

Carbon Dioxide (CO₂) Safety Program

Chemical and Physical Properties; Major Uses; Ethanol Manufacturing Production of CO₂; Physical and Health Hazards; and Guidelines for Maintaining Safe Working Conditions, Including Safety Awareness, Safe Handling, and Hazard Minimization



June, 2015

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Prologue

Carbon dioxide (CO₂) is a “sleeper hazard;” very little information outside scientific literature has been published to help facilities understand CO₂ health effects and control CO₂ exposures. This Carbon Dioxide Safety Program is designed to fill this gap.

We now know that CO₂ is a toxic gas – not a simple asphyxiant. In fact, data from the National Institute of Occupational Safety and Health (NIOSH) and other studies show that *even in the presence of normal concentrations of oxygen, death will occur at exposures of 7% CO₂ in only 5 minutes.* Several studies have demonstrated that breathing concentrations of 30% CO₂, even with 70% oxygen, leads to *unconsciousness in 30 seconds.* And since CO₂ is odorless, tasteless, and colorless, there is no indication that it is even there.

Breathing concentrations of 30% CO₂, even with 70% oxygen, leads to unconsciousness in 30 seconds

Use this Carbon Dioxide Safety Program to help your facility develop a CO₂ Management Program (a site CO₂ Identification and Control Program), the first step in controlling and preventing hazardous levels of carbon dioxide accumulation. Identify operational areas where CO₂ can collect, and then develop procedures and methods to ensure that CO₂ is dispersed to safe levels.

Your facility may have been doing what it has been doing for years, not knowing that circumstances can change just a little bit and lead to a terrible injury or fatality.

– Eric Fasnacht, Plant Manager, Archer Daniels Midland Co., Cedar Rapids, IA.

Learn how and when to use all three types of electronic monitors – review your exposures and then decide how best to use this technology. At the least, consider hand held multi-gas (5-gas) portable monitors with a CO₂ sensor for confined spaces, personal clip-on monitors for personal plant work, and mounted ones for fixed areas where CO₂ levels can be monitored remotely and measured continuously – and in some cases, interlocked with ventilation equipment.

Learn and remember the adverse health effects of CO₂ and the signs and symptoms of even low-level exposure;

Recognize that current practices may not be acceptable and use this manual to improve your program.

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CHAPTER 1: Best Practices for Recognizing, Preventing and Controlling Unsafe Levels of Carbon Dioxide

What Kinds of Situations Result in Exposures to Carbon Dioxide That Are Making People Sick or Killing Them?

EXAMPLE ACCIDENTS:

In October 2012, a beer manufacturer in Houston received multiple citations from OSHA for failing to protect workers from exposure to CO₂ and other workplace hazards while working in brewery cellars. This company was issued a proposed penalty of \$88,000 and was required to implement many engineering, equipment, training and program changes to reduce the probability of a recurrence, along with paying the hefty fine.

Just a few months later, in January 2013, two men were found unconscious as they did maintenance in an ethanol production facility. One died and one has residual neurological damage from the CO₂ overexposures. Details about this accident are given later in the section on Specific Cases of Accidental Injuries and Fatalities Involving Exposures to Carbon Dioxide in Ethanol and Beer Production.

Unsuspected Exposures to Hazardous Levels of Carbon Dioxide

What is the common thread in these two accidents? It is the failure to recognize how and where carbon dioxide gas can accumulate, to understand how dangerous it is to breathe, and to take action to protect workers.

Even up to relatively recent times, it had been commonly thought that carbon dioxide is a relatively non-toxic gas and it had been classed as a simple asphyxiant. This is because carbon dioxide is part of every breath we exhale. However, at the concentrations of carbon dioxide in our exhaled air, it is lethal in just a few minutes if inhaled. CO₂ is a toxic waste product that our body must eliminate. As we breathe out, it is diluted in the atmosphere negating its toxic effects.

Little safety information has been available to assist manufacturers in recognizing, controlling and preventing unsafe levels of carbon dioxide. Because of the lack of understanding of its hazardous effects, CO₂ is an unsuspected dangerous gas at elevated levels.

In 2012 however, it was conclusively demonstrated that concentrations as low as 1,000 ppm can impair thinking, concentration, and logical thought processes.¹

Fortunately, during the past decade, great strides have been made in developing accurate, rugged, and dependable carbon dioxide sensors at a reasonable cost. These

sensors can now be part of a multi-gas monitor, such as those used for confined space entry, or be a single gas monitor that is hand-held or worn by the worker. The industry is poised to embrace this technology and train workers to use them as a routine part of production work.

This *Carbon Dioxide Safety Program* provides an overview of the chemical and physical properties of carbon dioxide, explains where it comes from and how it is produced in the ethanol industry; its many uses; accidents that have resulted from CO₂ overexposures; the health and physical hazards associated with carbon dioxide in all its forms; the U.S. established worker exposure limits; and specific safety awareness, safe handling procedures, and methods for hazard minimization.

