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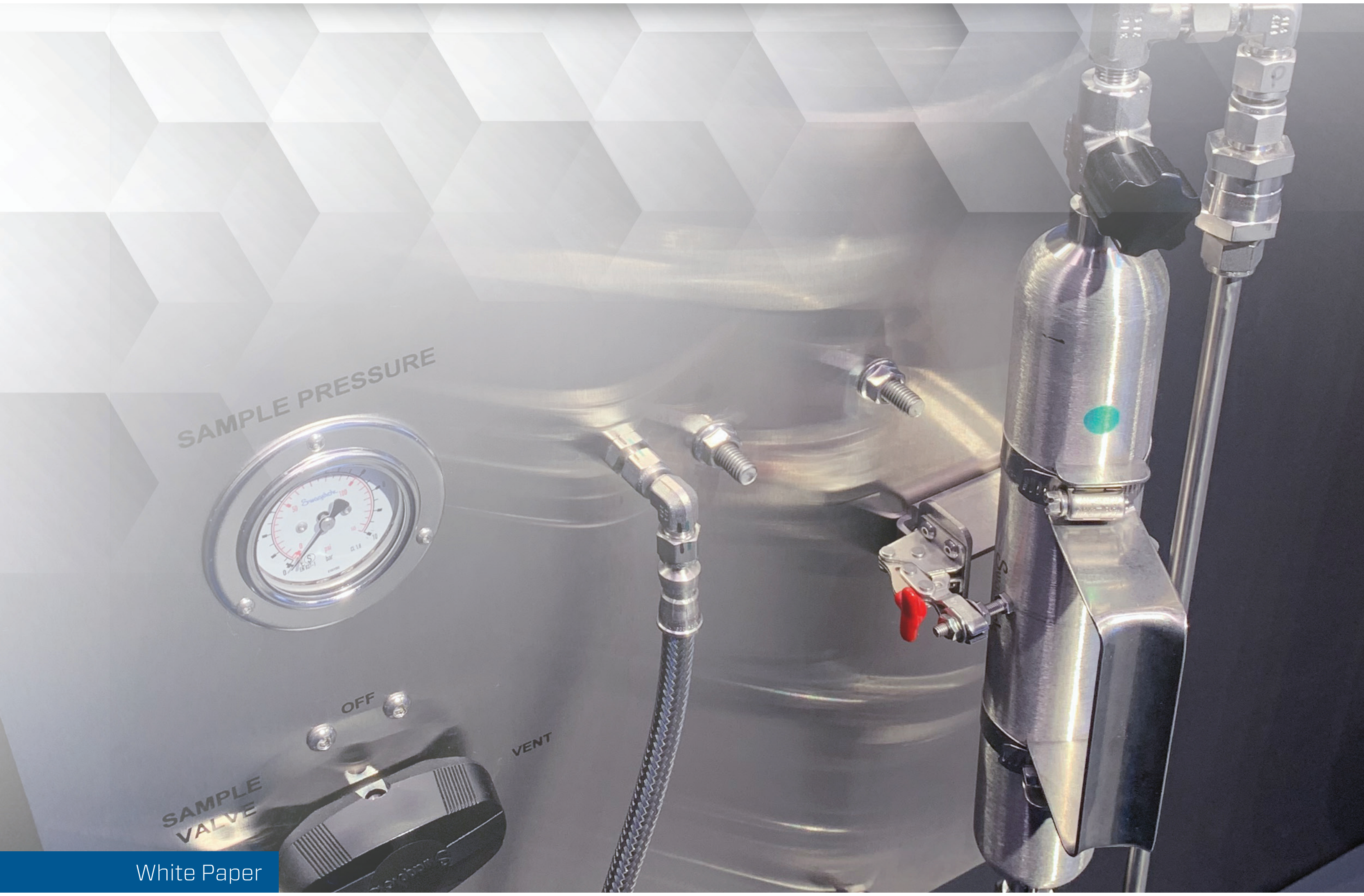

White Paper

Sampling Liquids in a Sample Cylinder: Vapor Space and Outage Tubes

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Abstract

Outage tubes are commonly used when collecting liquid samples in sample cylinders. They are intended to create a vapor space in the cylinder, thereby allowing for thermal expansion of the liquid. However, most designers do not understand how outage tubes work and how they can be affected by the operating parameters of the sampling system. By understanding how sample system design features, pressures, and operating procedures impact the function of outage tubes, designers can perform simple calculations to accurately predict performance of the outage tube. This enables them to identify and remedy problems related to thermal expansion before they manifest in the field.

Introduction

When sampling liquids using sample cylinders, there are few things more important than overpressure protection. Liquids typically have higher rates of thermal expansion than the metal sample cylinders in which they are contained, which can cause problems if the temperature of the cylinder rises after the sample is taken. Due to the incompressible nature of liquids, this expansion of the liquid can create immense hydraulic pressure that can damage or even rupture the sample cylinder.

The cylinder can be protected using rupture discs or relief valves, but both solutions usually result in the release of the sample, or a portion of the sample, to the atmosphere. This presents a myriad of problems, especially if the sample is toxic to the environment or to the personnel transporting the cylinder to the laboratory. As such, when taking liquid samples in a cylinder, rupture discs and relief valves are commonly seen as secondary methods of overpressure protection, not the primary method.

The most common primary method of overpressure protection is to avoid filling the cylinder 100% liquid-full in the first place. Leaving some gas, also known as a vapor space, in the cylinder with the liquid sample provides that sample a place into which it can expand in the event of a rising temperature. Because this vapor space is compressible, the liquid can expand into the space, compressing that gas. This will still result in a pressure rise but not the exponential and catastrophic increase that can be experienced by a cylinder that is 100% liquid-full.

There are many methods that can be used to create a vapor space, a few of which will be described below. However, one of the most simple and effective methods is to use an outage tube. The intent of this paper is to describe the use of outage tubes, explain how they can be used to create the requisite vapor space, and describe how to ensure that the resulting vapor space is sufficiently sized for the application.

Creating a Vapor Space

Note that the term vapor space refers to the volume of gas captured in the closed cylinder. Outage, on the other hand, expresses the volume of that vapor space as it relates to the overall volume of the sample cylinder, typically expressed as a percentage. Therefore, a 1000mL cylinder with 20% outage would be filled with 20% gas (200 mL vapor space) and 80% liquid (800 mL sample size). The required outage percentage is often defined by industry standards, plant/company procedures, and established best practices.

There are several methods for taking a liquid sample and ensuring that there is a vapor space in the cylinder, including the most common ones as follows.

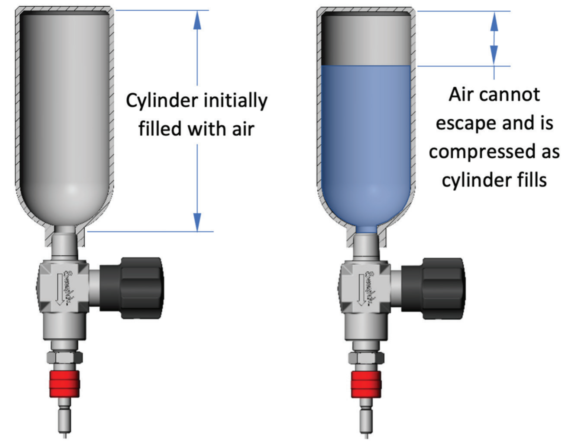


Figure 1: Filling a Single-Ended Cylinder

Single-Ended Cylinder

This method uses a cylinder with only one inlet connection. The opposite end is welded closed with a cap or is possibly plugged. When taking a sample, the cylinder is oriented vertically with the closed end of the cylinder pointing up. Filling from the bottom, the air that was originally in the cylinder is trapped above the liquid's surface and cannot escape, collecting at the closed end as shown in Figure 1.

This is an effective method because, as long as the gas is not soluble in the sample liquid, it guarantees that a vapor space will be present. However, when compared to traditional double-ended sample cylinders, single-ended cylinders are more expensive, less available, harder to clean, harder to obtain a representative sample in, and harder to extract the sample from. As such, use of single-ended cylinders is relatively rare.

Constant-Pressure Cylinders

With this method, a double-ended cylinder is used, but the cylinder includes a floating piston that can move from one end of the cylinder to the other. See Figure 2. Prior to taking a sample, one side of the cylinder is precharged with a gas, such as nitrogen. This precharge, typically higher than the process pressure of the liquid being sampled, pushes the piston to the opposite end of the cylinder. The opposite end is connected to the sample point.

