

Enhanced Performance of an Integrated Gas Chromatograph for Online Gas Analysis

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Abstract

The physical properties of the gas, the composition of the gas during upset, and the operation of the gas in hazardous locations can affect the analytical method development and the hardware design. The gas chromatograph must be compatible with the physical properties (e.g., the physical state) of the sample. The sample must be introduced to the gas chromatograph as a single phase. Since on-line gas chromatographs are installed at the pipeline to analyze sample continuously, the system must be designed for fast analyses and low maintenance.

The thermal conductivity detector (TCD) has been used extensively in the on-line gas chromatographs due to its simplicity, stability, durability, and universal detection. Many analyses require the measurement of fixed gases (H₂, O₂/Ar, N₂, CO and CO₂) and light hydrocarbons (C₁ - C₁₀) for which the TCD is ideally suited. Optimization of a thermal conductivity detector for on-line gas chromatography inevitably involves improvements in detectability and linearity, while minimizing degradation of column performance by the detector itself. To optimize the chromatography, the column module should be warmer than the valves and detectors while minimizing the interconnecting temperature gradients. With our patented design, the increased thermal mass and improved insulation minimizes the impact of environmental temperature changes.

By integrating the valves and detectors into a single structure, the lengths of interconnecting tubing and flow path can be greatly reduced. With this arrangement, the dead volume of the system has been reduced by approximately 60%. In addition, the maintenance process has been greatly simplified. This paper describes the enhanced operating characteristics and performance of a new integrated gas chromatograph. Of particular interest are design improvements, which greatly affect the data quality. In addition, repeatability data for a light hydrocarbon (C₁ - C₁₀) application is discussed. This data represents an order of magnitude improvement from data presented in previous publications.¹⁻⁴

Experimental

A prototype on-line gas chromatograph (Emerson Process Management Gas Chromatographs Division, Houston, Texas) equipped with dual 15- μ L thermistor detectors was used in this

evaluation. The detectors are located in the multi-valve system, which precisely controls sample injection, switching valve and detector temperature. The detector design is based upon the Danalyzer thermistor TC detector, which is CSA Class I, Groups C & D, Division I rated. The thermistors were 9 K ohm at 25°C and were operated at a bridge current of 23 mA (approximately 145°C).

Data acquisition was accomplished via prototype electronics, Model 2350 controller and PC-based MON software (Emerson Process Management Gas Chromatographs Division). Helium carrier gas with <0.5 ppm hydrocarbons was used for all data collection. Carrier and sample flow rates were measured using a digital bubble-type flowmeter (Alltech Associates, Deerfield, Illinois). Certified samples used in experiments for the determination of linear dynamic range and minimum detectable quantity were obtained from Aeriform (Pasadena, Texas).

Results and Discussion

The on-line gas chromatograph must be compatible with the properties (e.g., the physical state) of the sample. The sample must be introduced to the gas chromatograph system as a single phase. Accidental conversion from one phase to another can seriously alter composition. The dewpoint of a vapor mixture is the temperature at which condensation begins to occur at a given pressure. The dewpoint is lowered as the pressure is decreased. It is important to keep a gas heated at least 10°C above its dewpoint to prevent partial condensation.

Stream Switching System

A stream switching system (SSS) selects a single stream from multiple streamlines and introduces it into the gas chromatograph system. In the typical SSS, multiple individual valves are configured in a double block and bleed (DBB) structure. Since SSS are usually quite large, they introduce dead volume into the system, which can result in carry over from one stream to the next.

In addition to high maintenance costs, common problems with the traditional stream switching systems include sample condensation and cross contamination. In this design, a new compact, double block and double bleed (DBDB) stream

switching system has been developed with more heating flexibility to prevent condensation. In addition, the dead volume of the system has been greatly reduced with this arrangement.

Valve Structure

In this new stream switching system (SSS) (patents pending), the stream switching valves and the sample shut-off (SSO) valves are integrated into a single block, as shown in Figure 1.

