

Jet Expansion Module for Liquid-Sampled GC-Discharge Ionization Detection of Liquefied Gases

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A rugged jet expansion module was designed, built, and utilized to sample liquefied gas for gas chromatography-discharge ionization detector (GC-DID) analysis. The module is inserted at an intermediate stage between a higher pressure sample cylinder and lower pressure gas injection manifold. The title jet module permits selection of liquid-phase or vapor-phase sampling by setting the valve–cylinder orientation up or down (relative to gravity). It consists of a four-way stainless steel cross, plus the following components connected to pipe thread ports: (1) mechanical pressure gauge, –15 to +30 psig; (2) threaded nut with 0.010-in. jet orifice (connect to sample cylinder valve); (3) bellows valve (connect to GC manifold); (4) bellows valve (connect to expansion cylinder). Making use of the jet module, measurement of air concentration in [¹⁵N]ammonia and sulfur hexafluoride (single-component) samples was found to be significantly lower in the liquid phase by GC-DID. This compact apparatus enables phase-selective sampling, reduces primary manifold contamination, and improves operator safety.

Isotope-labeled products include various gases such as [¹⁵N]-ammonia that can liquefy if moderately compressed into cylinders. It is known that such liquefied gases can have different impurity profiles in the liquid-phase and vapor-phase spaces. Thus, meaningful measurement of impurities in liquefied gas requires phase-selective analysis. By combining the principles of compressed gas delivery¹ and vacuum technology,² specialized gas injection manifolds have been designed for gas-sampled GC analysis. However, for product cylinders that contain liquefied gas, it is highly advantageous to be able to separately sample impurity concentrations in both liquid phase^{3–5} and vapor phase.^{6,7} Toward this objective, a robust “jet expansion module” was designed to help regulate the flow of liquefied sample (at relatively high

pressure) to a vapor expansion reservoir (at lower pressure) prior to sample GC injection.

Interface of the jet expansion module to a gas chromatograph (GC) equipped with a pulsed discharge helium ionization detector (denoted GC-PDHID) permits measurement of component concentrations in the liquid phase or vapor phase of the sample. GC-discharge ionization detector (GC-DID)-type instruments are particularly adapted to this application since sub-ppm concentrations of impurity can be quantitated in the sample liquid phase.

EXPERIMENTAL SECTION

Stainless steel fittings were obtained from Cincinnati Valve and Fitting. Swagelok manual bellows valves with a working pressure limit of 1000 psig were used. The steel jet fitting was equipped with an 0.010-in.-diameter orifice. Steel sample cylinders were nominally 0.5-L capacity and equipped with 0.25-in. national pipe taper (NPT) ports. Each NPT port connection was sealed with PTFE tape. Attached to each sample cylinder was a diaphragm valve rated at 3000 psig (Matheson-Trigas). Pressure gauges were equipped with steel Bourdon tubes (McDaniel Controls). [¹⁵N]-Ammonia was prepared at Isotec from 99 atom % [¹⁵N]ammonium chloride precursor. Sulfur hexafluoride (99.8%) was further purified at Isotec by vacuum distillation. Appropriate safety procedures should be followed when working with liquefied gases, which by their nature are pressurized.

Two instruments were used for gas chromatography. An Agilent-6890 GC was modified by Wasson-ECE for vapor-phase sample injection. It was equipped with a PDHID from Valco Instruments. The other GC was a Finnigan 9001 equipped with helium DID. For both GC systems, stainless steel vacuum-pressure manifolds were designed and built at Isotec for handling moderate-pressure gas samples. Essentially the title jet module is an interface between a higher pressure, liquefied gas cylinder and the lower pressure gas injection manifold.

RESULTS AND DISCUSSION

Figure 1 is a two-dimensional drawing of the jet expansion module and sample cylinder (depicted in liquid-sampling mode). The module consists of one four-way stainless steel cross, plus the following standard components connected to pipe thread (NPT) ports: (1) pressure gauge, –15 to +30 psig; (2) threaded nut with 0.010-in. jet orifice (connect to sample cylinder valve); (3) manual bellows valve (connect to GC manifold); (4) manual bellows valve (connect to expansion cylinder).

