

Gas Buying 101 — Eliminating the Hassles Associated with Obtaining and Using Gases

This month's column suggests ways to rethink the criteria for selecting and using gases in laboratories. Knowing about gas grades, purities and impurities will help alleviate some of the problems associated with gases.

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Chromatographers and others who procure gases for their laboratories routinely say that gases rank relatively low — well below the top 10 — on the list of expenditures compared with other laboratory purchases. Yet, when asked to rank laboratory supplies by the associated headaches and hassles, gases usually bubble to the top of the list. What causes these problems and what can people do to find some relief?

This month's "GC Connections" column will help define the reasons for these complaints and provide some potential remedies. Analysts need to consider the selection of the right gas and whether product quality has been maintained to the point of use. They must also consider how the gas will be used and then manage a supply chain that includes returnable cylinders. How many other laboratory supplies come in containers that must be maintained and then returned to the distributor?

Selecting the Right Gas

When it comes to selecting carrier, make-up or fuel gases for analytical equipment, many laboratory users specify names and grades of gases. But what do these names mean? With few exceptions, the gas industry has no standards 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 could be radically different from what another company calls a 300-size, zero-grade helium.

In addition, most gas grade names are unregulated. For example, no universal standard exists for defining a zero-grade gas. Many users assume that zero-grade helium is 99.999% pure (or "five nines"). Yet, a review of published product specifications from manufacturers' websites reveals that no major speciality gas manufacturer has listed zero-grade helium as 99.999% pure. Purities of zero-grade helium range from 99.998% to 99.995% pure. In fact, one company has stopped selling zero-grade helium.

Some product grades and names are regulated. To call a gas medical grade, for example, it must meet certain US Food and Drug Administration (FDA) standards. In addition, some emissions-monitoring standards, such as those used for US Environmental Protection Agency (EPA) protocols, must meet strict standards outlined by EPA or other regulatory bodies. Yet, these are the exceptions; most gases used in analytical laboratories fall under the general rule. The lack of a universal standard for defining gas grades and names makes the selection of the right gas a complex process. Users who select gases by names alone can make poor gas selections.

Adding to the complexity is confusion surrounding the total purity paradox. Analysts might think that they want the purest gas — gas that is 99.999% pure. If they ever encounter a problem with their laboratory gas, they might demand even higher levels of purity. However, they

should be looking at the actual impurity found in the gas.

As an analogy, take two spoonfuls of sugar, each of which is nearly pure sugar. One is 99% pure and the other is 95% pure. Given a choice between the two, most people would take the sugar that is 99% pure. Smart analysts, however, need to know much more than the purity to make an informed decision. What if the small percentage of impurity found in the 99% pure spoonful is rat poison, and the 95% pure spoonful's impurity is salt? Now, which would be the better choice? It is possible that a gas with a higher assay could actually be more detrimental to an application than one with a lower assay.

Therefore, when chromatographers select gases, they need to look closely at the impurity that might affect their application. The impurities found in gases could be contaminants that could yield false readings, create noise or cause other analytical problems. These impurities can also cause equipment breakdowns that lead to downtime. Two parameters are necessary for understanding these impurities. First, what substance would be rat poison for the laboratory's application? Second, how much of that substance can the application tolerate without hindering analytical results or adding operating costs?

The three contaminants that affect most chromatographic applications are oxygen, moisture and hydrocarbons. Oxygen can accelerate column bleed, reduce column

life and change retention times. In some applications, oxygen can cause ghost or unexpected peaks. Moisture also affects performance in a number of ways. It can reduce column life, shift retention times and increase baseline noise levels. Hydrocarbons can increase baseline noise,

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degrade analyte quantification and cause ghost peaks. A host of other contaminants can also influence performance. For example, some mass spectrometry (MS) applications are sensitive to inert gases such as krypton, although these gases do not affect the performance of many other types of detectors. Most detectors are also sensitive to impurities that are similar to the analytes. Electron-capture detectors, for example, are sensitive to halogen contamination because these detectors are selective for halogens.

