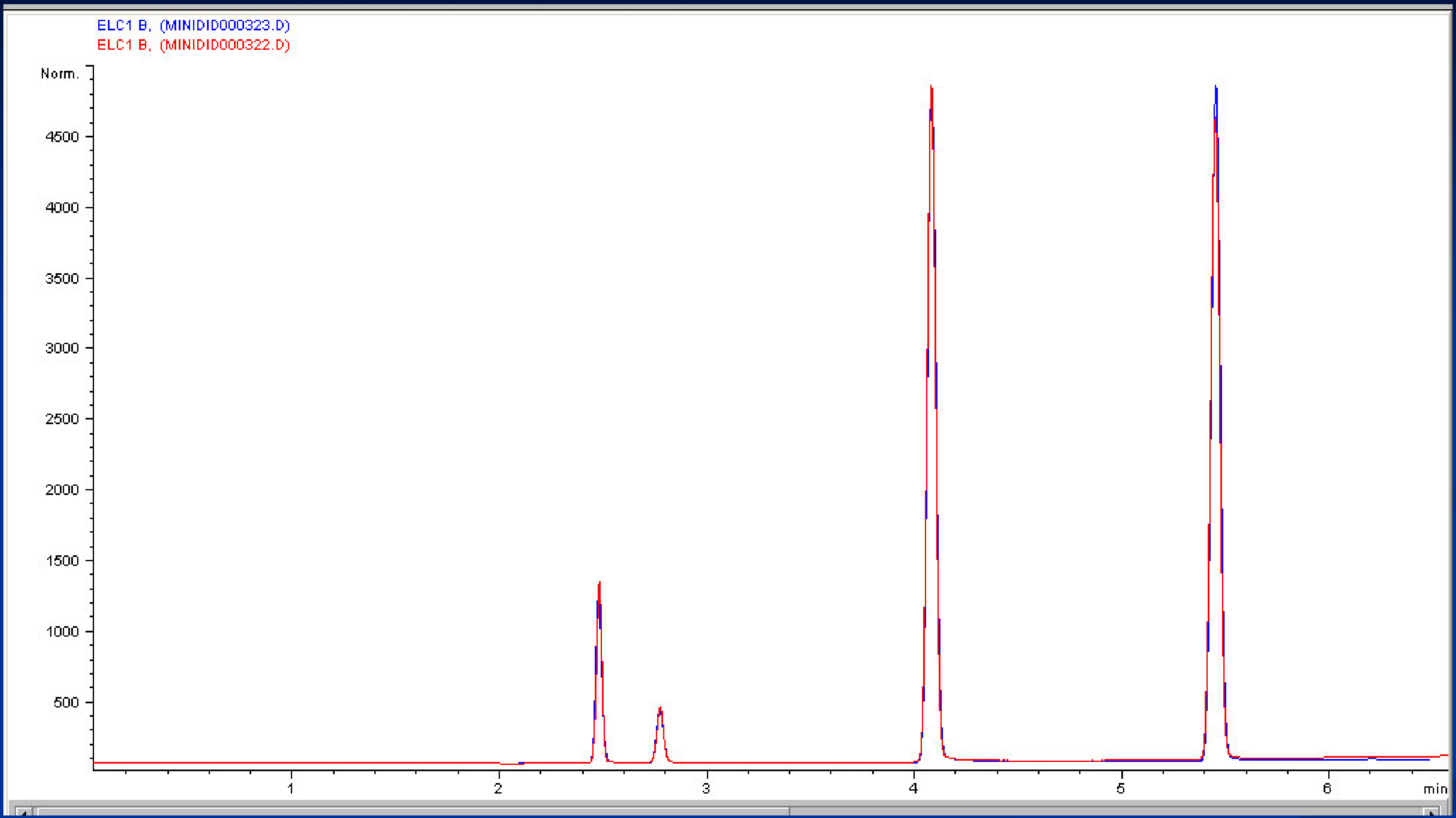


Argon mode: 60 meter, 50micron CP-Volamine, 40C/2min/25C per min/250C, 1 mL inj

1,3-Butadiene linearity

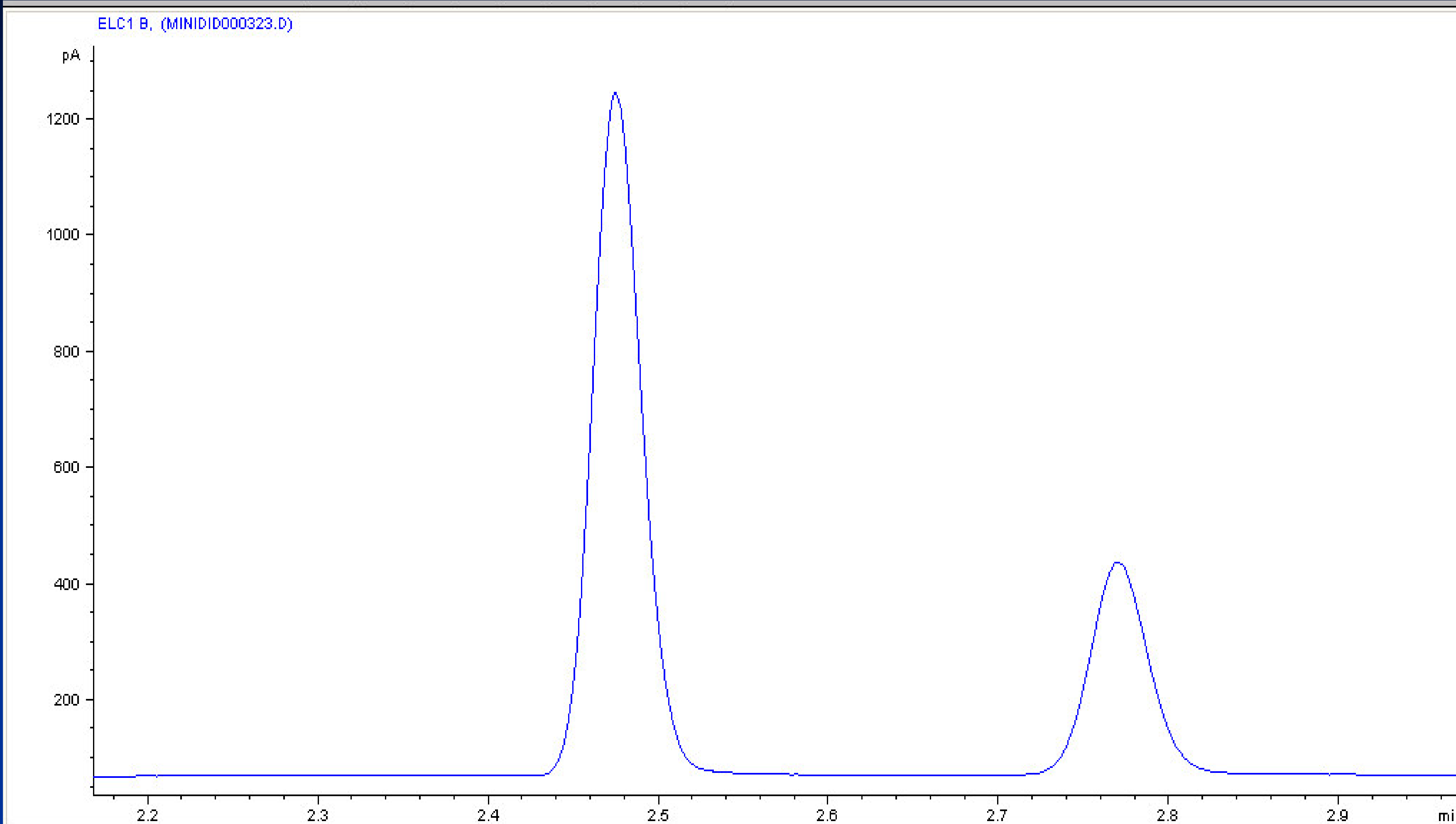