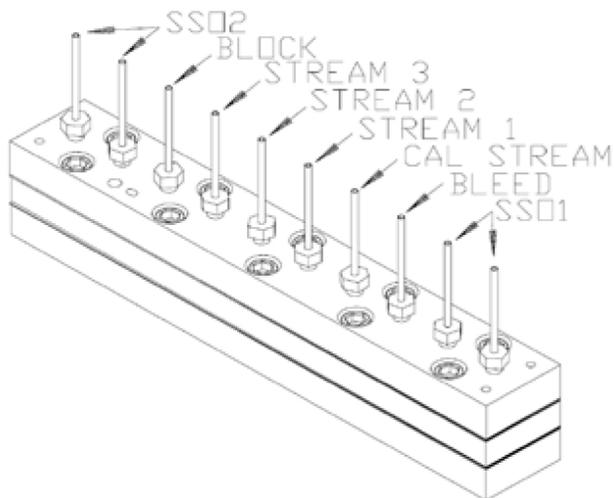


Figure 1. Schematic of a new stream switching system (SSS) (patents pending). It combines four stream valves (including calibration) and two sample shut off (SSO) valves into a single block structure.

The SSS is approximately seven inches in length, one inch in width and two inches in height. For rich gas applications, the SSS is placed into a cost-effective temperature controlled oven to prevent sample condensation. In the event of a power failure, the SSS is designed to be fail-safe (i.e., normally closed valves) to prevent contamination of the gas chromatograph system.

To prevent cross contamination, the SSS is designed in a double block and double bleed (DBDB) configuration. It has two flow blocks for each stream and two bleed paths for system purging. Since the standard system has four streams including calibration and two SSOs, it can be utilized for a wide variety of applications. If DBDB is not required the SSS can be configured for seven streams including calibration.

Multi-Valve System

In the typical on-line gas chromatograph, multiple individual valves are configured in a temperature-controlled oven. Since they are readily available in 4-port, 6-port, 10-port configurations (or more), most of the valves used in the field are diaphragm valves, slider valves and/or rotary valves. Diaphragm valves are most widely used because of their small size, low dead volume and durability. A diaphragm valve includes sample/carrier flow part and actuating part. Typically, one or more screws are used to tighten the valve system (i.e., the sample/carrier flow part and

the actuating part) into a single unit.

To provide a reliable gas chromatograph system, the valve system must be leak free and have a rapid response time. Since the gas chromatograph system can be contaminated during upset conditions, the valve system should be designed for easy maintenance. In this design, the valve system can be easily cleaned or replaced within minutes. In addition to high maintenance costs, the common problems associated with the traditional valve systems include internal leakage and large dead volume. By integrating the valves and detectors into a single structure, the lengths of interconnecting tubing and flow path can be greatly reduced. With this arrangement, the dead volume of the system has been reduced by approximately 60%.

Multi-Valve Structure

In this multi-valve system (MVS), the valves and detectors are integrated into a single block structure, as shown in Figure 2. The MVS is approximately five inches in diameter and three inches in height. Since the standard system has five 6-port valves and two thermal conductivity detectors, it can be easily adapted for a wide variety of applications. For very simple applications, the MVS can have two or three valves with only one detector or, for more complex applications, the MVS can have up to seven valves.

In the typical gas chromatograph system, nitrogen actuating gas or helium carrier is used to switch the valves. Since the actuating part of the valve is less susceptible to contamination than the sample/carrier flow part, it requires maintenance less frequently. In the MVS, the screw pattern is designed so that the upper sample/carrier flow part can be removed while the lower actuating part remains intact. In the typical gas chromatograph system, it can take several hours to replace the diaphragms in multiple individual valves. In this design, the maintenance time has been reduced to less than an hour.

Typically, the actuating part of the valve is separated from the driving part (solenoids) and located in the temperature-controlled oven. Since the temperature of the oven can be 80°C (or higher), it exceeds the temperature limit of most solenoids. The connective tubing used to separate the actuating and driving parts can increase the valve response time and construction costs for the system. In the MVS, a special plastic manifold was designed to interface the solenoids to the lower valve body, as shown in Figure 2. The plastic manifold material has been carefully selected for its mechanical strength and thermal insulation properties. Since the solenoids and the actuating part of the valve are connected directly through this manifold, the response time is greatly improved.

