Innovations in High-Pressure Liquid Injection Technique for Gas Chromatography: Pressurized Liquid Injection System

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Abstract

In gas chromatography (GC), highly volatile liquefied hydrocarbons are commonly injected using devices such as high-pressure syringes, piston valves, liquid rotary sampling valves, or vaporizing regulators. Although these techniques are adequate in some cases, there are known deficiencies. A new generation of sampling valve has been recently innovated and commercialized. Some of the highlights of the pressurized liquid injection system (PLIS) include compact size, the capability to directly couple to an injection port without the need for preinjection vaporization and transfer lines, and sample sizes ranging from 0.2 to 2.0 μL. Although the valve has a specification of helium leak-free rating of 82.7 bar (1200 psig), the valve passes a hydrostatic pressure test of up to 414 bar (6000 psig). In the unheated version of PLIS, vaporization of solutes occur mainly because of the sheering effect of carrier gas in combination with thermal energy drawn from an injection port or a heated adaptor. This was found to be adequate for solutes with high to medium volatility of up to nC_{14} hydrocarbon. A higher molecular weight range of up to nC_{44} hydrocarbon can be achieved with the implementation of a heated version of PLIS, in which the channel of the shaft can be resistively heated at a rate of up to 400°C/s. With its first introduction in May 2002, PLIS has gained acceptance amongst practitioners in GC because it addresses a key unarticulated need in sample introduction/enrichment and by specifically targeting many deficiencies encountered in contemporary high-pressure injection devices. In this paper, the design and performance of the various valve systems of PLIS, as well as industrial chromatographic applications, is presented.

Introduction

In gas chromatography (GC), highly volatile liquefied hydrocarbons are commonly injected using devices such as high-pressure syringes, piston valves, liquid rotary sampling valves, or vaporizing regulators. Although these techniques are adequate, there are known limitations. For instance, commercially available high-pressure syringes have a maximum pressure range of less than 27.6 bar (400 psig) (1,2), thus precluding them for use with very light hydrocarbons such as liquefied ethane. The design of piston valves such as Bendix or Mess Und Apparatetechnik types minimized sample fractionation, but these valves have a typical maximum pressure limit of 55.2 bar (800 psig) (3). Yet another limitation of the piston valve is its size; it is rather cumbersome to install on a bench-top GC. Liquid rotary valves and heated vaporizing regulators can handle very high pressure of up to 344.7 bar (5000 psig) (4,5); however, fractionation commonly occurs, especially in samples with wide boiling point ranges as in the case of diesel fuel in propane.

A new generation of sampling valve has been recently innovated and commercialized by Transcendent Enterprises Incorporated of Alberta, Canada. The pressurized liquid injection system (PLIS) enables a pressurized liquid or gas to be injected directly into a GC via a conventional septumless split/splitless injection port or a heated adaptor.

Two versions of PLIS were evaluated: (*i*) an unheated unit that relies solely on the sheering effect of carrier gas and the thermal energy drawn from a heated injector or adaptor to vaporize sample of interest and (*ii*) a heated unit in which the channel of the shaft can be resistively heated at a rate of up to 400°C/s.

This paper outlines the evaluation work and associated industrial GC applications developed using both the unheated and heated versions.
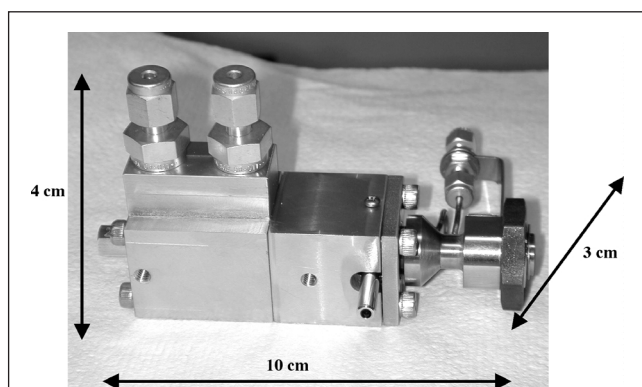
Experimental

The first three unheated prototypes [serial numbers (SNs) 42337-0001, 42337-0002, and 42337-0003] were made available by Transcendent in February, 2002 for evaluation and application developments. An improved unheated unit, designated as PLIS V2.0 (SN 43678-0013), was also made available in late December, 2002. In the same month, PLIS V2.2 represents the latest standard and is commercially available. The first prototype of the heated PLIS, equipped with a resistively heated shaft and a stand-
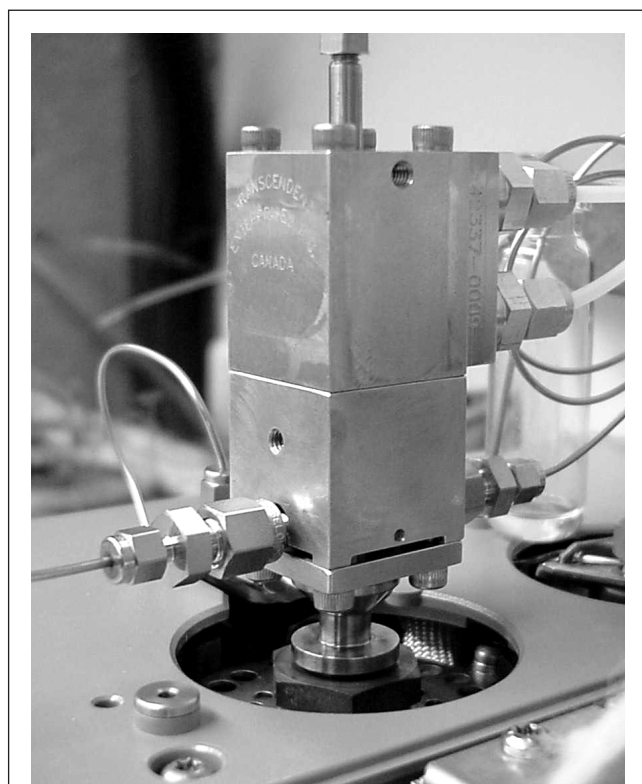
alone power control module, was made available for evaluation in January, 2003.

Figure 1 shows a picture of an unheated PLIS (SN 42337-0001) highlighting the compactness of the valve. Figure 2 shows a picture of a commercialized unheated PLIS V2.2 (SN 43678-0009) installed on an Agilent (Wilmington, DE) HP-6890A GC equipped with a double rod sulfur chemiluminescence detector (DR-SCD), and Figure 3 shows a picture of an unheated PLIS V2.0 (SN 43678-0013) installed on an Agilent HP-6890A GC equipped with a pulsed discharge detector (PDD) and flame ionization detector (FID).