Sulfur compounds, 100 ppm each, split 10:1



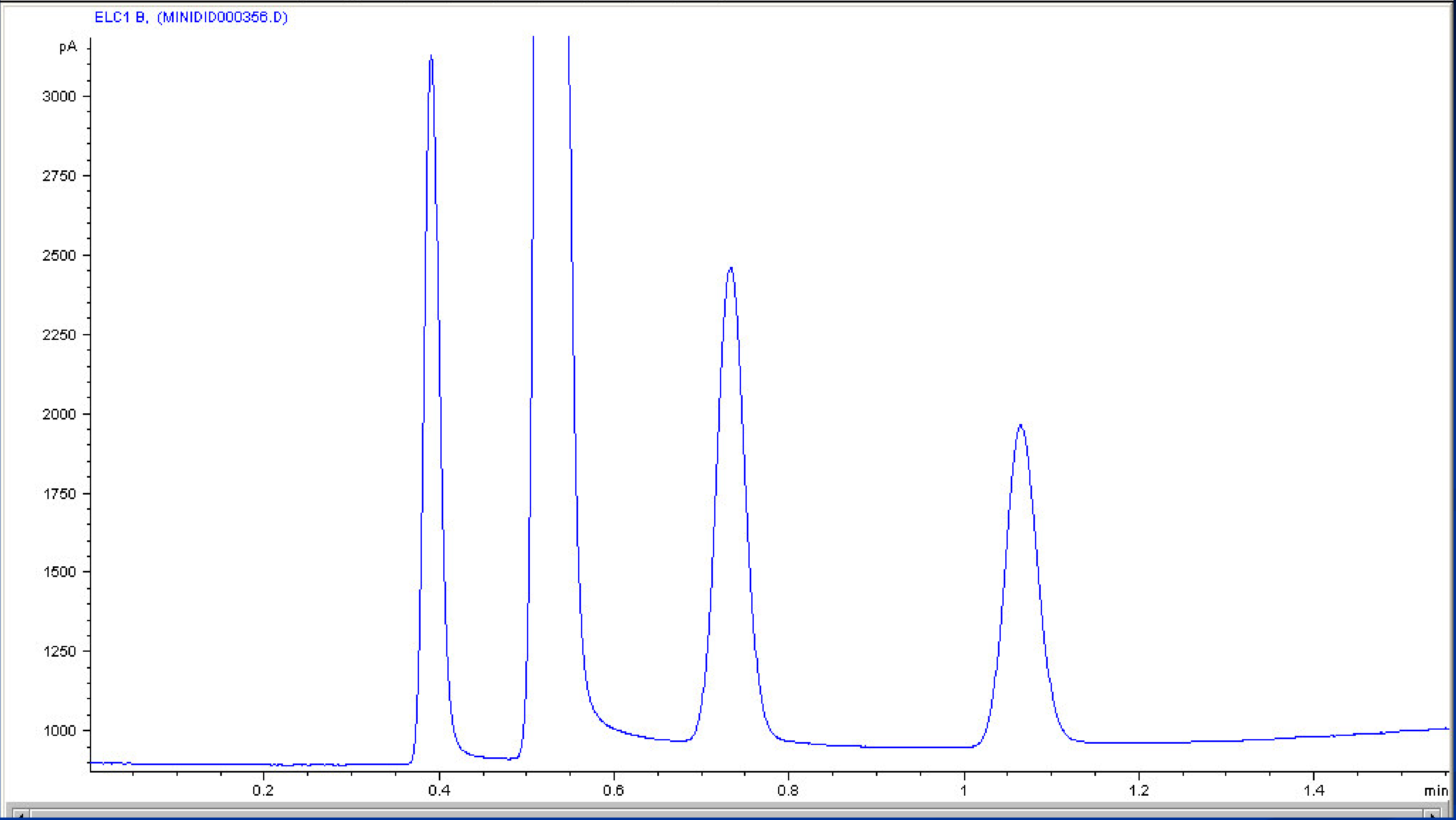
Argon mode: 60 meter, 50micron CP-Volamine, 40C/2min/25C per min/250C, 1 mL inj; H_2S, COS, Methyl Mercaptan, Ethyl Mercaptan