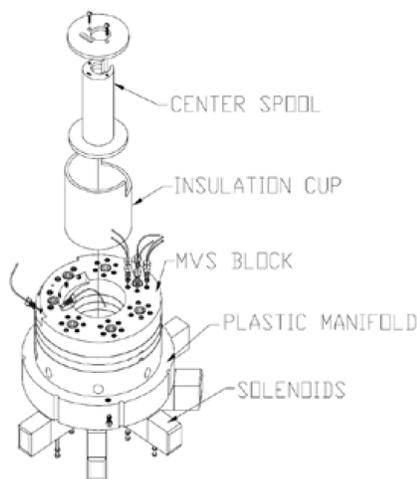


Figure 2. Schematic of a multi-valve system (MVS). In the MVS, five valves and two detectors are integrated into a single block structure. The column module is located in the center of the MVS block.

In trace level applications (i.e., ppm O₂, CO, CO₂, etc.), the valve system can be contaminated from diffusion (or leakage) through the diaphragm material. To minimize this problem, the diaphragm material has been carefully selected to be durable and impermeable. To eliminate internal leakage (across the diaphragm), the screw size, pattern and torque have been carefully optimized. Temperature Oven Through integration of the valve and the detector systems, the system performance (i.e., repeatability) can be greatly improved. In this design, the large thermal mass of the valve system is used to improve the thermal stability of the thermal conductivity detectors (TCD). In addition, the valve system provides a very stable environment for the column module, which is located in the center of the MVS. To optimize the chromatography, the valve system including the detectors and the column module are heated independently and precisely controlled within $\pm 0.05^{\circ}\text{C}$.

The first heated zone is composed of a band heater around the MVS block, insulation cover, and plastic manifold, as shown in Figure 3. The insulation cover is made of a btu powder material covered with steel sheet. The btu material has been selected to minimize the thermal leak out of the system. The second heated zone, the column module, has a cartridge heater located in center of an aluminum spool. To ensure uniform heating, the columns are wound tightly around the aluminum spool.

The insulation cup surrounding the column spool is thermally isolated from the valve and detector block with an air gap, and the insulation cover minimizes the heat leakage from the column module. With this arrangement, the temperature differential between the two zones can be up to 20°C. To minimize temperature fluctuations in the columns, the carrier gas is

preheated in tubing coils, which are upstream from the valves. The heated zones are controlled using temperature controllers and RTDs.

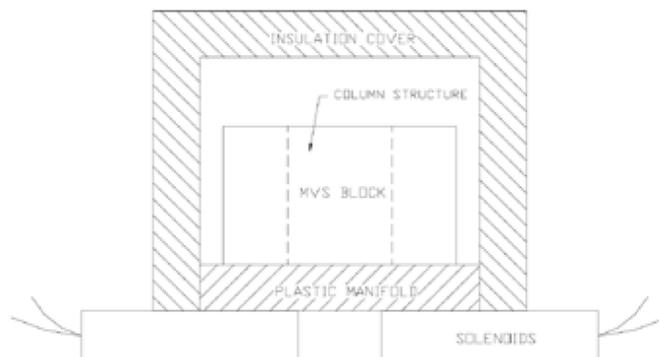


Figure 3. Schematic of a new multi-valve system (MVS) temperature-controlled oven. It is composed of a band heater around the MVS block, insulation cover, and plastic manifold. The solenoids are attached directly to the plastic manifold and located at the outside of the thermal oven.

Micro-volume Thermistor Detector

Optimization of a thermal conductivity detector for online gas chromatography inevitably involves improvements in detectability and linearity while minimizing degradation of column performance by the detector itself. Additionally, for on-line gas chromatograph systems, the detector design should be simple to maintain system durability. Reduction of the internal volume of the TCD results in less sample dilution in the cell, thereby increasing the effective concentration. By focusing design attention on reducing the internal volume, it was believed that the desired improvements for on-line analyses could be achieved. A number of experiments were performed to evaluate this effect. Additionally, a typical natural gas application is presented as evidence of the suitability of the new design for the on-line gas chromatograph environment.

