



Gas Cylinder Safety, Part I — Hazards and Precautions

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Many gas chromatographers are not fully aware of safe practices for handling high-pressure gas cylinders. Operators should be trained to properly transport, install, connect and maintain their gas supplies, as well as to deal with emergencies. In the first of a two-part series, this month's "GC Connections" examines the principal hazards and safety issues surrounding the compressed gas cylinder. The second instalment will present procedures for routine cylinder use.

A nightmare: It's Monday morning and a co-worker has found that one of the helium cylinders in the laboratory had emptied over the weekend. I watch as he reaches over the other gas cylinders, applies the big tank wrench and accompanied by a loud hissing sound, detaches the regulator fitting from the tank. Letting the regulator hang by its plastic connecting tubing, he moves the hydrogen and air cylinders into the corridor between the laboratory benches, tilts the empty cylinder on its bottom edge and rolls it into position near the door. He leaves the laboratory and returns in a moment pushing a furniture dolly in front of him. With a grunt, he tilts the cylinder sideways onto the dolly and pushes it down the hallway. Ten minutes later, he returns with a new cylinder on the dolly, which rolls away and bangs against the laboratory bench as he lifts the tank up to a vertical position. He removes the cylinder cap, holds it in one hand and uses his other hand to examine the cap that had come a couple of weeks ago with the empty tank. He puts both caps down with a shrug and grasps the neck of the new tank's exposed valve. With a grimace he ducks down slightly, cracks open the valve, and is rewarded with a 110 dB roar as the escaping gas expresses its new freedom. Satisfied with the demonstration, he rolls the tank into position and reattaches the regulator. Then he begins to return the other tanks to their original positions.

Someone near the door calls his name loudly and as he spins around to see who it is, his belt buckle catches one of the dangling gas lines. In dreamlike slow motion, the hydrogen tank begins to head for a horizontal position as its valve and regulator glance off the bench top on the way down. A bright orange-yellow light fills my eyes ... and I wake up with the morning sun streaming onto my face.

Certainly, no one would take all of the wrong actions that my dreamworld co-worker did, but how many of us have done just one of them? I've witnessed them all, and I'm guilty of a few myself from time to time, especially in exceptional situations such as setting up a demonstration in a conference room. I sincerely hope that everyone working in a laboratory treats flammable solvents and toxic chemicals with well-deserved respect and understands the short- and long-term risks involved with handling hazardous materials. So what leads some of us to fall short of giving compressed gas cylinders the respect they deserve? In terms of stored potential kinetic energy, they are bombs waiting to explode; in terms of suffocation potential or flammability, they can be as great a fire hazard and potentially as toxic as many solvents and solids.

Let's take a look at the hazards gas cylinders present and some procedures and practices that can maximize safety for those who work with them.

Cylinder Hazards

Gas cylinders present several obvious and some less-familiar hazards, including sudden decompression that can propel a cylinder remarkably quickly across a laboratory and displace breathing air; risk of explosion or reaction; possible acute toxicity; heavy-object hazards; and personal injury from high-pressure gas streams or cryogenic liquids. The Occupational Safety and Health Administration (OSHA) regulations *29 CFR Parts 1910.101–1910.105* provide specific guidelines for the use of compressed gases in the workplace. Gas chromatographers do not normally use some of the common hazardous gases such as acetylene, oxygen, nitrous oxide and propane in pure form, but they may encounter them in other laboratories and should be aware of the extra dangers that chemically reactive, fuel, or oxidizer gases pose. Table 1 lists hazard classes for commonly used gas chromatography (GC) gases.

Several commonly accepted first aid procedures address exposure to these hazards. However, I am no expert in this area. I strongly recommend that all personnel who use compressed gases be trained in basic first aid and that a few receive additional cardiopulmonary resuscitation (CPR) and other advanced training.

