DESIGNING ON-LINE CHROMATOGRAPH SYSTEMS
FOR LIQUID FRACTIONATION FACILITIES

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ABSTRACT

Liquid fractionation plants can optimize their operations by installing on-line gas chromatograph systems that have been properly designed to provide reliable, fast, accurate results.

One of the most important, but overlooked, facets of designing an on-line analytical system for gas processing facilities is the sample conditioning system (SCS). The sample delivered to the Gas Chromatograph (GC) must truly represent the process media if the measurement is to be accurate — or even meaningful. Samples may be transported to the GC in either gas or liquid phase, but they will ultimately be analyzed in the gas phase only. Selection of sample location and careful attention to sample phase (liquid or gas) is required to ensure optimum system performance.

Discussed in this paper are: typical process conditions, GC location, sample transport systems, and details of both vapor- and liquid-phase sample conditioning.

INTRODUCTION

The SCS , purchased from the GC vendor or separately along with an optional analyzer shelter and associated instrumentation, performs three functions:
>   1- Sample transport system,
>   2- Sample conditioning and stream switching, and
>   3- Sample injection.

All three parts must operate together to supply a clean, representative, *single-phase* sample to the analyzer. Each measurement stream has process-specific requirements centered around the need to transport and maintain a single-phase sample to the sample inject valve located in or near the analyzer oven. After sample injection, the sample is mixed with a light carrier gas and carried through the columns in the vapor phase for component separation and subsequent analysis. On-line gas chromatographs must provide fast, accurate, reliable results for any process control system to fully optimize plant performance. Key factors are:
>   1- Reliability,
>   2 -Analytical Speed, and
>   3- Cost.

THE PROCESS

Liquid fractionation towers (columns) can be controlled by optimizing the inlet feed flow rate, reflux flow rate, reflux temperature and column pressure. On-line chromatographs can provide measured results of both the composition in column overheads (gas phase), column bottoms and inlets (liquid phase) for process control. With GC data, changes in composition at the inlet to each column can be compensated for as part of the overall control scheme. Tighter overhead product specifications can then be met and reduced operating costs can result. (For a more complete description of the process, refer to GPA Engineering Data Book Volume II, Section 19).

The following process conditions, typical of an NGL fractionation facility, serve as an example for design of an analytical system as part of a larger process control system.
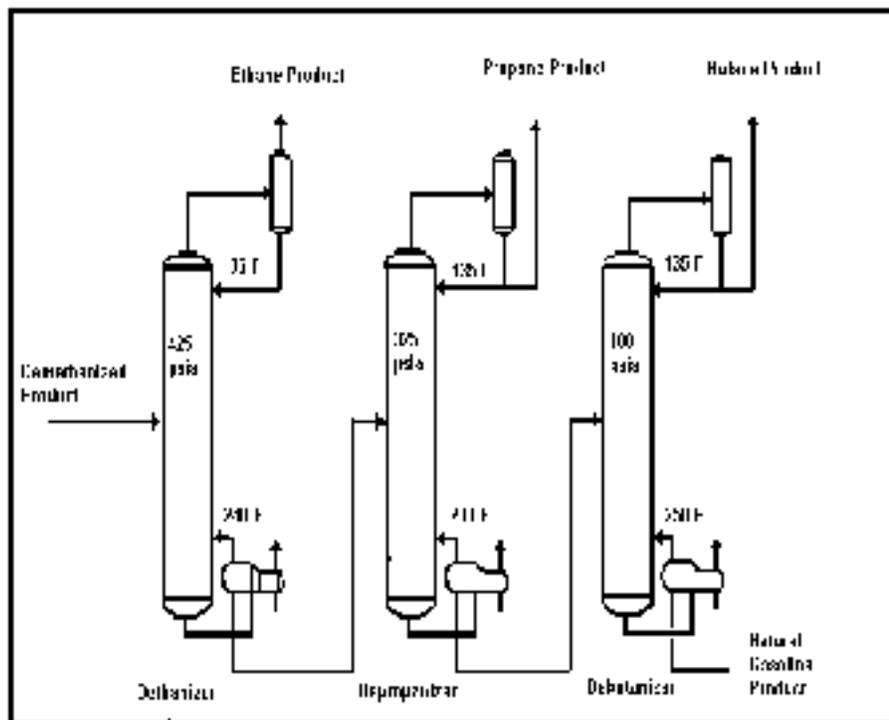