Cell Geometry Effects

Both filament- and thermistor-type TCDs have been widely utilized in on-line gas chromatographs. Thermistor detectors offer the advantages of reduced sensitivity to carrier flow perturbations and relative inertness to corrosive samples or samples containing trace amounts of oxygen. The filament-type TCD offers the advantage of a higher operating temperature range with the disadvantage of being susceptible to loss-of-carrier burnout. Since the thermistor detector sensitivity decreases as cell temperature increases, it is better suited to applications requiring relatively low operating temperatures (i.e., $<120^{\circ}\text{C}$). For these reasons, the thermistor-type TCD is ideally suited for the measurement of fixed gases (H₂, O₂/Ar, N₂, CO and CO₂) and light hydrocarbons (C₁ - C₁₀).

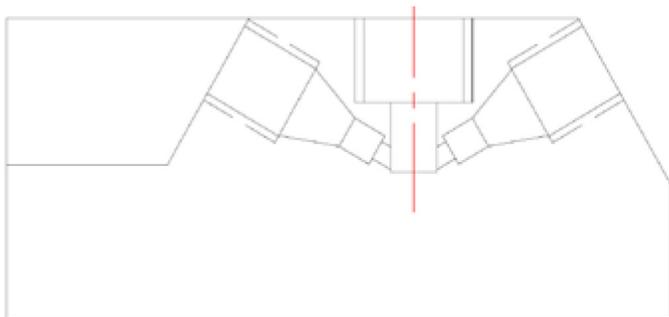


Figure 4. Schematic for micro-volume thermistor detector. The design of the detector on both the reference and measurements sides is identical.

The designs used for TCD are typically based upon flow-through-type or diffusion-type cell geometry. The flow-through-type cells have the advantage of retaining peak symmetry without the large volumetric time constants associated with larger-volume cells. They have the disadvantage of moderate detector noise (due to sensitivity to flow perturbations) which results in higher detection limits. Diffusion-type cells, while yielding very low detector noise, have the disadvantage of acting as a mixing or exponential dilution chamber. Hence, the actual chromatographic peak shape can be severely distorted with a diffusion-type cell. For this reason, our thermistor detector is based upon a pseudo-flowthrough design for the micro-volume detector cell. Figure 4 shows a cross-sectional view of our micro-volume thermistor detector. The design of the detector on both the reference and measurement sides is identical.

Any improvements achieved by reducing the cell volume can readily be lost by the creation of unswept regions in the detector block. In order to demonstrate that the desired cell geometry has been achieved without adverse effects, our micro-volume thermistor detector was evaluated with propane (in a balance of helium) as a sample for response as a function of flow rate (Figure 5). An apparent linear response was observed a several different flow rates (ranging from 5 to 20 mL/min), indicating an effectively swept detector volume, which results in minimal peak distortion in the micro-volume cell.

The TCD measures the changes in thermal conductivity of the carrier, which is altered when an eluting analyte is present. Since the TCD is a mass flow (concentration) detector, that is, responding to changes in analyte concentration in the detector cell, lower flow rates resulting from the use of micro-packed or capillary columns should favor the response of a micro-volume TCD. As a general rule, the detector cell volume should be no greater than 20% of the halfwidth of early eluting components.⁵ For the micro-volume thermistor detector described, this would include peaks as small as one sec in width (at a flow rate of 5 mL/min). Thus, capillary columns should offer the efficiency

required for this effective concentration increase.

Linear Dynamic Range

Since sample concentrations can vary from stream to stream, the linear dynamic range is an important factor with an on-line GC. Using propane as a sample, the linear dynamic range of our micro-volume thermistor detector was determined. The linear dynamic range was defined as the range of response factor based upon area measurement which varies by less than a specified quantity.⁶ Over a range of response factors of $\pm 10\%$, the linear range was found to be $10e5$. Using the generally accepted definition of MDQ (S/N ratio of 2), the micro-volume thermistor detector was found to have a detection limit of $4.8 \times 10e-9$ g/mL, corresponding to ca. 3-ppm propane in helium. These results were obtained with 9 K ohm at 25 °C thermistors operated at a bridge current of 23 mA (approximately 145 °C).