Rocket ship: The first thought that comes to my mind when discussing gas cylinders is their rocket potential. A 1-A cylinder of

helium contains 8.3 m³ (293 ft³) of room-pressure gas that's compressed into a space of less than 0.5 m³ (2.0 ft³) at a pressure of 18.1 MPa (2640 psi). The European L-size cylinders contain slightly more compressed gas. These cylinders weigh approximately 91 kg (200 lb) when empty and the weight of the helium within a fully pressurized cylinder is approximately 1.4 kg (3 lb). When the gas pressure is released rapidly through an opening the size of the valve stem, the cylinder — if it shoots in a straight line — can reach velocities of close to 30 m/s, 108 km/h or 66 mph. A 91 kg metal cylinder hurtling at high velocity can do tremendous damage almost instantaneously and a person can do nothing to stop it after a decompression incident starts. See the sidebar "How Fast Will a Cylinder Fly?" for the calculations that produced this velocity figure.

The thought of a heavy cylinder careening through the laboratory walls gets the attention of most chromatographers. This type of accident, however, is easy to avoid by always restraining cylinders with appropriate chains or brackets, transporting them in cylinder carts and keeping them capped at all times unless they are actually in use with a regulator or manifold attached. Any cylinder found to be damaged or that has a stuck valve should be returned immediately to its supplier. If the damage is to the cylinder body, the supplier should be notified and asked to remove it. Never try to vent a damaged cylinder.

Atmospheric displacement: Another problem can occur when the contents of any large gas cylinder — other than an air cylinder — vent rapidly, even if the cylinder is restrained. The sudden release of more than 8 m³ of unbreathable gas in the laboratory will reduce the level of oxygen in the air dramatically and present a real suffocation hazard. Liquefied gases expand as much as 1000-fold in volume when vaporized and can present a much greater hazard. Large liquid nitrogen Dewars contain enough nitrogen gas to make a room incapable of sustaining life if the gas is released rapidly. Carbon dioxide can cause immediate unconsciousness followed by death when breathed in any significant concentration. It is much denser than air and will settle in low, unventilated areas. Liquid carbon dioxide tanks, such as the ones used for GC cooling, can release especially large quantities of gas during a tank rupture.

If an event such as this happens, leave the area immediately, prevent others from entering the area and seek the assistance of personnel trained in the use of a self-contained breathing apparatus. Make sure the area has been well ventilated before returning. Don't try to reenter a hazardous area without the proper breathing equipment to assist someone else. Many unnecessary tragedies have occurred because of misguided rescue attempts.

Explosion and fire hazards: If a hydrogen cylinder vents into a laboratory in an uncontrolled manner, even if the leak is through the pressure-release disk on the

cylinder or regulator, leave the area immediately, close the doors, pull the fire alarm to evacuate the building, and call emergency services. Don't try to extinguish flame detectors or shut down anything in the laboratory — just get out quickly. Hydrogen has a flammable concentration in air of 4% so a venting cylinder can easily create an explosive concentration in moments. In its favour, hydrogen rapidly diffuses in air so the flows typically encountered with flame detectors or carrier gases present no significant hazard under normal conditions.

The same evacuation procedure is required with other flammable gases such as propane and acetylene or reactive gases and oxidizers such as oxygen and nitrous oxide. Breathing air contains approximately 20% oxygen, but high oxidizer concentrations will accelerate combustion dangerously and can cause serious burn injuries. Remember that clothing, paper, paint and plastic can all burn rapidly in the presence of high oxidizer concentrations.

If a gas fire starts and the gas leak cannot be stopped safely and positively, don't try to extinguish the flame. Unburned gas can accumulate and explode if an ignition source is present. Hydrogen particularly presents a special hazard because it burns in excess air with an invisible flame. Never try to investigate a possible hydrogen fire by approaching the suspected flame area; leave it to the professionals. Although the combustion by-products of hydrogen are non-toxic, the fire can burn other nearby items such as

Table 1: Hazard classes for commonly used GC gases and other gases found in the laboratory.