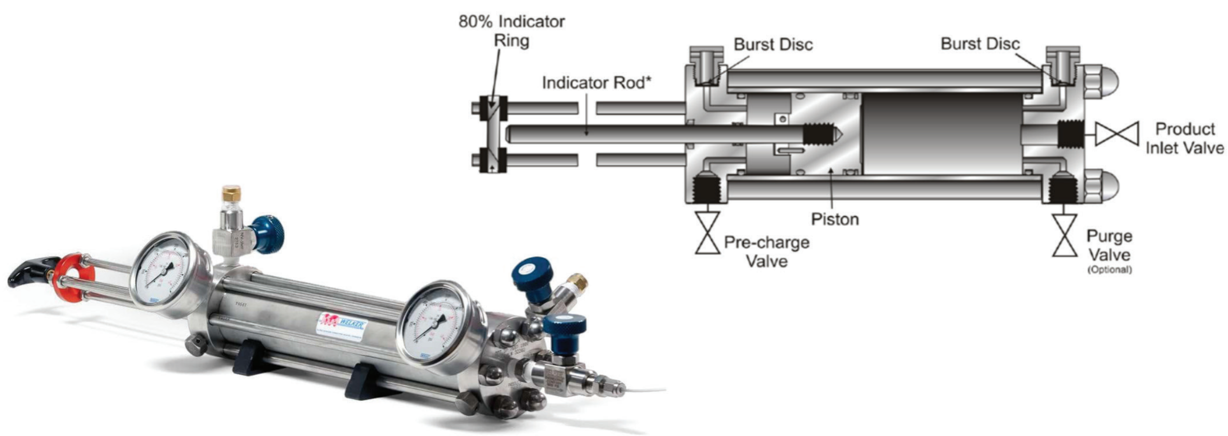
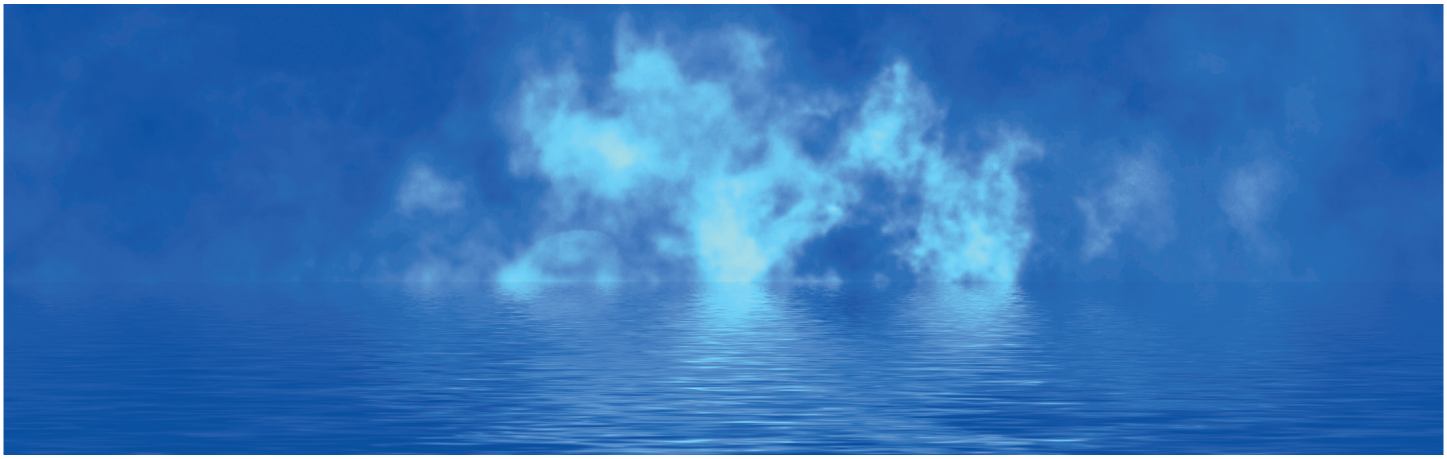


Figure 2: Constant-Pressure Cylinder (images courtesy of Welker)

Creating a Vapor Space (Cont.)



Because the precharge is at a higher pressure than the process, the sample cannot enter the cylinder and move the piston until that precharge pressure is relieved. To take a sample, the operator will open a vent valve, releasing some of the precharge gas. This allows the process pressure to move the piston, filling the cylinder with sample liquid. The operator can monitor the position of the piston, and therefore the sample size, by means of a position indicator on the exterior of the cylinder. When the appropriate amount of liquid sample has been drawn, the operator closes the vent valve to trap the remaining precharge gas, which then acts as a vapor space. Any thermal expansion of the sample liquid will push the piston a little farther, compressing the precharge gas.

This method has two primary benefits over the single-ended cylinder method:

1. The piston isolates the sample fluid from the vapor space, which eliminates any issues that could come as a result of the gas being soluble in or reactive with the sample liquid.
2. The sample is kept at the process pressure, hence the name "constant-pressure cylinder." This helps to keep volatile samples from vaporizing as they fill the cylinder, which could compromise the representativeness of the sample and/or even eliminate the vapor space.

However, constant-pressure cylinders also have a number of drawbacks:

1. Due to their complexity—piston, end caps, gauges, position indicator, etc.—they are significantly more expensive than traditional sample cylinder assemblies.
2. They can be prone to damage during transportation because of the gauges, relief valves, and position indicators installed on the cylinder. Care must be taken when transporting, including potentially using a hard-sided case to protect the cylinder.
3. Maintaining a vapor space is not guaranteed but rather relies on the operator. If they were to release all the precharge gas (or if it leaks out) then the piston could come to a hard stop at the end of the cylinder, and the effect would be the same as a cylinder that is 100% liquid-full. Assuming the problem is recognized, which is not guaranteed, the sample panel would require additional functionality to enable the operator to safely vent excess sample (potentially altering the sample composition) and/or recharge the cylinder to restore the vapor space.

Creating a Vapor Space (Cont.)

Traditional Liquefied Petroleum Gas (LPG) Sampler

As shown in Figure 3, Step 1, with a traditional LPG sampler, the cylinder is installed in a sample panel, and sample liquid flows through the cylinder. After the cylinder is flushed and a representative sample is achieved, the panel is switched to a bypass mode. In addition to allowing the sample flow to bypass the panel, it also isolates a loop on the sample panel, including the sample cylinder. Note that at this point the cylinder is 100% liquid-full.

Once the loop is isolated, a vent valve is opened, which allows the pressure to drop. Because LPG is a volatile liquid, dropping the pressure allows the liquid to begin boiling and the vapors to collect at the top of the isolated loop (Figure 3, Step 2). The liquid level will slowly drop as more and more of the sample changes phase from a liquid to a gas. Eventually the liquid level will drop to the point where there is a 20% vapor space in the cylinder, which is dictated by ASTM D1265, Standard Practice for Sampling Liquefied Petroleum (LP) Gases (Manual Method). The operator can see this liquid level because on the side of the loop opposite the cylinder, a sight flow indicator or level gauge is strategically positioned so that the liquid level is visible when the cylinder has a 20% outage. Alternatively, a temperature-indicating strip might be affixed to the exterior of the cylinder, which would also be a good indication of liquid level. Once at this position, the operator closes the vent valve to stop the boiling, isolates the sample in the cylinder, and removes the cylinder from the panel (Figure 3, Step 3).

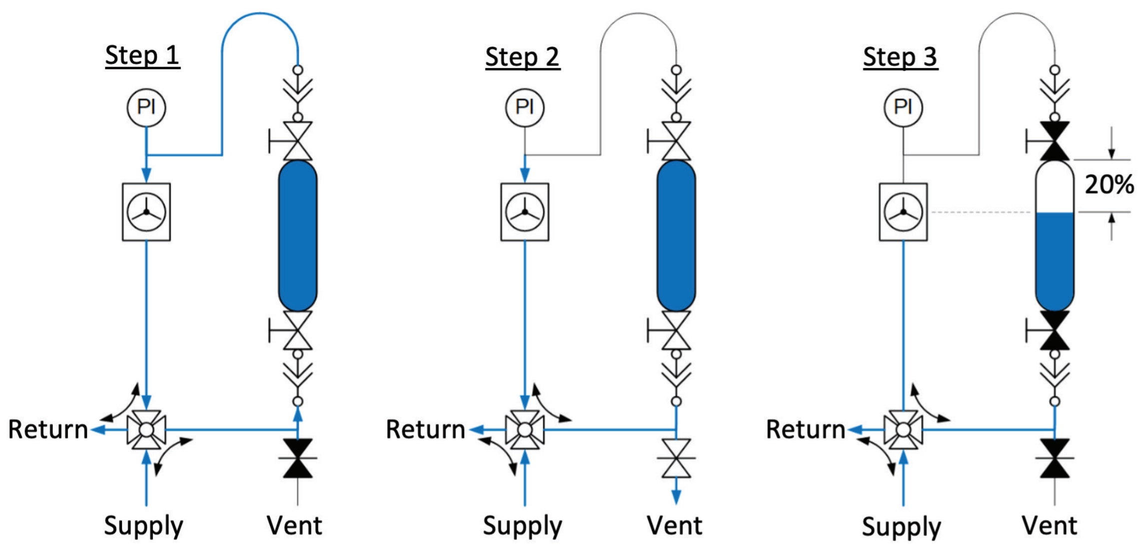


Figure 3: Traditional LPG Sampling Steps

While this method offers the advantage of visual confirmation of the presence/volume of the vapor space, it has one enormous drawback: Allowing the sample to boil fundamentally changes the sample. When the pressure drops and the sample starts to boil, it is the light components in the sample that will boil first—ethane, propane, butane, etc. They will boil away, leaving the heavier components behind in the liquid state. Therefore, these light components will be underrepresented in the remaining sample liquid. The sample is no longer representative of the process from which it was extracted. Additionally, this method again relies on the operator to not only create the vapor space, but also to create the correct volume vapor space. Failure to do this properly could result in a cylinder or sampling system that is overpressurized.