Three Agilent HP-6890 GCs and a Varian (Middleburg, the Netherlands) CP-4900 micro GC were used: (*i*) an HP-6890A, equipped with a split/splitless and PTV injection ports, two onboard pneumatic valve actuators, an FID, and Valco vacuum pulsed discharge helium ionization detectors; (*ii*) HP-6890Plus, equipped with two split/splitless injection ports, two onboard pneumatic valve actuators, an Ionics Instruments (Boulder, CO) DR-SCD, and an FID; (*iii*) HP-6890Plus, equipped with two split/splitless injector ports, two onboard pneumatic valve actuators, an FID, and an atomic emission detector; and (*iv*) a Varian CP-4900 micro GC equipped with four modules was also used to evaluate an unheated PLIS equipped with a heated adaptor for liquid injection into the micro GC.

The following columns were used in the evaluation: a (*i*) Varian Chrompack 50-m, 0.32-mm-i.d., 5-µm CP-Sil 5CB column; (*ii*) Varian Chrompack 30-m, 0.25-mm-i.d., 1-µm CP-Sil 5 CB-MS column; (*iii*) Varian Chrompack 5-m, 0.53-mm-i.d., 20-µm PoraBOND Q column; (*iv*) Varian Chrompack 5-m, 0.53-mm-i.d., Al_2O_3–KCl column; (*v*) Scientific Glass Engineering, 4-m, 0.15-mm-i.d., 0.4-µm BPX-5 column; and (*vi*) Varian Chrompack, 50-m, 0.53-mm-i.d., 5-µm CP-Sil 5 CB column.

Chemical standards were obtained from Aldrich (St. Louis, MO)

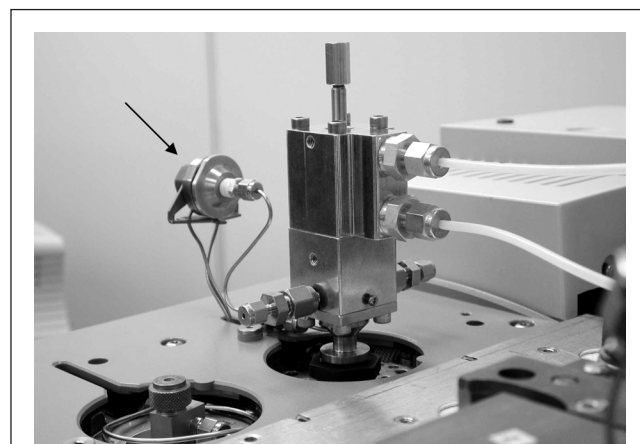**Figure 1.** An unheated PLIS V1.0 (SN 42337-001). Note the compactness of the valve (10 × 3 × 4 cm).

Figure 2. An unheated version of PLIS V2.2 installed on injection port A of an Agilent HP-6890A equipped with an FID and DR-SCD.
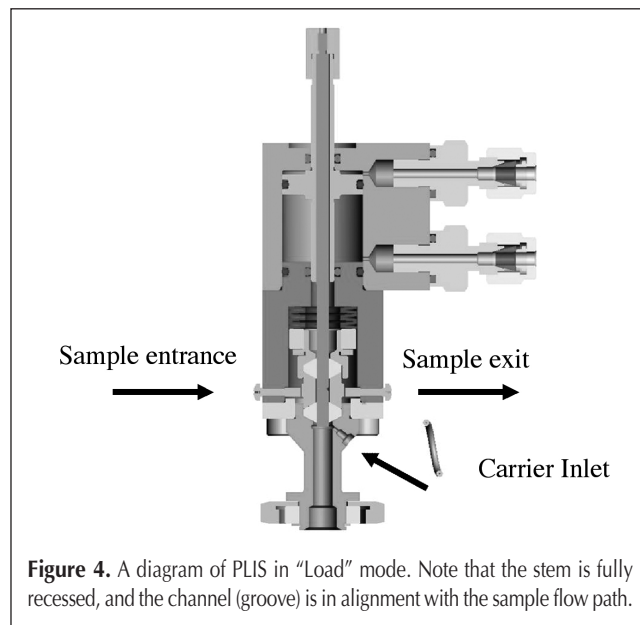

Figure 3. An unheated version of PLIS V2.0 installed on injection port B of an Agilent HP-6890A equipped with an FID and PDD—carrier pick up adaptor indicated by arrow on the left side of the valve.

Figure 4. A diagram of PLIS in "Load" mode. Note that the stem is fully recessed, and the channel (groove) is in alignment with the sample flow path.

and Supelco (Bellefonte, PA), and the samples used for testing were obtained onsite from the hydrocarbons, ethylene oxide–ethylene glycol, and vinyl chloride–ethylene dichloride plants.

The valve was actuated pneumatically using a solenoid on the Agilent HP-6890A GC with 90 psig air pressure. To charge the valve, liquid samples were allowed to purge across the sampling shaft for a predetermined period of time and then blocked in using a Whitey 1/16-inch block valve (Whitey, Highland Heights, OH). This approach offered good overall reproducibility. A GowMac (Chandler, AZ) helium detector was used to check the valve for possible leakage at various pressure settings prior to use.

Results and Discussion

Valve fundamental design features
Integrated pneumatic actuator to manipulate the sampling shaft

Viton seals are used to maintain internal air or helium pressure for valve actuation. The actuator is very compact in size with dimensions of only $4 \times 3 \times 3$ cm. Up to 140 psig of helium has been successfully applied to the actuator assembly without any detectable leak, offering a very high speed of injection. The actual speed of injection is not measured because of the unavailability of optical sensing devices. However, we proved that unlike the rotary valve, in PLIS, speed of injection has much less impact on chromatographic performance. This finding will be discussed later in this paper.

Sampling shaft with a channel that is reciprocal between a sampling and injection position

In the load mode, liquid or gas sample flows across the shaft and fills the channel (as shown in Figure 4). The sampling shaft was made out of chromatographic-grade stainless steel (SS-316). The sampling shaft is attached to the piston of the actuator with a brass nut. This facilitates the movement of the shaft from the sampling to inject position upon the valve being activated. The size of the channel corresponds to the size of the sample being injected, with sample size ranging from 0.2 to 2.0 µL. Figure 5
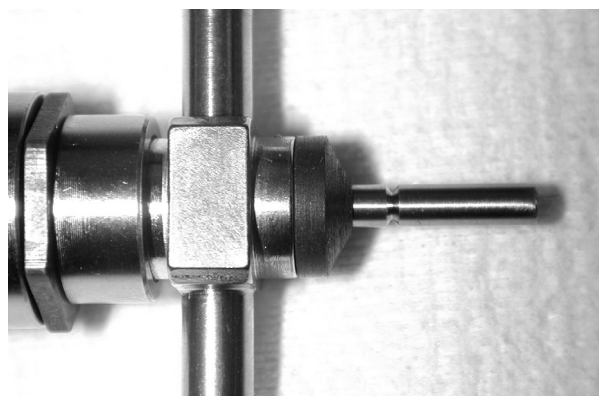
shows a photograph of the sample chamber and an unheated sample shaft. The sample groove shown was nominally 2 µL in volume. A channel size of greater than 2 µL was mainly used not for liquid, but gas injection as per the method described as microvolume injection technique (6).

