High Performance Pressurized Liquid Injection System (HPLIS) for Fast Gas Chromatography

Jim Luong and Ronda Gras
Dow Chemical Canada Inc

Richard Tymko
Transcendent Enterprises Inc
Outline

- Merits for Fast Gas Chromatography
- PLIS as a sample introduction device for faster GC
  - Conventional fast GC
  - Vacuum outlet GC and selective detector
  - Silicon micromachined gas chromatography
  - Microvolume injection
- Conclusions
- Acknowledgements
Merits for Fast Gas Chromatography in industries

- Improve chromatographic performance
  - Reproducibility and detectability
  - Address the needs for real time data
  - Higher sample throughput

- Typical industrial applications for fast GC:
  - Combinatorial chemistry
  - Industrial hygiene/environmental monitoring
  - Catalyst studies
  - Productivity improvements
Liquid Sample Introduction Systems

- Introduction of semi-volatile liquid via automated liquid sampler and split/splitless injector

- 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
  - Tert-butyl catechol (TBC) in butadiene
  - Diethylhydroxylamine (DEHA) in butadiene
  - Alcohols in hydrocarbon feedstreams

- Fractionation (vapourizer, rotary, diaphragm, slider valves)
- Speed of injection too slow for fast gas chromatography
PLIS Design Criteria & Key Features

- Fast injection speed
- High pressure of up to 1200 psig
- Minimal fractionation
- Sample size from nL to 12 uL
- Low dead volume
- Low maintenance and user-friendly
Impact of Speed of Injection

Impact of Actuation Valve Pressure (Speed of Injection) on Peak Width in PLIS

0.23
0.235
0.24
0.245
0.25
0.255
0.26
0.265
0.27

35 45 55 65 75 85 95

Actuation Pressure (Psig Air)

Peak Width (min)

Peak Width of Methane (min)
Pressurized Liquid Sampling Injection System (PLIS)
Load and Inject Positions

Courtesy of Transcendent Enterprises Inc.
www.transcendent.ca
PLIS Technologies

Unheated PLIS  
Resistively Heated PLIS (HPLIS)
Resistively Heated PLIS Technology

Heated PLIS Valve Assembly
Shaft exposed – Non energized

Heated PLIS Valve Assembly
Shaft exposed – Energized
Shaft Design

Shaft:

Heating Cartridge:

Sample Channel:
Performance of HPLIS

Comparison of syringe injection, energized and non-energized valve from nC$_7$ to nC$_{32}$

Stainless steel shaft (320C)

Enlargement from C$_{24}$ to C$_{32}$
Performance of HPLIS

Comparison of various PLIS injection modes - Each case, ratio to nC₇

Syringe S/S: conventional syringe split/splitless injection
SS(E) - stainless shaft, energized (ca 320°C)
SS(NE) stainless steel shaft, non-energized (radiant heat from injection port only)
Performance of HPLIS

Comparison of various PLIS injection modes - Each case, ratio to nC₇

Syringe S/S: conventional syringe split/splitless injection
SS(E) - Stainless shaft, energized (ca 320°C)
SS(NE) Stainless steel shaft, non-energized (radiant heat from injection port only)
HPLIS with Conventional Approach for Fast GC

- Hydrogen carrier gas
- Rapid temperature programming
- Narrow bore, short capillary column
- Oven Insert
ASTM D-2887 standard diluted 10:1

4 metre, 0.15 mm id, BPX-5 Column Technology

50 C - 0.3 min - 70C/min - 350 C, u = 100 cm/sec Hydrogen

5.5 min
Comparison of energized and non-energized PLIS Injection for Light Hydrocarbon Condensate
30 metre, 0.32 mm id, 1 micron CP-Sil 5CBMS

Light condensate - unheated PLIS

Light condensate - heated PLIS
Comparison of energized and non-energized PLIS Injection of Heavy Hydrocarbon Condensate
30 metre, 0.32 mm id, 1 micron CP-Sil 5CBMS

