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
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 affect 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
Pressurized Liquid Injection System (PLIS)

Courtesy of Transcendent Enterprises Inc.
PLIS in Pieces
PLIS on Agilent HP-6890 GC
A Look At Interface
PLIS on 6890 GC
PLIS / Vacuum GC/DR - SCD Technology
Elimination of pressure vaporizer
Temperature Profile of Injector vs. Vaporizing chamber (°C) - Unheated version

Temperature Profile of Injector vs. Cone (°C)

Set Temperature (°C)

Actual Temperature (°C)

- Injector Temperature (°C)
- Cone Base Temperature (°C)
Selected Chromatographic Applications
A chromatogram of Alberta Natural Gas
GC/FID - Al₂O₃/KCl technology
Repeatability – Natural Gas GC/FID

PLIS Quantitative Repeatability of Natural Gas Injections
Retention Time (min)

Injection Number

Retention Time (min)

Ethane
Propane
i-Butane

Rel. Prec. (95%) = 1.2%
Rel. Prec. (95%) = 0.8%
Rel. Prec. (95%) = 0.7%
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

C4-P403 PLIS/GC/DR-SCD 1:5
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
Stack Injection Technique
100°C-1 min-50°C/min-260°C 5 psig
Lowox Column Technology

1. Methanol
2. Ethanol
3. Propanol
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
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 μL
- Helium actuation not necessary and has no impact on overall chromatography obtained.
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

![Graph showing FID B (CALD0085.D) with pA on the y-axis and minutes on the x-axis. Peaks are visible at different time points.]
Future Research

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