	Decompression	Flammability	Asphyxiation	Toxicity	Cryohazard
Acetylene	✓	✓	✓		
Air	✓				
Argon	✓		✓		✓*
Carbon dioxide	✓		✓	✓	✓*
Chemical reagents (reactive compressed gases)	✓	✓	✓	✓	
Helium	✓		✓		✓*
Hydrogen	✓	✓	✓		✓*
Nitrogen	✓		✓		✓*
Oxygen	✓	✓†			✓*
Propane	✓	✓	✓		

* Liquefied gas

† Accelerates combustion

plastics, which can produce toxic combustion by-products.

High-pressure gas cylinders can rupture explosively when heated in a fire. All cylinders include a thermal fuse that is supposed to melt and release the cylinder contents in a semicontrolled manner before the internal pressure reaches a safe upper limit. However, if the cylinder has been mechanically stressed by a fall or the impact of another cylinder, it can burst before the pressure relief valve can act. A chain-reaction effect sometimes occurs in large fires in areas where many cylinders are stored.

Toxicity: GC gases aren't generally toxic. That is, after a victim has been removed from an accident area and has received first aid, the immediate effects of gas exposure

such as dizziness and difficulty breathing will diminish rapidly. Sample or reaction gases, alternatively, can present a real toxic health hazard and a significant disposal problem. If even a small leak of a toxic gas is detected, leave the area and call trained personnel to move the leaking cylinder to a safe place. Each type of gas has an associated material safety data sheet, which must be sent in advance to the purchaser, who must then keep the information on file for access by any employee. Material safety data sheets contain extensive information about the use, storage and disposal of chemicals, including compressed gases; their toxicity; and any other relevant information. Refer to the appropriate material safety data sheet when you have any questions about a particular material.

Many years ago, I saw lecture bottles of methyl bromide, cyanogens, hydrogen fluoride, carbon monoxide and various highly reactive silanes — not all in the same laboratory — carelessly stored on shelves above floor level with unprotected valves. No analytical or chemical laboratory can justify operation under such hazardous conditions. Improperly stored or deployed toxic gas cylinders have no place in anyone's workplace. If any are found, it's good procedure to evacuate the area and call a hazardous materials team to remove the danger. In any case, never try to move or dispose of hazardous or unknown chemicals in gaseous, liquid or solid form by yourself — it's not worth the risk.

Heavy lifting: No one should attempt to lift a cylinder that weighs more than approximately 12 kg (26 lb). Heavy cylinders belong on the floor and they should be restrained to a bench or a wall. Always use a cylinder cart to move cylinders, even from one part of a laboratory to another. The practice of rolling a cylinder on its bottom edge, although prevalent, risks injuries to feet and toes — and risks a cylinder becoming unbalanced and falling. Never place a cylinder on its side and roll it; the sidewalls are the thinnest parts of a cylinder and aren't designed to support any weight. You might create a dangerously weak cylinder that could explode the next time it's filled with gas.

Liquid carbon dioxide cylinders, which are used for cryogenically cooling GC components, weigh much more when full because of liquid carbon dioxide's density, and they can be deceptively heavy. Always pay special attention to these cylinders. In all instances, it's good practice to wear protective eyewear, shoes, gloves and clothing when manipulating large gas cylinders.

Cryocooling: Cryogenic liquefied gases such as liquid nitrogen or carbon dioxide present additional hazards in the laboratory. Carbon dioxide, a liquid when stored under pressure at room temperature, cools to subzero temperatures when decompressed because of both expansive and evaporative cooling. Liquid nitrogen is stored under low positive pressure in a special Dewar tank at $-195\text{ }^{\circ}\text{C}$. Both liquefied gases can cause immediate frost burns on exposed skin. Liquid nitrogen also presents a cryogenic freezing hazard that embrittles almost any object it contacts in bulk, including fingers. Connecting tubing that conducts cryogenic liquids also presents a freezing hazard — the tubing should always be insulated or shielded to prevent accidental contact. Again, appropriate protective wear such as thermal gloves,

How fast will a cylinder fly?