*Seals and compression fittings to maintain appropriate set pressure*

Polymeric seals such as Teflon, graphite–Teflon, and polyetheretherketone can be used to seal around the sampling shaft and between the liquid stream and the injection port of the GC. To maintain proper sealing, compression fittings are used. The compression fittings compress the seal and force it into better sealing engagement with the reciprocating sampling shaft. Although this is not as elegant as in the constant pressure-loaded shaft seal design as taught by Ruiz (3), it is much easier to maintain and service. If a leak occurs, this can be eliminated by increasing the gap between the lock-nut and the seal holder, which, in turn, increases the force applied to the seal, or it is possible to simply replace with a new seal.

Vaporizing cone and a coupling connecting the valve directly onto a septumless standard injection port

Upon injection, the shaft is lowered from the sampling chamber into the vaporizing chamber where the entire sample, residing in the sample channel, is vaporized by the heat from the injection port and from the sheering effect of the carrier gas (as shown in Figure 6).

In this version of PLIS, the shaft is not directly heated, offering the highest degree of simplicity in design and operation. Figure 7 shows a photograph of a disassembled unheated PLIS valve. The four main compartments shown are the sample chamber, sample vaporization chamber, spring housing block, and pneumatic actuator.

Extensive testing and performance evaluations of PLIS V1.0 over a six-month period led to the introduction of PLIS V2.2 in December, 2002. Although PLIS V2.2 and its predecessors share

Figure 5. A photograph of the sample chamber and an unheated sample shaft. The sampling channel shown is 2 µL.
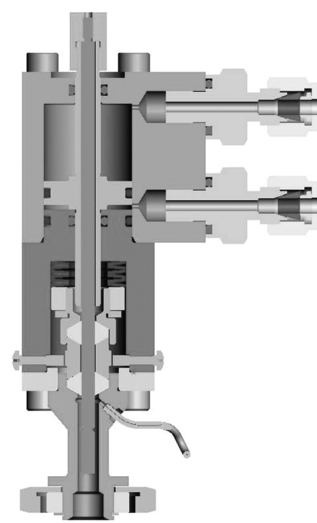

Figure 6. A diagram of PLIS in "Inject" mode. Note that the sampling shaft is protruding into the sample vaporizing chamber.

the same fundamental design, many enhancements on functionality and ease-of-use were made, including an improved sample chamber to reduce the purge time required between samples, a new sampling shaft with a high degree of concentricity and optimized channel angle to improve seal life, a unified vaporizing adaptor that drastically decreases the internal void volume from 360 to 80 µL, improved carrier adaptor, and new design carrier support bracket to protect the carrier gas weldment assembly. Despite the number of changes, PLIS V2.2 is backward compatible with its predecessors. Figure 8 shows a side-by-side picture comparing PLIS V1.0 and V2.0 with the changes mentioned.

Physical performance, valve handling, and interfacing
Interfacing with Agilent chromatographs

One of the main modes of operation for PLIS is to be directly coupled with a standard Agilent split/splitless injection port. Connecting the valve to a split/splitless injection port can be carried out easily with the provided coupling nut, which is similar to an Agilent weldment assembly nut for a split/splitless injector. Figure 9 shows a photograph of an inside view of the coupling nut. Also shown on the photograph is the carrier inlet connector. The carrier gas pick-up assembly, an accessory for PLIS (as
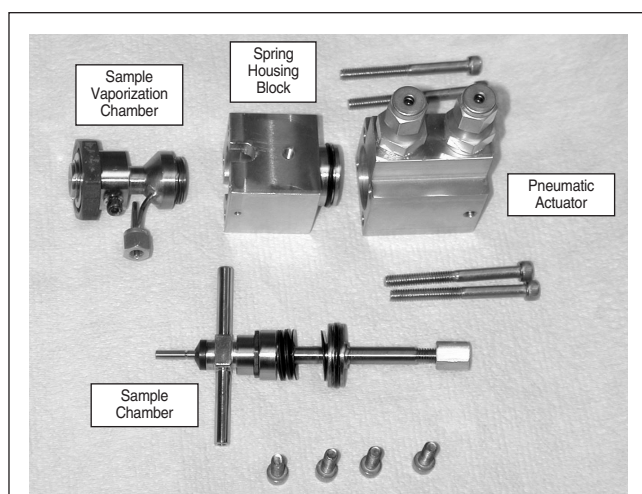
Figure 7. A disassembled unheated PLIS valve. The four main compartments shown are the sample chamber, sample vaporizing chamber, spring housing block, and pneumatic actuator.
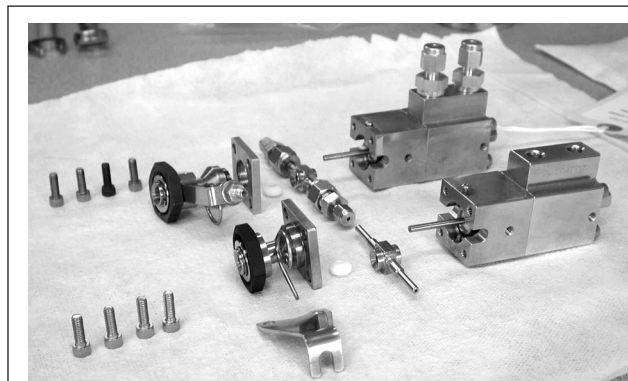
Figure 8. A side-by-side picture comparison of PLIS V1.0 (top) and V2.0 (bottom).

shown in Figure 3), allows rapid switching between the conventional split/splitless injection and PLIS by coupling the part described to the weldment assembly already in place. This accessory was found to work well.

PLIS as a stand-alone injection device

The valve can be operated as a stand-alone vaporizing device. In this mode, PLIS is fitted with a stand-alone assembly including a heated adaptor and a four-way solenoid valve. PLIS is used to vaporize a liquid sample into a gas stream for sampling. It is in this configuration, PLIS can be interfaced to the Varian CP-4900 micro GC. This adaptation of PLIS to commercially available micro GC works well, and indirectly enhances the analytical capability of micro GC by offering micro GC with a liquid sampling capability.