LIQUID FRACTIONTION TRAIN

Figure 1

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Table 1
Typical Stream Compositions (mole%)

Component (mole%)	Inlet feed	De-eth over-hd	De-prop over-hd	De-but over-hd	De-eth bottom	De-prop bottom	De-but bottom
Nitrogen	Trace	Trace	0	0	0	0	0
Methane	0-3%	0-2%	0	0	0	0	0
C02	0-3%	0-2%	Trace	0	0	0	0
Ethane	0-35%	0-100%	0-10%	Trace	0-10%	Trace	0
Propane	0-35%	0-20%	0-100%	0-5%	0-60%	0-5%	Trace
Iso-Butane	0-15%	0-2%	0-5%	0-50%	0-20%	0-30%	0-2%
N-Butane	0-15%	Trace	trace	0-70%	0-40%	0-50%	0-15%
Iso-Pentane	0-5%	0	0	0-2%	0-5%	0-10%	0-30%
N-Pentane	0-5%	0	0	0-2%	0-5%	0-10%	0-35%
Hexanes +	0-3%	0	0	Trace	0-10%	0-40%	0-55%

Table 2
Typical Process Conditions

Process Conditions	Inlet feed	De-eth over-hd	De-prop over-hd	De-but over-hd	De-eth bottom	De-prop bottom	De-but Bottom
Pressure at sample point	400 psig	30 psig	15 psig	20 psig	400 psig	260 psig	100 psig
Temperature at sample point	70 F	95 F	80 F	130 F	220 F	260 F	200 F
Phase at sample point	Liquid	Vapor	Vapor	Vapor	Liquid	Liquid	Liquid
Phase to sample system oven	Vapor	Vapor	Vapor	Vapor	Liquid	Liquid	Liquid
Phase to analyzer oven	Vapor	Vapor	Vapor	Vapor	Vapor	Liquid	Liquid

THE GAS CHROMATOGRAPH

This paper does not attempt to discuss the merits of one application method over another or the differences in design from one manufacturer to another. GC components such as valves, columns, detectors, electronic hardware and software can be configured in a multitude of ways for the same application. When evaluating various methods, these quality criteria should be considered:

  1- Analytical speed (the time it takes to transport, separate and measure each component of interest),

  2- Complete baseline separation of all measured components from one another on a chromatogram, and

  3- Suitability for packaging in an analyzer building, three sided shelter or outdoors.

GC Location

The GC should be located as close to the sample point as possible to allow for short sample transport lines. This is frequently a compromise between location of the analyzer building and available site space to locate the building. GC location will determine the sample system lag time which can account for the majority of the overall system lag time.

There is a trade-off between cost and analytical speed when considering the location of a common analyzer building. Sample transport time (lag time) can introduce a large delay into the response of the analytical system. The best solution for minimizing sample lag time is to reduce the volume of sample in the transport lines and the sample conditioning system. By minimizing the volume, the velocity at which the sample travels can be increased. Shorter sample lines and smaller diameter tubing (1/8 inch from 1/4 inch) both help to reduce sample volumes.

Vaporizing liquid samples will reduce the sample volume and increase the sample velocity a great deal. Once a liquid or heavy vapor phase sample has been vaporized, the sample transport tubing must be heat-traced. Heat tracing can be costly when multiple sample lines travel several hundred feet. Installation costs for liquid sample lines are substantially less than for heat-traced vapor phase sample lines.

The sample return flow rate can also be set in the SCS to increase sample flow on either liquid or gas phase sample lines depending on the suitability of returning higher volumes of sample to the process return point. For example, it may be considered wasteful to return high volumes of on-spec products to the flare stack.

An alternative solution is to locate the GCs outdoors close to the sample point rather than in a central analyzer building.

This can greatly reduce the installed cost and increase the speed of the overall system, thereby improving plant control system performance. There is considerable disagreement within industry about the merits of locating GCs outdoors.

The perceived disadvantages with outdoor installations include the following:
  1- Difficult to service in adverse weather conditions,
  2- Reduced operational life associated with exposing electronics to the outside environment
  3- Measurement stability.

A partial solution is to locate the GC controller, with the majority of the electronics, in a control room environment. Technicians can then perform maintenance work with PC-based software from the control room or offsite via modem thereby minimizing technician time at the actual GC.