After laboratory personnel understand the impurities that could affect their application, they need to select the gas that has the lowest level of the impurities that their system can tolerate. This choice will enable them to produce the results they seek and to do so at the lowest possible cost. Selecting a gas that is higher in purity than required can waste money with no reasonable improvement in performance.

After selecting the right gas for the application, laboratory personnel then need to consider two additional issues: First, what is the gas supplier doing to prevent impurities from entering the cylinder? Second, what assurances or proof is the supplier providing to ensure the quality of the delivered product?

Ensuring Gas Quality

Gas users must be sure that gas quality is verified at every step of the process — from raw materials to bulk transfers and from cylinder filling to delivery — to ensure that no part of the supply chain enables the introduction of impurities.

The most important verification is that of the final product. For applications that require a certificate of analysis, the supplier should provide a certificate of analysis for the product in the cylinder. Without this certificate of analysis, users cannot be certain that the cylinder is free of contaminants that could affect their process. Sometimes a laboratory needs a gas that conforms to standards but is not

individually analysed. Therefore, the gas might come with a certificate of conformance. Beware of any supplier that tries to represent a certificate of conformance (a promise to meet a specification) for a certificate of analysis (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 instance 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 certificate of analysis is for the end-use product in the cylinder and not the raw material. In the majority of instances, problems with gases have more to do with the gas cylinders' cleanliness than the raw material. The three most troublesome contaminants — oxygen, moisture and hydrocarbons — are also the contaminants that have the greatest potential to work themselves into the cylinder during the filling process. Some examples of these possible contaminant sources include raw material sources, hydrostatic testing, gas leakage during filling, cylinder service changes, top filling and zero cylinder pressure.

Raw material source contamination:

Raw materials are contaminants less often than some people might think. In a few instances, however, raw material can influence analytical performance. For example, helium used for analytical applications should be sourced from a supply that was liquefied at one time. Although liquefied helium is more expensive, the use of this source minimizes the potential for contamination because most contaminants are removed during the helium liquefaction process. The way to avoid low levels of inert compounds that can affect MS applications is to purchase helium from a liquid source.

Another example is synthetic air for flame ionization detectors. Air supplied for a flame ionization detector should have hydrocarbon levels less than 1 ppm and even less for low-level analysis. The best way to minimize hydrocarbon content is to purchase a synthetic air blended from liquefied gases. Air cylinders intended for instrumentation will have a CGA 590 valve fitting (although the proper valve is not

enough assurance that it is proper for the application). If an air cylinder delivered for flame ionization detector service has a CGA 346 fitting, it is the wrong supply.

Hydrostatic testing: Every 5 or 10 years, high-pressure cylinders must be pressure tested to ensure their integrity. Usually, gas suppliers will test their cylinders hydrostatically, filling them to five-thirds of their working pressure with water to measure steel expansion. If a cylinder leaks or does not stretch and then return to normal size, it is scrapped. Otherwise, it is stamped and put back into service. Unless hydrostatically tested cylinders are properly baked out to remove moisture, hydrostatic testing can introduce moisture contamination. A newer technique called ultrasonic testing does not expose the cylinder to moisture and eliminates this potential contamination source.

Gas leakage during the filling process:

Although gas suppliers intend for the gas-filling process to be a one-way street, the Venturi effect means that any leak could allow a countercurrent of air to flow back into the system — air that usually contains approximately 21% oxygen and a lot of moisture and hydrocarbons. If gas is leaking out, a countercurrent of air — with all that oxygen, moisture and hydrocarbons — could be working its way into the gas stream. Depending upon the make-up of the local air, it could contain approximately 60 ppm total hydrocarbons. Suppliers who routinely perform a prescribed leak check during filling can minimize this contamination source.

