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Shift your cylinder gas procurement and usage paradigms

Rethinking current systems can eliminate many analytical problems while improving costs

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While ranking relatively low on expenditure lists, specialty and packaged gases used in the hydrocarbon processing industry (HPI) usually cause the most annoyances and problems. Why would there be more complications with gases than almost any other lab product?

There are numerous reasons for this. Selecting the right gases and/or grades is not a simple process. Nor is managing product quality to the point of use. Add to this challenges associated with managing administration and logistics, such as waste, movement and inventory, as well as cylinders that must be maintained and then returned to the gas vendor. There are many potential remedies that can relieve problems and provide cost savings for gas procurement and use.

Selecting the right gas. When it comes to selecting carrier, make up or fuel gases for analytical equipment, many cylinder gas users specify names and gas grades. But what do these names mean? With few exceptions, there are no standards in the gas industry for naming gases or grades. Gas grades, specifications and cylinder size vary from vendor to vendor. What one company calls a 300-size, zero-grade helium (He) may be radically different than what another company calls it.

In addition, most gas grade names are not regulated. For example, there is no universal standard for defining a zero-grade gas. Many end-users assume zero-grade He means the gas is 99.999% or "five nines" pure. Yet, reviewing published product specifications from manufacturers' Websites reveals that there is no major specialty gas manufacturer with zero-grade He listed as five nines pure. Zero-grade He purities range from 99.998% to 99.995% pure. In fact, one company has stopped offering any zero-grade He.

There are some product grades and names that are regulated. In order to call a gas medical grade, it must meet certain FDA standards. In addition, some emissions monitoring standards must meet strict rules outlined by the EPA or other regulatory bodies. Yet, these are the exceptions; most gases used in analytical applications fall into the general rule. The lack of a universal standard for defining gas grades and names makes selecting the right gas a complex process.

Adding to the complexity is confusion surrounding the total purity paradox. Analysts may think they want the purest gas—gas that is 99.999% pure. If a problem is ever encountered with cylinder gas, they may demand even higher purity levels. Instead, what should be looked at is the actual *impurity* found in the gas (Fig. 1).

For example, take two spoonfuls of sugar, each consisting of nearly pure sugar. One is 99% pure and one is 95% pure. Given a

	Company A	Company B	Company C
O_2	5	3	1
Ar_2	NA	NA	4
CO_2	NA	1	1
CO	NA	1	1
H_2	NA	NA	1
THC	NA	1	1
H_2O	5	4	1
Purity	99.999%	99.999%	99.999%

Are these really the same?

FIG. 1 Which "five 9" nitrogen would you buy?

choice between the two, most people would choose the sugar that is 99% pure. Yet, a smart analyst needs to know much more than the purity in order to make an informed decision. What if the impurity found in the 99%-pure spoonful is rat poison, and the 95%-pure spoonful's impurity is salt? Now which one would you choose? It is not the purity, but the impurity that causes problems. It is possible that a gas with a higher assay may actually be more detrimental to an application than one with a lower assay.

Therefore, when analysts are selecting a gas, they need to look closely at the impurity or "rat poison" that might affect an application. Impurities found in the gas could be contaminants that may give false readings, create noise or cause other analytical problems. These can also cause equipment breakdowns leading to downtime. There are two parameters to understanding these impurities. First, what is the impurity for the application? Second, how much of that substance can the application tolerate without hindering analytical results or adding operating costs?

Impurities. The three contaminants that affect most chromatographic applications are oxygen (O_2), moisture and hydrocarbons. O_2 can accelerate column bleed, reduce column life and change retention times. In some applications, O_2 can also cause ghosts or unexpected peaks. Moisture also impacts performance in numerous ways. It can reduce column life, shift retention times and increase baseline noise levels. Hydrocarbons can also increase baseline noise, degrade analyte quantification and cause ghost peaks. There are many other contaminants that can also affect performance. For example, some mass spectrometry applications are sensitive to inert gases, like krypton, although these gases do not affect many other detectors' performance. Most detectors also are sensitive to impurities that are similar to analytes, i.e., electron capture detectors (ECDs) are sensitive to halogen contamination because ECDs are halogen selective.