H2S/COS expanded view



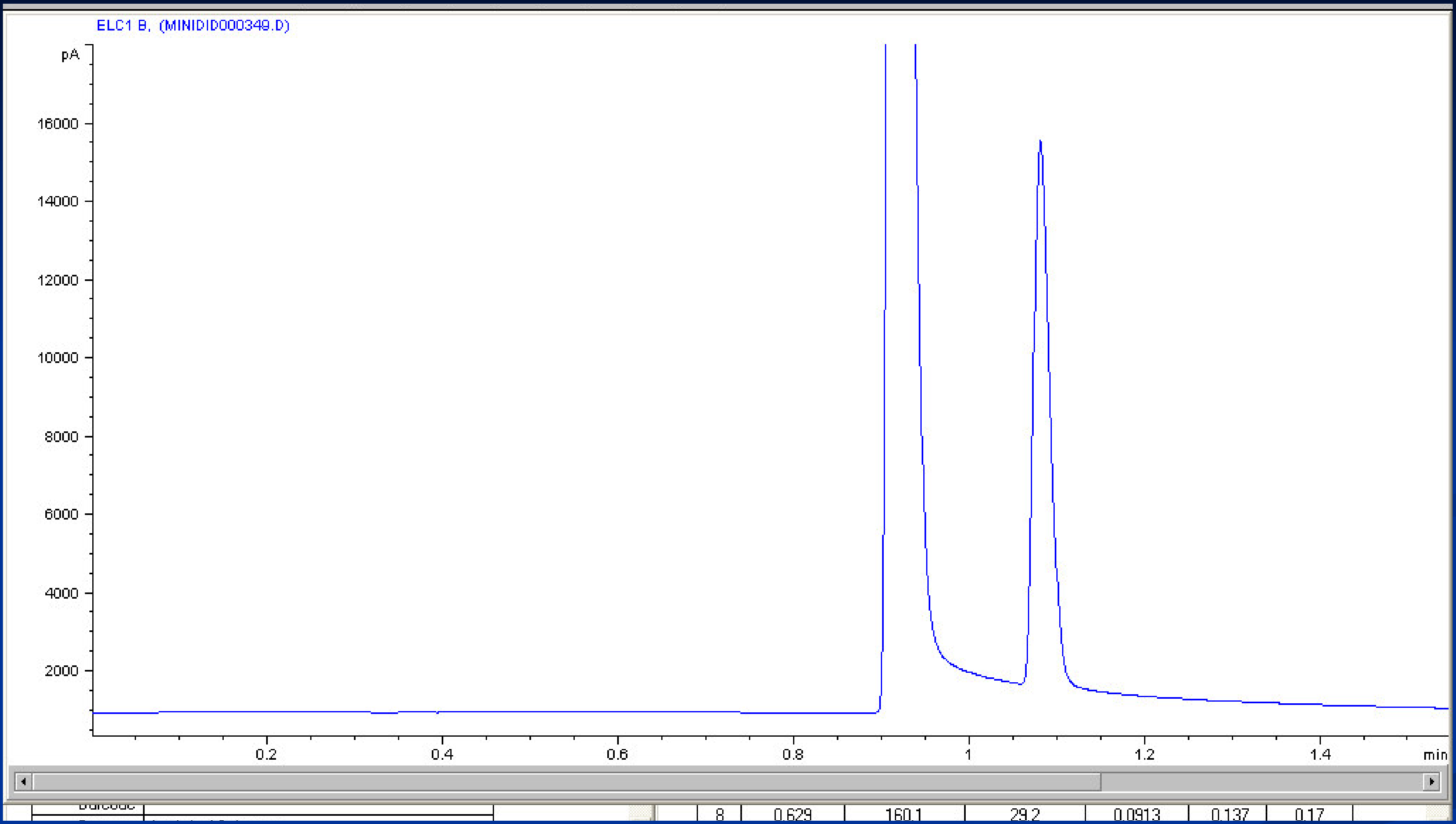
Argon mode: Note excellent peak shape for sulfur compounds, especially H2S

Fixed Gases, split 10:1



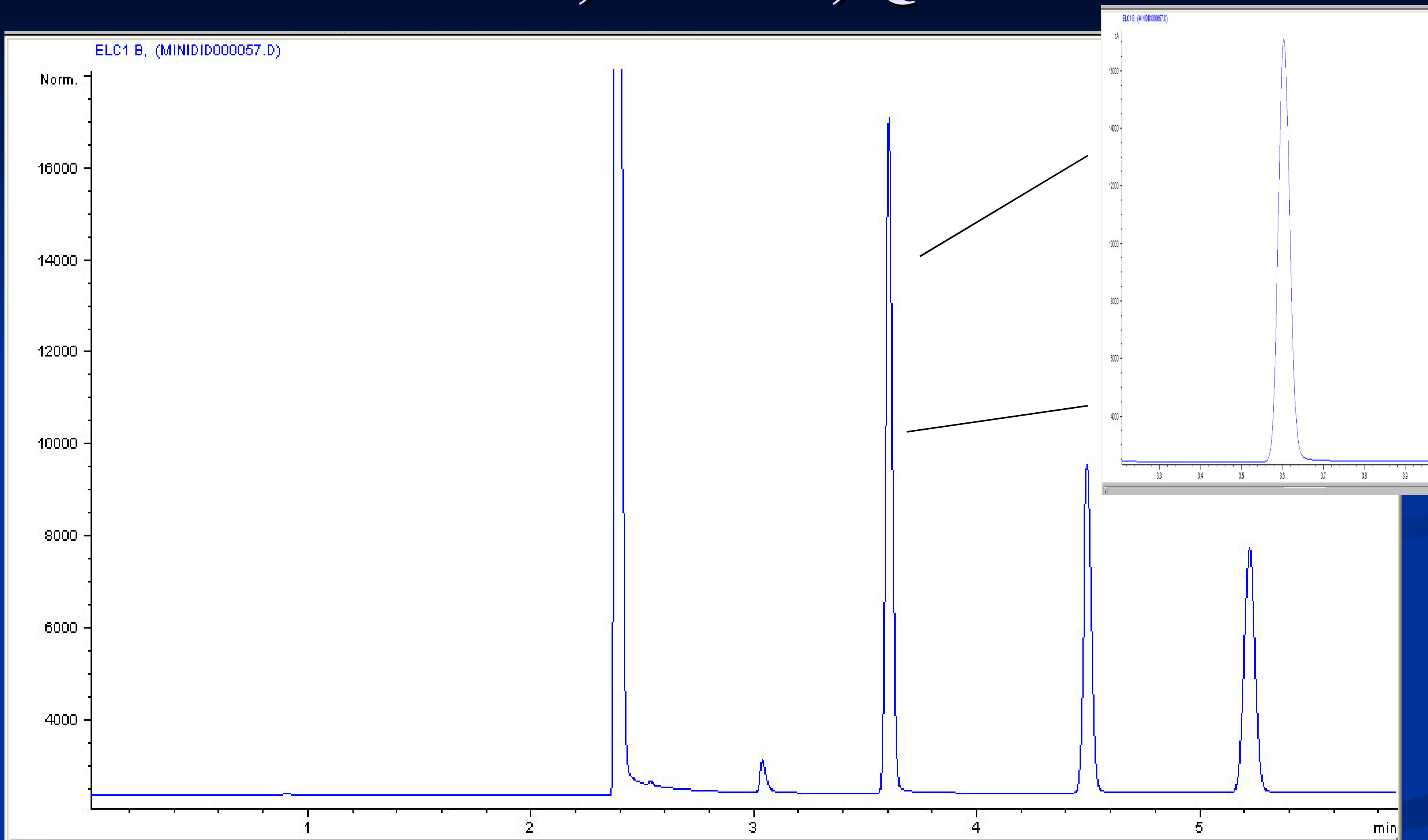
Helium mode: 1 meter, CP-MS 5A, 50C/0.5min/50C per min/100C, 0.1 mL inj; Oxygen (70ppm), Nitrogen (500 ppm), CO2 (40 ppm), CO (70ppm)