Communications

In recent years there has been a trend in the process industry toward open protocols and open systems as opposed to proprietary data highways. Technology is changing rapidly and the ability to keep pace and support proprietary data highways is increasingly difficult. Several well-established protocols are fully supported by the control systems vendors for serial interfacing to DCSs and PLCs. These interfaces are usually designed around a dedicated protocol converter often referred to as a gateway. These gateways plug into a DCS or PLC bus and provide a serial interface to other field devices using the same protocol. As a minimum, the GC should have conventional protocol support on redundant serial ports. There is no real need for proprietary high speed data highways to pass GC data that does not change for several minutes. A serial interface is more than adequate for on-line readings as well as full diagnostics, chromatograms and other troubleshooting tools.

THE SAMPLE CONDITIONING SYSTEM

Basic Rules of Sample System Design

The first rule in sample system design is to ensure that sample probes extract a sample from a point 1/3 to 2/3 of the distance into the process piping. This will help ensure a representative sample with minimal contaminants from piping internal walls.

In general, the required single-phase samples are maintained by temperature (heat) on vapor streams and pressure on liquid streams. Vaporization can occur at several points depending on the composition and the practicality in keeping the sample completely in a single phase from sample point to sample valve.

Vapor Phase Samples

The Sample Transport System

The compositions listed in Table 1 represent the highest full-scale range for each component; typical operating ranges may be less. To determine the heat-tracing requirements, the full- scale range of the heaviest components must be used. This ensures that a representative sample will be delivered under all process and environmental conditions. The temperature, pressure and composition at the sample point will determine the initial sample phase. The same principles hold true for the sample transport system and the sample conditioning system.

Vapor Phase Sample Inject

As noted, all streams must be in the vapor phase after the sample valve for GC analysis. Table 2 shows that the inlet feed and dethanizer bottoms are sampled in the liquid-phase.

Figure 2 shows the inlet stream is vaporized at the sample point and transported to the GC in the vapor-phase. The dethanizer bottoms stream is sampled and transported to the GC in the liquid phase and vaporized in the GC sample conditioning system. In either case, the vaporizing pressure regulator (VPR) adds heat at the exact point where the sample pressure is dropped to counteract the cooling effect that occurs when pressure is reduced (Joules Thompson effect). The greater the pressure drop, the greater the cooling and the greater the heat requirement to maintain complete vaporization of the heavier components. The remaining two streams (dethanizer overhead & depropanizer overhead) are vapor-phase at the sample point with heat tracing installed to simply maintain the sample in the vapor phase. Additional pressure reduction occurs in the sample system oven which operates at an elevated temperature (170° F/70 °C in this case).

Vapor-phase samples should be injected at atmospheric pressure to increase the repeatability of the measured sample volume. To accomplish this, a sample shut off valve (SSO), located in the analyzer oven, typically shuts off sample flow about five seconds prior to sample injection. This references the sample loop to atmospheric pressure to improve the repeatability of the sample volume injected. The sample vent and measure vents from the analyzer should be returned to atmospheric pressure.

Sample Conditioning

To ensure a single phase for vapor streams in figure 2, the SCS should increase sample temperature as the sample travels closer to the sample valve.

For instance, sample temperature should increase by 5° C (after pressure regulation) from the sample transport system to the sample conditioning system and again from the sample conditioning system to the analyzer oven. A vaporizing pressure regulator (VPR) can be used at the sample point to assist in temperature control (refer to the inlet stream on figure 2). The remaining streams (dethanizer overhead, dethanizer bottoms and depropanizer overheads) are already in the vapor phase at the sample point. Pressure regulation on these streams does not occur until the sample has traveled into the SCS oven where adequate heat is available. The low sample pressures will be required to transport the samples to the sample conditioning system where pressure will be regulated. Depending on the pressure loss over the distance traveled, there may be very little sample pressure available at the sample system. In most cases 2-5 psig of sample pressure is adequate. Individual stream pressures should be set for balanced sample flow, as indicated by the sample flow meter prior to sample vent two. The stream to stream purge is set from the lower solenoid purge flow to eliminate cross stream contamination.

