Innovations in High Pressure Liquid Injection Technique for Gas Chromatography

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Outline

- Requirements of sample introduction systems
- Liquid sample systems
- Pressurized Liquid Injection System *(PLIS)*
- Performance and applications
- Conclusions
- Future plans
- Acknowledgements

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Requirements of sample introduction system

- **The sample introduction process should not depend upon column operating temperature**
- **Thermal degradation, adsorption, rearrangements or other solute reactions should be negligible**
- **The sample system should not effect column efficiency – input band critical**

Liquid Sample Introduction Systems

- **Introduction of semi-volatile liquid in GC via ALS**
- **Introduction of volatile liquid in GC via valve or vapourizer**
  - **Rotary valve (Valco Vici, Rheodyne)**
  - **Diaphragm valve (Valco)**
  - **Slider valve (ABB, Applied automation)**
  - **Piston valve (M.A.T)**

Limitations of Sample introduction for volatile liquid

- **The main challenges:**
  - **Dissimilar boiling point solutes (high boiling point compounds in low boiling point matrices)**
    - **Examples:**
      - **Diesel in ethane**
      - **Pole oil in ethylene**
      - **TBC in butadiene**
      - **DEHA in butadiene**
      - **Alcohols in hydrocarbons feedstreams**
  - **Fractionation (vapourizer, rotary, diaphragm, slider valves)**
  - **Speed of injection too slow for fast gas chromatography**

Stem valve concept

- **Merits in injection technique**
  - **M.A.T**
  - **Siemens**
  - **Most recently, *PLIS* (transcendent)**

PLIS Design Criteria & Key Features

- **Fast injection speed**
- **High pressure of up to 1200 psig**
- **No fractionation**
- **Sample size from nL to 2 uL**
- **Heatable of up to 300 C (radiant with V1.0)**
- **Low dead volume**
- **Low maintenance and user-friendly**

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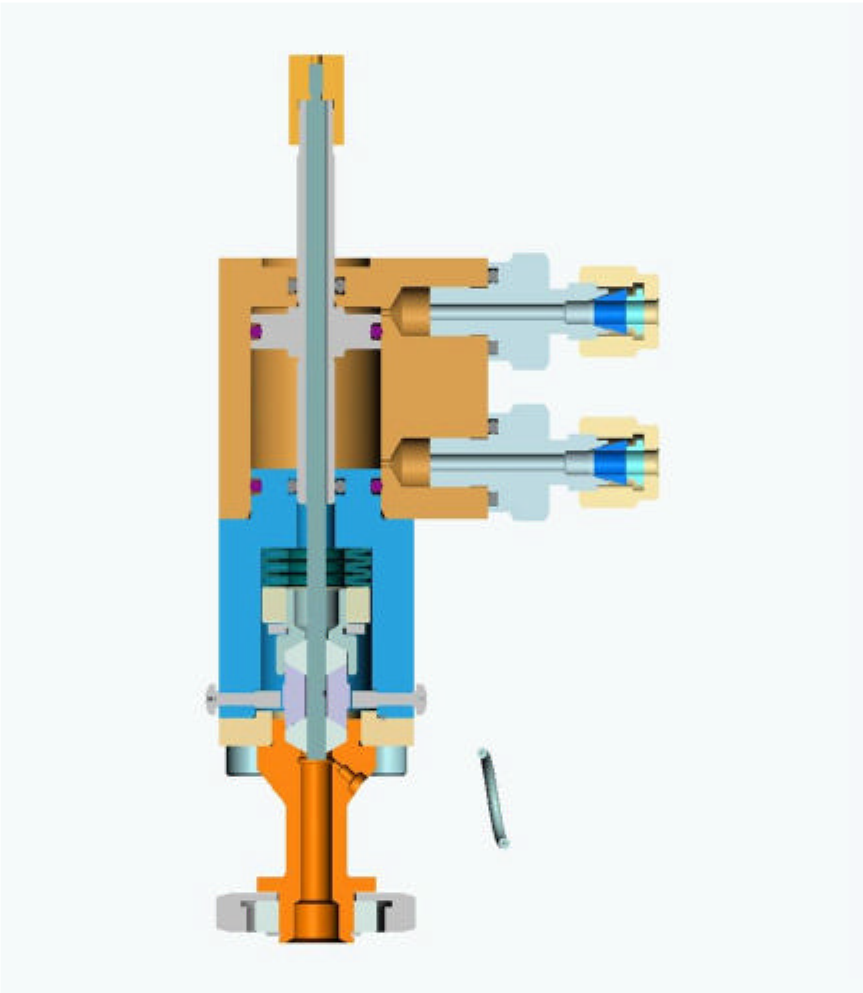
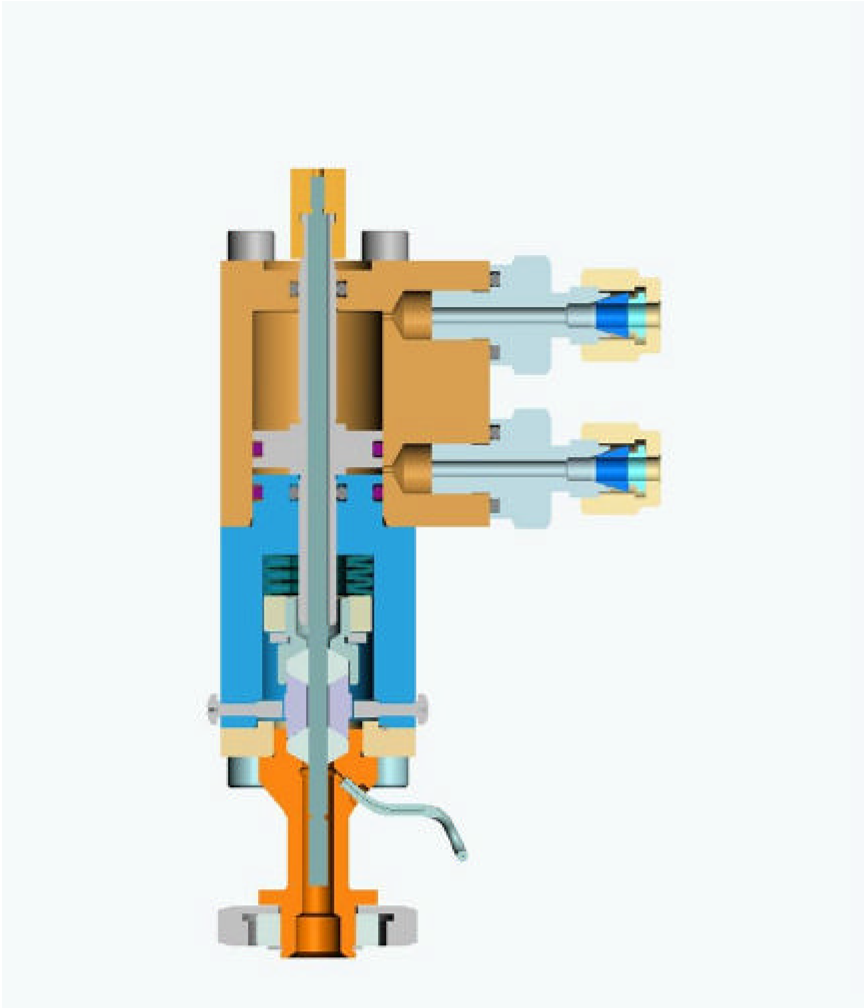
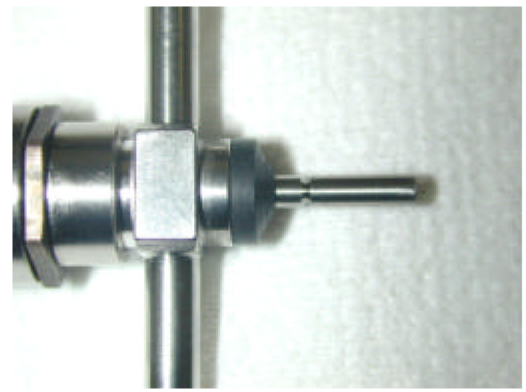
Pressurized Liquid Injection System *(PLIS)*