Creating a Vapor Space (Cont.)

Venting Cylinder to Atmosphere

This method, once common, has dwindled in popularity due to environmental and health concerns. With this method, a cylinder is filled with sample liquid. In some cases, the cylinder is fitted with an outage tube (see page 7), which ensures some amount of vapor space in the cylinder. In other cases, the cylinder is filled 100% liquid-full. In either case, after removing the cylinder from the sample panel, the top valve on the cylinder is opened and the cylinder is allowed to vent to atmosphere.

If the cylinder has an outage tube, opening this valve allows the compressed vapor space to expand and push the liquid out of the cylinder. Once the operator sees that there is only gas coming out of the top of the cylinder, that is an indication that the liquid level has fallen below the tip of the outage tube. The operator can then close the valve ensuring that the vapor space in the cylinder is equal to the length of the outage tube.

If the cylinder does not have an outage tube, then opening the valve will allow a pressure drop of the cylinder contents. Like with the traditional LPG sample method noted on the previous page, the volatile liquid will start to boil, and the light components will escape out the top of the cylinder as they vaporize.

This method has all the same concerns/drawbacks of the traditional LPG sampler. Additionally, there are obvious concerns about the environmental exposure, personnel exposure, and the possibility of a potentially flammable cloud finding an ignition source.

Expansion Chamber

With this method, in addition to the sample cylinder used to collect/transport the sample, the sampling panel includes a second vessel, called an expansion chamber, which is permanently affixed in the system. When the sample process begins, this expansion chamber is empty and at zero pressure. The liquid being sampled is flushed through the panel, and the cylinder used for sample collection is allowed to fill 100% liquid-full (Figure 4, Step 1). At that point, the valves on the panel are switched to allow the cylinder to connect to the expansion cylinder (Figure 4, Step 2).

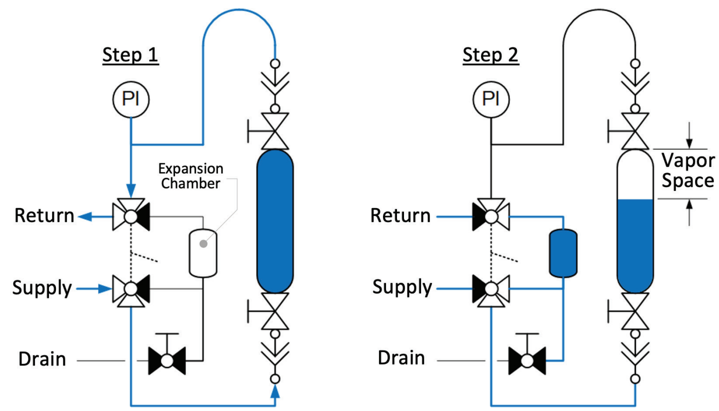


Figure 4: Grab Sample Panel With Expansion Chamber

For nonvolatile liquid samples, the liquid will simply find the lowest elevation and flow into the expansion chamber. This draws liquid out of the sample cylinder, creating a vapor space at the top of the cylinder. The cylinder is then isolated and removed for transport to the laboratory. With volatile liquids, in addition to the liquid finding the lowest level, the resulting pressure drop will also allow the sample to begin to vaporize.

This method is advantageous because it results in a consistent volume of vapor space. However, while this method does take the operator out of the equation for determining the volume of the vapor space, it still relies on the operator to switch the valves appropriately to ensure that the vapor space is created in the first place. It is also necessary for the operator to drain the old sample from the expansion chamber. If the operator fails to do either of these properly, then the result could be transporting a cylinder that is 100% liquid-full. Additionally, like previous methods, the expansion cylinder has the potential to fundamentally alter the sample by allowing volatile samples to partially vaporize.

Creating a Vapor Space (Cont.)

Outage Tube

Sometimes called an ullage tube or dip tube, an outage tube is installed at the top end of a sample cylinder, which is oriented vertically as the sample is collected. See Figure 5. The length of the outage tube is typically expressed as the percentage outage that it is intended to produce when sampling at atmospheric pressure. As noted below, increased pressure can impact the volume of the vapor space created by the outage tube. In fact, if the system pressure is too high, then the resulting vapor space may be insufficient and remedial measures must be taken or a different method must be employed to ensure the requisite vapor space.

At the top of the cylinder, the outage tube creates a vapor space from which the gas cannot escape. As liquid fills the cylinder from the bottom up, the liquid will reach the tip of the outage tube. With the gas in the vapor space occupying the top of the cylinder, the liquid is forced to flow up and out of the outage tube.

The primary advantage of using an outage tube is that it is not reliant on the operator to create the vapor space. If installed properly, an outage tube guarantees that a vapor space will be present. However, there is a major drawback in that there are a number of factors that can impact the volume of the vapor space created by an outage tube. Improper installation, the pressure of the sample, the pressure of the sample return, the design of the sampling system, and the sampling procedure can all impact the volume of the vapor space. This can result in a vapor space that is too small to accommodate the thermal expansion of the captured liquid sample, potentially leading to a damaged or ruptured cylinder.

The remainder of this document will address how to use outage tubes to ensure that the vapor space is large enough to safely absorb any expected thermal expansion of the liquid being sampled.

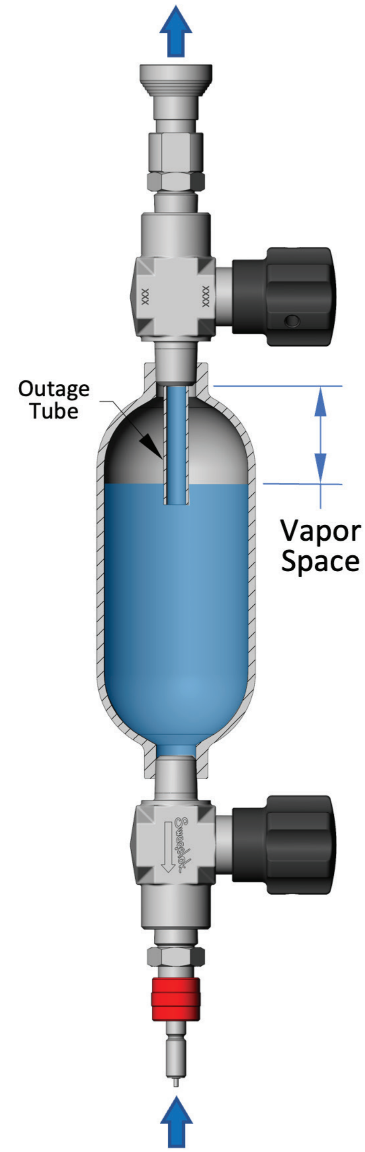


Figure 5: Cylinder with Outage Tube

Understanding Vapor Space Compression

Though an outage tube is designed to create a specific volume of vapor space, compression of that vapor space can result in a significantly smaller outage than expected. This compression is a function of pressure, procedure, temperature, and sample system design.

Compression Due to Pressure

Once a liquid fills the sample cylinder to the point where the liquid level reaches the tip of the outage tube, the vapor space will be compressed by the sample supply pressure, P_S, and return pressure, P_R, according to Boyle's law.

Equation 1:

$$P_1V_1 = P_2V_2$$ [1]

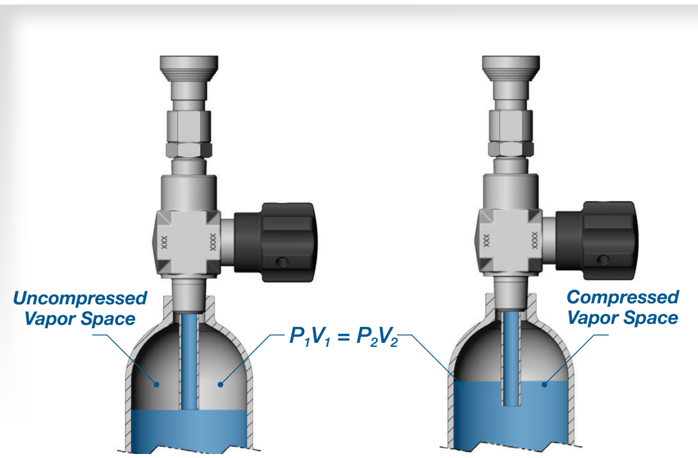


Figure 6: Vapor Space Compression

P_1 and V_1 are the initial pressure and volume of the vapor space when the liquid reaches the tip of the outage tube. P_2 and V_2 are the final pressure and volume of the compressed vapor space. Rearranging the formula to solve for V_2, it becomes evident that the volume of the compressed vapor space, V_2, is a function of the ratio of the pressure change.