Sample transport lines require heat tracing from 55° C - 70 ° C (120 ° F - 170 ° F). When installing heat-traced sample lines it is important to ensure there are no cold spots after the sample probe or VPR. During winter conditions a few inches of cold tubing can be enough to cool samples such as these enough to drop out heavier components into the liquid phase. The filters shown on streams one, two, three and four in figure 2 can be a coalescing type or a membrane type. Either type of filtration method is designed to remove solids and liquids while allowing vapor phase samples to proceed. Membrane filters offer superior liquids removal in saturated conditions without allowing downstream carryover. Once saturated, coalescing filters allow liquids to pass. Coalescing filters offer a more rugged solution for streams containing excessive particulate.

The process conditions at the sample point may vary from the conditions listed in table 1 due to access to process piping for installation of the sample probe. The closer the sample probe can be located to the tower overheads and bottoms the better for the system response time, but it may be more practical to install the sample probe on the reflux accumulator, inlet feed or piping to product storage if the desired stream is an overhead stream. As noted, the phase at the sample location and the sample transport phase to the SCS must be carefully considered.

Obviously, the greater the difference in pressure from the sample point to the sample return point the greater the sample flow rate and the faster the sample system can deliver a representative sample to the GC in the vapor phase. From an analytical point of view, sample vents should vent to atmosphere or atmospheric pressure. The initial sample pressure for the depropanizer and debutanizer overheads is so low that they may have to be returned to a flare stack. Any samples returning to a low pressure flare should have check valves to eliminate reverse flow conditions into the SCS when the plant goes to flare.

Vapor-phase samples can be transported more rapidly than liquid-phase samples for decreased lag time. Sample velocity, through sample tubing, increases as the volume decreases. An additional benefit is the reduced sample volume removed from the process and returned to the low pressure sample return point. In some cases the sample may tend to be two-phase. It is easier to heat two-phase samples for transport in the vapor phase than it would be to cool them, or boost the pressure, for transport in the liquid phase. Vapor phase sample transport is the preferred method on the inlet stream and all the overhead streams (dethanizer, depropanizer and debutanizer). The VPR shown at the sample point on the inlet stream is required due to the Joules Thompson effect but heat tracing alone is adequate on the remaining streams.

Care must be taken to ensure that sample transport tubing is heat-traced to about 70°C (160°F) and insulated depending on ambient temperature. Heat tracing must be installed right up up to the entrance to the sample system oven to eliminate cold spots on the tubing that would cool the vapor-phase sample and liquify the heavier components.
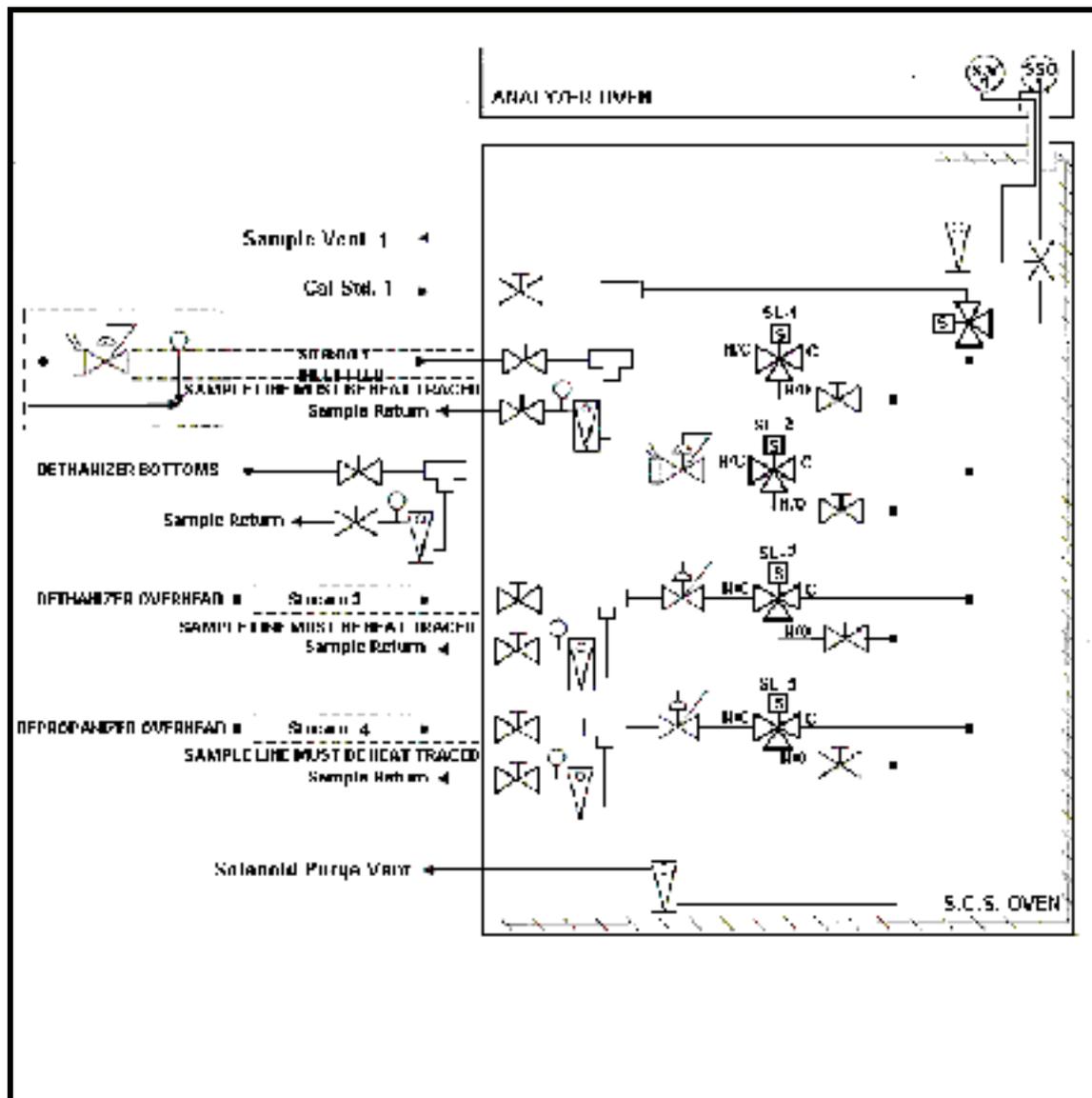