PLIS in Pieces



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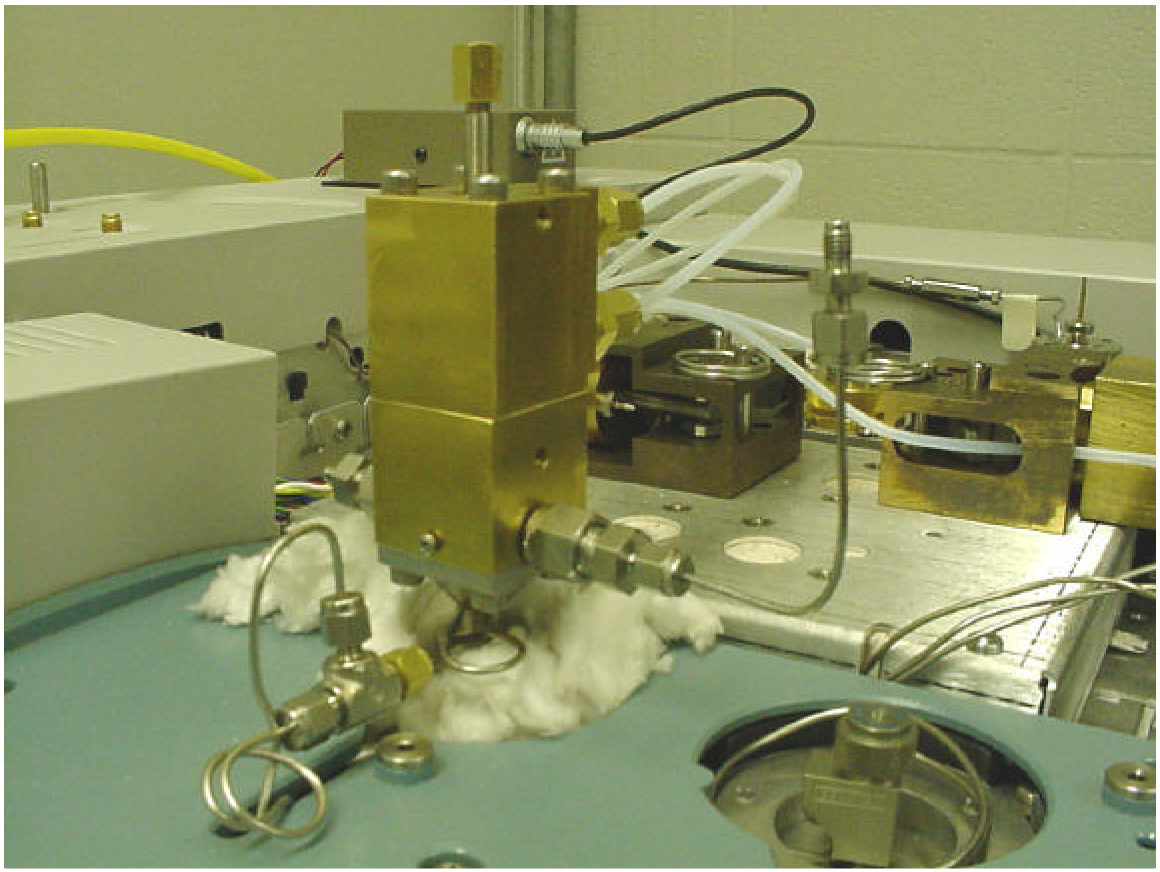
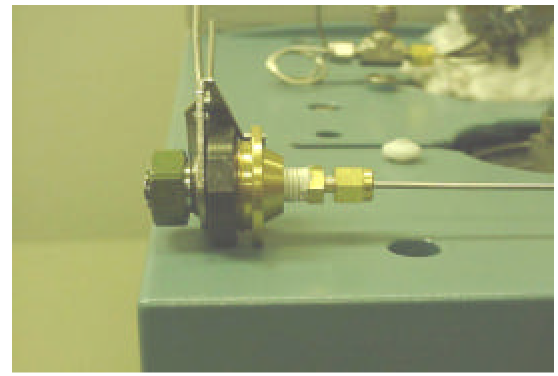
PLIS on Agilent HP-6890 GC
A Look At Interface





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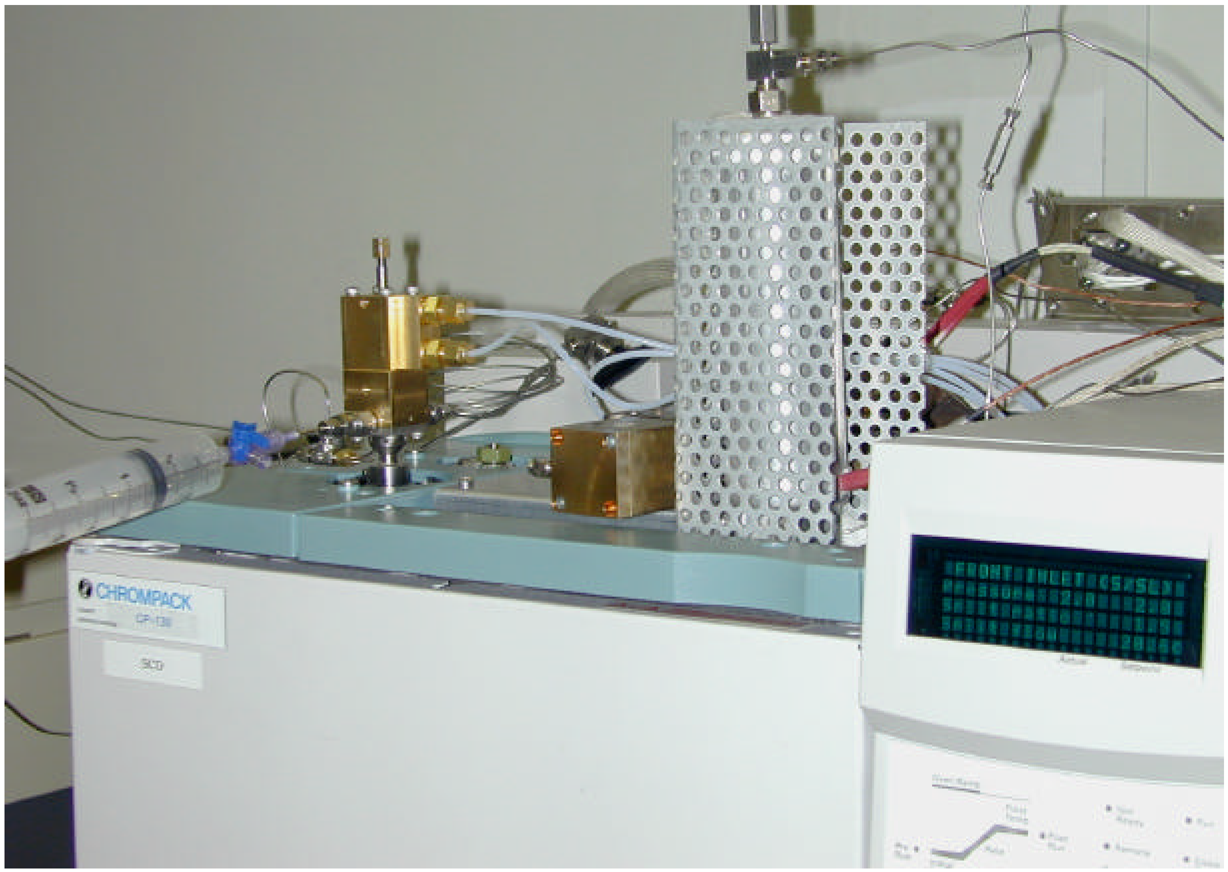
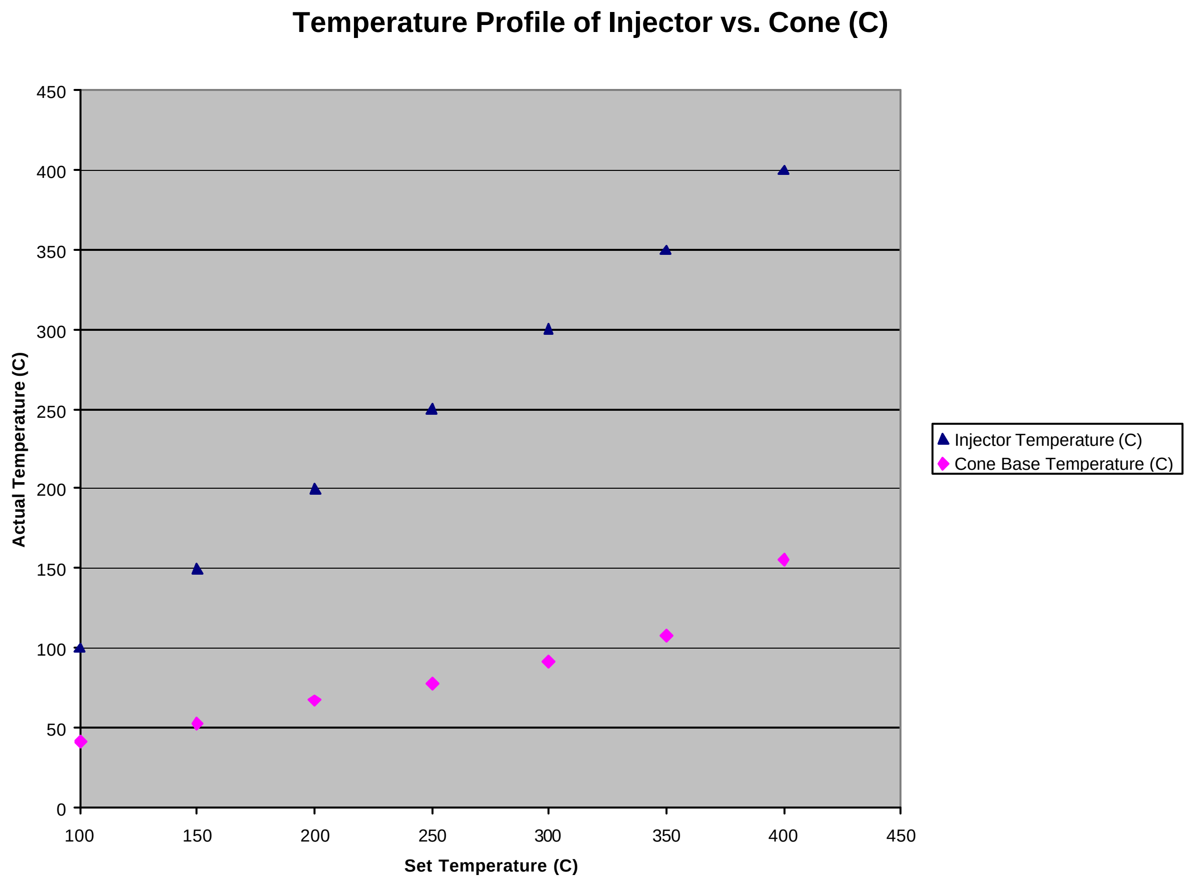
PLIS on 6890 GC
PLIS /Vacuum GC/DR-SCD Technology
Elimination of pressure vaporizer