Hydrocarbon contamination is especially problematic for flame air supply to a flame ionization detector (FID), a very common detector in hydrocarbon applications. Frequently, one sees technicians running high-grade He as a carrier and hydrogen (H_2) as a flame gas, yet run low-quality air as flame support. The probability of picking up trace hydrocarbon levels in high-grade He and H_2 high enough to impact FID performance is fairly low, especially if the He is supplied from a once-liquefied source. Yet, technicians will use breathing-quality air to run the FID. It is best to use synthetic air blended from liquefied gases to reduce the hydrocarbon contamination probability.

Once users understand the impurities that might affect an application, they then need to select the gas that has the lowest level of impurities their system can tolerate. This will enable them to produce the results being looked for, and do so at the lowest possible cost. Selecting a gas that is higher in purity than required may waste money with no reasonable improvement in performance.

After selecting the right gas for the application, gas users then need to consider two additional issues. First, what is the gas supplier doing to ensure that impurities don't get into the cylinder? Second, what assurances or proof is the supplier providing to ensure product quality?

Gas quality. Users need to be sure that gas quality is verified at every process step from raw materials to bulk transfers, to cylinder filling, to delivery; thus ensuring that no part of the supply chain allows introduction of impurities.

The most important verification is the final product. For those applications that require a certificate of analysis (COA), the supplier should provide it for the cylinder product. Without this COA, a user cannot be sure that the cylinder doesn't contain a contaminant that could affect their process. Sometimes a laboratory needs a gas that conforms to standards, but is not individually analyzed. Therefore, the gas may come with a certificate of conformance (COC). Beware any supplier that tries to represent a COC, a promise to meet a specification, for a COA, an actual analytical result.

In addition, if a gas company represents a specification as typical, it is a dead giveaway that the assurance is not tied to a specific analysis. Typical in this case means that the company is stating that, "more often than not, this gas will meet specifications, but if it doesn't, tough luck." It is also important to check that the COA is for the end-use product in the cylinder, not the raw material.

In most cases, problems with gas have more to do with the gas cylinder's hygiene than the raw material. The three most troublesome contaminants—O_2, moisture and hydrocarbons—are also the contaminants that have the greatest potential to work themselves into the cylinder during filling.

Raw materials. This is less of a contamination problem than some may think. However, there are a few cases where raw materials will impact analytical performance. For instance He for analytical applications should be sourced from a supply that was liquefied at one time. Although liquefied He is more expensive, using this source minimizes contamination potential, as most contaminants are separated out during the liquefaction process. One way to avoid some low levels of inerts, that may impact mass spectrometry applications, is to purchase He that has come from a liquid source.

Hydrostatic testing. Every five or ten years, high-pressure cylinders must be pressure tested to ensure integrity. Usually, the gas supplier will test the cylinder hydrostatically, filling it to five-thirds its working pressure with water to measure steel expansion. If the cylinder leaks or does not stretch and then return to normal size, it is scrapped. Otherwise, it is stamped and put back into service. When hydrostatically tested cylinders are not properly baked out to remove moisture, hydrostatic testing can introduce contamination. A newer technique, ultrasonic testing, does not expose the cylinder to water, thus eliminating this potential contamination source.

Gas leakage. While gas suppliers intend for the gas filling process to be a one-way street, the Venturi effect caused by any leak could allow air into the system—air that usually contains about 21% O_2, and large quantities of moisture and hydrocarbons. Depending on the local air makeup, there could be about 60 ppm total hydrocarbons. Suppliers who routinely go through a prescribed leak check during filling can minimize this contamination source.

Cylinder service. Suppliers sometimes take a high-pressure steel cylinder out of service for one gas, repaint it and then reuse it for another gas. If the proper standard operating procedures are not followed, these can serve as a contamination source. For instance, if a gas supplier converted cylinders from sulfur hexafluoride service to He service, it typically would not be a problem, as both products are considered inert.

However, let's assume a gas user hooked up a converted He cylinder to an electron capture detector. In this example, the converted cylinder can cause problems because electron capture detectors look for halogens. Thus it will detect the fluorine in any residual sulfur hexafluoride from prior service.