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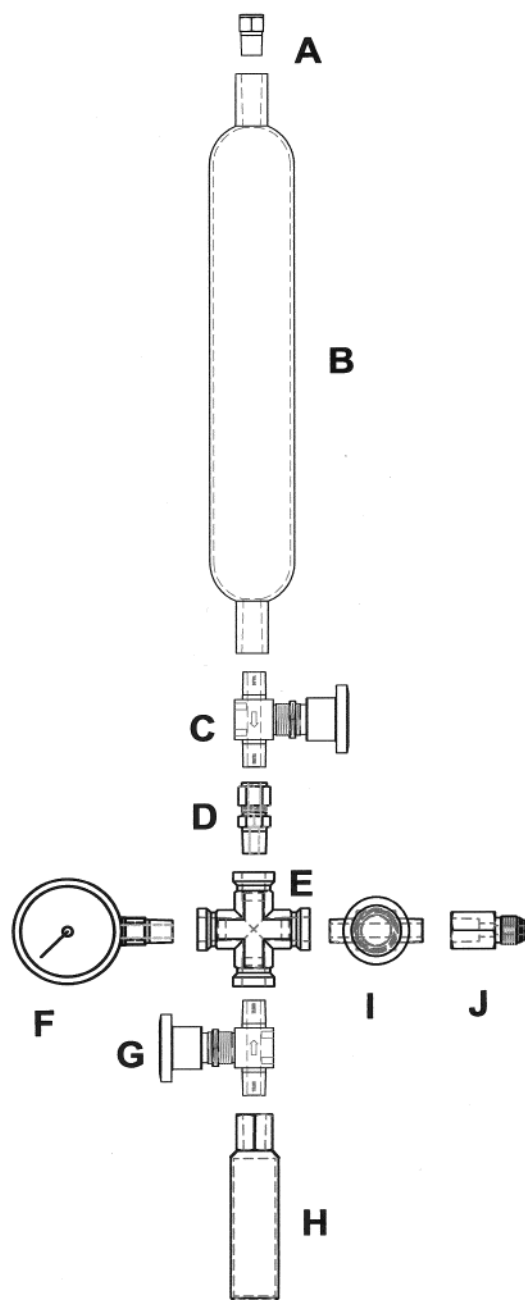


Figure 1. Exploded view drawing of the jet expansion module and sample cylinder. Module components are labeled as follows: (A) 0.25-in. NPT plug; (B) 0.5-L steel sample cylinder with 0.25-in. NPT ports; (C) sample cylinder diaphragm valve with 0.25-in. NPT ports; (D) 0.25-in. NPT fitting equipped with 0.010-in. jet orifice (in practice the jet subassembly can be fabricated using various component combinations); (E) 0.25-in. NPT cross; (F) pressure–vacuum gauge with steel Bourdon tube and 0.25-in. NPT port; (G) expansion cylinder bellows valve with 0.25-in. NPT ports; (H) expansion cylinder with 0.25-in. NPT port; (I) interfacial bellows valve; (J) adapter 0.25-in. NPT to VCR (also connected to GC-injection manifold).

GC sample testing starts with attachment of the sample cylinder valve (see Figure 1C) to the high-pressure end of the 0.010-in. jet fitting (Figure 1D) and attachment of the jet expansion module to the GC-injection manifold through an interface valve and VCR fitting (Figure 1J). With the GC-injection manifold under dynamic vacuum, the jet expansion module is then evacuated by opening the interface valve (Figure 1I). Note that the sample

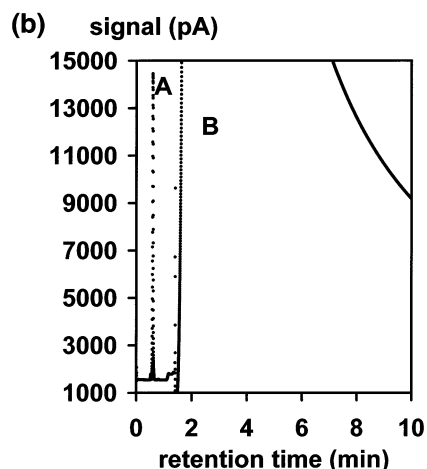
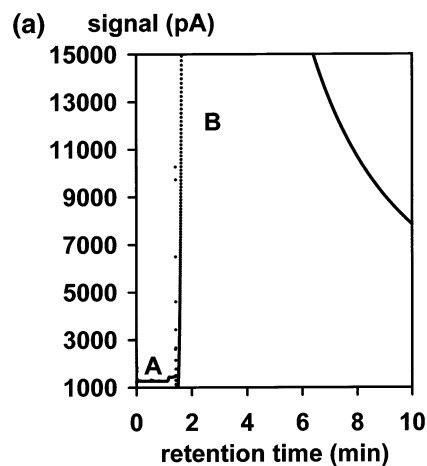