Figure 2

Stream Switching

Once the sample has been filtered, pressure regulated to about 2-20 psig and heated to maintain a single phase sample, stream switching can occur. Three common design options for switching streams are:

1- Solenoid purge,
2- Double block and bleed, and
3- Single block.

Solenoid Purge: Solenoid purge designs are used to ensure that cross-stream contamination does not occur in multi-stream sample systems. Off streams are purged with a split flow from the selected stream.
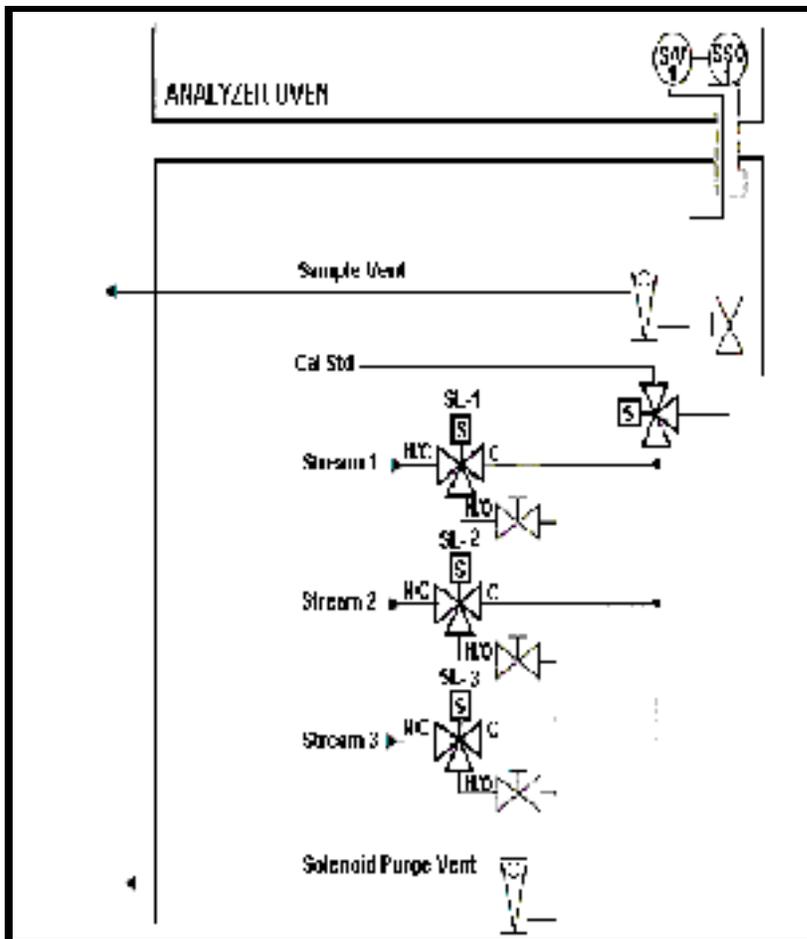