Temperature Profile of Injector vs. Vaporizing chamber (^{o}C) - Unheated version



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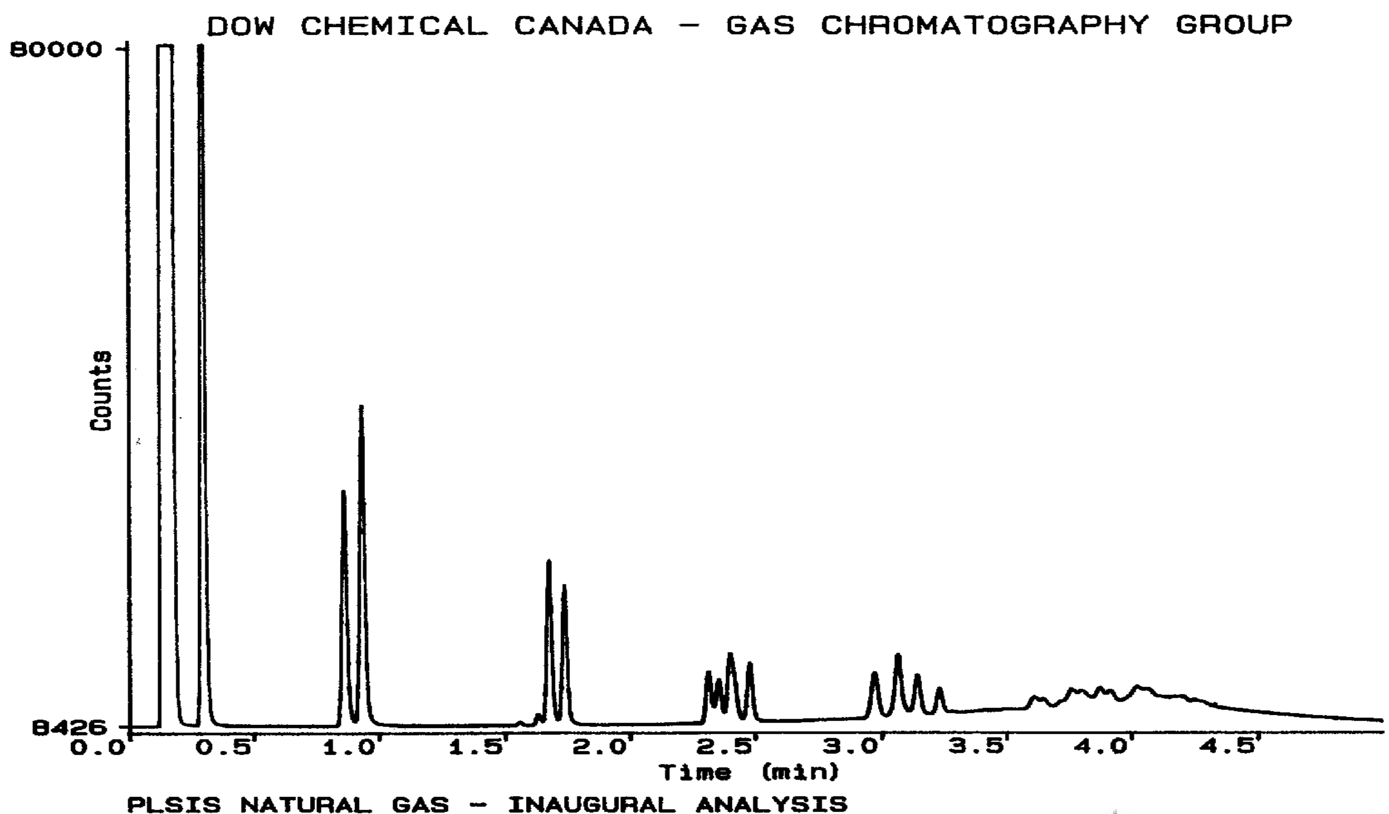
Selected Chromatographic Applications