Resistively heated PLIS

Unlike the unheated PLIS version, in which vaporization of the sample depends solely on the sheering effect of the carrier gas and the thermal energy drawn from either the injector it is coupled to or a heated block it is interfaced with, in this heated variant, the channel of the valve shaft can be resistively heated at a rate of up to 400°C/s with a final temperature reaching in excess of 350°C. The temperature at the channel can be adjusted by changing the duration current that is applied to the shaft. By carefully applying heat to the channel of the shaft synchronized with sample delivery, faster vaporization of solutes can be attained. This leads to overall improvements in chromatography.

Ease of service

The valve can be disassembled and reassembled easily in less than 15 min. All the components of the valve are engineered for ease of service. It is imperative that the valve assembling instructions are followed closely (7). Failure to do so might result in leaks at much lower pressure than designed values.

Temperature

In this unheated version of PLIS, radiant heat from the injection port is used to help vaporize the sample upon injection. Figure 10 shows a graph of temperature of injector versus temperature at the lower vaporizing chamber of PLIS. When the split/splitless injector is set at its maximum temperature of
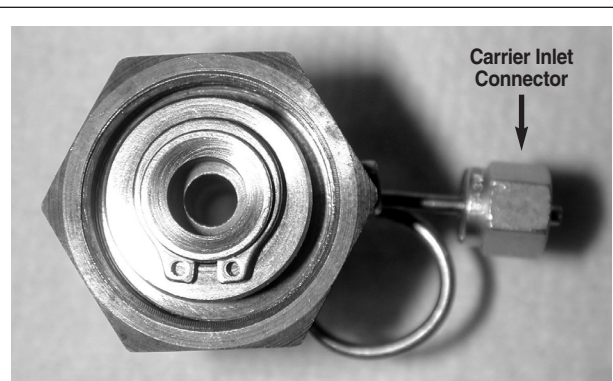
Figure 9. A photograph of an inside view of the coupling nut. Also shown in this photograph is the carrier gas inlet.

400°C, the temperature of the vaporizer adaptor of the PLIS reaches 150°C. This is well within the operating temperature of the Teflon seals. We recommend that the lower vaporizing chamber be insulated in order to prevent cold spots for applications in which heat is required. Though keeping the temperature of the vaporizing chamber high has its desirable effects, it is important to keep in mind that a colder temperature in the sampling chamber aids in minimizing premature vaporization of the sample. Additional cooling of the sample chamber can be achieved by purging the sampling chamber block with air using an adaptor provided.

Chromatographic performance

Impact of speed of injection

Speed of injection is an important parameter in GC for the attainment of a quality chromatographic profile, especially when the sample is introduced by a mechanical sampling device such as a rotary valve. Typically, a diaphragm or rotary valve injection speed ranges from 10 to 100 ms, and various concepts were used to measure the speed of injection (8). Although this is a crucial parameter for a rotary valve, it is unclear whether this is applicable in PLIS. Unlike the rotary valve design, in which port-to-port sample diffusion can be an issue upon valve rotation, with the PLIS injection technique—at least in theory—this diffusion can either be minimized or eliminated. This is because of its inherent design of a shaft traversing a seal, thereby instantaneously exposing the entire sample to the uninterrupted carrier gas stream. Measuring the speed of injection can be rather diffi-
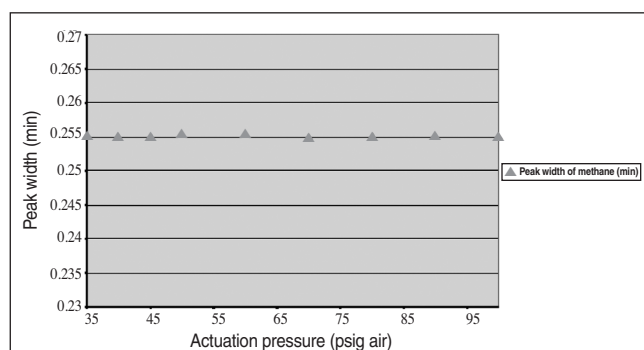
cult and might require sophisticated equipment such as a proximity detector (Hall detector) or laser; indirect measurement can be made quite simply by varying the pressure of the actuator. The speed of injection is inversely proportional to the pressure applied on the actuator. Marked differences in injection speed can be observed when actuator pressure is changed from 45 to 90 psig. Figure 11 plots the actuator pressure versus peak width of methane in minutes. Peak width of methane remains constant throughout the entire pressure range. Methane was chosen as a test solute because it has a k' value approaching zero, with little to no column trapping effect. Therefore, any chromatographic effect is mainly attributable to the injection system. From this result, it can be concluded that the impact of speed of injection, if any, is quite insignificant in a practical sense when PLIS is used as an injection device.

Unlike in the case of a rotary valve, it is not necessary to cycle the valve quickly between inject and load modes to maintain good chromatographic profile, especially in solutes with low k'. Figure 12 shows an overlay of propane in ethane with PLIS cycled back to load mode after 0.1 min and an injection with PLIS left in the inject mode through the entire run. As shown in Figure 12, no observable difference in peak width was seen in the chromatography obtained.

N-alkanes were used to assess both chromatographic performance of the valve and the maximum molecular weight of compounds that can be injected by the valve without direct heating
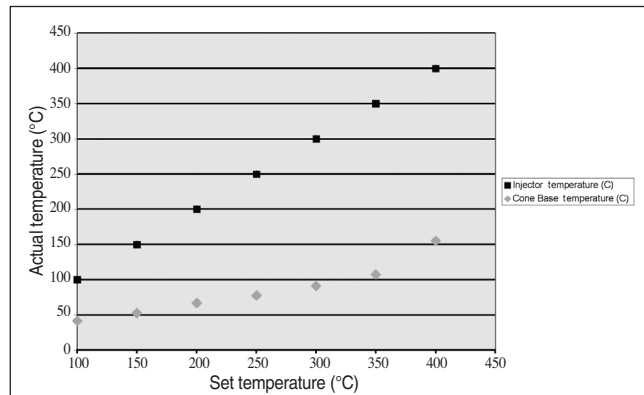
Figure 10. Temperature profile of injector versus cone (C). Temperature correlation between the valve vaporizing cone (V1.0) and injection port.

Figure 12. An overlay of propane in ethane with the PLIS valve recessed after 0.1 min and at the end of the run.

Figure 11. Impact of actuation valve pressure (indirect speed of injection) on peak width in PLIS.
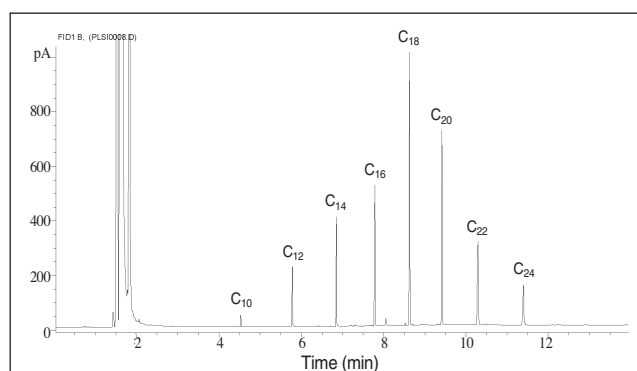
Figure 13. A chromatogram of nC_{10} to nC_{24} in hexane by PLIS–GC–FID.

of the channel. Figure 13 shows a chromatogram of straight chain alkanes in hexane ranging from nC_{10} to nC_{24}.