Figure 3

The selected stream energizes its solenoid to allow sample flow from the normally closed (N/C) port to the common (C) port. A split in the flow occurs allowing the sample to flow in two directions. The first path flows upward to the sample valve for analysis, the second path flows from C to normally open (N/O) for the off streams to carry potential leaks from off stream solenoids away from the selected stream flowing to the sample valve. The solenoid purge vent carries the purge flow from the sample system to a low pressure return point in the process. Each stream must be vapor-phase and pressure balanced up to the stream select solenoids

The calibration standard uses a single block to conserve valuable calibration gas. In addition, it is assumed that calibration gas is similar in composition to the selected stream and potential leaks will not seriously bias the results.

Double Block and Bleed: A double block and bleed design also ensures that cross stream contamination does not occur in multi-stream sample systems. The primary source of cross-stream contamination is leaky solenoids and areas of unpurged tubing common to more than one stream.
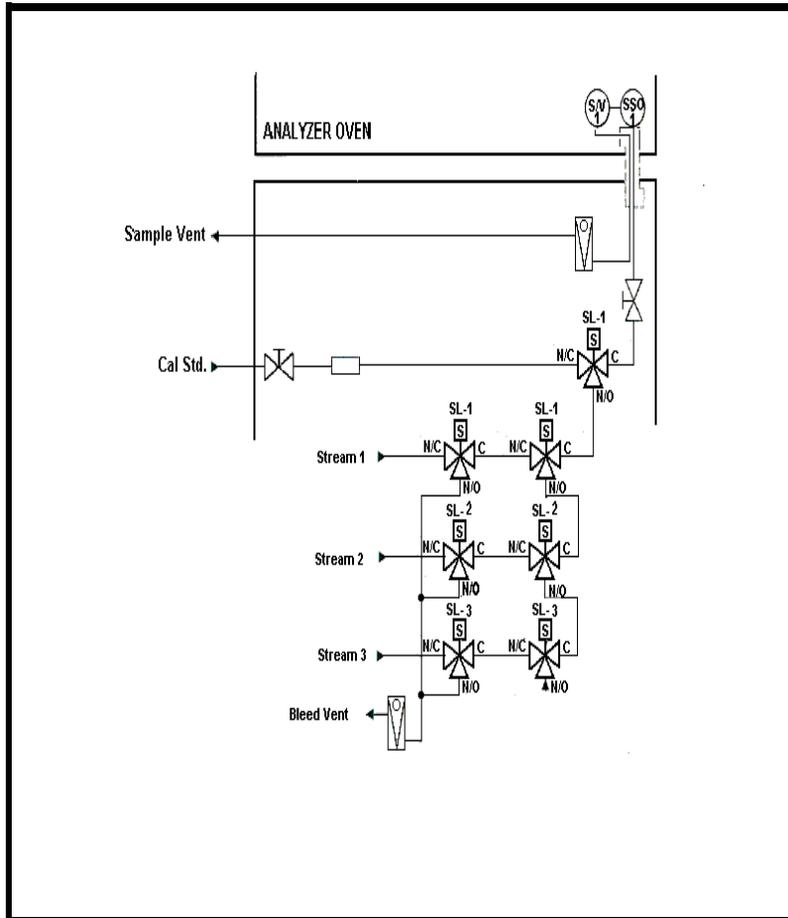
This design allows sample flow from the selected stream to pass through two solenoids en route to the sample valve. The other streams are double blocked with two solenoids and a low pressure vent to allow flow from either potentially leaky solenoid to escape out the bleed vent. The selected stream energizes both solenoids to allow sample flow from the normally closed port (N/C) to the common port (C). The other streams flow from N/O to C. This method uses more solenoids than the solenoid purge design to accomplish the same result.