Analysis of Natural Gas

The analysis of natural gas is important for several reasons: calculation of physical properties (i.e., calorific value), identification of source and measurement of gas quality. The accuracy required from the analysis strongly influences the selection of analytical technique. As an alternative to direct measurement, gas chromatographs provide sufficient detail and precision to allow the calculation of several natural gas properties from a single analysis.

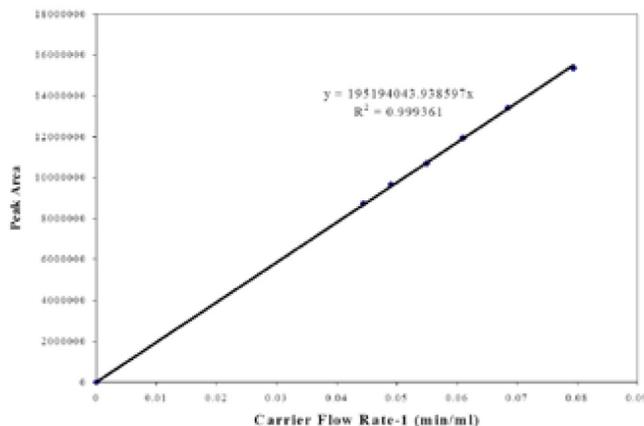


Figure 5. Response Vs flow rate for the micro-volume thermistor detector using propane as a sample and helium as carrier.

For the calculation of calorific value, relative density and compressibility, the heavier hydrocarbons are typically measured as a composite (e.g., C6+). The calorific value of natural gas is typically calculated within one British thermal unit (Btu). However, to calculate phase properties (e.g., hydrocarbon dewpoint), the heavier components should be further characterized. Small variations in the composition, especially

in the heavier hydrocarbons, can result in large variations of hydrocarbon dewpoint.

Natural Gas Application

To improve the performance of our natural gas applications, the chromatography was optimized for our prototype gas chromatograph. In order to deal with the analytical constraints, 316 SS primary plates were selected for the multi-valve system (MVS) and the stream switching system. To prevent partial condensation of the sample, the sample transport lines, the stream switching system including the sample shut off valves, and the sample valves were heated above $>60^{\circ}\text{C}$.

The MVS included five 6-port valves and two thermal conductivity detectors (TCD). The MVS including sample valves, switching valves and detectors was held isothermal at 80°C . For the first column train, the valves were configured for a backflush to detector with a series bypass and; for the second column train, the valves were configured for a backflush to detector. The resulting hardware configuration is illustrated in Figure 6.

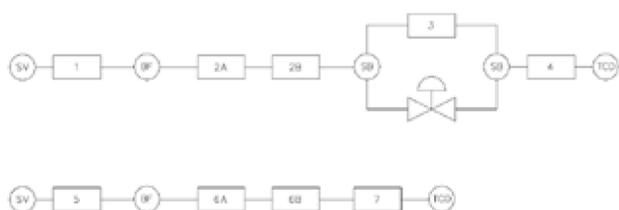


Figure 6. Hardware configuration for the analysis of natural gas. Components: sample valves (SV), backflush valves (BF), series bypass valve (SB) and thermal conductivity detectors (TCD).

For the analysis of typical natural gas (approximately 1000 Btu), a vapor calibration blend containing nitrogen, carbon dioxide, methane, ethane, propane, isobutane, butane, neopentane (2,2-dimethyl propane), isopentane, pentane, isohexane (2,2-dimethyl butane), and hexane was selected for the methods development. The composition for this calibration blend is shown in Table 1. For the analysis, 165 μL of vapor calibration blend was injected. The sample size was optimized to minimize the tailing of methane due to column over loading while retaining the required precision for the pentanes.