Top filling. In order to reduce raw material costs, some gas companies may be tempted to fill on top of the residual product in a returned cylinder, especially if the cylinder has an expensive raw material, like He. Yet, this shortcut could also introduce contaminants. How does this happen? High-pressure cylinders are usually returned once they reach a minimum pressure and are never really emptied. Yet, if the user's operating pressure is higher than the residual cylinder pressure, contaminants from the user's systems can get backed into the cylinder, even if there is positive pressure on the cylinder.

When the cylinder is returned and the supplier takes the shortcut of top filling, the next cylinder user may pick up the contaminants from the prior user. This is the analytical equivalent of using a dirty needle. Cylinders should be cleaned properly before they are filled by going through a systematic purge and evacuation procedure to minimize residual gas-phase contaminants. Another way to minimize contamination is for the gas company to use valves that prevent back flow.

Zero cylinder pressure. Another contamination source can be found when a cylinder is completely emptied. The higher upstream pressure can cause liquid-phase contaminants to enter the cylinder. A normal purge and evacuation procedure will remove gas-phase contaminants, but it may not be robust enough to remove liquid-phase contaminants.

The only way to remove some liquid contaminants is through a bake-out procedure (if it is not a flammable liquid) or overnight vacuum. A gas company should remove the valve on zero-pressure cylinders and inspect for liquid condensation. Gas users usually avoid charges for this expensive de-valving process by returning cylinders with positive pressure, anywhere from 100 psig to 150 psig. Yet, when they don't, the supplier must follow procedures assuring contaminants are removed.

Drinking through a dirty straw. If technicians are sure of the gas purity selected, but are still not getting desired results, they need to investigate whether their own on-site gas delivery systems may be introducing impurities. In other words, they may be "drinking clean water through a dirty straw." For example, improper piping, regulators or other laboratory equipment can also be a contamination source. Here are some general rules to ensure your delivery system is not causing problems:

1. *Proper analytical regulators.* Usually, big is bad. Regulators should have low dead volume, stainless steel diaphragms with packless valves and should be lubricant free. Some regulators labeled analytical regulator contain hydrocarbon- or halocarbon-based lubricants, which can impact analytical performance on FIDs, ECDs, mass spectrometers and other detectors. In addition, regulators for chromatographic applications should be designed specifically for the intended service.

2. *Minimize gas delivery system leaks.* Remember the Venturi effect. If gas is leaking out, an air countercurrent—with all that O_2, moisture and hydrocarbons—may be working its way in. Use stainless steel tubing (be sure that it is the right type for the specific application) and minimize connections. Also, many flexible pigtails are porous enough that small-molecule gases like He and H_2 can diffuse through the pigtail wall, wasting in excess of 10% of the usable gas product (Fig. 2). Make sure pigtails are suitable for He and H_2 service.

3. *Proper change-out procedures.* Many gas users are concerned with O_2, moisture and hydrocarbon contamination; yet they introduce air every time they change out a gas cylinder, defeating the purpose of buying a high-purity gas. Users can minimize this contamination source during cylinder change-out by using proper purge and evacuation procedures.

The gas supply chain. The final source of trouble associated with gases includes all the complexities of managing a gas supply chain that, among other things, includes returnable, rented containers. Once the product is used, the user needs to replace the cylinder with a full one and then return the used cylinder to the supplier. Gas is one of the few laboratory supplies that requires a two-way supply chain—introducing additional challenges.

Many procurement systems have difficulty managing cylinder rentals because the actual rental costs fluctuate depending on end-of-month cylinder balances. If balances go up, so does the monthly rental charge, and vice versa.

FIG. 2 Proper tubing, cleaning and leak elimination = reduced cost and better gas utilization.

Assume a user pays $5 per month per cylinder rental and has a 100-cylinder balance at the end of the month. The facility would be invoiced $500 for rent. If the cylinder balance creeps up to 120 cylinders at the end of the following month, the facility would be billed $600. A user's system that pays on reconciliation to a specific part number may have difficulty managing and interpreting rental items because the amount is not standard each month. Rental allocation within a facility's operation can be complicated, especially in an HPI complex that has numerous users, end-use points and cylinder stockpiles. Most choose to do flat allocations in which each user is allocated a set portion of the bill each month.