Recommended practices for maintaining a safe work environment are also presented. Specific attention is given to principles for implementing renewed facility-wide safety procedures, ventilation methods, instruments that can be used to detect carbon dioxide, and special precautions to use when conducting confined space entry work. In addition, how carbon dioxide is used, the ways exposure incidents have occurred in the past, specific health hazard exposure symptoms, and detailed procedures and methods for eliminating these exposures – or at least controlling them to an acceptable degree – are all presented.

¹ Satish U., Mendell M. J., et al 2012. "Is CO₂ an Indoor Pollutant? Direct Effects of Low-to-Moderate CO₂ Concentrations on Human Decision-Making Performance." (<http://ehp.niehs.nih.gov/wp-content/uploads/2012/09/ehp.1104789.pdf>). *Environmental Health Perspectives* 120 (12).

Best Practices: Develop a CO₂ Management Program

Many specific procedures, specialized equipment, and engineering controls are presented below to help keep workers and property safe from adverse carbon dioxide exposures. The following sections of best practices have been developed for manufacturing industries that may possibly produce unsafe levels of carbon dioxide in their facilities. It is up to each manufacturer to determine whether all of these activities, or a combination of select activities from this list, are suitable for effectively managing carbon dioxide levels in a specific facility.

KNOW YOUR PROCESS! RECOGNIZE THE HAZARDS!

Recognize Where Carbon Dioxide Can Accumulate – Especially During Different Processes, Seasons and Weather Conditions

Whether the facility uses wet or dry corn milling, or cellulosic materials in its ethanol production process, large amounts of carbon dioxide are generated and can accumulate in many areas. It is a common myth that unsafe levels of carbon dioxide are only present in Confined Space areas, when in fact, depending upon weather and other conditions, carbon dioxide can be found in nearly all areas.

Many areas exist where under the right conditions, CO₂ can reach very high levels in a brief amount of time. Hazard assessments are critical for evaluating where CO₂ can collect. It has happened at other facilities – look where you can have a catastrophic level of CO₂ under the right conditions.

Areas identified below are examples of places that could all fall prey to CO₂ accumulation:

- ▶ Ground floor locations and other low-lying areas, including those outdoors and around the water treatment containment areas (including anaerobic and aerobic tanks),
- ▶ In grain receiving areas due to new crop respiration and limited ventilation, including under the corn receiving tunnels,
- ▶ Locations where carbon dioxide is given off from processes, including inside the buildings that house the fermentation tanks, the fermentation tanks themselves, yeast propagation, grain receiving and unloading areas, hoppers, slurry/mash “steep” tanks, and drains that collect liquid materials and pump it out,

- ▶ Areas where carbon dioxide is collected and discharged, especially the carbon dioxide scrubber, and baghouse,
- ▶ Locations with restricted or limited ventilation whatever the elevation, especially those areas where people rarely need to go, and
- ▶ Confined areas and confined spaces, including diked areas around any kind of tank.

Although carbon dioxide is heavier than air, **warm or heated CO₂ rises and floats away**. It can then travel to remote locations as it cools, collecting in unsuspected areas, depending upon air temperature, wind direction and speed.

Develop a Carbon Dioxide Facility Review Process

- ▶ Conduct a comprehensive walk-through survey of the entire facility looking for areas where carbon dioxide can collect, including areas of limited air exchange; low-lying areas; places where stover, organic waste, and wastewater are stored and can collect; and process areas known to have elevated CO₂ levels. Survey must include indoor as well as outdoor areas.
 - » These surveys should be conducted with a hand-held CO₂ monitor to allow for greater flexibility identifying CO₂ levels across the facility.
 - » Be sure to survey on a day when the air is still (very little wind, <5mph) in order to detect pockets where CO₂ can collect. Wind plays an important part in dissipating CO₂.
 - » Include all areas of the manufacturing site, not just areas expected to have carbon dioxide present such as fermentation areas.
 - » Be sure to survey the facility under both normal and abnormal process conditions to establish normal vs. abnormal CO₂ levels.
 - » Conduct multiple surveys throughout the year and repeat walk-throughs during various weather conditions in order to understand any effects that changes in ambient temperatures may have on CO₂ levels. This will give the most comprehensive results. The differences can be surprising.
- ▶ Carbon dioxide pressure relief devices (PRD's), or pressure release valves (PRV's) often allow carbon dioxide to be vented directly out of its respective process vessel. The CO₂ released is one of the significant sources of fugitive CO₂ emission within any production facility. If at all possible, these PRD's/PRV's should be directed to a safe release point such as a scrubber, collection system, or elevated exhaust stack so that CO₂ dispersion does not present a safety hazard. Do not allow CO₂ PRD's/PRV's to discharge into work areas, especially indoors.