CO2 in Nitrogen



Helium mode: 500 ppm, 10:1 split, 0.1 mL inj;
Demonstrates ability to eliminate methanizer.

Alcohols, Helium, Qualitative



Helium mode: 60 meter, CP-Volamine, 50C/1min/15C per min/100C/ 5min;
Air, water, methanol, ethanol, isopropanol

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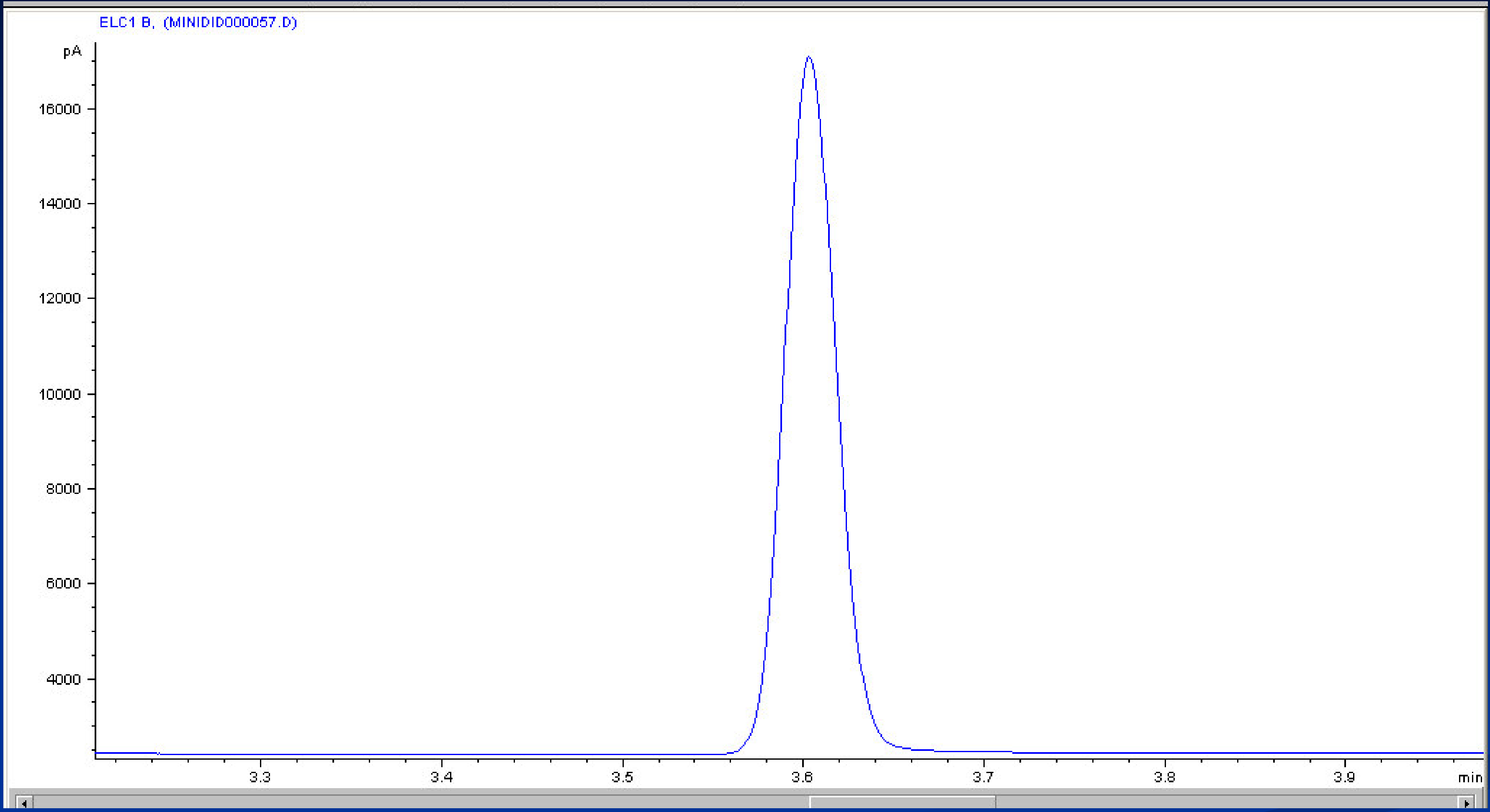
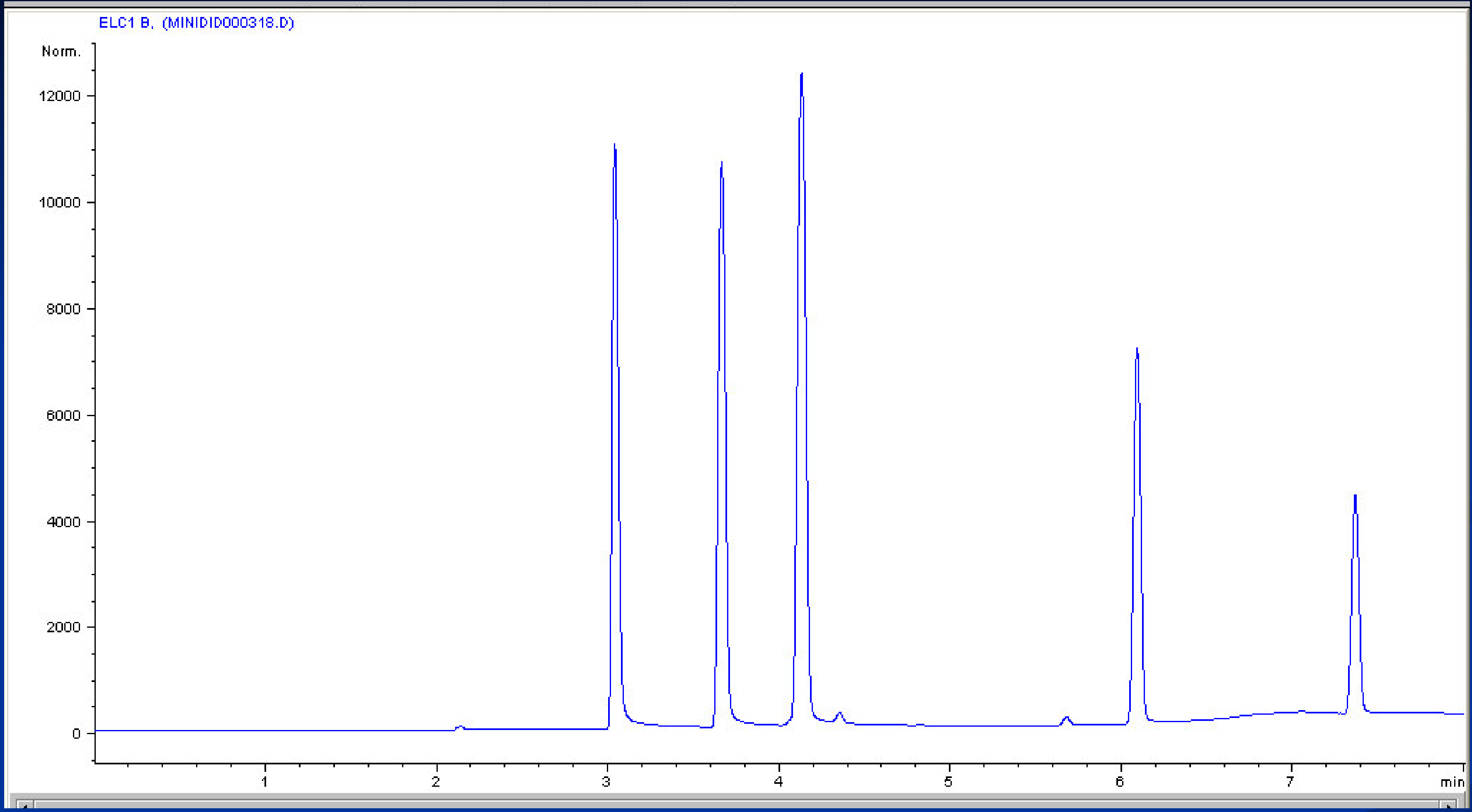
Methanol, Helium, Expanded View