A chromatogram of Alberta Natural Gas
GC/FID - Al_2O_3/KCl technology



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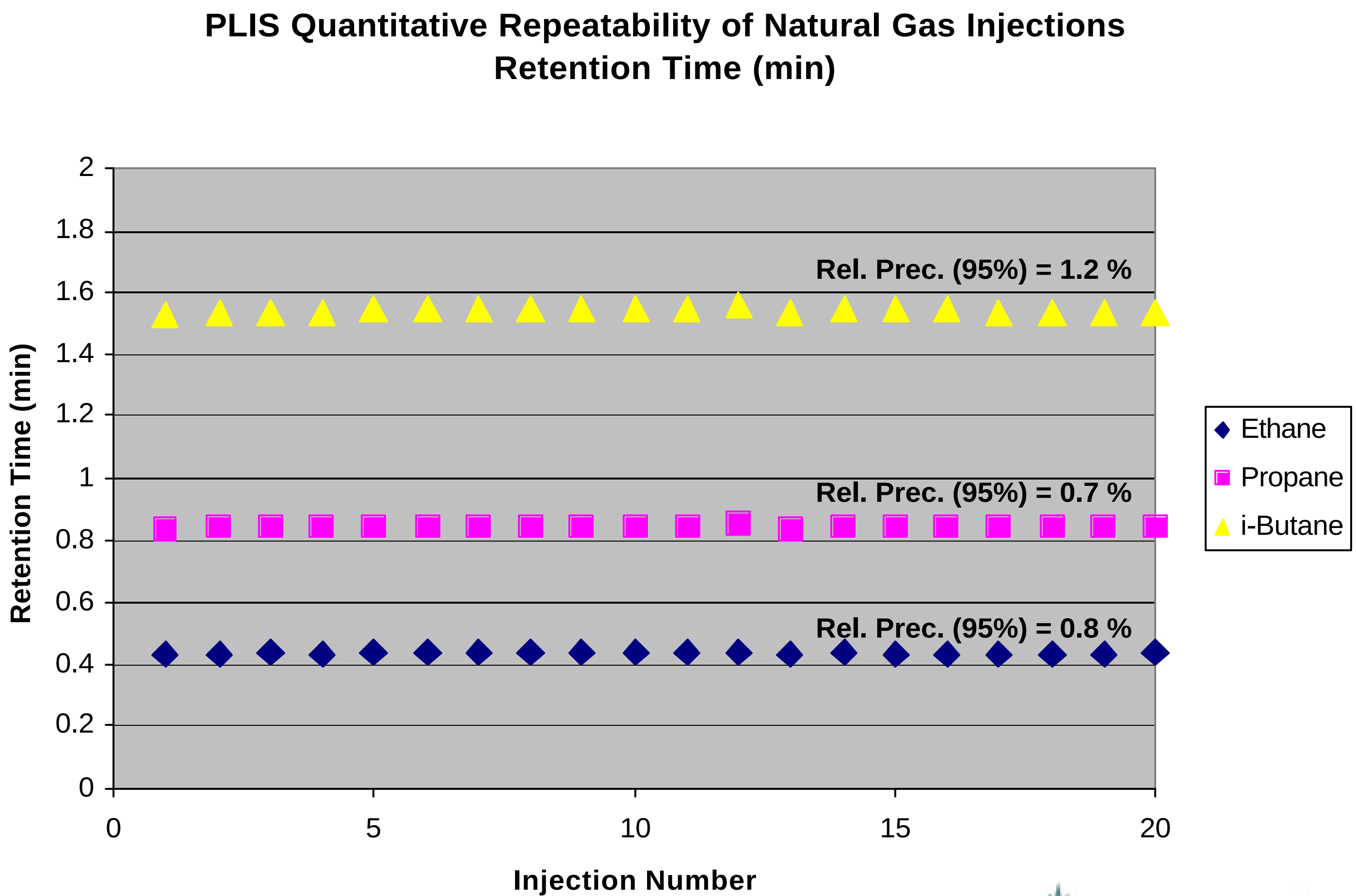
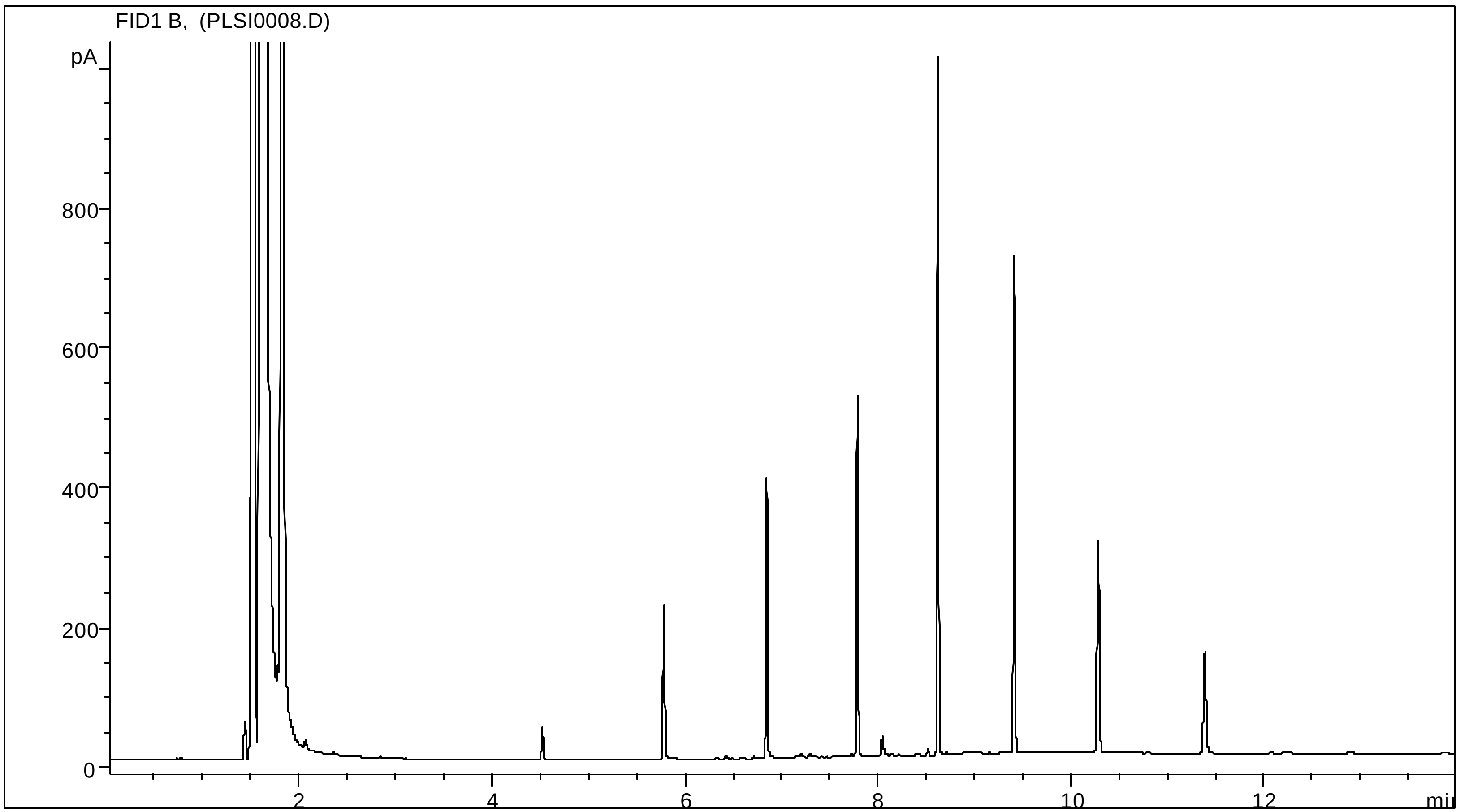
Repeatability – Natural Gas GC/FID