Cylinder service changes: Suppliers sometimes take a high-pressure steel cylinder out of service for one gas, repaint it and use it for service with another gas. If the supplier does not follow proper standard operating procedures, these service changes can serve as a contamination source. For example, if a gas supplier converted cylinders from sulphur hexafluoride service to helium service, it would typically be no problem because both gases are considered inert. However, if a gas user connected a converted helium cylinder to an electron-capture detector, the converted cylinder could cause problems because electron-capture detectors are extremely sensitive to halogens and will detect the fluorine in any residual sulphur hexafluoride from the prior service.

The larger the gas company's cylinder fleet, the less likely it is that it will swap cylinder service. Users can tell if a company is swapping service by checking the paint job on the cylinder. Most companies paint cylinders different colours for different

product classes. If you see a multicoloured cylinder, with different undercoats of colour showing through chips and scratches in the topcoat, chances are the company has been swapping cylinder service.

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Top filling: To reduce raw material costs, some gas companies might be tempted to fill on top of the residual product in a returned cylinder, especially if the cylinder contains an expensive raw material such as helium. This shortcut could also introduce contaminants. How does this happen? High-pressure cylinders are usually returned after they have reached a minimum pressure but are not empty. If the user's operating pressure is higher than the residual cylinder pressure, contaminants from the user's systems can back up into the cylinder, even if positive pressure is on the cylinder. When the cylinder is returned to the gas company and the supplier takes the shortcut of filling on top of the residual gas, the next cylinder user can get the contaminants from the prior user. Think of top filling as the equivalent of using a dirty needle. Gas suppliers should clean cylinders properly before refilling them by performing a systematic purge-and-evacuation procedure to minimize these residual gas-phase contaminants. Another way to reduce this risk of contamination is for the gas company to use valves that prevent back flow.

Zero cylinder pressure: Another source of contamination can result when a cylinder is emptied completely. 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 might not be robust enough to remove liquid-phase contaminants. The only way to remove some liquid contaminants is by subjecting cylinders to a bakeout procedure (if it is not a flammable liquid) or overnight vacuum. Gas companies should remove the valves on zero-pressure cylinders and inspect them for liquid condensation. Laboratory personnel usually avoid charges for this expensive devalving process by returning cylinders with positive pressure (100–150 psig). If they don't, the supplier must follow procedures to ensure contaminants are removed.

Drinking through a Dirty Straw

If chromatographers are sure of the purity

of the gas they selected but are still not obtaining the desired results, they need to investigate whether their own on-site gas delivery systems could be introducing impurities. In other words, they could be

“drinking clean water through a dirty straw.” For example, improper tubing, regulators, or other equipment in the laboratory can also be a source of contaminants.

The following general rules will help ensure that your delivery system is not introducing impurities:

- Use the proper analytical regulators. Generally, big is bad. Regulators should have low dead volumes and stainless steel diaphragms with packless valves and they should be lubricant free. Some regulators labelled “analytical regulator” contain hydrocarbon- or halocarbon-based lubricants, which can affect the analytical performance of flame ionization, electron-capture, MS and other detectors. In addition, regulators for chromatographic applications should be designed specifically for the service intended.
- Minimize leaks in the laboratory gas delivery systems. Remember the Venturi effect. Use stainless steel tubing (be certain that it is the right type for the specific application) and minimize the number of connections. Also, many flexible pigtailed are porous enough that small-molecule gases such as helium and hydrogen can diffuse through the pigtail wall and waste more than 10% of the usable gas product. Make sure pigtailed are suitable for helium and hydrogen service.
- Use proper change-out procedures. Many gas users are concerned with oxygen, moisture and hydrocarbon contamination, yet they introduce air every time they change out a gas cylinder, which defeats the purpose of buying a high-purity gas. Users can minimize this contamination potential during cylinder change by using proper purge-and-evacuation procedures.

Managing the Gas Supply Chain

The final source of problems associated with gases incorporates all the complexities of managing a gas supply chain that, among other things, includes returnable, rented containers. After a product is used, laboratory workers must replace the cylinder with a

full one and then return the empty or nearly empty cylinder to the supplier. In fact, gas is one of the few laboratory supplies that require a two-way supply chain, a situation that introduces additional challenges.