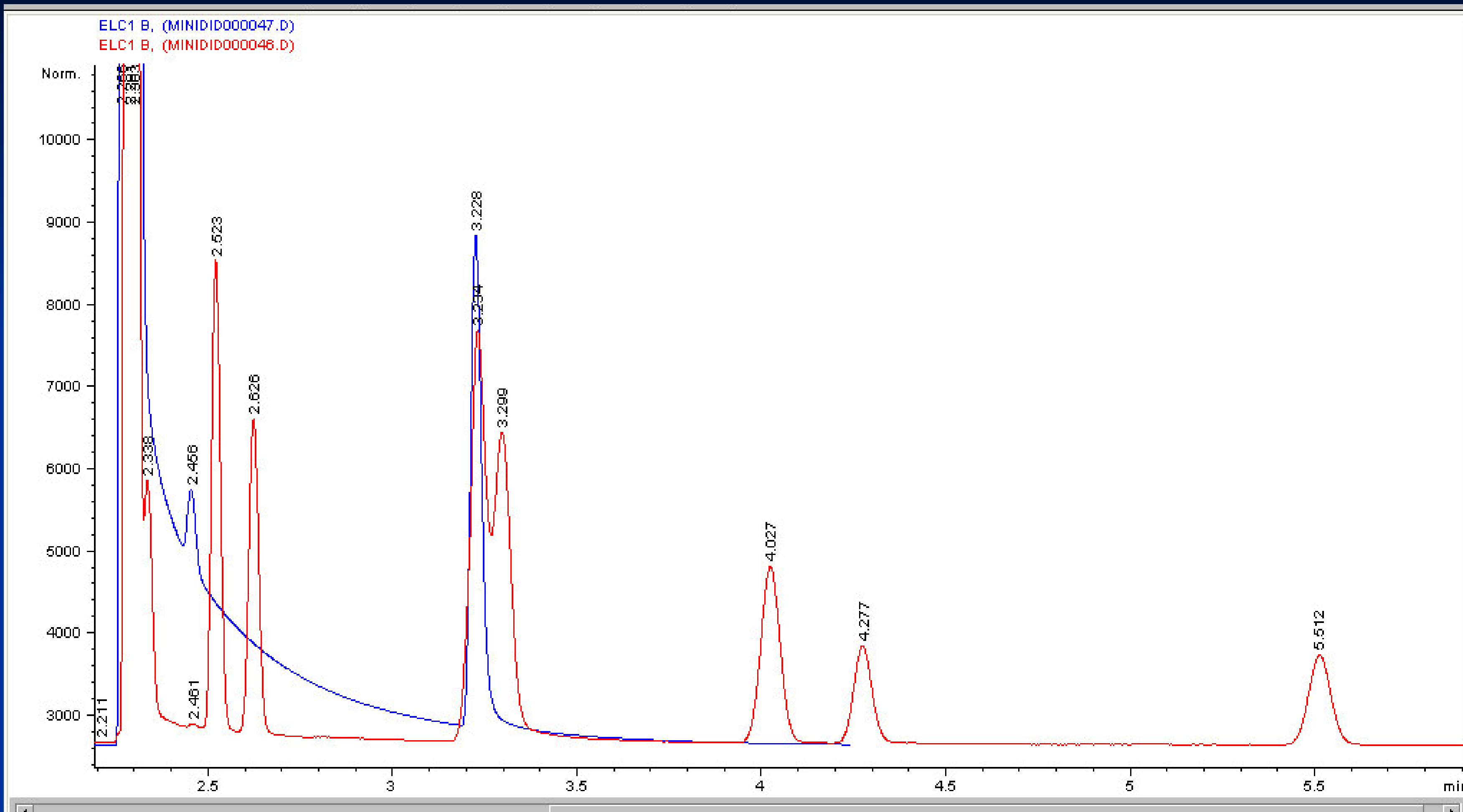
Helium mode: Note Gaussian peak shape

Alcohols, Argon, 10 ppm, split 10:1



Helium mode: 60 meter, CP-Volamine, 40C/2min/25C per min/250C, 1 mL inj; Methanol, ethanol, propanol, (I,I), butanol, pentanol. Note minimal baseline disturbance with oven programming. Note, as expected, minimal air disturbance.