Figure 2. (a) Liquid-phase and (b) vapor-phase GC-PDHID of [¹⁵N]-ammonia. Component peaks are labeled as follows: (A) air; (B) ammonia. For each run, the cylinder vapor pressure was ~130 psia, injection volume 0.5 mL, injection pressure 0 psig. The GC column was Porapak-Q at 30 °C, 2 m × 3.2 mm × 2 mm with helium flow 25 mL min⁻¹. The PDHID temperature was 150 °C, and helium glow gas flow 30 mL min⁻¹. Helium supply gas purity was ≥99.9999%.

cylinder valve (Figure 1C) remains closed up to this point. The selection of sampling liquid or vapor depends on cylinder–valve orientation. To sample liquid phase, the cylinder (Figure 1B) would be positioned “up” (relative to gravity). Next, the interface valve (Figure 1I) is closed. At this stage, liquid-phase material could be valve-throttled through the jet flow restriction and into a static expansion volume (Figure 1E–H). In the present design, the cylinder valve–jet tandem provides regulated mass transfer of sample to a 50-mL expansion reservoir. The expansion reservoir is typically filled such that a pressure difference of >100 psia across the jet orifice is maintained while the sample valve (Figure 1C) is cracked open. Once sample vapor is isolated at lower pressure, it is straightforward to transfer it through an interfacial bellows valve (Figure 1I) to the primary gas GC-injection manifold.

In general, the jet expansion module has been used to determine phase-select chemical purity of single-component gases. The 0.010-in.-diameter jet was chosen to enable “reasonable” fluid flow control while minimizing droplet formation under working conditions. Representative chemical applications include ammonia, sulfur hexafluoride, and methylamine. Panels a and b of Figure 2 are gas chromatograms of [¹⁵N]ammonia liquid phase and vapor phase, respectively, under similar GC-PDHID conditions. Note the

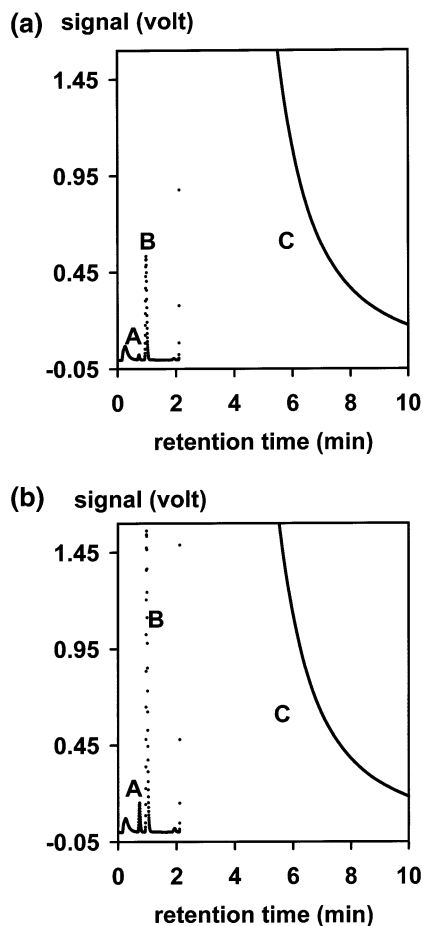


Figure 3. (a) Liquid-phase and (b) vapor-phase GC-DID of sulfur hexafluoride. Component peaks are labeled as follows: (A) air; (B) carbon tetrafluoride; (C) sulfur hexafluoride. For each run, the cylinder vapor pressure was ~ 335 psia, injection volume 1.0 mL, injection pressure 760 Torr. The GC column was Porapak-R at 40°C , $6\text{ ft} \times 0.125\text{ in.} \times 0.085\text{ in.}$ with helium flow 25 mL min^{-1} . The DID temperature was 150°C , and helium glow gas flow 50 mL min^{-1} . Helium supply gas purity was $\geq 99.9999\%$.

comparative absence of air components in liquid-sampled ammonia. Indeed, the air component (commonly denoted “composite peak”) was measured to be 0.2 (liquid-phase) versus 150 ppm (vapor phase) based upon a 1 ppm external calibrant gas. Under similar conditions, dynamic vacuum blank GC-PDHID runs gave air component concentrations of <0.1 ppm. Such two-phase GC results can be valuable for purposes of quality certification or further purification.