Table 1: Composition of Typical Natural Gas Calibration Blend

Compound Name	Concentration (Mol %)
Nitrogen (N ₂)	0.603
Carbon dioxide (CO ₂)	0.403
Methane (CH ₄)	97.1154
Ethane (C ₂ H ₆)	1.009
Propane (C ₃ H ₈)	0.500

Isobutane (C ₄ H ₁₀)	0.100
Butane (C ₄ H ₁₀)	0.100
Neopentane (C ₅ H ₁₂)	0.050
Isopentane (C ₅ H ₁₂)	0.050
Pentane (C ₅ H ₁₂)	0.0495
Neohexane (C ₆ H ₁₄)	0.0101
Hexane (C ₆ H ₁₄)	0.010

A 14-inch porous polymer column (Emerson Process Management) was used to separate isohexane for backflush to the detector. The isohexane and heavier components are measured as a C₆₊ composite. The lighter components (<C₆) were subsequently transferred from the backflush column to a four-foot boiling point column coupled to three-foot porous polymer column (Emerson Process Management) for further separation. The critical separation for the coupled column is the ethane/propane separation for the series bypass valve switch. Propane, isobutane, butane, neopentane, isopentane, and pentane were bypassed to the TCD for quantitation.

A third column, a seven-foot porous polymer column (Emerson Process Management) was used to separate nitrogen, methane, carbon dioxide and ethane. Finally, a five-inch glass bead column (Emerson Process Management) was used to dampen the pressure pulses at the TCD from valve switches. Figure 7 shows the resulting chromatogram. The cycle time for the typical natural gas was achieved in four minutes.

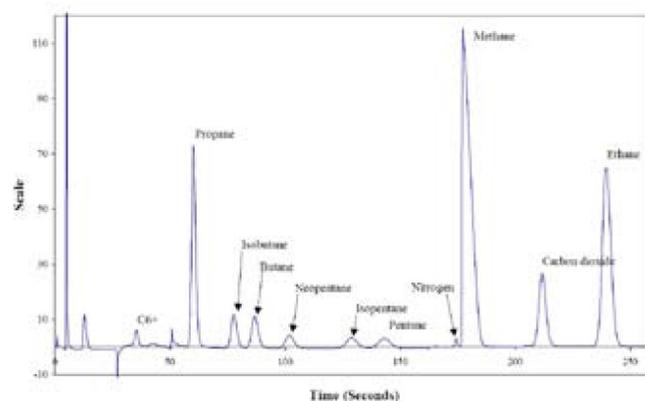


Figure 7. TCD chromatogram of typical natural-gas (approximately 1000 Btu) calibration blend utilizing micro-packed columns and isothermal oven conditions.

For the analysis of rich natural gas (> 1100 Btu), the second detector is used to further characterize the heavier components (C₆₊). For the second column train, a vapor calibration blend containing nitrogen, carbon dioxide, methane, ethane, propane, isobutane, butane, isopentane, pentane, isohexane, hexane, heptane, octane, and nonane was selected for the methods development. The composition for this calibration blend is shown in Table 2. For the analysis of the second column train,

745 µL of vapor calibration blend was injected. The sample size was optimized to provide adequate detection for octane.

A 12-inch boiling point column (Emerson Process Management) was used to separate the C9s for backflush to the detector. The C9 and heavier components are measured as a C9+ composite. The lighter components (<C9) were subsequently transferred from the backflush column to a nine-foot boiling point column coupled to two-foot glass bead column (Emerson Process Management) was used to separate C6s, C7s and C8s. Again, a five-inch glass bead column (Emerson Process Management) was used to dampen the pressure pulses at the detector. Figure 8 shows the resulting chromatogram. The cycle time for the heavier components was achieved in four minutes.