C1-C3 Hydrocarbons split 10:1



Helium mode: 60 meter, CP-Volamine 5 micron film, 40C Isothermal, 1mL inj;

C_1-C_3 Hydrocarbons in Helium Mode

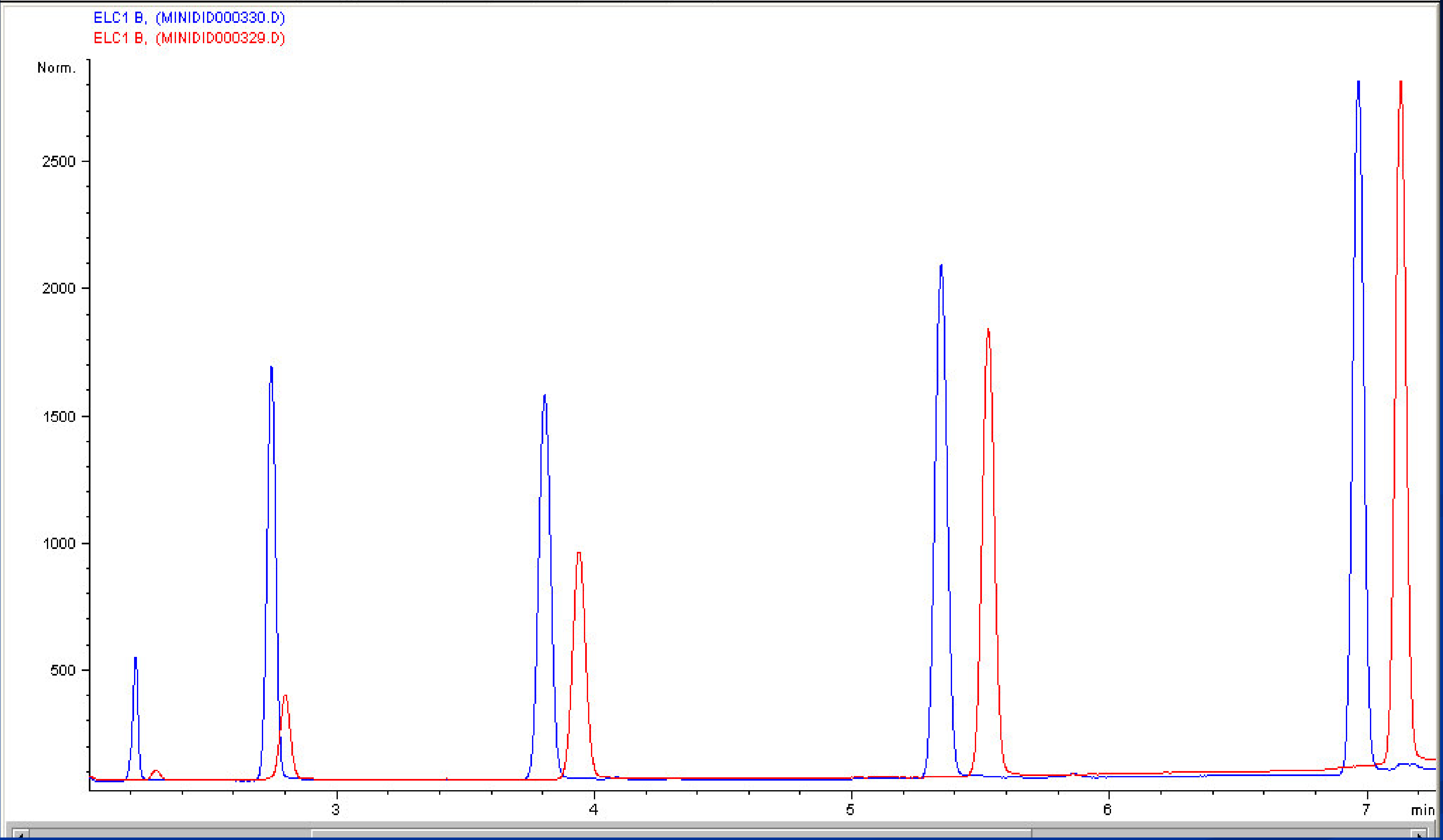
Components

- Air/Methane
- Ethylene/Acetylene
- Ethane
- Propylene/Water
- Propane
- Cyclopropane
- Acetaldehyde
- Ethylene Oxide