Figure 4

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<u>Single Block</u>: The single block design does not take into account potential leaks from solenoids. There is no stream-to-stream purging to eliminate cross-stream con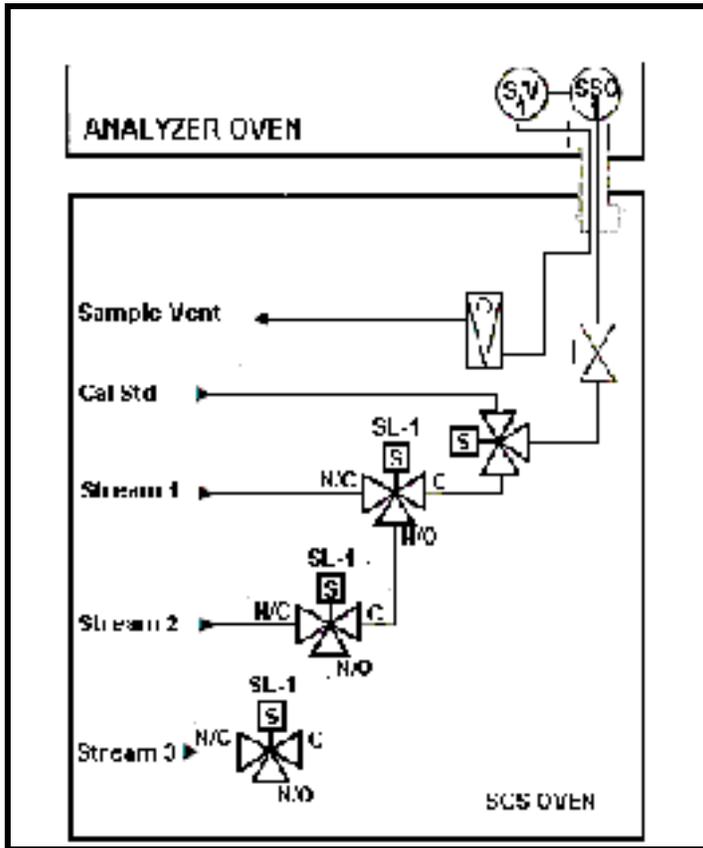tamination should one of the solenoids leak. This design minimizes cost, but should only be used in cases where alternate streams are very similar in composition and SCS oven temperatures are relatively low. Solenoids that operate at higher temperatures are more prone to leaks and generally experience a higher failure rate. This design does not purge samples other than the sample flowing to the sample valve. For example: Calibration gas in figures 2,3, and 4 is switched on with a single block design to minimize unnecessary loss through a purge or bleed vent. Small leaks across this solenoid will mix similar samples with a minimal effect on readings.

Figure 5

Liquid Phase Samples

Sample Transport System for Liquids

To determine sample pressure for transport of a liquid-phase sample from the probe to the GC, the full scale range of the lightest components must be used. This ensures a representative sample will be delivered to the GC without "bubbling" of the lighter components under all process and environmental conditions.

For liquid streams there are basically three choices for the point at which the sample is vaporized: the sample point, the sample conditioning system or the sample valve. In figure 2, the inlet stream was vaporized at the sample point with a VPR and heat tracing to the sample conditioning system. This greatly reduced the sample transport time (lag time) and also reduced the amount of sample returned to the process.

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Although this stream was liquid phase, in the process it was treated as a vapor phase sample within the analytical system because the compositions were light enough to allow for vaporization without excessive heat requirements. The remaining column overheads and dethanizer bottoms streams in Figure 2, were sampled as a vapor from the process and maintained in the vapor phase with heat tracing to the SCS.

The heavier streams, (i.e. the depropanizer and debutanizer bottoms), are too heavy to vaporize easily: temperatures in excess of 100° C would be required to maintain a vapor-phase sample for the higher concentrations of these heavier components. These streams are sampled from the process, transported to the sample system and delivered to the sample valve in the liquid phase.

Liquid Phase Sample Inject

Depropanizer bottoms and debutanizer bottoms are sampled and transported in the liquid phase at fairly high pressures and temperatures. As a result, care must be taken that the lightest component, propane, does not bubble into the vapor phase as a result of the higher temperatures. Any reductions in sample pressure may cause propane to vaporize. In this case both bottoms products will be liquid phase right up to the sample valve in the GC oven without pressure regulation until after the sample valve. This back pressure regulator maintains a constant pressure in the sample valve at the highest possible pressure to ensure a single phase liquid sample for injection.