**Heavy condensate - unheated PLIS**

**Heavy condensate - heated PLIS**

FID1 B, (HPLIS080.D)

FID1 B, (HPLIS079.D)

40 min
Heavy and Light Hydrocarbon Condensate with Heated PLIS/GC/FID

4 metre, 0.15 mm id, 0.4 micron BPX-5
Hydrogen carrier, 100 cm/sec, 50°C – 0.3 min – 70°C/min – 350°C

Heated PLIS - Heavy Condensate

Heated PLIS - Light condensate
Tert-butyl catechol in butadiene by HPLIS/GC/FID

30 metre, 0.32 mm id, 1 micron CP-Sil 5 CBMS

Unheated PLIS

Overlay

Heated PLIS
Comparison of sensitivity of Monoethylene Glycol (MEG) with Heated vs. Non Heated PLIS Injection

30 metre, 0.25 mm id, 0.5 micron Stabilwax-DA
50 C – 1 min – 20C/min – 200C
HPLIS with Microvolume Injection for Fast GC

- Low pressure gas chromatography
- Short, wide bore capillary column
- Rapid temperature programming
- Small sample size
PLIS for Microvolume Injection Technique

Channel exposed

Channel covered by seal
Analysis of light hydrocarbons C₁ to C₃
5 metre, 0.53 mm id, Al₂O₃/KCl, 12 uL Channel, inlet pressure 1.3 psig
50°C – 0.1 min – 70°C/min – 150°C

1. Methane
2. Ethane
3. Ethylene
4. Propane
5. Propylene
6. Acetylene
7. Impurity
8. Impurity
HPLIS with Vacuum Gas Chromatography
Selective Detector for Fast GC

- Vacuum outlet GC
- Highly selective detector
Multiple injections of a mixed sulfur standard by PLIS/GC/DR-SCD
5 metre, 0.25 mm id, 0.25 micron CP-Sil 5CBMS, 250 C Isothermal, 225 cm/sec Helium

Dow Chemical Canada—Total Sulfurs PLIS/GC/DR-SCD
Figure of merit
Precision at 12.3, 123.2, and 1232.2 ppm S (w/w)

Reproducibility of Total S by PLIS/GC/DR-SCD

Area Counts

RSD 2.82%
RSD 1.75%
RSD 4.14%
HPLIS with Micromachined Gas Chromatography

- Silicon micromachined injection system
- Mechanism for introduction of liquid sample
Analysis of Liquid sample with microGC using AVS
AVS System Coupled to a MicroGC

SV – Solenoid Valve
EXH – Exhaust/Vent
AVS – An experimental product of Transcendent Enterprises Inc.
Injection of 0.2 uL of liquid hydrocarbons mixture with AVS

8 metre, 0.32 mm id, CP-Sil 5 CB Module Varian CP-4900 MicroGC
Constraints

- HPLIS is designed for “medium” high speed gas chromatography
- Limitations associated with split/splitless continues to exist
- Trade off between “cool” sample chamber vs. “hot” vaporization cone
Conclusions

- The advent of HPLIS provides a new dimension in sampling for fast gas chromatography

- PLIS was demonstrated to be compatible with a wide variety of techniques in fast GC

- Despite some constraints, HPLIS has the potential to further enhance the overall performance and flexibility of gas chromatography

- PLIS results tracked conventional needle split/splitless injection technique in split mode:
  - Up to C18 in unheated mode
  - Up to C24 in heated mode
Acknowledgements

- Analytical Sciences, Separations Team
- Analytical Sciences, Separations Leadership Team
- Professor Dr. Karel Cramers, TU/e
- James Griffith, Analytical Sciences
- Dr. Mary Fairhurst, Analytical Sciences
- Ian Moss, Moss and Son Engineering, Canada
- Dr. Randy Shearer, Ionics Instruments
- Varian International