Let's assume that helium is allowed to vent unobstructed through a 1.1 cm (0.5 in.) orifice, such as the cylinder valve stem, during a 10 s interval. That's just my guess at a time frame that seems reasonable. The thrust or force exerted on the cylinder at any moment will be the sum of two terms: the mass flow of the helium times its exit velocity through the orifice and the pressure differential across the orifice times its area, as delineated in Equation 1:

$$F = qV_e + A_e(p_e - p_a) \quad [1]$$

where q is the rate of helium mass flow, V_e is the exit velocity through the orifice, A_e is the orifice cross-sectional area, and p_e and p_a are the cylinder and ambient pressures, respectively.

The helium must expand through the orifice, which has an area of 0.000095 m^2 , into an 8.3 m^3 volume in 10 s, which produces an average exit velocity during the release of 87 m/s. That's approximately 314 km/h, 200 mph or 25% of the speed of sound, and these numbers accentuate the hazards of rapid decompression. The exit velocity will be higher at first and then slow as the tank pressure decreases. This reaction mass of the helium will impart an average force of approximately 12 kg m/s^2 . Acting for 10 s against the mass of the cylinder — we'll ignore the loss of the helium's mass — this average force will impart a velocity change of approximately 4.8 km/h or 3 mph. That number is not very impressive, but it seems right for a relatively small mass of helium acting against a heavy cylinder.

The rocket effect primarily comes from the second term of Equation 1, which involves the high-pressure drop from the cylinder to the atmosphere. At the first instant of decompression from a full cylinder at 18.1 MPa, a force of 1710 kg m/s^2 will be exerted by the pressurized gas across the orifice. This force is so much larger than the first term that we can ignore the helium reaction mass effect, as Equation 2 shows below. As the remaining gas pressure drops, the force will also decrease and reach zero after 10 s, for all practical purposes. Recalling that $F = ma$ (force equals mass times acceleration) and then integrating the decreasing acceleration across time, Equation 2 describes the situation for an exponential decay in pressure:

$$v = \frac{A_e(p_e - p_a)}{m} \times \int_0^{\infty} e^{-kt} dt = \frac{A_e(p_e - p_a)}{mk} \quad [2]$$

where v is the cylinder velocity after the gas has escaped, k is the pressure decay constant, and t is the time interval. A pressure decay rate of 50%/s, where k is $1 - 1/e$ or 0.632, reduces the pressure to less than 0.2% after 10 s. With a 91 kg cylinder mass, the terminal velocity is approximately 30 m/s, 108 km/h or 66 mph. Even if the pressure drop decreased more rapidly and approached zero after 5 s, the velocity would still be as high as 19 m/s, 68 km/h or 42 mph.

eyewear and skin-covering clothing helps prevent accidents.

High pressure: The co-worker in my nightmare liked to crack open the high-pressure valve without a regulator attached. I suppose his idea was to blow out any dust particles and to see if the tank was pressurized, but this behaviour is never a good idea. The force exerted by gas decompressing from high pressures is tremendous. If he happened to have part of his hand or arm in front of the cylinder fitting, he could have suffered a serious abrasion, deep cut or worse. A much better way to clear the dust is to spray the area with clean, dry compressed air from a good air source or a small can. Never spray a halocarbon-based material onto the cylinder fitting — the gas can get into the lines and cause problems with electron-capture and mass spectrometry detectors.

Conclusion

I've addressed many of the hazards associated with compressed and liquefied gases in this month's "GC Connections." The four most important considerations when dealing with compressed gas cylinders are proper physical restraint, personal protection, knowledge of potential hazards and appropriate emergency procedures. After a cylinder is in place in a laboratory, the next step is to hook it up and put it in service. In the next article, I'll present some good procedures to follow when installing, using and replacing gas cylinders and pressure regulators.

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