Equation 2:

$$V_2 = \frac{P_1}{P_2} \times V_1$$

Because the initial volume is defined at the point where the liquid is at the tip of the outage tube, V_1 will be equal to the nominal outage percentage. In other words, for a 20% outage tube, V_1 = 20%[2]. Also note that because the volume is multiplied by the ratio of the pressures, it follows that the closer those pressures are to each other, the lesser the impact will be on the compression of the vapor space. In the worst-case situation, P_1 would be very low and P_2 would be equal to the sample supply pressure, P_S.

As an example, suppose that the nominal outage percentage V_1 = 20%, the supply pressure $P_S = P_2$ = 10 bara, and the initial pressure P_1 = 1 bara:

$$V_2 = \frac{P_1}{P_2} \times V_1 = \frac{1\ \text{bara}}{10\ \text{bara}} \times 20\% = 2\%$$

In making this calculation, the final pressure, P_2, is typically known (or assumed to be equal to the supply pressure, P_S), as is the nominal outage percentage, V_1. Therefore, only P_1 needs to be identified to calculate the outage of the compressed vapor space. But this initial pressure is more difficult to identify than it initially seems. To understand it, one must first understand how a cylinder fills.

1. Absolute pressure must be used for this calculation.
2. Because the units for V_1 and V_2 cancel each other out, the same calculation can be made with percentages or with volume units. This example will be worked with percentages to make it more general.

Understanding Vapor Space Compression (Cont.)

How a Sample Cylinder Fills

In most cases, sample cylinders are empty and unpressurized when initially coupled into a sampling panel. Opening the cylinder valves and the isolation valves on the sampling panel connects the cylinder to the process. At that point, the differential pressure between the sample supply, P_S, and the empty cylinder, P_C, causes liquid to flow into the bottom of the cylinder ($P_S > P_C$). However, note that in most applications, the sample return pressure, P_R, is also higher than the empty cylinder ($P_R > P_C$). Thus, without the use of a check valve or other device to prevent or restrict back flow, this differential pressure will cause liquid to flow backwards from the sample return into the top of the cylinder. It is this backwards flow that many designers fail to consider.

As the liquid flows into the cylinder from both ends, the air that was initially in the cylinder is compressed. It is prevented from escaping by the liquid flowing in through the top of the cylinder. This continues until the pressure in the cylinder equalizes with the sample return pressure ($P_R = P_C$). At that point, the incoming sample supply pressure causes the flow at the top of the cylinder to reverse ($P_S > P_R$). One of two scenarios will be present, depending on the return pressure. To determine which scenario will apply, both must be evaluated to determine which will result in the smaller vapor space.

Scenario 1, Relatively Low Return Pressure:

If the return pressure is relatively low, the liquid level will be below the tip of the outage tube when the flow reversal happens, as shown in Figure 7. In this scenario, some of the air that was initially in the cylinder will escape out the top as the cylinder continues to fill from the bottom. Because the flow through the valve at the top of the cylinder will be air at a relatively low flow rate, the pressure loss through this valve will be negligible. Therefore, it is safe to assume that the pressure in the cylinder will be equal to the sample return pressure, P_R.

This continues with $P_C = P_R$ until the liquid level reaches the tip of the outage tube, at which point the liquid will flow up the outage tube and out the top of the cylinder. The worst-case situation that could result in the smallest, most compressed vapor space would be when the sample return (outlet) valve is then closed and the sample supply (inlet) valve remains open. This would allow liquid to pump into the cylinder until the cylinder pressure equalizes with the supply pressure. This compression can be calculated using Equation 2 with $P_1 = P_R$. and $P_2 = P_S$.

Understanding Vapor Space Compression (Cont.)

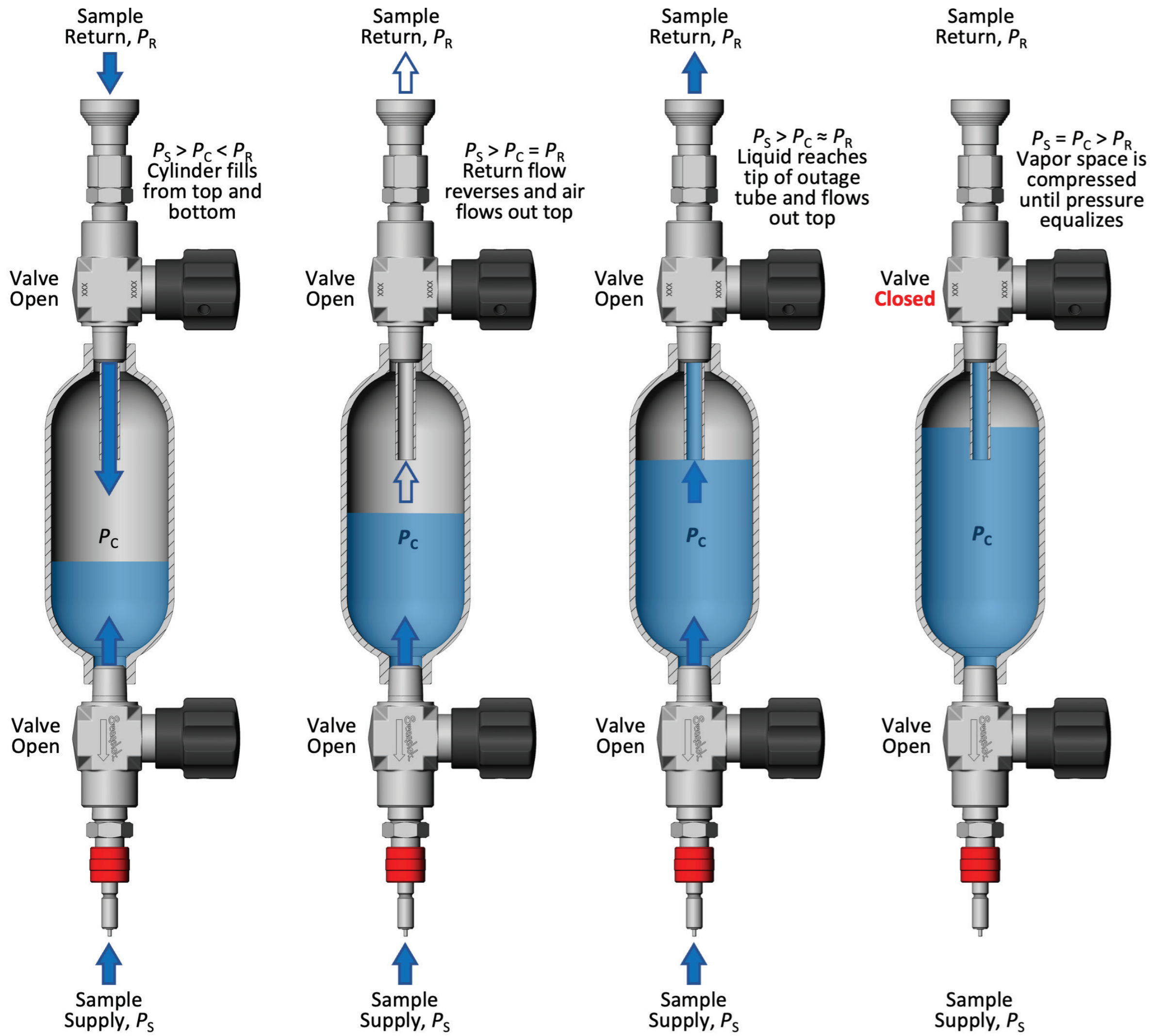


Figure 7: How a Cylinder Fills, Scenario 1

Returning to the example in the previous section, if the supply pressure P_S = 10 bara = P_2 and the return pressure P_R = 4 bara = P_1:

$$V_2 = \frac{P_1}{P_2} \times V_1 = \frac{4 \text{ bara}}{10 \text{ bara}} \times 20\% = 8\%$$

This illustrates the significant impact that the return pressure can have on the volume and compression of the vapor space. By increasing P_1, the amount of compression is significantly decreased and therefore the volume of the vapor space is significantly increased.

Scenario 2, Relatively High Return Pressure:

If the return pressure is relatively high, then the liquid level will be above the tip of the outage tube when the flow reversal happens, as shown in Figure 8. In this scenario, no air will flow out of the cylinder because it will already be trapped in the vapor space by the outage tube. Only liquid will flow out the top of the cylinder. All the air that was initially in the cylinder is compressed and remains trapped in the vapor space at the top of the cylinder.