The GC conditions were as follow: Agilent HP-6890A GC; injector, split/splitless equipped with an unheatd PLIS injector; PLIS injector sample volume, 0.2 µL; injector temperature, 300°C; split ratio, 10:1; column, 30 m, 0.25-mm i.d., 1 µm CP-Sil 5CB MS; carrier gas, helium; flow velocity, 43 cm/s (4.2 psig); temperature profile, initial at 40°C, held 0.5 min, rate 70°C/min
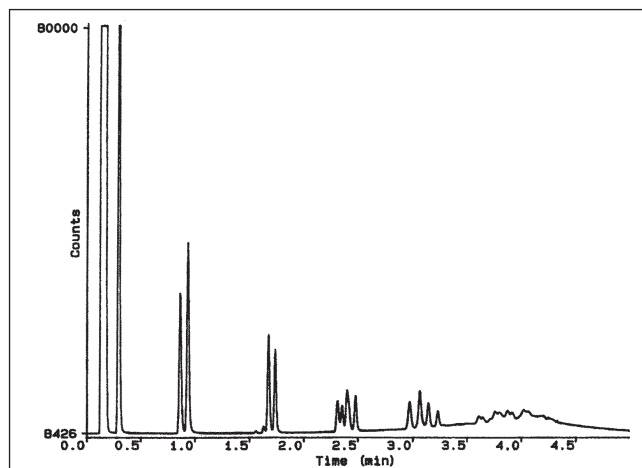

Figure 14. A chromatogram of Alberta natural gas (Canada).

to a final temperature of 280°C (held 5 min); and detector, FID (temperature, 300°C; hydrogen, 30 mL/min; air, 400 mL/min; and nitrogen, 25 mL/min). Excellent chromatographic peak symmetry was obtained for all compounds.

GC applications
Unheated PLIS

Natural gas. The analysis of natural gas components is one of the most common applications in GC, especially in gas producing regions such as Alberta, Canada. Figure 14 shows a chromatogram of Alberta natural gas. The GC conditions were as follow: Agilent HP-6890A GC; injector, split/splitless equipped with an unheatd PLIS injector; PLIS injector sample volume, 0.2 µL; injector temperature, 100°C; split ratio, 10:1; 5-m, 0.53-mm-i.d. Al_2O_3–KCl column; carrier gas, helium; flow velocity, 57 cm/s (4.2 psig); temperature profile, initial at 40°C, held 0.4 min, rate 50°C/min to a final temperature of 180°C (held 5 min); and detector, FID (temperature, 300°C; hydrogen, 30 mL/min; air, 400 mL/min; and nitrogen, 25 mL/min). Excellent chromatographic peak symmetry was obtained for all compounds.
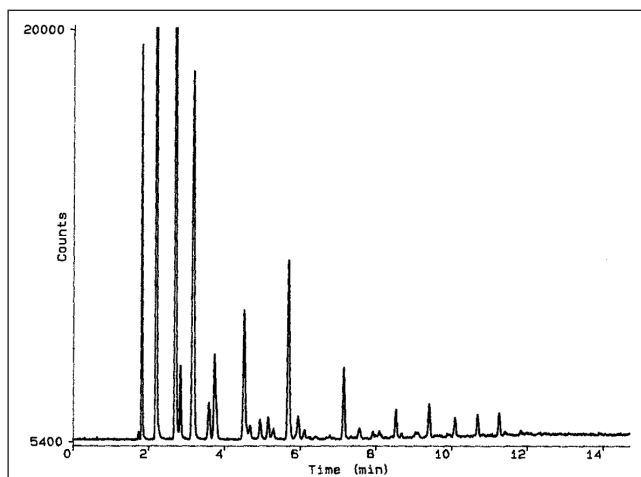
Reproducibility of retention time and an area counts studies were conducted using this natural gas sample. The results obtained were tabulated in Tables I and II, respectively. Excellent repeatability with relative precision (95% confidence level) better than 5% for area counts and 1.2% for retention time were obtained for ethane, propane, and iso-butane.

Table I. PLIS Quantitative Repeatability for Area Counts for 2 µL of Natural Gas Injections

Injection no.	Ethane	Propane	i-Butane
1	121754	39884	10916
2	123649	40520	11033
3	121831	40223	10939
4	123160	40371	10933
5	122336	40152	10885
6	121277	39571	10763
7	120943	39479	10708
8	121000	39534	10700
9	120826	39492	10699
10	120956	39182	10610
11	119346	38687	10449
12	120108	38830	10510
13	121442	39213	10535
14	120292	39002	10494
15	121420	39315	10533
16	122217	39382	10568
17	122473	39489	10636
18	120791	38955	10488
19	120275	38846	10417
20	118799	38182	10270
Ave.	121245	39415	10654
SD*	1194.5	598.7	205.4
%RSD†	1.0	1.5	1.9
RP‡	2.2	3.3	4.2

* SD, standard deviation.
† %RSD, percent relative standard deviation.
‡ RP, relative precision at 95% confidence level.

Table II. PLIS Repeatability for Retention Time for 2 µL of Natural Gas

Injection no.	Ethane	Propane	i-Butane
1	0.433	0.841	1.529
2	0.431	0.842	1.536
3	0.435	0.844	1.537
4	0.433	0.844	1.54
5	0.437	0.847	1.542
6	0.438	0.848	1.541
7	0.437	0.849	1.544
8	0.437	0.849	1.541
9	0.436	0.847	1.543
10	0.435	0.848	1.544
11	0.437	0.848	1.541
12	0.438	0.851	1.557
13	0.433	0.841	1.54
14	0.436	0.847	1.548
15	0.433	0.844	1.541
16	0.431	0.843	1.541
17	0.432	0.843	1.537
18	0.433	0.844	1.538
19	0.433	0.846	1.54
20	0.435	0.846	1.537
Ave.	0.435	0.846	1.541
SD	0.002	0.003	0.35
%RSD	0.52	0.34	0.35
RP*	1.2	0.7	0.8

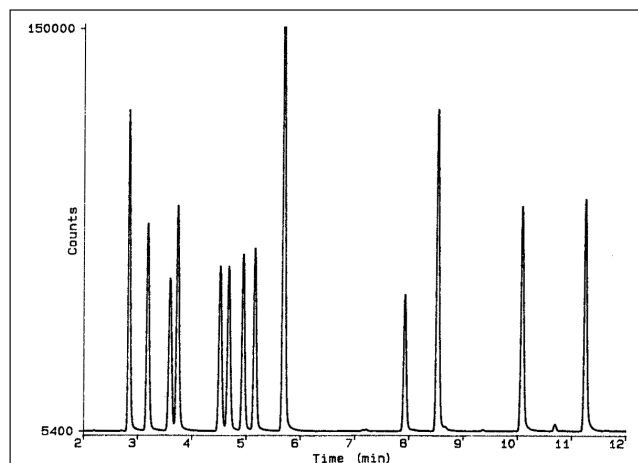* RP, relative precision at 95% confidence level.