Any bubbling of lighter components at this point will affect the measured volume injected into the columns for measurement. This injected volume must be repeatable from one analysis to another to ensure reliable, accurate results. In most cases the process pressure is adequate for these types of liquid streams. If the potential for bubbling is too great, the stream may be better suited to vapor-phase sample handling.

A low pressure sample return point will be required from the process with a large enough differential to create flow in the sample transport system (figure 6). These liquid samples remain in the liquid phase for sample injection. Vaporization occurs after sample injection when oven heat and a light carrier gas (usually helium) combine to vaporize these heavy samples.

Very significant differences exist in design considerations for liquid sample systems as opposed to gases. The primary difference centers around the fact that liquids are less active than gases and do not adequately purge common tubing and a common sample valve. For this reason each liquid stream should have its own isolated flow path and sample valve. Gas molecules are much more active.

As a consequence, they are more suited to multi-stream sample systems where stream-to-stream purging techniques like solenoid purge or double block and bleed can adequately purge common tubing.

In figure 6 the manual block valves (BV-1 and BV-2) allow for manual introduction of a common liquid calibration standard for each sample valve, as opposed to the solenoid actuated calibration standard that was shown in figure 2. Manual control is preferable on liquids because of an increased need for operator attention during liquid calibrations to ensure accurate results. The back pressure regulators (BPR-1 and BPR-2) are required to maintain a suitable back pressure on the liquid sample volume in the sample valve to ensure that a single phase liquid sample is injected. As stated earlier, bubbling of the lighter components must not occur or the injected volume will not be repeatable. Stream bypasses must return to a lower pressure to ensure sample flow.

Sample flow and back pressure settings can be critical factors in determining the sample transport lag time. Consideration must be given to liquid volume in the sample transport system and distance the sample must travel to the sample valve. For example, a high pressure liquid sample (400 psig) traveling 300 feet with a stream bypass returning to the process at 370 psig is going to create a great deal of lag time. As a result the overall system will have a very slow response time regardless of how fast the GC is.

CALIBRATION STANDARDS

Vapor-Phase Calibration Standards

If the sample system produces two-phase samples en route to the GC, an error will be introduced into the GC analysis that is dependent upon ambient climate conditions. The same considerations must be given to vapor-phase calibration standards and the sample transport tubing that carries the calibration standard to the GC. These standards are mixed with the highest possible pressure based on *the lowest ambient temperature* stated. As a result, a heated calibration standard not only ensures that the heavier components are maintained in the vapor phase, but contains more volume for virtually the same price. These calibration standards can be very costly, and care must be taken to ensure they are properly installed as cold temperatures will liquify the heavier components and render them useless.

Figure 6

In colder regions a heated insulated cabinet is frequently attached on the outside of an analyzer building. In warmer regions the calibration standards can be placed outdoors provided the transport tubing and standards are heated to maintain the temperature above the lowest ambient temperature specified for that mixture. To conserve the calibration standard, 1/8 th inch sample transport lines are recommended to reduce the volume required to purge the sample system with sample prior to a calibration.

Liquid-Phase Calibration Standards

If the sample conditioning system supplies a liquid-phase sample to the sample valve for injection in the liquid phase then the calibration standard must also be liquid phase. The same is true for vapor-phase samples. Certified liquid calibration standards, however, are considerably more expensive than certified gas standards. In some cases, the user may choose to certify their own liquid standards form laboratory analysis of liquid samples. Although this procedure may save on cost, any errors in the collection of the samples or the subsequent laboratory analysis will introduce errors into the process GC.

SUMMARY

To ensure reliable, accurate, timely results are available for process control the SCS must be designed specifically for the process conditions on each individual stream. An integrated approach to designing the sample transport system on site, to match the sample conditioning system that arrives with the GC, will help ensure reliability and faster analytical results. When GC results are in question calibration standards can be used as a quick reference check for operations to easily verify on-line GC results. Only then can the full benefits of on-line chromatographs be fully realized to optimize plant performance and meet tighter product specifications.

References
"Fractionation and Absorption," Gas Processors Association, Engineering Data Book, Volume II, Chapter 19.