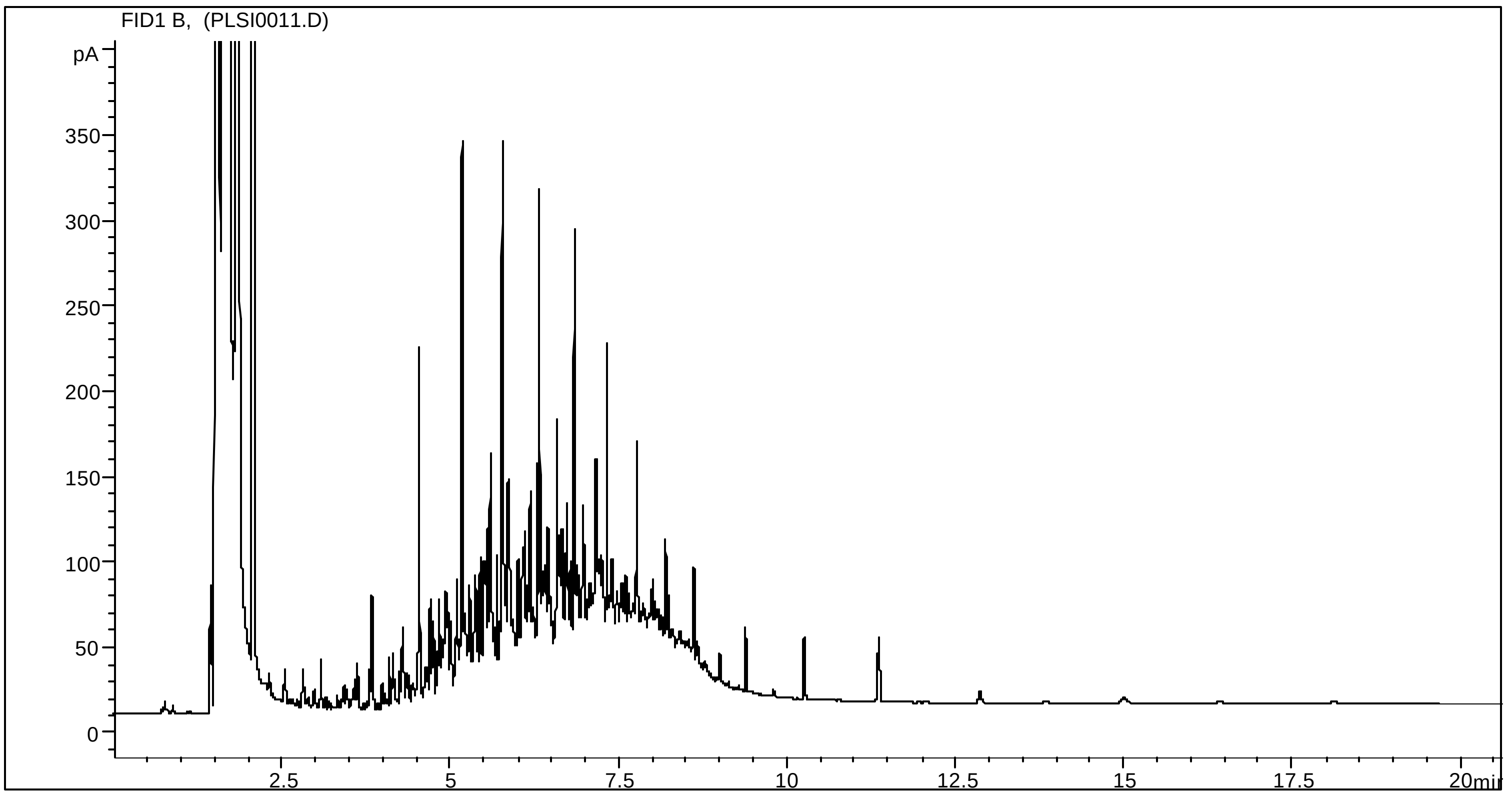


A chromatogram of nC10 to nC24 in Hexane

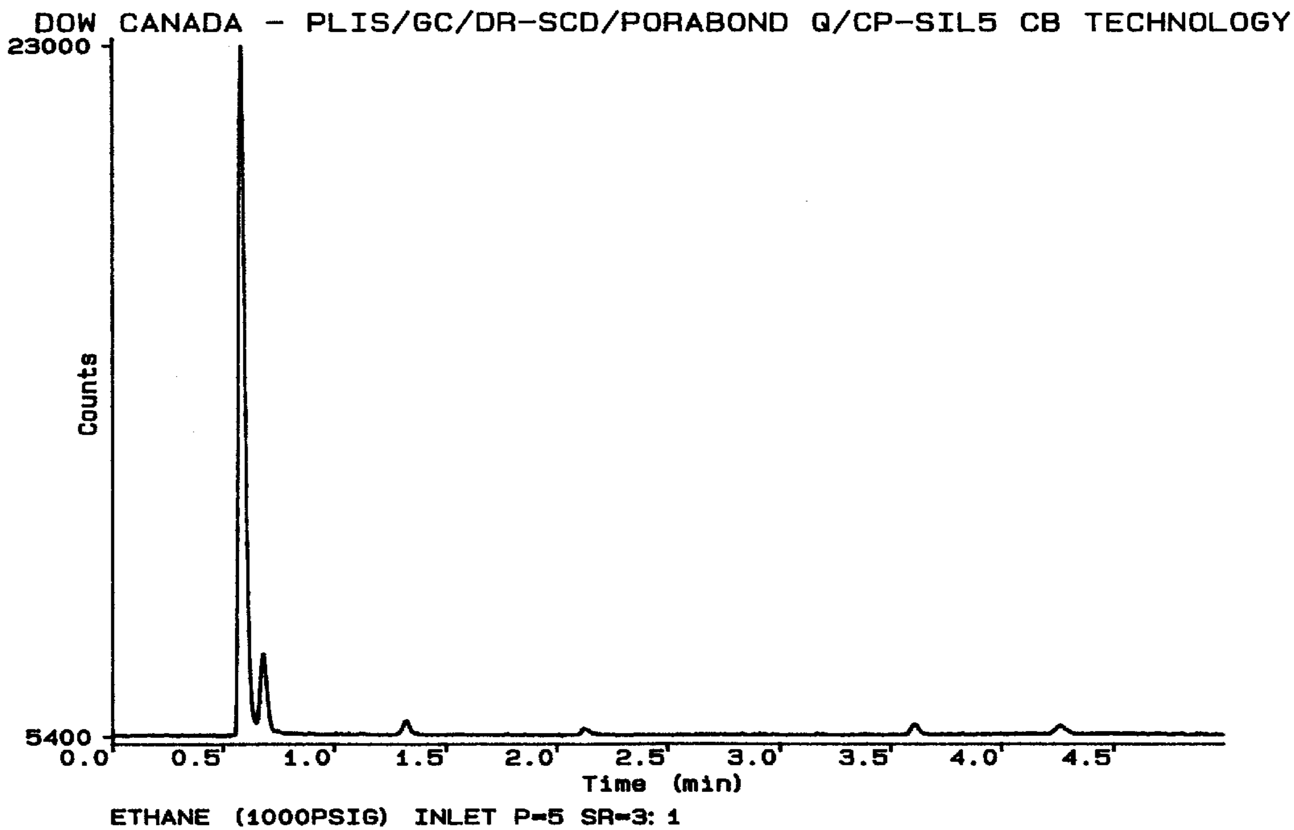
GC/FID - 30 metre, 0.25 mm id, 1 micron CP-Sil 5 CB-MS



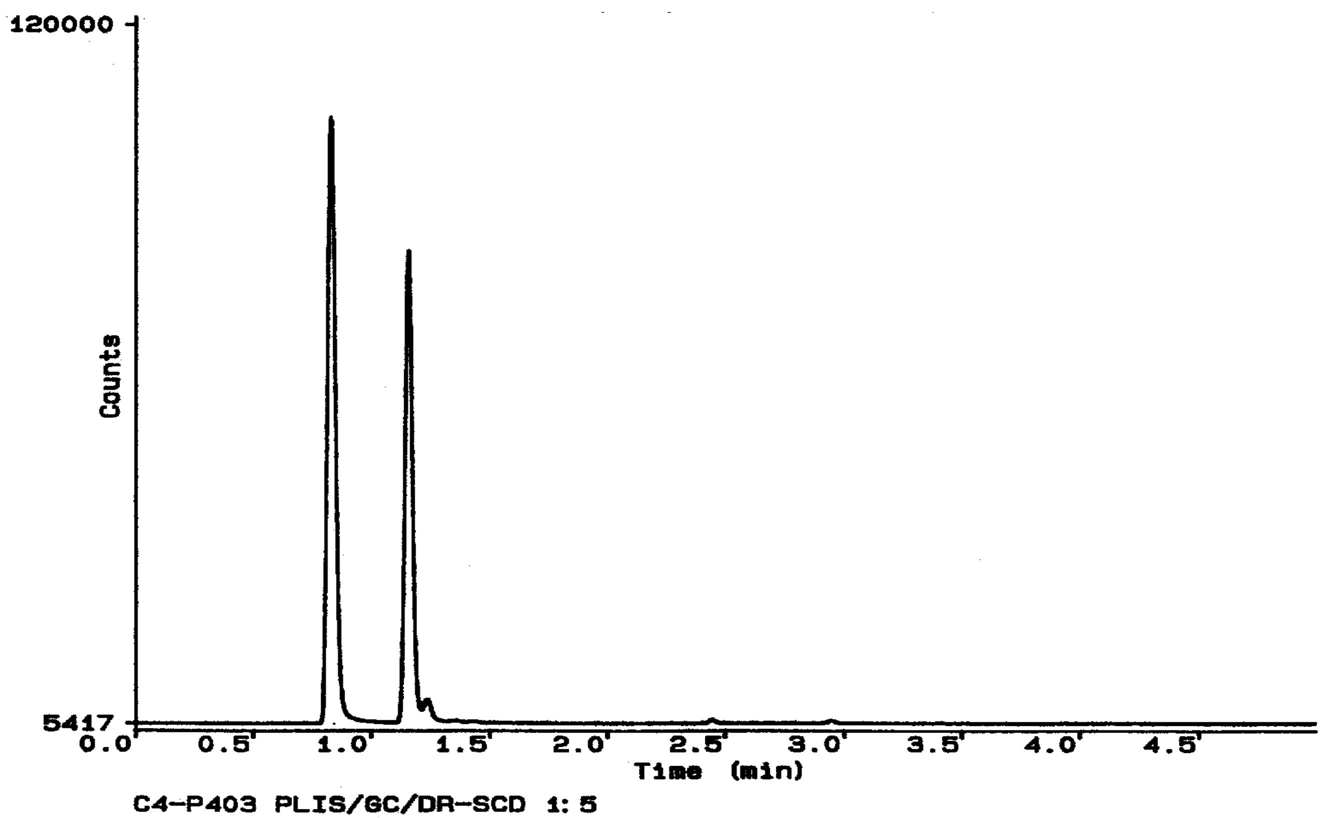
A chromatogram of Diesel in Hexane
GC/FID - 30 metre, 0.25 mm id, 1 micron CP-Sil 5 CB-MS