Many procurement systems have difficulty managing cylinder rentals because the actual rental costs fluctuate depending upon end-of-month cylinder balances. If balances go up, so does the monthly rental charge, and vice versa. For example, assume a laboratory pays €5 per month per cylinder rental and has an end-of-month balance of 100 cylinders. The laboratory would be invoiced €500 for rent. If the cylinder balance increases to 120 cylinders at the end of the following month, the laboratory would be billed €600. A user's system that pays on reconciliation to a specific part number can have difficulty managing and interpreting rental items because the amount fluctuates each month. Rental allocation within a laboratory's operation can be complicated. Most laboratories 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 a relatively low expense, many end users do not actively monitor cylinder balances. They simply want the gas to be available when they need it, much like a utility. The result is that they typically overstock; most users keep many months' inventory on site even though their gas suppliers might make deliveries a few times a week.

Rental might be an insignificant cost for each end user but when totalled for an entire complex, 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 the number of months that cylinders stay at a site, users should divide the number of total units purchased per month by the end-of-month balance (an end-of-month balance can be found on any monthly rental statement). For instance, if a user purchases an average of 50 cylinders per month and has an average 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 €2500 per month or €30 000 per year. A reduction in cylinder turn from 10 to 5 months would result in €15 000 in cost savings per year. Again, if the gas supplier is delivering gases a few times a week, even 5 months' inventory could be excessive. Users should calculate cylinder turn — many will be surprised at

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how long cylinders sit idly at their facility and add unnecessary costs.

As discussed earlier, if a gas supplier maintains good cylinder hygiene and minimizes the probability of cylinder contamination, cylinders can be used to pressures as low as 100 psig. In many chemical, petrochemical and refinery applications, however, it's almost an unwritten rule that cylinders are changed 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 justifiable reason would be that the cost of wasted gas is outweighed by the costs associated with running out of gas. If users target 500 psig, they're probably changing at higher pressures, which often happens on Friday afternoons when users connect fresh cylinders to ensure that they have enough gas to last through the weekend.

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

Laboratories can help reduce logistical headaches and hassles by changing to more-efficient gas packaging — such as liquid Dewars that hold the equivalent of more than 12 high-pressure cylinders; micro-bulk systems, which hold as much as 100 times a cylinder's volume of product; or bulk tank systems for even larger needs. In addition, users can assess whether they even need cylinders; instead, they could consider generated gas, an investment that can have a payback in as little as a few months.

Problems can also be eliminated in the administration of ordering and managing invoices. Most users continue to use paper purchase orders; some even continue to

use one purchase order per gas, which leads to even more low-dollar purchase orders and adds to the time and cost of order processing. More efficient ways of working with suppliers include summary billing or on-line ordering to improve ordering time, efficiency and cost. According to Aberdeen Research Inc. (Boston, Massachusetts, USA), electronic procurement can reduce the cost of goods and services by 5–10%, speed fulfillment cycles from 8.4 days to an average of 2.3 days, and cut administrative costs from \$114 to an average of \$31 per requisition.

What It Comes Down to...

People who use gases in laboratories are looking for solutions to the headaches and troubles that they face in buying and using the right gases for their applications. These solutions become even more critical when you consider the costs associated with the problems.

Evaluating gas supply cost is like evaluating an iceberg — the part you cannot easily see could be the part that gets you in trouble. Look carefully at the total cost of the gas supply, above and below the waterline. For every euro spent on gas, cylinder rental and transportation, you typically have €2–3 in hidden costs associated with inefficiencies in gas selection, gas distribution, excess administration, waste and downtime. Working with a supplier to reduce these inefficiencies — headaches and hassles — 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 supplier that is willing to work closely with its customers to understand their processes and recommend the best gas and equipment solutions to meet their needs. Typically, the customers and vendors stick to their zones of responsibility. Getting the gas company involved can help you get the most out of the gas you buy.

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