Note peak shape for AA and EO

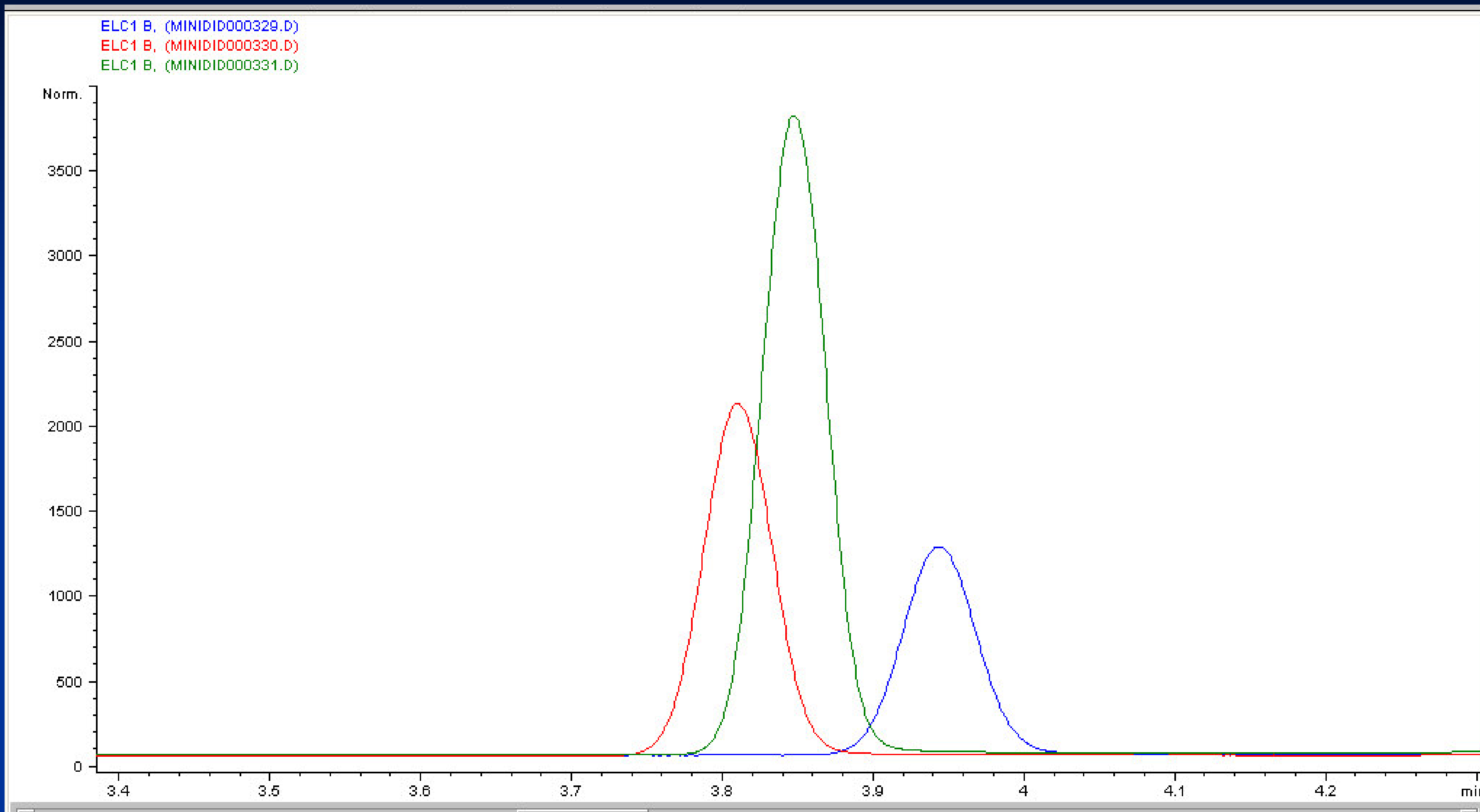
Note that water can be a co-eluting interference and separations must take this component into account in helium mode (not an issue in argon mode.)

C_2-C_6 Hyrdrocarbons: Alkanes, Alkenes, 10:1



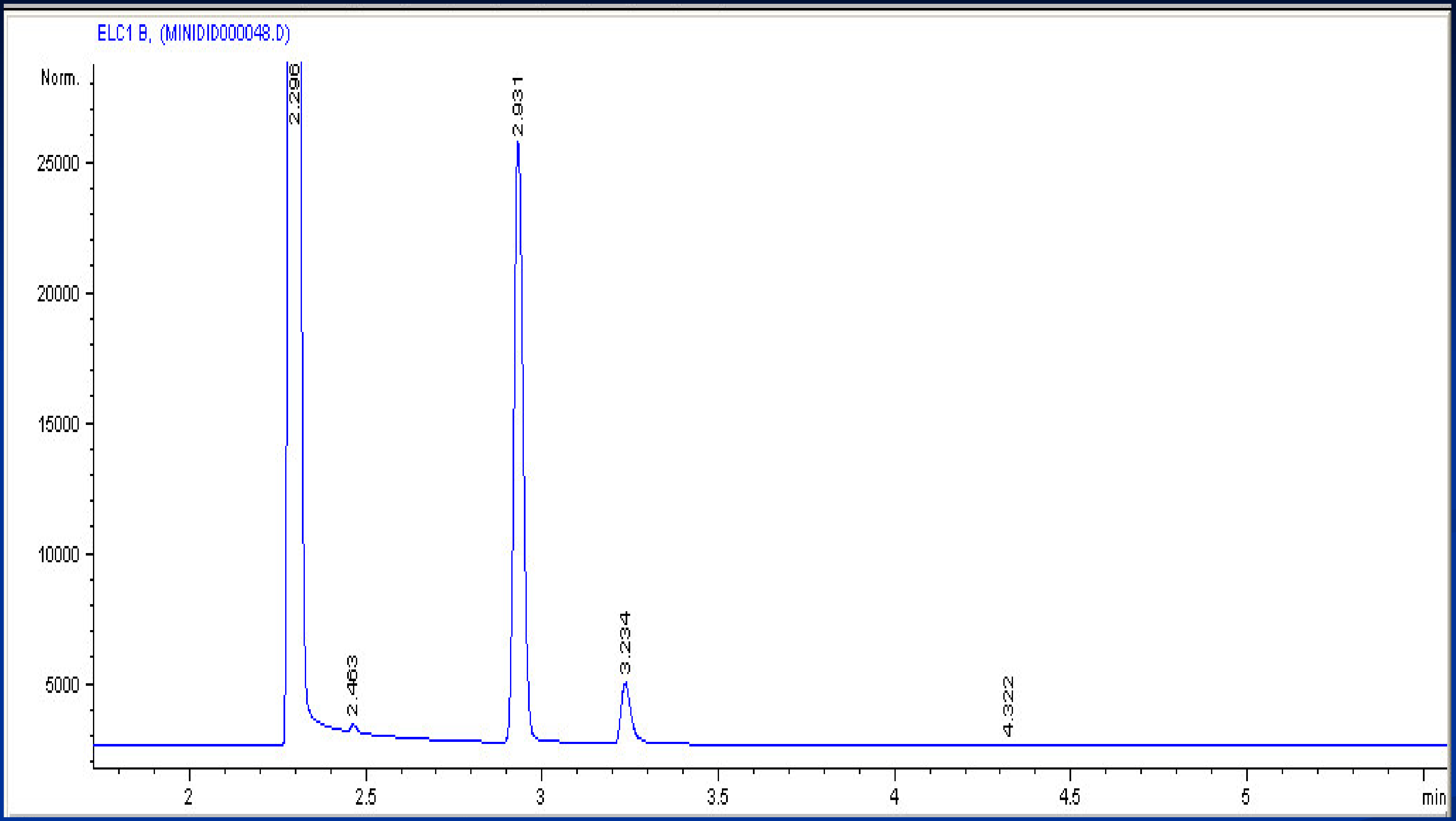
Argon mode: 60 meter, CP-Volamine 5 micron film, 40C Isothermal, 1mL inj;
Note suppressed response of C2; note reduction of alkene effect with increasing carbon #