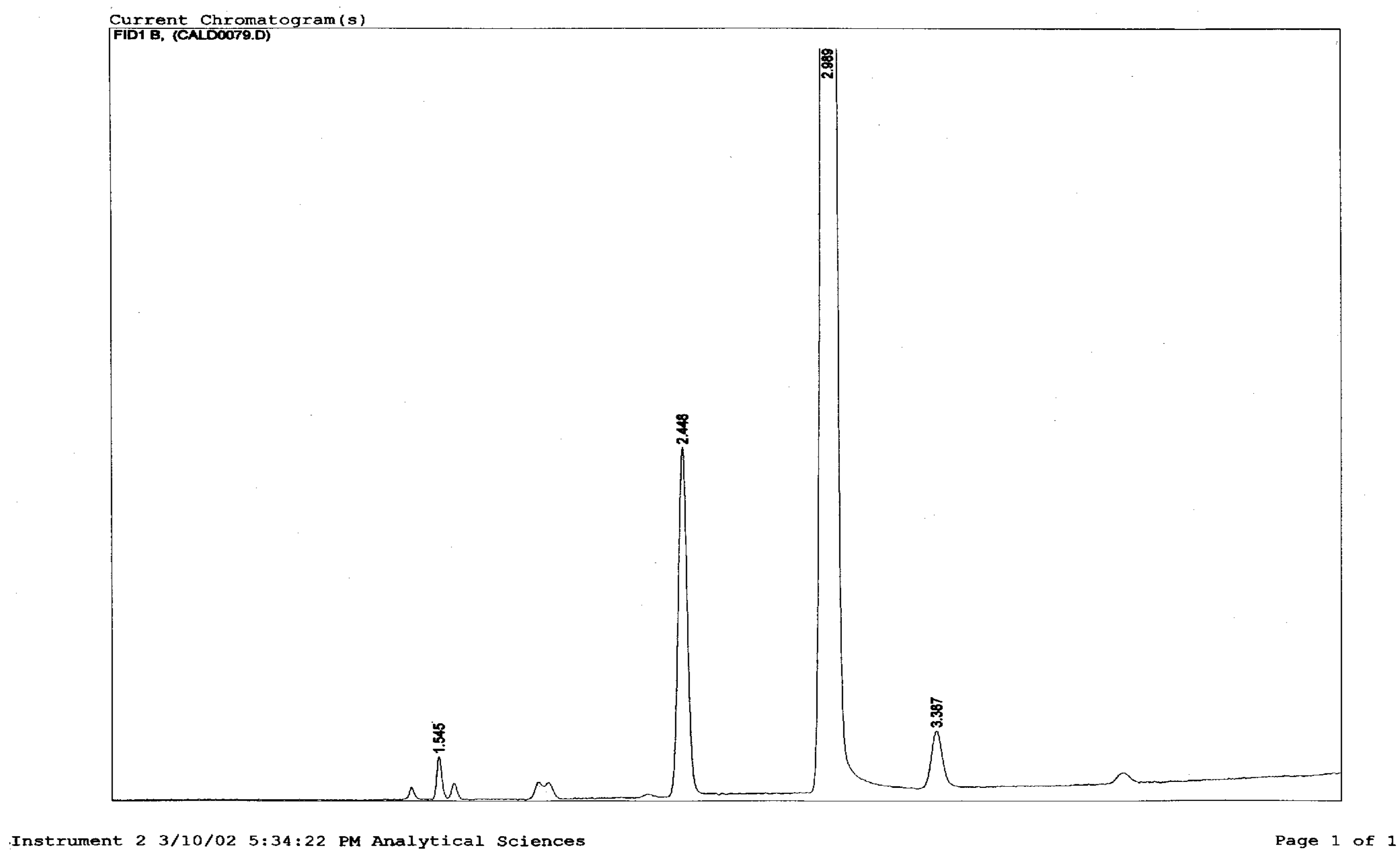
A chromatogram of Sulfurs in Ethane
hydrogen sulfide and carbonyl sulfide
PLIS / VGC/DR-SCD
30 meter, 0.32 mm, 5 micron CP-Sil 5 CB-MS



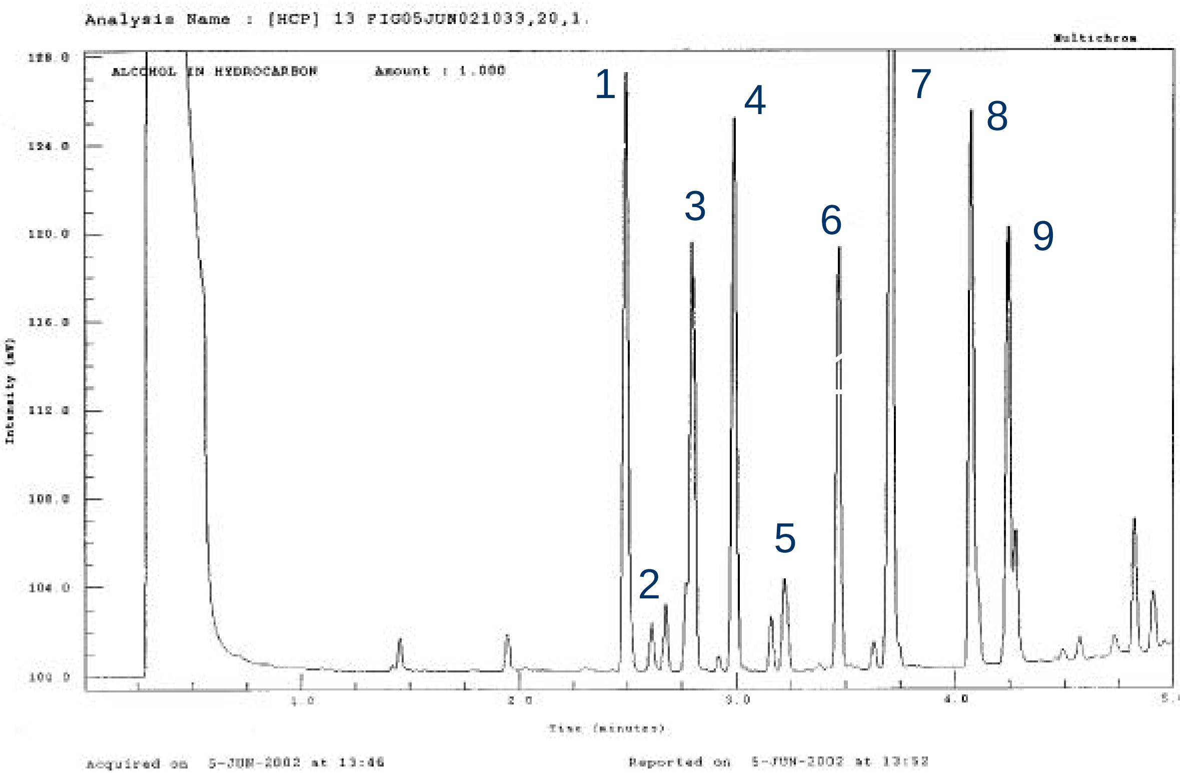
A chromatogram of Sulfurs in Butane Methyl and ethyl mercaptan – *PLIS* /VGC/DR-SCD 30 meter, 0.32 mm, 5 micron CP-Sil 5 CB-MS



Volatile Oxygenated Compounds MeOH, AA, EO, and EtOH GC/FID, 50 meter, 0.32 mm id , 5 micron CP-Sil 5



Hydrocarbons and Oxygenates
10 metre, 0.53 mm id, Lowox Column Technology



1. nC14
2. Methanol
3. Acetone
4. nC15
5. Ethanol
6. nC16
7. Propanol
8. Iso-butanol
9. Butanol