Understanding Vapor Space Compression (Cont.)

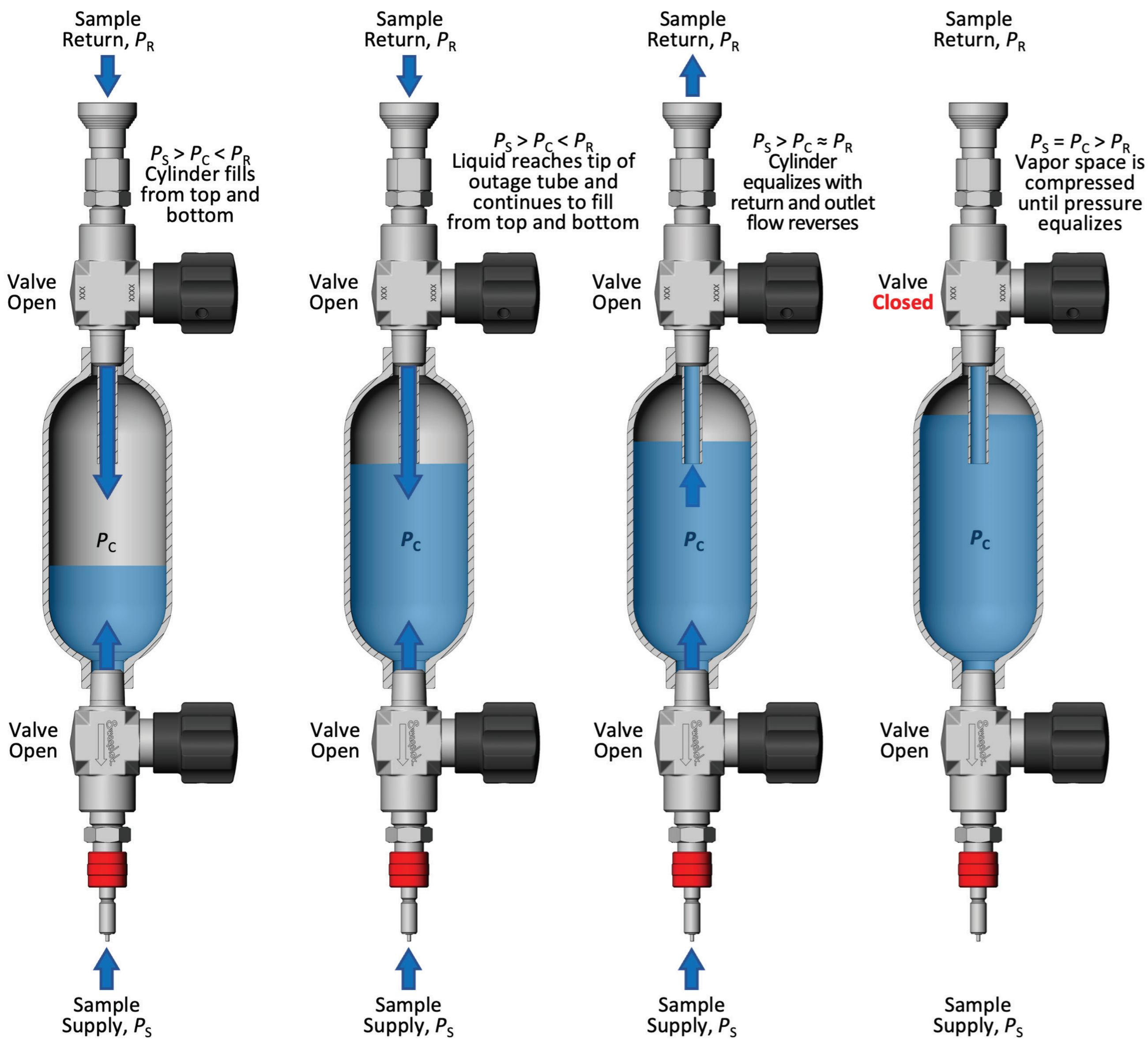


Figure 8: How a Cylinder Fills, Scenario 2

As before, the worst-case situation would be where the sample return valve is closed and the sample supply valve remains open. Because none of the air has escaped, the initial volume of the air, V_1, was equal to the entire volume of the cylinder, 100%, and that air was initially at some pressure, P_1. Knowing that the final pressure, P_2, of the air is equal to the supply pressure, P_S, it is relatively easy to calculate the final volume of that air using Equation 2.

Returning to the example
and assuming P_1 = 1 bara:

$$V_2 = \frac{P_1}{P_2} \times V_1 = \frac{1 \text{ bara}}{10 \text{ bara}} \times 100\% = 10\%$$

Understanding Vapor Space Compression (Cont.)

Which Scenario Applies?

So, which scenario applies to a given situation? As it turns out, the scenario that results in the smallest outage percentage is the one that will be applicable. The determining factor is the sample return pressure. If it is high enough to prevent any of the air that was initially in the cylinder from escaping, then Scenario 2 would apply and would produce the smaller, more compressed vapor space. If the return pressure is relatively low, then some of the air will escape from the cylinder and Scenario 1 would apply, producing the smaller vapor space. Therefore, it is necessary to calculate both scenarios and use the lesser value produced by the two calculations.

To see why, it is beneficial to further examine Scenario 2 and calculate the pressure of the vapor space at the point where the liquid level first reaches the tip of the outage tube. Again, Boyle's law, Equation 1, can be used, rearranging to solve for pressure:

Equation 3:

$$P_2 = \frac{V_1}{V_2} x\ P_1$$

Like the previous calculation in Scenario 2, the initial volume of air, V_1, is simply equal to the total volume of the sample cylinder. For this calculation, the final volume would be the nominal outage percentage. Knowing that the air was initially at some pressure, P_1, Equation 3 can be used to solve for the final pressure, P_2, which is the pressure at the nominal outage percentage.

Returning to the previous example:

$$P_2 = \frac{V_1}{V_2} x\ P_1 = \frac{100\%}{20\%}\ x\ 1\ bara = 5\ bara$$

In this specific example, the calculated pressure is higher than the sample return pressure (4 bara). Of course, this is not possible. The cylinder would reach the sample return pressure at some point before the liquid level reaches the tip of the outage tube. Once that happens, rather than being compressed further, air would simply flow out the top of the cylinder until the liquid reaches the tip of the outage tube. This matches our description of Scenario 1, so the Scenario 1 calculation would apply.

The Effect of Backpressure

The previous example assumes that the sample return pressure acts directly on the top of the cylinder. But what if there is some other device/component installed between the sample cylinder and the sample return? What impact will that have on how the cylinder fills and how the sample is compressed? There are three components that are commonly used that could possibly create a backpressure and influence the volume of the vapor space—a check valve, a backpressure regulator, and a needle valve.

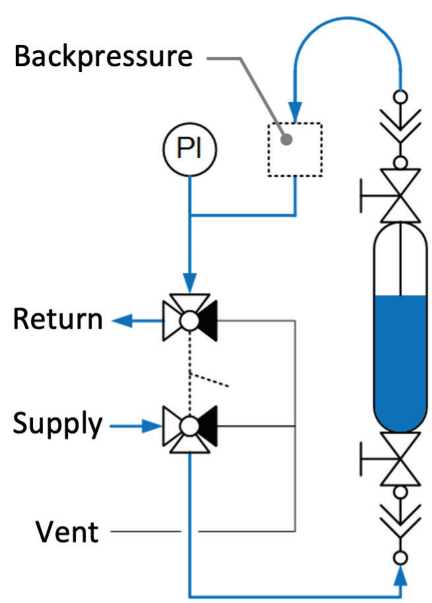


Figure 9: Grab Sample Panel with Backpressure Device

Understanding Vapor Space Compression (Cont.)

Check Valve

Installing a check valve downstream of the sample cylinder has two primary effects on the sample panel:

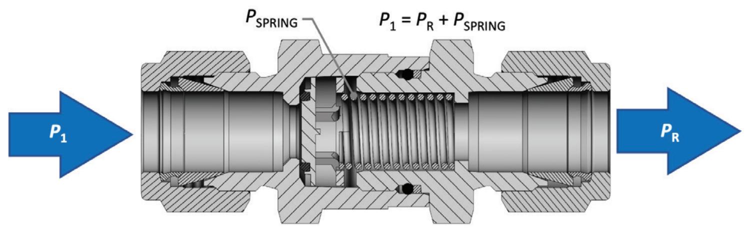


Figure 10: Check Valve Backpressure

1. By design and intent, the check valve prevents flow from the sample return into the sample cylinder. Therefore, the cylinder will only fill from the bottom up.
2. The check valve creates an additional backpressure that inhibits the air in the cylinder from escaping. This backpressure is caused by the force of the spring in the valve and by the sample return pressure pushing on the back side of the valve's poppet.