C4: Alkane, Alkene, Diene; 100 ppm each



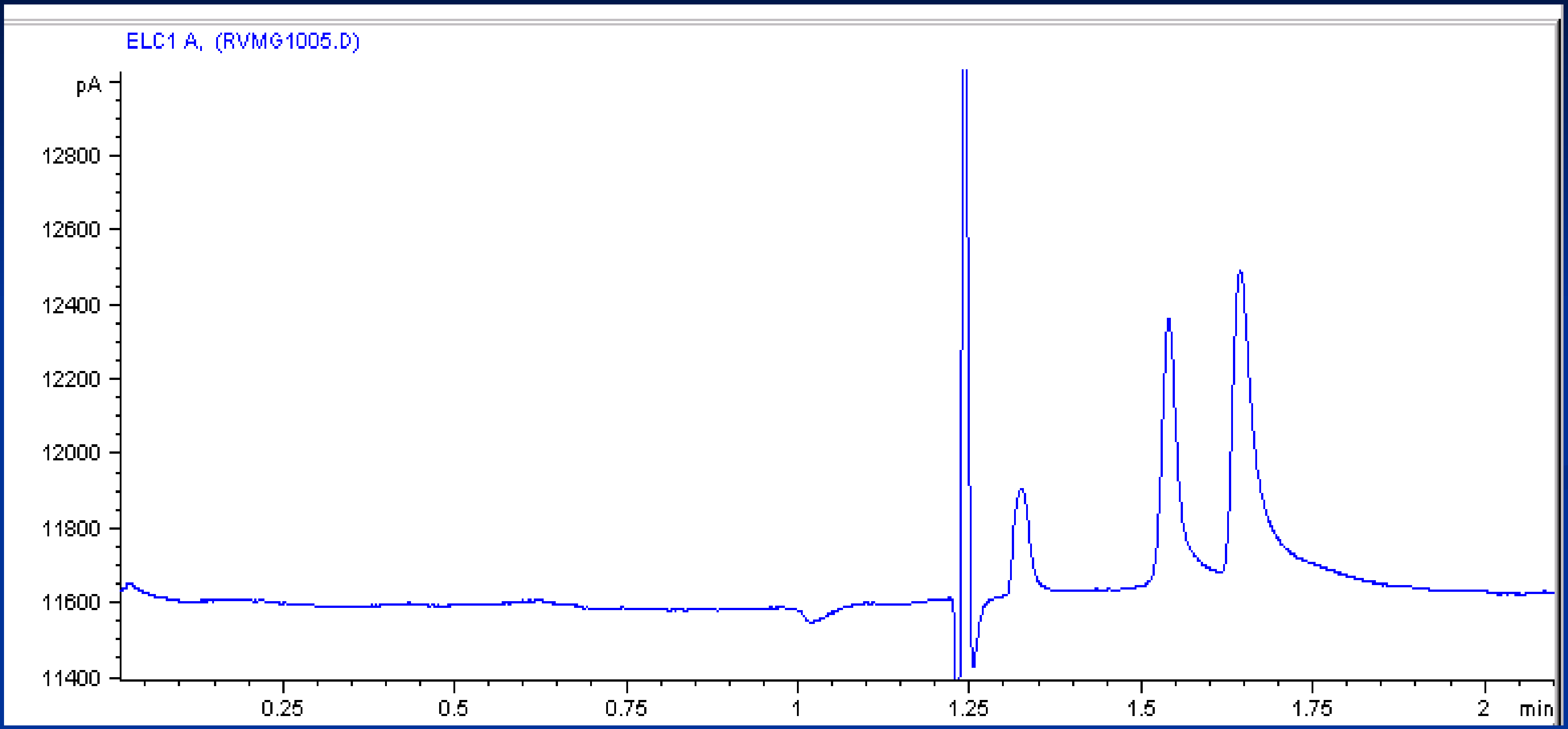
Argon mode: 60 meter, CP-Volamine 5 micron film, 40C/2min/25C /250, 1mL inj; Butene, Butadiene, Butane; diene ~2X over butene and ~ 7X over butane

Formaldehyde, qualitative



Helium mode: 60 meter, CP-Volamine 5 micron film, 40C/2min/25C /250, 1mL inj; Air, CO2, Formaldehyde, Water

Arsine (R.T.=1.6 min) , 960 ppb diluted in helium



Helium mode: 50 meter, CP-Sil8 5 micron film, 45C/2min/s5C per min/250C; 0.25mL inj; Nitrogen/helium, (I), Arsine, Water

Able to recover quickly from cylinder change over
Slide from other set

Observations: Detector characteristics

Sensitive, universal detector operating in helium mode

Sensitive, selective detector operating in argon mode

Very low gas consumption, especially in argon mode

Stable in day-to-day operations in both helium and argon modes

Consistent and reliable plasma ignition (aided by increased temperature in argon mode)

Observations: Continued

- Minimal electrode wear even after two years
- Care must be taken in helium mode to minimize impurities in gas system
- Dow has developed procedure for changing out helium cylinders which minimizes down time.
- Generally low reactivity: H_2S, methanol, AA, EO and formaldehyde have excellent peak shape
- High level analytes or matrix tend to tail on Mini; work underway to identify causes of this effect
- Spurious signal with very high helium reaction flows (>200mL/min)

Conclusions

DBD Detectors are a new commercial detector which utilize a robust plasma for analyte ionization.

DBD detectors demonstrate excellent sensitivity for components such as 1,3-butadiene and fixed gases.

DBD detectors are able to easily switch between argon and helium modes

DBD detectors, operating in argon or helium mode, are applicable to a wide range of challenging applications.

Acknowledgements

Dow Chemical Separations Leadership Team

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Vicki Carter, Analytical Sciences

Bill Winniford, Dow Chemical Company

In Memorium

AIC Corporation would like to acknowledge the work of the late Professor Dr. Wayne Wentworth. His work, ranging from the Wentworth equation for linearization to microwave plasma based detectors and, finally, his work with the pulsed discharge detector has been thoroughly studied and appreciated.