Because this in-house charge is a flat fee and is a relatively low expense, many end-users do not actively monitor cylinder balances. They simply want the gas to be available when it is needed, much like a utility. This may result in overstock, with most users keeping many months of inventory onsite even though their gas supplier may make deliveries a few times a week. In HPI facilities, it is not uncommon to find eight cylinders somewhere in the system for every one cylinder in use.

Rental may not be a significant cost for each end-user, but when added up across an entire facility, the cost, and potential savings in reducing inventory, can be great. Calculating cylinder turn (the length of time it takes a cylinder to travel through a site) can help identify if overstocking is occurring.

To determine how long cylinders stay at a site, users should divide the number of total units purchased per month into the end-of-month balance (an end-of-month balance can be found on any monthly rental statement). For instance, if a user purchases, on average, 50 cylinders per month and has, on average, a 500-cylinder end-of-month balance, it takes 10 months for a cylinder to travel through the facility. Assume the same user pays $5 in rental per cylinder. That's $2,500/month or $30,000/year. A reduction in cylinder turn from 10 months to five months would result in **$15,000** in cost savings/year. Again, if the gas supplier is delivering gases a few times a week, even five months' inventory may be excessive. Users should calculate cylinder turn—many will be surprised at how long cylinders sit idly at a facility, adding unnecessary costs.

Selecting gas mixtures. In addition to carrier, makeup and fuel gases, many gas chromatographic applications require calibration standards. In the HPI, these standards can be a complex mixture of hydrocarbons and/or volatile organic compounds. Additional factors must be understood in order to make an informed gas mixture selection:

- **Mixture safety.** With all mixtures, the first item that needs to be determined is whether it can be safely blended. Flammables and oxidant concentrations are especially tricky. The flammable components must be kept reasonably below the lower explosive limits respective to oxidant concentration, thus ensuring safety.
- **Mixture stability.** Will the components remain stable over time or will they begin to react? Component compatibility and reactivity need to be factored into gas cylinder manufacture and storage. For example, components like nitric oxide will react in the presence of trace amounts of O_2 and turn to nitrogen dioxide. This reaction can cause nitric oxide numbers to degrade over time. Proper precautions need to be taken by the gas manufacturer to ensure nitric oxide stability. The inverse is true as well. Without the presence of an amount of O_2 in nitrogen dioxide standards, its values may degrade as it converts to nitric oxide. As another example, components, such as 1,3 butadiene, in gas mixtures may dymerize and fall out if not kept at cool temperatures. Gas mixture handling and control may impact stability.
- **Acceptable tolerance or error.** It is impossible to make a zero-error mix—calibration standards are reference standard copies. The copy's quality/accuracy needs to be defined. The better the copy, the more expensive the mix. Mix quality and accuracy are generally expressed using terms such as primary, certified, unanalyzed or a variety of other names. However, just as with the total purity paradox, gas users need to understand what gas manufacturers actually mean when they refer to a mixture as primary or certified. For instance, error associated with certified standards is not universal from one gas company to the next.

There are two types of tolerance or error that gas companies should specify when naming a standard: the preparation tolerance (the error associated with mixing the gas components) and the analytical or certification tolerance (the error associated with naming the gases in the cylinder). As with pure gases, these definitions are not standard with suppliers. Production method, gas filler skill and production conditions can impact preparation tolerance. Analytical equipment and method, gas sampling technique and the gas company's reference standard accuracy can impact analytical tolerance. Knowledge and understanding of both tolerances will help ensure selecting the correct standard.

- **Sampled material phase.** Most gases used as support in chromatography applications are in gas phase. However, mixtures of gases used to calibrate instrumentation may be in either gas or liquid phase. Nonliquefied gases are essentially homogenous and taking a representative sample of the gas in the cylinder is fairly easy. However, liquefied gas cylinders contain both a liquid and gas phase. The product in the cylinder is not homogenous; contaminant and mix concentration levels vary with phase and a representative sample is difficult to obtain.