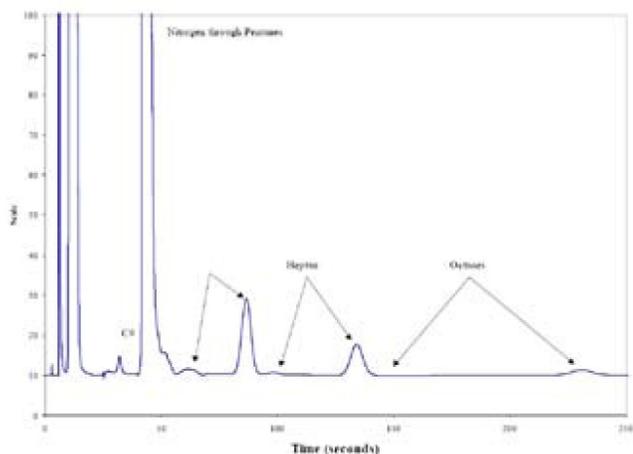


Figure 8. TCD chromatogram of rich natural gas (approximately 1100 Btu) calibration blend utilizing micro-packed columns and isothermal oven conditions.

Repeatability Data

To demonstrate the enhanced performance of the integrated gas chromatograph, a typical natural gas application has been selected as a benchmark. Most commercial gas chromatographs with a typical natural gas application are advertised as repeating within ± 0.5 Btu/1000 Btu. Over a 24-hour period, Emerson’s integrated gas chromatograph produced repeatability data that was within ±0.054 Btu/1000 Btu, as shown

Table 2: Composition of Rich Natural Gas Calibration Blend

Compound Name	Concentration (Mol %)
Nitrogen (N2)	2.5020
Carbon dioxide (CO2)	1.0010
Methane (CH4)	90.5246
Ethane (C2H6)	4.0020
Propane (C3H8)	1.0000
Isobutane (C4H10)	0.3000
Butane (C4H10)	0.3000

Isopentane (C5H12)	0.0999
Pentane (C5H12)	0.0999
Hexane (C6H14)	0.0998
Heptane (C7H16)	0.0500
Octane (C8H18)	0.0159
Nonane (C9H20)	48.9 ppm

in Figure 9. To further demonstrate the data quality, for the same 24-hour period, nitrogen repeated 0.585 ± 0.0004 Mol %, methane 97.196 ± 0.0027 Mol %, propane 0.5797 ± 0.0009 Mol % and pentane 0.0564 ± 0.001 Mol %. This data represents an order of magnitude improvement (and better) than data presented in previous publications.¹⁻⁴

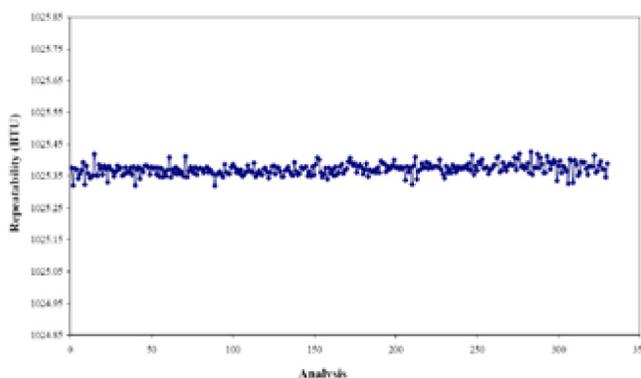


Figure 9. Repeatability data collected for 24-hours (1025.37 ± 0.055 Btu) using typical natural gas (approximately 1000 Btu) calibration blend.

To achieve an order of magnitude improvement in data quality, several key requirements were satisfied. The dead volume of the system was greatly reduced, which minimized the component band spreading. This provided for narrower chromatographic peaks, which resulted in better component separations for valve switches. Furthermore, the large thermal mass of the valve system was used to improve the stability of the detectors and to provide a stable environment for the column module. In addition, the carrier gas was preheated before introduction to the column train. This minimized temperature fluctuations in the columns, which resulted in more consistent component retention times. Finally, the reduced detector volume and noise resulted in increased sensitivity. This allowed more flexibility in optimizing sample size, which improved column efficiency.

Summary

The demand for improved system performance and reduced maintenance costs has resulted in the need to design a new on-line gas chromatograph. Through the integration of the valve and detector systems, the system performance can be greatly improved. The large thermal mass of the valve system is used to improve the stability of the thermal conductivity detectors and to

provide a stable environment for the column module. With this arrangement, the dead volume of the system has been reduced by approximately 60%. This paper describes the enhanced operating characteristics and performance of a new integrated gas chromatograph.

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