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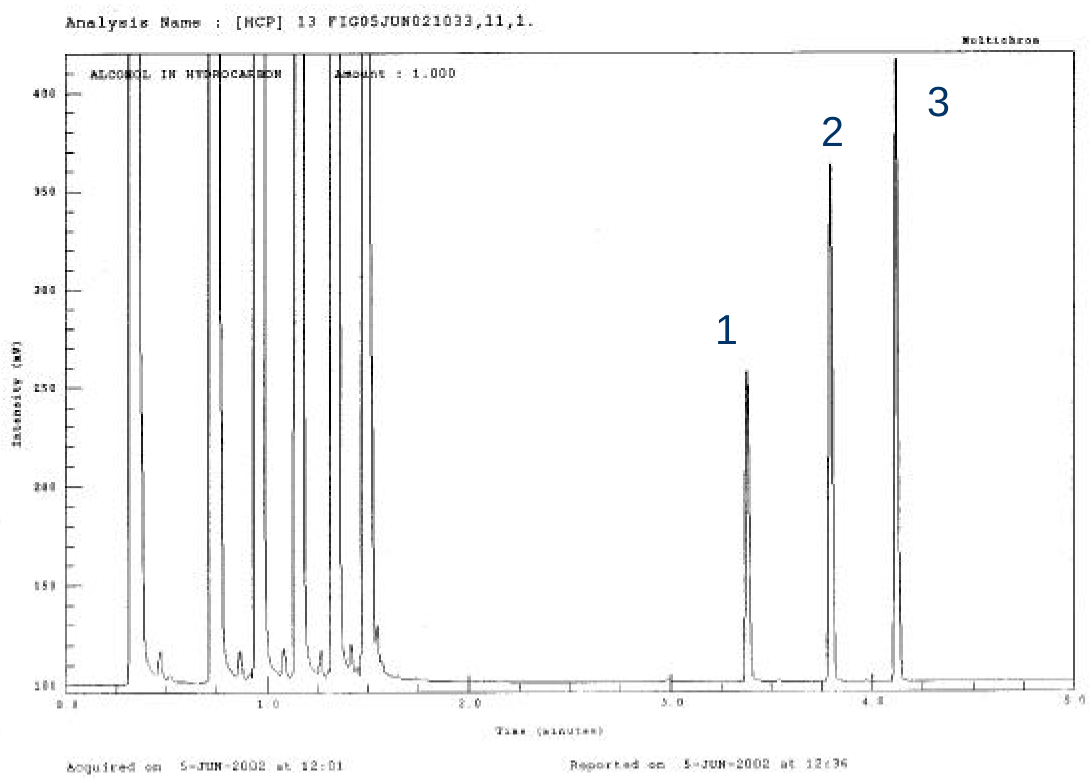
Stack Injection Technique
100 C-1 min-50C/min-260C 5 psig
Lowox Column Technology



1. Methanol
2. Ethanol
3. Propanol

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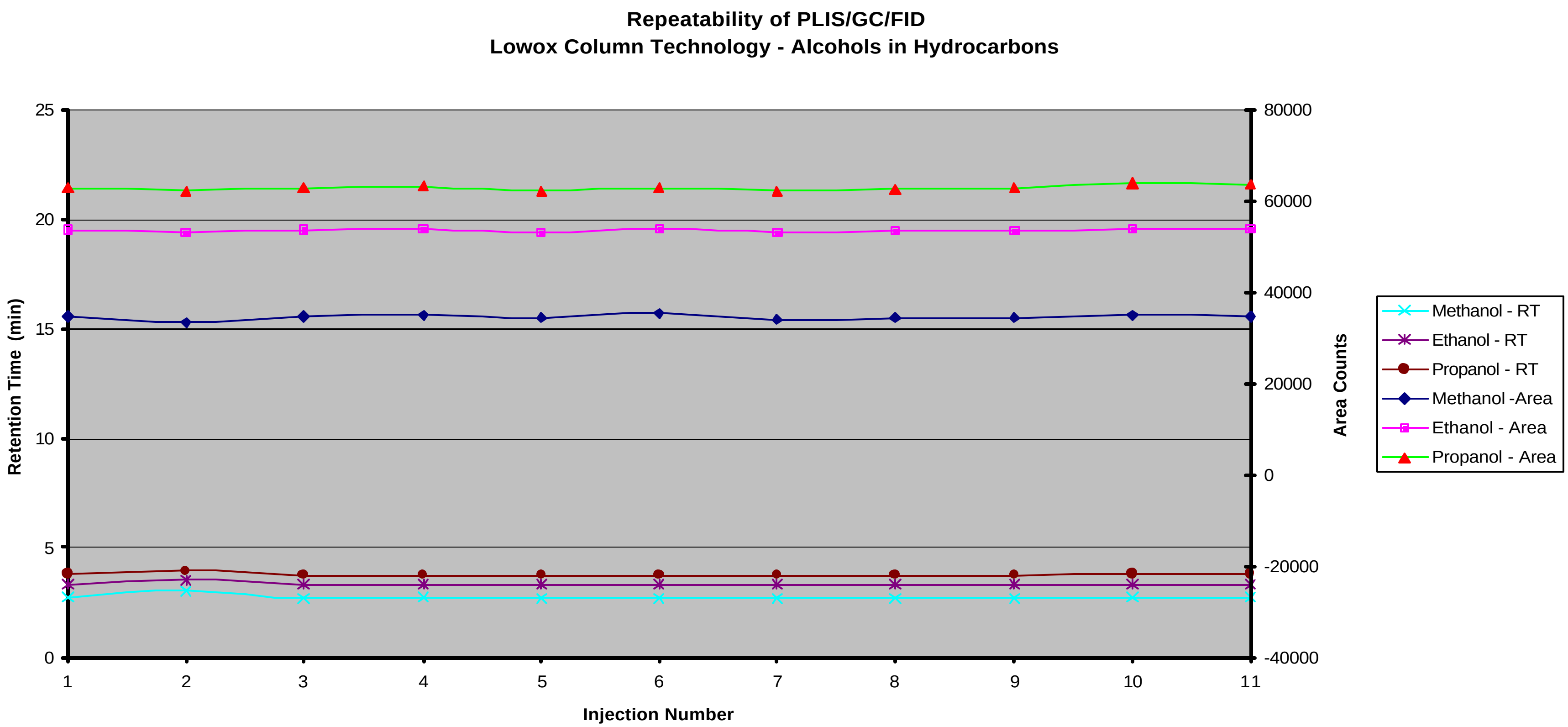
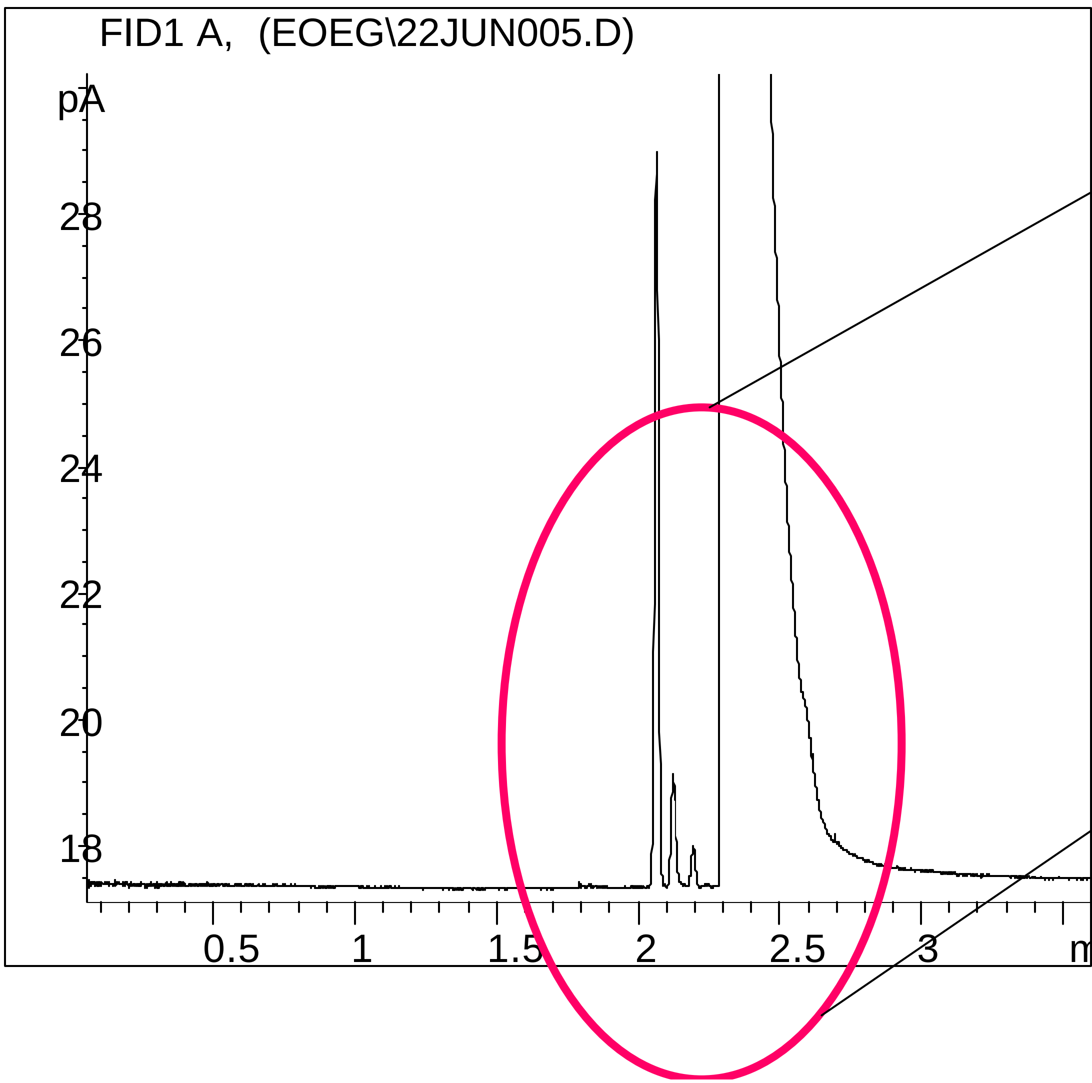
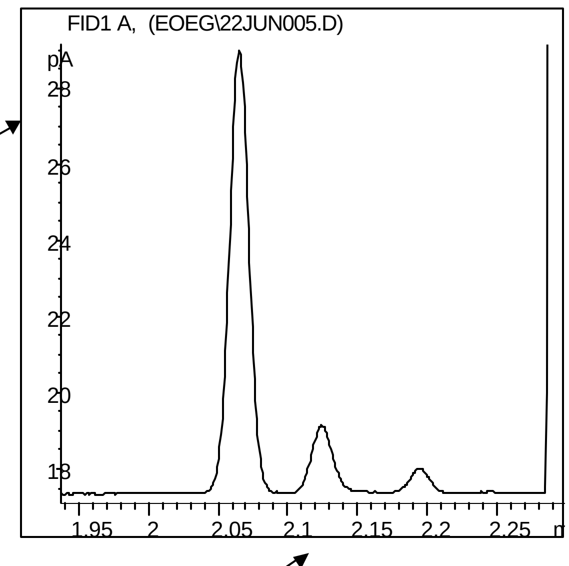
PLIS / GC / FID
Lowox Column Technology – Alcohols in Hydrocarbons
Reproducibility of Retention Time (min) and Area Counts