Volatile organic sulfur-containing compounds in liquid ethane, propylene, propane, butane, and butadiene. Sulfur-containing compounds in the hydrocarbon streams are commonly analyzed using a regulating vaporizer such as Tescom 4400 series in combination with a selective detector (such as an SCD). The inertness of PLIS, as well as its capability to handle high-volatility, high-pressure liquids, was tested using liquid ethane, propylene, propane, butane, and butadiene. In all cases, the valve performed well, including when liquid ethane was padded with nitrogen pressure as high as 1300 psig. Even at this high pressure, no sample leak was detected. Figure 15 shows a chromatogram of sulfurs in crude ethane. Figure 16 shows a chromatogram of 13 sulfur-containing compounds in hexane. A relative standard deviation (95% confidence interval) of less than 0.1% was obtained for all compounds, highlighting the high degree of precision of the chromatographic system. Except for dipropyl disulfide, equal molarity of sulfur compounds (within 10% analytical error) was obtained for the rest of the sulfur compounds tested, demonstrating the valve's compatibility with highly reactive sulfur compounds. One plausible explanation for the lower response for dipropyl disulfide is the decrease of

volatility because of its higher boiling point when compared with the rest of the sulfur compounds tested. Using a higher temperature setting for the vaporizing chamber temperature can rectify this situation. As shown in the data obtained, despite that the inner surface of the valve is not treated with passivation processes such as Silcosteel or titatium nitride deposition, the valve offers sufficient inertness that volatile sulfur compounds can be successfully analyzed. The results obtained are tabulated in Tables III and IV.

The GC conditions were as follow: Agilent HP-6890A GC; injector, split/splitless equipped with an unheatd PLIS injector; PLIS injector sample volume, 0.2 μL; injector temperature, 250°C (insulated) and valve 2 on 0.0 min then off 0.1 min; split ratio, 10:1; columns, 50-m, 0.32-mm-i.d., 5-μm CP-Sil 5CB connected to a 5-m, 0.25-mm-i.d., 0.25-μm CP-Sil 5 CB; carrier gas, helium; flow velocity, 71 cm/s and 6.5 mL/min; temperature profile, initial at 100°C, held 2 min, rate 15°C/min to a final temperature of 250°C (held 5 min); and detector, Ionics Instruments

Figure 15. A chromatogram of sulfurs in crude liquid ethane by PLIS–GC–DR-SCD (sample pressure at 1300 psig).

Figure 16. A chromatogram of 13 sulfur-containing compounds in hexane. Sulfur compounds (from left to right) are: (1) dimethyl sulfide, (2) isopropyl mercaptan, (3) tert-butyl mercaptan, (4) propyl mercaptan, (5) sec-butyl mercaptan, (6) iso-butyl mercaptan, (7) dimethyl sulfide, (8) butyl mercaptan, (9) dimethyl sulfide, (10) dipropyl sulfide, (11) diethyl disulfide, (12) diisopropyl disulfide, and (13) dipropyl disulfide.

Table III. Reproducibility of Retention Time of 13 Sulfur Compounds by an Unheated PLIS V2.2

Run/compound	Retention time (min) of compounds												
	1	2	3	4	5	6	7	8	9	10	11	12	13
1	2.84	3.19	3.60	3.74	4.52	4.67	4.95	5.16	5.69	7.93	8.53	10.09	11.25
2	2.84	3.18	3.59	3.73	4.51	4.67	4.94	5.15	5.69	7.92	8.52	10.08	11.25
3	2.84	3.18	3.60	3.74	4.52	4.68	4.94	5.16	5.69	7.93	8.53	10.09	11.25
4	2.84	3.18	3.60	3.74	4.52	4.68	4.94	5.16	5.69	7.92	8.53	10.09	11.25
5	2.84	3.18	3.60	3.74	4.52	4.68	4.94	5.16	5.69	7.92	8.53	10.09	11.25
6	2.84	3.19	3.60	3.74	4.52	4.68	4.95	5.16	5.69	7.93	8.53	10.09	11.25
7	2.84	3.18	3.60	3.74	4.52	4.67	4.94	5.16	5.69	7.92	8.53	10.09	11.25
8	2.84	3.18	3.60	3.74	4.52	4.68	4.94	5.16	5.69	7.92	8.53	10.09	11.25
9	2.84	3.19	3.60	3.74	4.52	4.68	4.95	5.16	5.69	7.93	8.53	10.09	11.26
10	2.84	3.18	3.60	3.74	4.52	4.68	4.95	5.16	5.69	7.93	8.53	10.09	11.25
Ave.	2.84	3.18	3.60	3.74	4.52	4.68	4.94	5.16	5.69	7.92	8.53	10.09	11.25
%RSD (*n* = 10)	0.05	0.06	0.05	0.06	0.05	0.05	0.05	0.04	0.04	0.03	0.02	0.02	0.02

DR-SCD, at 820°C, pressure 475 torr, reactor at 10.6 torr, ozone at 5 psig. Excellent chromatographic peak symmetry was obtained for all compounds.

Gasoline and diesel in hexane. Heavier hydrocarbons such as diesel, alkyl naphthalenes, and mine oil are often used to shape ethylene storage caverns. Upon removal of ethylene from the caverns, invariably, these oils exist as contaminants in the product being stored. This analysis has been done regularly in the past by supercritical fluid chromatography (9) mainly because it is impossible to prevent the sample from being fractionated upon injection. To simulate this condition, a sample of diesel fuel in hexane was analyzed, and the resulting chromatogram is shown in Figure 17. The design of PLIS allowed the entire sample to be vaporized at once with minimum fractionation, making it an ideal sample introduction system for the application mentioned. This would be difficult or impossible if a conventional diaphragm or rotary valve is used.