Gases with a low boiling point and high vapor pressure, such as nitrogen, will tend to concentrate in the vapor phase. As product is initially withdrawn from the cylinder, vapor phase gases will be at their highest levels. Mixture components with a high boiling point and low vapor pressure, such as heavy hydrocarbons and moisture, will tend to concentrate in the liquid phase. These heavier gases become more concentrated as the cylinder is emptied. A gas vendor can improve its assay by analyzing vapor phase contaminants in liquid and vice versa. It is important to stipulate the phase analyzed and ensure that multiple vendors are sampling and analyzing consistently.

- **Units of measure.** When a cylinder is analyzed, contaminant levels of pure gases and concentration levels of gas mixtures should be listed with the appropriate measurement unit. Levels can be listed in either %volume or %weight. The listed amounts will differ depending on the unit of measure. Ensure that specifications are evaluated in identical units to limit evaluation bias.

More ways to save. There are a few more ways to find incremental savings. As discussed earlier, if a gas supplier maintains good cylinder hygiene and minimizes cylinder contamination probability, cylinders can be used to as low as 100 psig. However, in many chemical, petrochemical and refinery applications, it's almost an unwritten rule that cylinders are changed out at 500 psig. Why do they change so much earlier than needed? The most common answer is "that's the way we've always done it."

The only possible justification for this would be that the wasted gas cost is outweighed by the costs associated with running out of gas. Changing cylinders at 500 psig is equal to wasting one usable cylinder for every six cylinders purchased. In addition, if a user targets 500 psig, they're probably changing at higher pressures. This is often seen on Friday afternoons, when users will put on fresh cylinders to ensure that they have enough to last through the weekend.

Newer, easy-to-use gas manifold systems allow cylinders to be changed at the lowest practical pressure, giving users an extra measure of security and supply reliability. After a cylinder reaches its lowest-use-pressure, the system will automatically switch to a backup cylinder. Once a cylinder is switched and the backup is in use, the empty cylinder can be replaced. The result is that more gas is withdrawn from a cylinder. This also reduces the need to monitor gases—the automatic switchover does that—while giving an extra security measure. Implementing a system such as this may result in one free cylinder for every six purchased.

Gas users can help reduce logistical headaches and hassles by changing to more efficient gas packaging, such as multi-cylinder packs; liquid dewars, which hold the equivalent of more than a dozen high-pressure cylinders; micro-bulk systems, which hold up to 100 times a cylinder's product volume; or bulk tank systems, for even larger needs.

In addition, users can assess whether they even need cylinders, and, instead, they may consider generated gas, an investment that can have a payback in as short as a few months.

Generated air can get hydrocarbon purity to the sub-one ppm

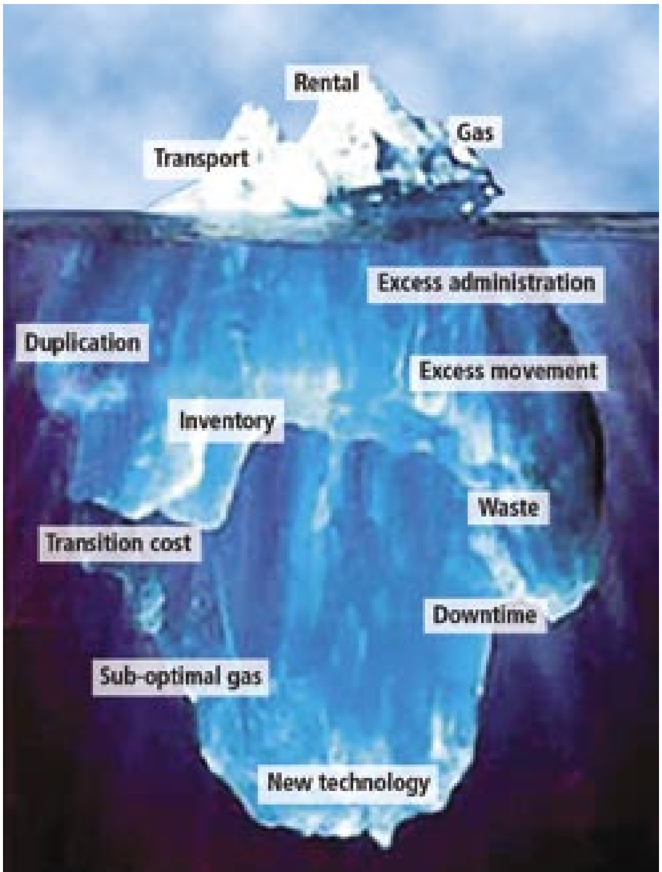


FIG. 3 Analyze thoroughly both above and below the water.

level, good enough to run most FIDs, as long as the feed air is oil-free (air generators have a heated catalyst that picks off light hydrocarbons). If you have fairly clean house air supply, payback on systems can be as quick as two months, depending on the volume and current cylinder price.