Effect number 1 has no practical impact from a vapor space compression perspective. However, effect number 2 does have an impact. Because Scenario 2 (from the previous section) does not take sample return pressure into account, this added backpressure does not impact the Scenario 2 calculation. However, the additional backpressure imposed by the check valve's spring increases the chance of encountering Scenario 2 because there is now additional pressure that the air in the cylinder must overcome before it can escape. This extra pressure factors into the calculation from Scenario 1. The same calculation can be made, except that the initial pressure, P_1, from the Scenario 1 calculation would now be the summation of the sample return pressure, P_R, and the backpressure added by the check valve itself, P_{SPRING}, as shown in Figure 10. Note that P_{SPRING} is a differential pressure and therefore there is no need to convert it to an absolute pressure. Simply use the cracking pressure supplied by the valve manufacturer. Returning to the example and assuming a check valve has a spring that yields a 2-bar cracking pressure, P_{SPRING}, Equation 1 gives:

$$V_2 = \frac{P_1}{P_2} \times V_1 = \frac{P_R + P_{SPRING}}{P_2} \times V_1 = \frac{4 \text{ bara} + 2 \text{ bar}}{10 \text{ bara}} \times 20\% = 12\%$$

The resulting 12% outage is larger than the outage in the Scenario 2 calculation (10%), so Scenario 2 would be used to determine the volume of the vapor space. But still, adding the check valve did increase the outage percentage from 8% (original Scenario 1) to 10% (Scenario 2). Therefore, adding a check valve can be used to increase the outage when the sample return pressure is low.

Understanding Vapor Space Compression (Cont.)

Backpressure Regulator

Installing a backpressure regulator has a similar effect to a check valve. While a backpressure regulator does not absolutely prevent back flow; it severely restricts it to the point where it is rather unlikely in most applications. However, the regulator's primary purpose is to add an artificial backpressure downstream of the sample cylinder. Where it differs from a check valve is that the backpressure introduced by the regulator is referenced to atmosphere, not the downstream sample return pressure.

Therefore, instead of a differential pressure, this backpressure, P_{SPRING}, can be considered an absolute pressure that is only negligibly impacted by the sample return pressure. The caveat is that the backpressure will not be less than the return pressure, P_R. As such, when calculating Scenario 1 using Equation 2, the initial pressure, P_1, would be equal to the backpressure regulator setpoint, P_{SPRING}, or the return pressure, P_R, whichever is greater. See Figure 11. Supposing for this example that the backpressure regulator is set to 7 bara (P_{SPRING}) and the return pressure (P_R) is still 4 bara:

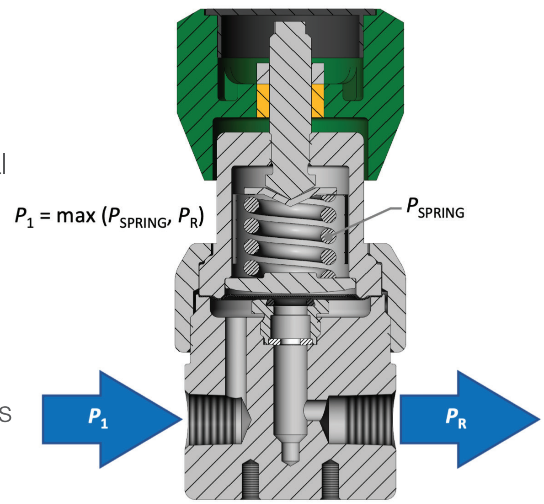


Figure 11: Backpressure Regulator

$$V_2 = \frac{P_1}{P_2} \times V_1 = \frac{\max(P_{SPRING}, P_R)}{P_2} \times V_1 = \frac{\max(7\ \text{bara}, 4\ \text{bara})}{10\ \text{bara}} \times 20\% = 14\%$$

Like with the example for the check valve above, the resulting 14% is larger than the outage in the Scenario 2 calculation (10%), so Scenario 2 would apply. Also like the check valve, a backpressure regulator might be introduced when the sample return pressure is low, with the added benefit that it will maintain a constant pressure, even if the sample return pressure fluctuates. This will help to maintain consistency and predictability in the sample panel operation.

Needle Valve

Needle valves are often installed downstream of a sample cylinder to control the flow of liquid through the system. It may be paired with a flowmeter to measure/indicate the flow rate or it could be installed by itself. In either case, the needle valve creates a backpressure, but only when liquid is flowing through it.

The needle valve will typically be adjusted to some setting that achieves the desired flow rate or backpressure for the liquid being sampled. However, when flowing a gas through the same valve at that same setting and same volumetric flow rate, the backpressure will be negligible because the gas is so much less dense and viscous than the liquid. Likewise, if the flow is stopped, whether gas or liquid, the backpressure will be zero because the backpressure created by a needle valve is dependent on the flow.

Like with the check valve and the backpressure regulator, Scenario 2 is not affected by backpressure and would therefore not be impacted by a needle valve. Scenario 1 is impacted by backpressure, but remember that with Scenario 1, the initial pressure, P_1, that is fed into Equation 2 is the pressure inside the cylinder when the liquid level first reaches the tip of the outage tube. However, at that point in time, it would be air that is flowing out the top of the sample cylinder and through the needle valve, not liquid. As noted previously, flowing air through the needle valve (which is set for a specific liquid flow rate) will result in only a negligible backpressure. Therefore, it can be assumed that the pressure acting on the cylinder is equal to the return pressure, P_R, and that the needle valve has no impact on the volume of the vapor space.

Understanding Vapor Space Compression (Cont.)

The Effect of Sampling Procedure

In addition to the pressure, the sampling procedure can also have a significant impact on the volume of the vapor space.

Sample Cylinder Orientation

All of the previous calculations and examples assume that during the sampling process the cylinder is held in the vertical orientation with the outage tube installed at the top. It is recommended that the panel be designed in such a way that it is impossible for the operator to install the cylinder in any other orientation. Having a clamp or cradle that holds the cylinder vertically is a best practice. Another best practice is to install quick connects of opposing genders on opposite ends of the cylinder (stem on one end, body on opposite end), which will prevent the cylinder from being installed upside down.

A cylinder that is installed horizontally will render any outage tube ineffective. However, because of the air trapped in the larger diameter of the sample cylinder, this orientation will result in a vapor space, even without an outage tube. The effect will be similar to Scenario 1 with a 50% outage tube. Despite this benefit, the bottom half of a horizontal cylinder will tend to collect sediment and other contaminants. For this reason, a horizontal cylinder is not recommended for most applications.

Valve Sequence

Varying the sequence in which valves are opened/closed can result in a vapor space of varying volume. In the previous example, the worst-case situation (smallest vapor space) was when the sample return valve was closed and the sample supply valve was kept open. This allowed liquid to flow into the cylinder until the cylinder pressure equalized with the supply pressure, compressing the vapor space.

Conversely, if the supply valve were to be closed first, then the pressure in the cylinder would decrease until it equalizes with the sample return. In this case the volume of the vapor space would increase. However, such a pressure drop could be problematic if sampling a volatile liquid and the return pressure is low. It might allow a portion of the sample to vaporize, which would compromise the representativeness of the sample.

The ideal sampling procedure would be one where the sample supply and return valves are closed at the same time, avoiding both of these situations. This can be addressed via procedure, with the instructions for the panel describing this simultaneous operation, but eventually the procedure will be misunderstood, ignored, or otherwise not followed. The best practice is to gang these two valves together so that they must be operated together, as shown in Figure 12.

If these valves are closed/switched simultaneously, then the cylinder pressure, P_C, after initially capturing the sample will be somewhere between the sample supply pressure, P_S, and the sample return pressure, P_R ($P_S > P_C > P_R$). This cylinder pressure would then be inserted for P_2 in the Scenario 1 and 2 calculations. It is not always clear what the value of P_C will be, though it can generally be estimated using manual calculations or flow simulation software.