Oxygenated compounds. Volatile oxygenated compounds like methanol, ethanol, and 2-propanol are commonly analyzed in various hydrocarbon products. Figure 18 shows an overlay of 10 chromatograms of 1000 ppm (v/v) of methanol, ethanol, and 2-
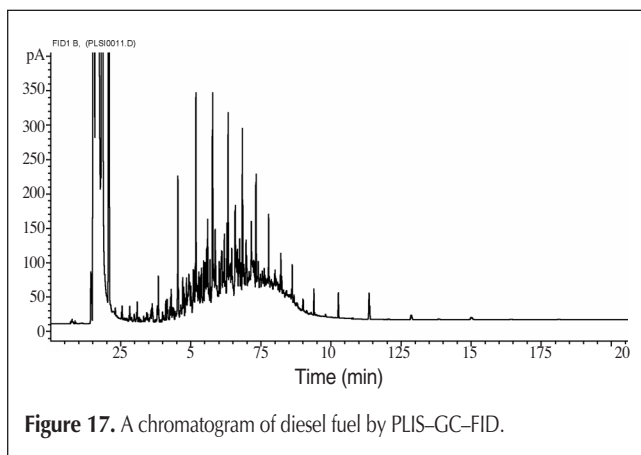
propanol in hexane. Hexane was used instead of liquefied high pressure hydrocarbons for ease of handling. Relative precisions for area counts at 95% confidence were found to be 2.2%, 3.1%, and 3.1% for methanol, ethanol, and 2-propanol, respectively. The high degree of inertness of the valve is clearly demonstrated with excellent peak symmetry even for highly polar compounds such as alcohols. Because of its design, the valve is directly coupled to an injector port without the requirements of transfer lines. The elimination of active metal sites and cold spots often encountered with transfer lines further improved the chromatography obtained.

Resistively heated PLIS

Although all the applications carried out by the unheated PLIS can certainly be conducted with the heated PLIS in the nonenergized mode, the heated PLIS variant offers new and extended analytical capability.

High-molecular-weight hydrocarbons. Figure 19 shows a chromatogram of ASTM-D-2887-simulated distillation standard. nC_{44} can be chromatographed in less than 6 min. Figure 20
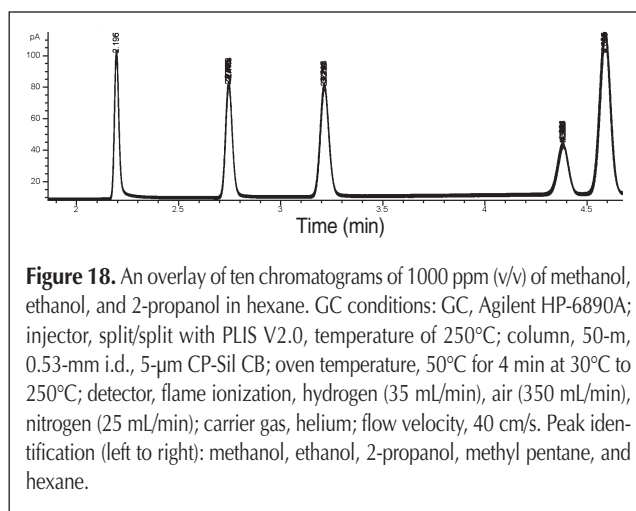

Figure 18. An overlay of ten chromatograms of 1000 ppm (v/v) of methanol, ethanol, and 2-propanol in hexane. GC conditions: GC, Agilent HP-6890A; injector, split/split with PLIS V2.0, temperature of 250°C; column, 50-m, 0.53-mm i.d., 5-μm CP-Sil CB; oven temperature, 50°C for 4 min at 30°C to 250°C; detector, flame ionization, hydrogen (35 mL/min), air (350 mL/min), nitrogen (25 mL/min); carrier gas, helium; flow velocity, 40 cm/s. Peak identification (left to right): methanol, ethanol, 2-propanol, methyl pentane, and hexane.

Figure 17. A chromatogram of diesel fuel by PLIS–GC–FID.

Table IV. Equal Molar Response of 13 Sulfur Compounds by an Unheated PLIS V2.2 GC–DR-SCD

Compound	Name	Retention time	Area counts	SD	%RSD*	ppm (w/w) of sulfur	Equal molar response
1	dimethyl sulfide	2.84	363269	3929.19	1.08	263	1.00
2	isopropyl mercaptan	3.18	280956	3980.17	1.42	213	0.96
3	tert-butyl mercaptan	3.59	238356	2456.50	1.03	171	1.01
4	propyl mercaptan	3.73	318149	2824.05	0.89	213	1.08
5	sec-butyl mercaptan	4.51	251016	2456.19	0.98	178	1.03
6	iso-butyl mercaptan	4.67	249881	2777.30	1.11	178	1.02
7	diethyl sulfide	4.94	251564	2249.69	0.89	179	1.02
8	butyl mercaptan	5.15	261558	2925.44	1.12	180	1.05
9	dimethyl disulfide	5.69	636877	7979.32	1.25	429	1.08
10	dipropyl sulfide	7.92	187971	2125.44	1.13	137	1.00
11	diethyl disulfide	8.52	439551	9299.08	2.12	314	1.02
12	diisopropyldisulfide	10.08	310291	7574.99	2.44	243	0.93
13	dipropyl sulfide	11.25	267779	8570.15	3.20	247	0.79

* $n = 10$, df = 9.

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shows an overlay of chromatograms of heavy and light hydrocarbon condensates using a heated PLIS valve. The extra energy derived from heating the sample channel aids in vaporizing high-boiling-point solutes such as nC_{44} hydrocarbon.