Payback on H_2 generators to supply FID flame gas is a little more difficult to justify when comparing product cost alone. Given H_2 generator cost and the relatively low use of H_2 flame gas on an FID, payback on H_2 generators may be a few years. However, consider using H_2 as both your flame and carrier gas. The payback period can be much faster and justify the generator cost, and H_2 is a better carrier than He. Why is He used more often than H_2 as a carrier gas? People remember the Hindenburg—they are afraid of H_2's flammability characteristics. However, the risk associated with having H_2 trickle coming off an H_2 generator is much less than risks associated with having a cylinder in your lab filled to rocket-like pressures; most high-pressure cylinders are filled to over 2,000 psi.

Hassles can also be eliminated in ordering and managing invoices. Most users continue to use paper purchase orders; some even continue to use one purchase order/gas, leading to even more low-dollar purchase orders, which add to the time and cost to process all those orders. There are more efficient ways to work with the supplier, including summary billing or online ordering to improve ordering time, efficiency and cost. According to one consulting company, e-procurement can reduce goods and services cost by 5% to 10%, speed up fulfillment cycles from 8.4 days to an average of 2.3 days, and

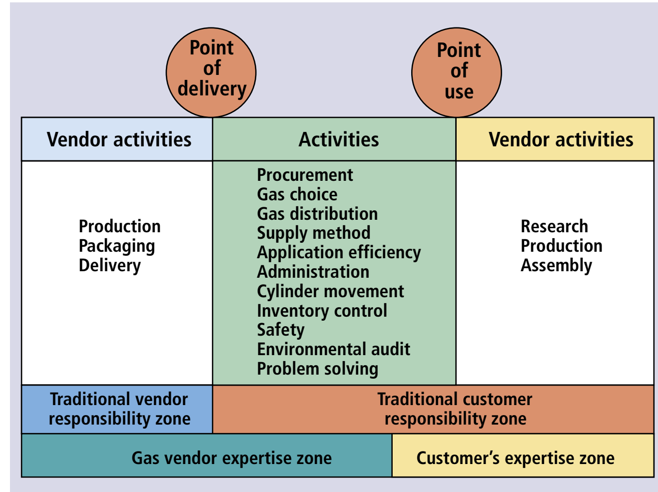


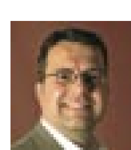
FIG. 4 Get the gas company involved.

cut administrative costs from $114 to an average of $31 per requisition. Some vendors even allow customers to access other paperwork, like COAs, online.

What it comes down to. People who use gases are all looking for solutions to problems faced in buying and using the right gas(es) for their applications. These solutions become even more critical when you consider the very real dollars associated with this.

Evaluating gas supply cost is like evaluating an iceberg: the part you may not easily see may be the part that gets you in trouble. Look carefully at the total gas supply cost, above and below the waterline (Fig. 3). For every dollar spent on gas, cylinder rental and transportation, there are typically two to three dollars in hidden costs below the waterline associated with inefficiencies in gas selection, gas distribution, excess administration, waste and downtime. Working with a supplier to reduce these inadequacies will help alleviate problems and get the most out of the gas you buy. Ideally, look for a company that has a unique understanding of packaged gases, technical expertise in analytical applications, first-rate supply chain management skills and many years of experience in the packaged gas industry.

Also, look for a company that is willing to work closely with its customers to understand their process and recommend the best gas and equipment solutions to meet their needs. Typically, the customer and vendor stick to their responsibility zones (Fig. 4). Getting the gas company involved can help you get the most out of the gas you buy. **HP**



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