“Chemical grade” sulfur hexafluoride (99.8%) can be further purified by distillation. Panels a and b of Figure 3 show chromatographic runs for vacuum-distilled SF_6 liquid phase and vapor phase, respectively. Note that, for this particular sample, the air component was found to be 2 (liquid phase) versus 11 ppm (vapor-phase) based upon a 5 ppm external calibrant gas. Indeed, the latter phase-dependent trend was also observed for SF_6 impurities carbon tetrafluoride and carbon dioxide (see Table 1). Under similar conditions, dynamic vacuum blank GC-DID runs gave air component concentrations of <0.5 ppm. The precision of liquid-sampled GC-DID was estimated by repeat injections of liquefied sulfur hexafluoride. Relative standard deviations (RSDs) of im-

Table 1. GC-PDHID and GC-DID Results for Chemical Impurities in $^{15}\text{NH}_3$ and SF_6

	concn, ppm	
	vapor phase	liquid phase
^{15}N ammonia (Porapak-Q, 30°C)		
air	150	0.2
sulfur hexafluoride (Porapak-R, 40°C)		
air	11	1.6
carbon tetrafluoride	160	55
carbon dioxide	1.9	0.7

purity peak areas (1–60 ppm range) did vary; however, all area RSD values were $<6\%$.

GC injection of liquefied gas from both liquid-phase and vapor-phase space is an important issue for the gas production and petroleum industry. The title jet expansion module can selectively sample either fluid space (confined in a metal cylinder) by means of a 180° manual rotation of the module. Choice of GC-DID-type systems for chemical purity analysis provides requisite sensitivity to detect low-level impurities in the liquid phase. The title jet expansion module was primarily designed for phase-selective chromatographic analysis of minor impurities that are dissolved in a single-component matrix. Due to differential vaporization effects through the jet, the quantitative application of this device might be limited to samples having one major component (that is, pure gases).

It is interesting to estimate the initial flow rate from a 0.25-in. (0.0064-m)-inner diameter pipe through an 0.010-in. (0.000 25-m) orifice. Under conditions of “frictionless”, incompressible fluid flow, the following calculation can be used to predict linear velocity:⁸

$$v = [2g_C V_S (\Delta p) / (1 - (A_2^2 / A_1^2))]^{1/2}$$

where v is the linear velocity of liquefied gas (along pipe axis, m s^{-1}), g_C is a constant (converts mass \times acceleration to force, $g_C = 1\text{ kg m s}^{-2} \text{ N}^{-1}$), V_S is the specific volume of liquid or vapor ($\text{m}^3 \text{ kg}^{-1}$), Δp is the pressure difference across jet (N m^{-2}), A_2 is the jet cross sectional area (m^2), and A_1 is the feed pipe cross sectional area (m^2).

Though the process of expanding liquefied gas into a lower pressure closed reservoir is dynamic, the equation above can provide a rough estimate of initial flow velocity. For liquid ammonia near room temperature, the initial velocity that results from a 130 psia ($8.96 \times 10^5 \text{ N m}^{-2}$) pressure drop would be $\sim 55\text{ m s}^{-1}$. A similar calculation for liquid sulfur hexafluoride results in an initial velocity of $\sim 50\text{ m s}^{-1}$ for a 335 psia ($2.31 \times 10^6 \text{ N m}^{-2}$) pressure difference. The latter Δp pressure values were chosen on the basis of material vapor pressure at 21°C . To provide some context for gas flow rates through the jet module, the initial jet flow velocities are about 2 orders of magnitude higher than typical gas velocity within the downstream GC columns.

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CONCLUSION

The title "jet expansion module" is a useful apparatus for both liquid sampling and vapor sampling of single-component, liquefied gases. Its modular design with minimal moving parts has resulted in mechanical reliability. At present, about 100 liquefied gas samples have been analyzed using jet modules interfaced to GC-DID instruments. Since most of its mechanical components are commercially available, adaptations of the present jet module could also be interfaced to other gas analyzers.

ACKNOWLEDGMENT

The authors acknowledge the Isotec division of Sigma-Aldrich Corp. for support.

Received for review June 3, 2002. Accepted December 31, 2002.

AC0203692