Monoethylene glycol in hydrocarbons. Monoethylene glycol (MEG) is commonly used as a heat exchanger fluid in the hydrocarbons industry. Because of its very low vapor pressure and the polar nature of the compound, it is difficult to chromatograph MEG in volatile hydrocarbons. A common technique involves the laborious extraction of the sample with water and the extract analyzed. Figure 21 shows an overlay of MEG in hexane using an unheated and heated PLIS valve. In this example, the unheated PLIS was found to be unsuitable for use in MEG analysis because of a severe asymmetric peak profile, yet excellent peak fidelity
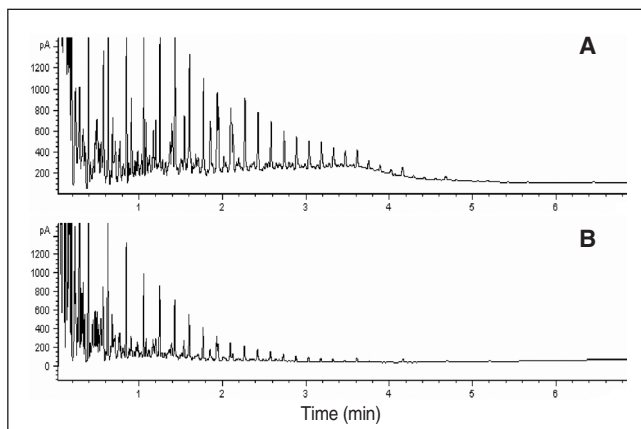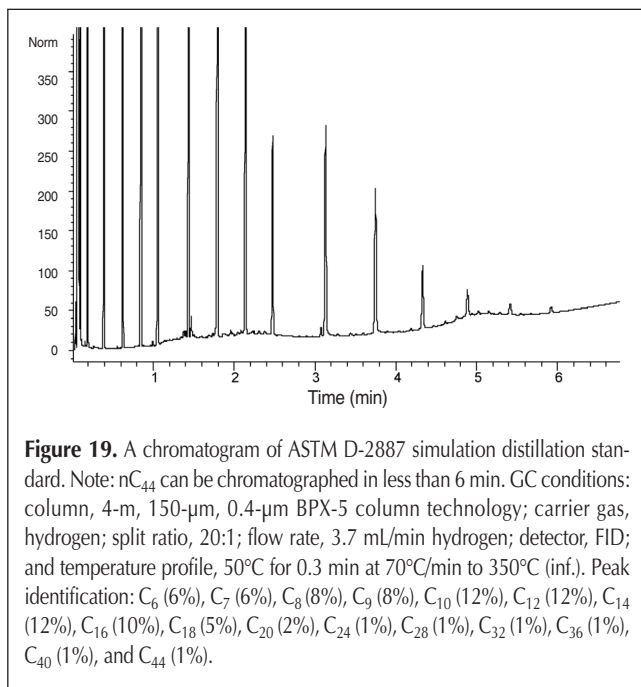
and symmetry were obtained with the heated variant. The advent of heated PLIS enhances the overall analytical capability of PLIS.

PLIS as a stand-alone vaporizing device. As mentioned earlier, the valve can be operated as a stand-alone vaporizing device. In this mode, PLIS is fitted with a stand-alone assembly including a heated adaptor and a four-way solenoid valve. Figure 22 shows a chromatogram of 2 µL liquid hexane injected using a PLIS valve coupled to a Varian CP-4900 micro GC. With a heated adaptor, PLIS can be effectively used to reproducibly convert liquid to a gas sample with minimum fractionation.

Conclusion

The development and commercialization of PLIS represents one of the important advances in sample introduction systems for GC, particularly in dealing with very high pressure, highly volatile liquids such as volatile hydrocarbons, and with wide boiling point range samples. With a rated pressure of 1200 psig, PLIS can handle the most demanding high-pressure liquid such as ethane. Despite that the inner surface of the valve is not

Figure 19. A chromatogram of ASTM D-2887 simulation distillation standard. Note: nC_{44} can be chromatographed in less than 6 min. GC conditions: column, 4-m, 150-µm, 0.4-µm BPX-5 column technology; carrier gas, hydrogen; split ratio, 20:1; flow rate, 3.7 mL/min hydrogen; detector, FID; and temperature profile, 50°C for 0.3 min at 70°C/min to 350°C (inf.). Peak identification: C_6 (6%), C_7 (6%), C_8 (8%), C_9 (8%), C_{10} (12%), C_{12} (12%), C_{14} (12%), C_{16} (10%), C_{18} (5%), C_{20} (2%), C_{24} (1%), C_{28} (1%), C_{32} (1%), C_{36} (1%), C_{40} (1%), and C_{44} (1%).

Figure 21. An overlay of MEG in hexane using an unheated (A) and heated (B) PLIS valve. Compound with retention time at 1.15 min—MEG.
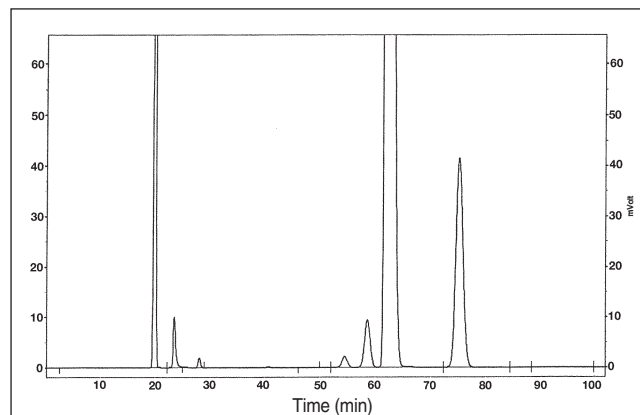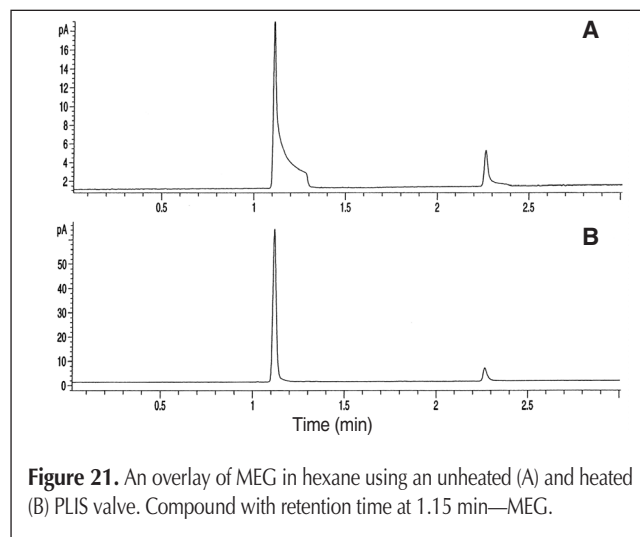

Figure 20. An overlay of chromatograms of commercially available heavy and light hydrocarbon condensates using a heated PLIS valve. Heavy condensate (A) and light condensate (B). GC conditions: column, 4-m, 150-µm, 0.4-µm BPX-5 column technology; carrier gas, hydrogen; split ratio, 20:1; flow rate, 3.7 mL/min hydrogen; detector, FID; and temperature profile, 50°C for 0.3 min at 70°C/min to 350°C (0 min).

Figure 22. A chromatogram of 2 µL liquid hexane injected using a PLIS valve coupled to a Varian CP-4900 micro GC. Compound identification (from left to right): air, water, butane, pentane, hexane (matrix), and heptane.

treated with passivation processes such as Silcosteel or titatium nitride deposition, the valve offers sufficient inertness so that volatile sulfur compounds can be successfully analyzed.

PLIS was found to be highly reliable, easy to service, and interfaced well with a conventional split/splitless injector such as an Agilent HP-6890. With a heated adaptor, PLIS can be used to reproducibly convert liquid to gas sample with minimum fractionation, thereby making it suitable for use as a sample introduction device for micromachined GCs.

The novel heated variant of PLIS further extends its applicability particularly for high-molecular-weight, high-boiling-point compounds of up to nC_{44} hydrocarbon.

Acknowledgments

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