Impurities in Ethylene Oxide





1. Cyclopropane
2. Acetaldehyde
3. Vinyl chloride
4. Ethylene Oxide

Key Learning's

- ***PLIS*** **offers key advantages:**
  - **Small and compact (10 x 3 x 4 cm)**
  - **Capability to direct couple valve to injector reducing void volume, cold spots, active sites**
  - **Minimize fractionation of sample**
  - **Simplicity – ease of maintenance**

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Key Learning's

- **Unlike a rotary valve, speed of injection is not critical in delivering good chromatography**
- **Reduction of void volume between valve and injector port – critical**
  - **Reduction of liner volume**
  - **Reduction of volume of vapourizing chamber**
  - **Volume of vapourization chamber determined to be 360 uL**
- **Helium actuation not necessary and has no impact on overall chromatography obtained**

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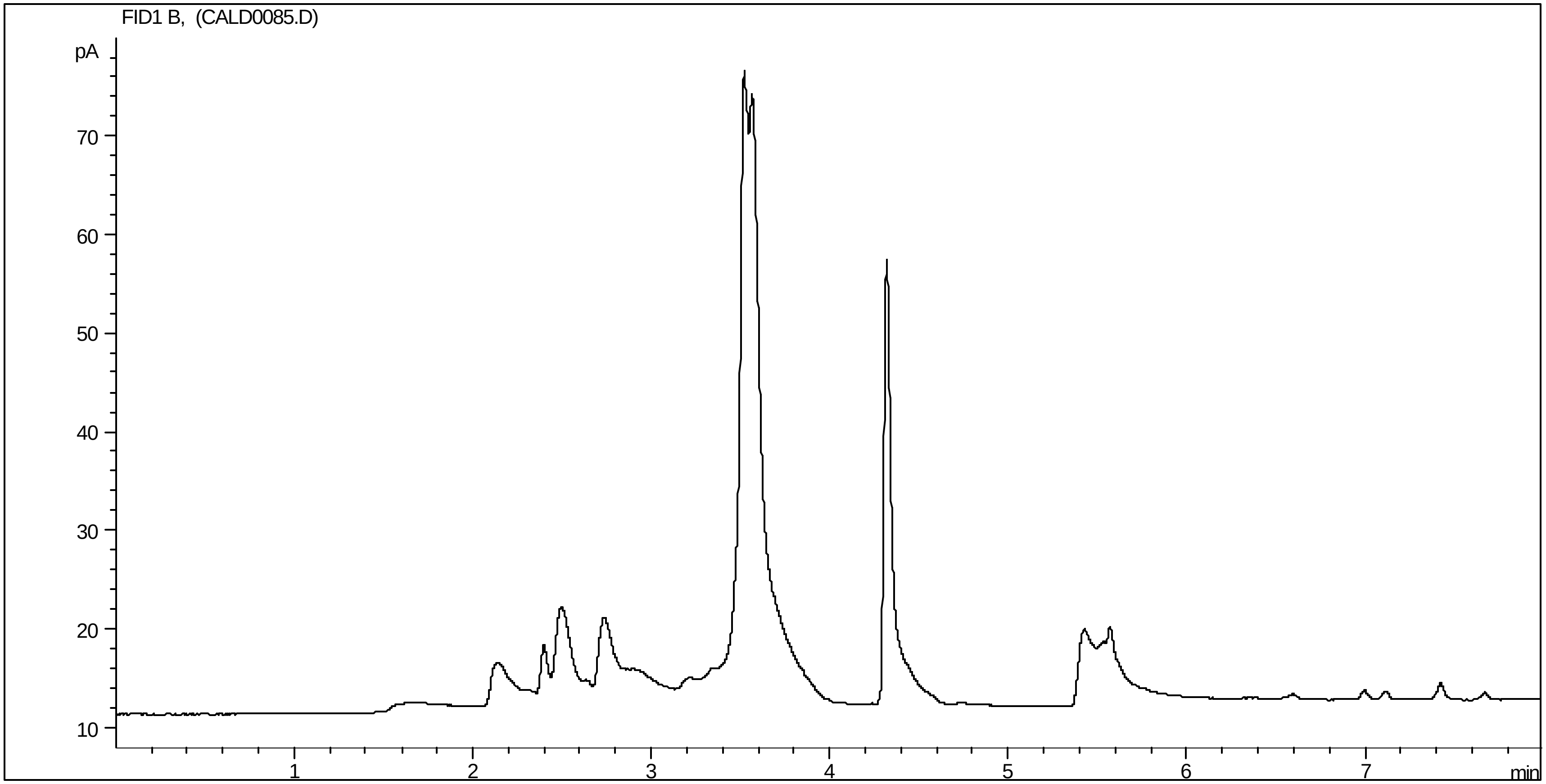
Limitations

- **Unheated version not suitable for high boiling polar compounds**
- **No long term performance data on seal(s)**

MEG, DEG, and TEG
GC/FID - 30 metre, 0.25 mm id, 1 micron CP-Sil 5 CB-MS



Future Research

- **Study effect of fractionation**
- **Void volume reduction**
- **Surface deactivation**
- **Applications development**
- **Resistively heated version**

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Acknowledgements

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