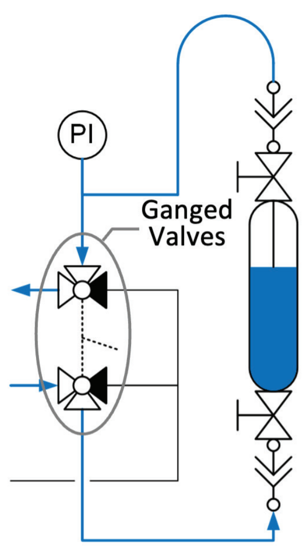


Figure 12: Sample Panel with Ganged Valves that Must Be Operated Together

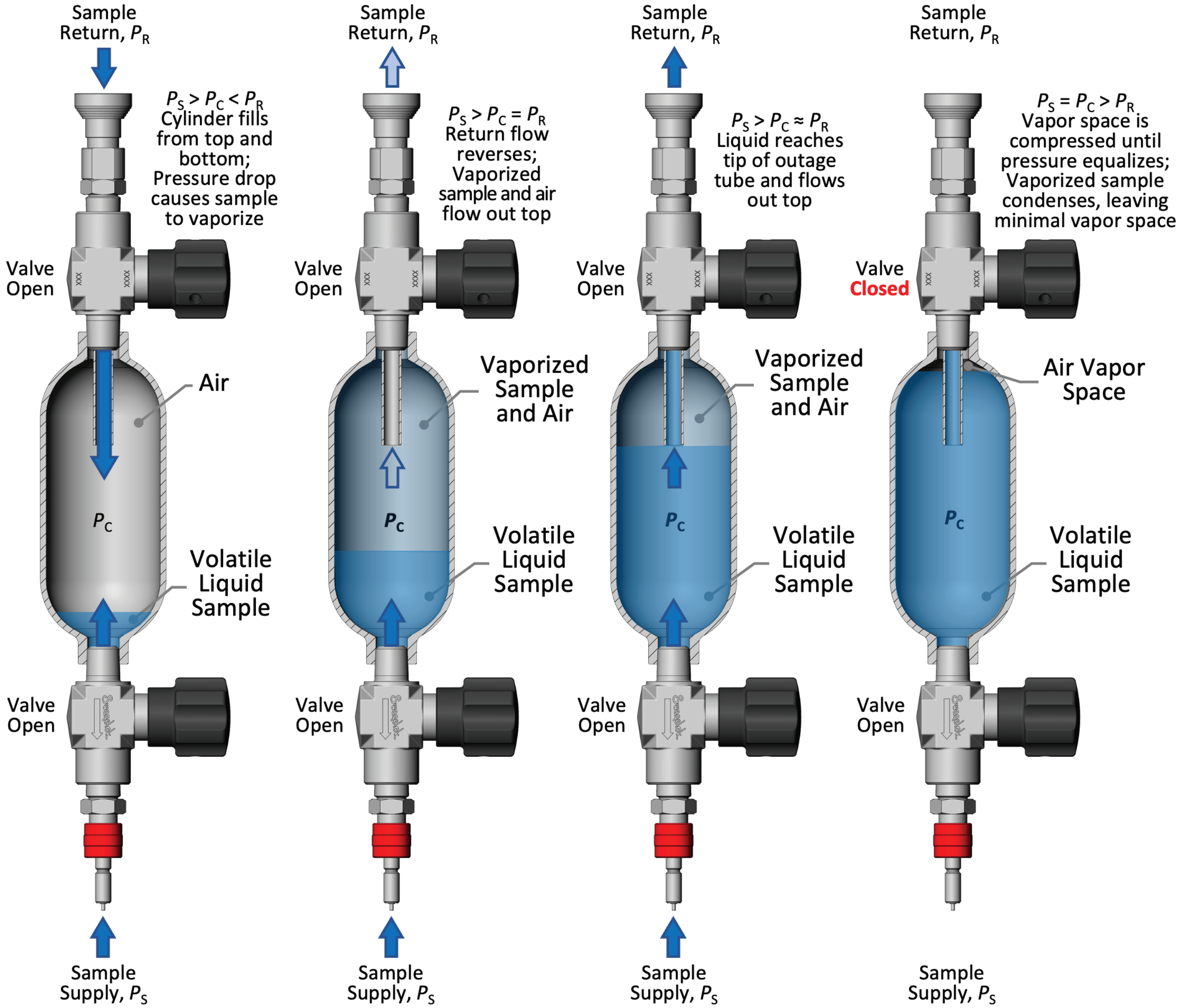
The sample return valve and sample supply valves refer specifically to the valves on the sampling panel, but the same undesirable situations would result from closing the valves on the cylinder assembly in the same sequence. Therefore, it is best to only close the cylinder valves after closing/switching the sample supply and return valves. At that point, the fluid in the cylinder will be static and the sequence for closing the cylinder valves will not have any impact.

Understanding Vapor Space Compression (Cont.)

Volatile Liquids and Liquefied Gases

When sampling highly volatile liquids or liquefied gases, there is another danger that is not readily apparent. As the volatile liquid enters the cylinder and the pressure drops, the liquid will begin to vaporize. This vapor will mix with and can possibly displace all the air in the cylinder. If the sample return valve is then closed and the sample supply valve is left open (the worst-case scenario previously mentioned), liquid will continue to flow into the cylinder, repressurizing the vapor. As the vapor is pressurized, it will condense, allowing even more liquid to flow into the cylinder. This process will repeat continuously to the point where the cylinder is 100% liquid-full, regardless of whether an outage tube is installed. Because all (or most of) the air was displaced by the sample vapor, the entirety of the vapor space can condense and leave the cylinder without a vapor space at all. This is illustrated in Figure 13.

Figure 13: Filling Cylinder with Volatile Liquids



Understanding Vapor Space Compression (Cont.)

To prevent this situation, the air must be prevented from escaping the cylinder. The surest way to do this is to introduce backpressure on the sample return that prevents the air from flowing out. The backpressure needs to be high enough to cause the vaporized sample to condense, or better yet, prevent it from vaporizing in the first place. If the sample return has enough backpressure, then maybe no further design changes are necessary. But if the sample return pressure is low or if the sample return is connected to a low-pressure vent/flare, then the sample system design should be modified to create a backpressure.

The easiest and least expensive way to create backpressure would be to install a check valve or backpressure regulator. These can trap the air in the cylinder until the pressure reaches the set point/cracking pressure. If the check valve or backpressure regulator is set high enough, then the pressure in the cylinder can build to the point where any vaporized sample will reliquefy. In this case, since the air will not have escaped, the vapor space calculations will be the same as for a nonvolatile liquid.

Even better would be to combine the use of a backpressure device with a sample cylinder that was precharged with pressurized air/nitrogen. If charged properly, this elevated pressure in the empty cylinder can prevent the sample from vaporizing, which can otherwise still happen in an unpressurized cylinder. As the pressurized liquid enters the unpressurized cylinder, the sample will begin to vaporize until the cylinder reaches the sample's vapor pressure. At that point, the vaporized sample will begin to recondense. By using a cylinder that is precharged with air/nitrogen at an elevated pressure, this vaporization can be avoided.

Finally, this is an excellent application for a constant-pressure cylinder. As described previously, constant-pressure cylinders include a piston that prevents the sample liquid from interacting with the gas in the cylinder. That pressurized gas can also be used to prevent the sample from vaporizing.

Thermal Expansion of Liquid Sample

Once the volume of the vapor space is known, the next step is to consider the potential thermal expansion of the liquid sample to determine if the vapor space is sufficient. If the thermal expansion is less than the volume of the vapor space and the pressure in the cylinder is not too high, then the outage tube implementation will be sufficient. If not, then the sampling system will need to be altered to ensure safety.

Final Sample Volume

Calculating the change in volume of the liquid is relatively easy. It is simply a function of the liquid's density at the initial and final temperatures. Starting with the formula for density:

Equation 4:

$$\rho = \frac{m}{v}$$

Here, ρ is the density, m is the mass of the sample, and V is the volume. This formula can be rearranged to solve for the mass:

Equation 5:

$$m = \rho V$$

It is known that the mass of the sample will not change—the cylinder valves trap the sample in the cylinder so no mass can escape. Therefore, it can be said the initial density and volume of the sample liquid will equal the final density and volume:

Equation 6:

$$\rho_1 V_1 = \rho_2 V_2$$

The initial volume, V_1, is known since it can be calculated as explained previously. The initial density, ρ_1, and final density, ρ_2, of the sample at the given temperatures can be found in various published references and/or software such as REFPROP. Therefore, the only unknown is the final volume of the sample, V_2, which can be solved for by rearranging Equation 6:

Equation 7:

$$V_2 = \frac{\rho_1 V_1}{\rho_2}$$

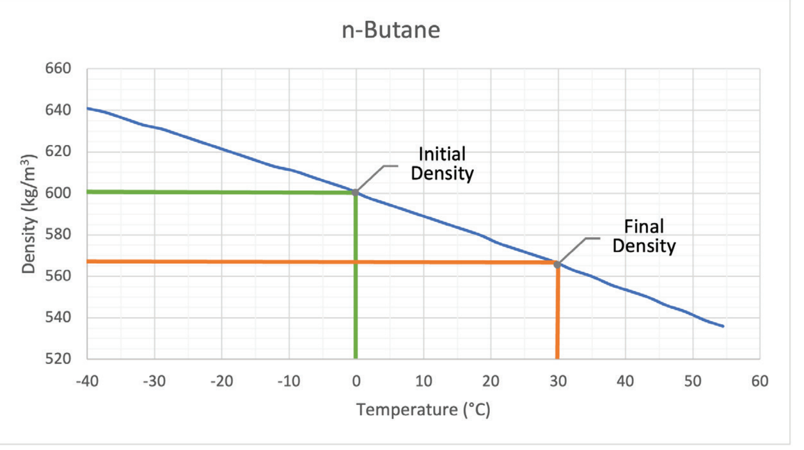


Figure 14: Temperature vs. Density for n-Butane

In the previous example, it was calculated that with Scenario 1, there would be an 8% outage and therefore the sample volume, V_1, would be 92% (100% - 8%). For this example, it will be assumed that the sample fluid is butane, which was initially collected at 0°C and then allowed to warm up to 30°C. Given these initial and final temperatures, Figure 14 can be used to determine the initial density, ρ_1, and final density, ρ_2.

Entering these values into Equation 7, along with the initial volume:

$$V_2 = \frac{\rho_1 V_1}{\rho_2} = \frac{600\frac{kg}{m^3}\, 92\%}{566\frac{kg}{m^3}} = 97.5\%$$

Here, the final sample volume of 97.5% is less than the total cylinder volume 100%, so the cylinder is unlikely to rupture. However, to verify this, the final cylinder pressure must also be determined.

Thermal Expansion of Liquid Sample (Cont.)

Final Cylinder Pressure

To calculate the final pressure of the cylinder, Boyle's law is once again used. In this case, the initial pressure, P_1, and volume, V_1, are the pressure and volume of the vapor space prior to thermal expansion, 10 bara and 8%, respectively. The final volume is 2.5% (100% - 97.5%). These values can be inserted into Equation 3 to solve for the final pressure:

$$P_2 = \frac{V_1}{V_2} \times P_1 = \frac{8\%}{2.5\%} \times 10 \text{ bara} = 32 \text{ bara}$$

This calculated pressure can then be compared to the rated pressure of the sample cylinder. Most sample cylinders are rated to 125 bara, so in this example, the sample pressure is well below that rating and there is little risk of rupture.

If the Vapor Space Is Not Large Enough

If the final sample volume is larger than the cylinder volume or if the final cylinder pressure exceeds the rated pressure of the cylinder, then the sampling system will need to be changed. There are a number of strategies that can be employed:

- The easiest and most obvious solution is to use a longer outage tube to increase the initial volume of the vapor space.
- Alternatively, a check valve or backpressure regulator could be installed immediately downstream of the sample cylinder assembly. When there is a low sample return pressure, the backpressure added by a check valve or backpressure regulator can help prevent air from escaping the cylinder. This will force the cylinder into Scenario 2, described previously, which will result in the largest possible vapor space.
- Another strategy is to precharge the cylinder with air, nitrogen, or some other gas. This helps to increase the initial pressure, P_1, in the Scenario 1 and 2 calculations. However, precharging the cylinder makes it more likely that the cylinder will be in Scenario 1, which means that some of the precharge will flow into the process by way of the sample return. As such, the process must be tolerant of the precharge gas.
- As noted in the Valve Sequence section on page 15, it can also help to ensure that the sample supply and return valves are opened/closed at the same time. This is most reliably achieved by using valves that are ganged together to operate with a single handle.
- In some cases, the use of a constant-pressure cylinder to collect the sample may be the best option. As described previously, if the proper procedure is followed, a constant-pressure cylinder can ensure a vapor space.

Proper Installation of Outage Tubes

The final step in the implementation of an outage tube is proper installation. An outage tube needs to be cut to the proper length, installed at the top of a sample cylinder, and be leak-free.

Cutting Outage Tubes

The length of the outage tube will vary based on the size of the cylinder in which it is installed. This length depends primarily on the length of the sample cylinder. For example, a tube that is sized for 20% outage in one cylinder would have a different outage percentage in a longer/shorter cylinder. Refer to the literature of the sample cylinder manufacturer to identify the proper cut length for the specific cylinder being used. Likewise, the outage tube manufacturer can provide instructions for how to properly measure and cut outage tubes, as shown in Figure 15.

Outage Tube Lengths

Tube OD, in.	Cylinder Ordering Number	Minimum Outage, %				
		10	20	30	40	50
		Tube Length, in.				
1/4	304L-HDF2-40	0.87	1.11	1.35	1.59	1.84
5/16	304L-HDF4-50	0.85	1.07	1.28	1.50	1.71
	304L-HDF4-75	1.02	1.34	1.66	1.98	2.31
	304L-HDF4-150	1.12	1.45	1.79	2.13	2.46
	304L-HDF4-300	1.65	2.32	2.99	3.67	4.34
	304L-HDF4-400	2.00	2.90	3.79	4.69	5.59
	304L-HDF4-500	2.26	3.38	4.50	5.62	6.74

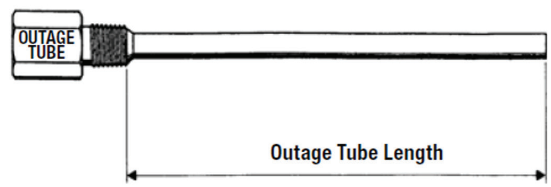


Figure 15: Outage Tube Instructions (Courtesy of Swagelok)

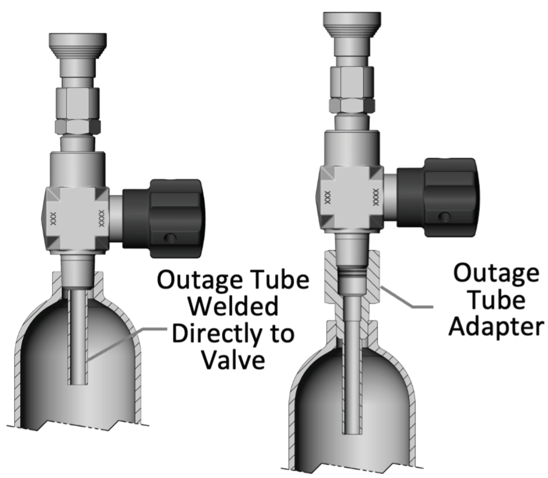


Figure 16: Outage Tube Adapters vs. Outage Tube Welded to Valve

Installing Outage Tube on Top of Cylinder

Outage tubes are available welded to adapter fittings or to other cylinder accessories, such as cylinder isolation or relief valves. Regardless of which type is used, the outage tube will be useless if it is installed on the bottom of the cylinder or if the cylinder is coupled to the sample panel in the wrong orientation. Obviously, care must be taken to ensure that the outage tube is actually installed and that it is installed on the top end of the cylinder, not the bottom. As shown in Figure 16, this is easy to verify visually when an outage tube adapter is used. However, when the outage tube is welded directly to a relief valve or cylinder isolation valve, careful inspection is required to confirm that the valve's part number or other markings indicate that an outage tube is included.

Additionally, the sample panel needs to be designed to ensure that the cylinder is installed vertically. This is usually accomplished using clamps, cradles, etc., that secure the cylinder to the panel in one specific orientation. Furthermore, the sample supply should be connected to the bottom of the cylinder, so the panel needs to be designed to route the sample liquid appropriately.

Finally, best practices dictate that cylinder assemblies are configured in such a way to guarantee that the cylinder cannot be coupled to the sample panel upside down. Cylinders can be marked with labels to note the orientation, but ultimately a visual label is considered insufficient because it relies on the operator to see and understand the markings. A more robust and common way to ensure that the cylinder is properly coupled to the panel is to install a quick connect stem on one end of the cylinder and a quick connect body on the other end. Because a stem can only couple to a body, the operator is forced to install the cylinder in the correct and upright orientation. Similarly, keyed quick connects can be made to ensure that the cylinder is installed in the correct orientation.

Proper Installation of Outage Tubes (Cont.)

Sealing Outage Tubes

The outage tube needs to be effectively sealed to the cylinder end connection to avoid leaks. If leaks are present when filling the cylinder, gas can leak through the joint and the vapor space will be reduced or eliminated altogether. To ensure a leak-free connection, it is essential to select components with quality pipe threads and use a thread sealant such as anaerobic thread sealant, PTFE tape, or graphite paste, as shown in Figure 17. Follow the instructions from the sealant manufacturer and leak test the connection afterwards.

Figure 17: Anaerobic Thread Sealant, PTFE Tape, and Grafoil Paste

Conclusion

When collecting a liquid sample in a sample cylinder, it is crucial to ensure that there is a vapor space in the cylinder to absorb any thermal expansion of the liquid. While there are many methods to create this vapor space, one of the most widely used and simple methods is the outage tube. However, this simple device is not well understood by most designers, and it is not as foolproof as many believe. But by understanding the fluid mechanics inside the sample cylinder and through careful sample system design, an outage tube can be an effective tool to ensure the safety of the sampling operation.

References

ASTM D1265, Standard Practice for Sampling Liquefied Petroleum (LP) Gases (Manual Method)

swagelok.com

Contact your local authorized
Swagelok sales and service center.