- ▶ If possible, install the exhaust stack of the CO₂ scrubber at well above the highest structure, and prior to its installation, consider how CO₂ disperses from that area (Compressed Gas Assc., gas dispersion pamphlet), including determining the prevailing wind directions, terrain, relative elevations, and other factors that will impact dispersion.
- ▶ PRD's/PRV's can sometimes stick open or be open for other reasons, then the areas around this device can accumulate IDLH CO₂ concentrations in a short amount of time. Carefully consider dispersion of CO₂ from these sources.
- ▶ Remember, although carbon dioxide is heavier than air, **warm or heated CO₂ rises and floats away**. It can then travel to remote locations as it cools, collecting in unsuspected areas, depending upon air temperature, wind direction and speed.
- ▶ Off-gassing from fermenters can cause localized areas of high CO₂ concentrations that can be unsuspected. Open manways and venting PRD's/PRV's can result in transient but catastrophically high CO₂ levels. Take CAUTION to identify all areas where equipment or specific jobs can result in these high CO₂ concentrations. Take the appropriate precautions to warn about and minimize exposures. If possible, vent these release lines to the scrubber if permitting allows. If not, make sure that adequate warnings are posted and that workers wear personal CO₂ monitors. Consider setting up remote sensors with automatically activated forced draft ventilation to reduce these potentially hazardous areas to a minimum.
- ▶ Whenever possible, install piping, plumbing connections, and vents that contain CO₂ above grade and in very well-ventilated areas. Further, consider plumbing connections directly into the carbon dioxide scrubber or collection system.
- ▶ Include risks of unsafe levels of carbon dioxide as possible hazards in Job Hazard Analysis (JHA) programs.
- ▶ Identify carbon dioxide monitoring equipment that complements your plant site's safety program. There is a wide variety of monitoring equipment available today at reasonable costs. If multiple gas monitors are selected for your safety program, include carbon dioxide as one of the gases.
- ▶ Initiate a routine procedure for instituting process and systems modifications and changes, including any time a piece of equipment is changed. For the risk evaluation, conduct the review during the design consideration stage, and consider materials of construction, ease of maintenance, and hazards presented by new systems in carbon dioxide service.
- ▶ Institute a documented routine inspection and testing program for all equipment, including process vessels, piping, valves, pressure relief design, hoses, ventilation systems, and detection instruments.



Prevent Unsafe CO₂ Levels

- ▶ Determine the lowest acceptable level of CO₂ that your facility can operate under to effectively protect workers' thinking and cognitive abilities. Trial and error may work to establish this point, which may be different in different parts of the facility. Keep in mind that the eight hour time weighted average workplace exposure level established by OSHA in 1970 was 5,000 ppm, so under no circumstances should this level be higher than this.
- ▶ Ensure mechanical ventilation of work areas, especially those areas in corners or the sides of buildings and vessels where carbon dioxide can collect. The ventilation does not need to run continuously; however, it needs to be able to be activated remotely, before workers enter those areas, or be automatically activated when a carbon dioxide remote monitor reads levels that exceed your facility's critical set point.
- ▶ Having many remote sensors is not enough. Give careful consideration to the placement of these sensors. It is all too common for remote monitors to be placed in the middle of buildings, to get broad representative readings of the general work area. However, this sometimes backfires and results in sensors located along walkways and open areas that have good ventilation. This gives everyone a false sense of security. Instead, the sensors should be located, or relocated, to dead areas and remote corners of buildings and areas where little ventilation is present. This will give a much better indication of actual CO₂ accumulation and where dead spaces are that can jeopardize worker safety. Consider locating one CO₂ monitor at the supplied air fan point of entry (discharge) to the work area to ensure to know if CO₂ is being blown into work area.
- ▶ Install remote sensors and implement a preventive maintenance program for proper operation of these CO₂ continuously monitoring sensors. This stationary monitoring equipment needs to have local audible and visual alarms. Consider tying the signals into control rooms to notify operators. Also consider installing interlocks from the electronic monitors so that ventilation equipment will automatically start up when critical set points are exceeded, which should not be more than 5,000 ppm CO₂. See bullet item above.



Evaluate and Upgrade Confined Space Entry Procedures

Before the federal OSHA General Industry Confined Space Entry Standard, 49 CFR 1910.146 was promulgated in January, 1986, more people died doing confined space entry work than anything else, except for over-the-road vehicle accidents. Now, decades later, although not the biggest single killer, it is still the *#1 cause of multiple fatalities in the workplace*.

To emphasize how inherently hazardous confined space entry is, the following facts have been compiled from the statistics of the 10-year, nation-wide study – commissioned by the National Chemical Safety and Hazard Investigation Board – of incidents involving the most common gas on earth: nitrogen². This study was also conducted by Mary C. DeVany (president of DeVany Industrial Consultants, Vancouver, WA), author of this RFA CO₂ Safety Program. Unfortunately these facts apply to confined spaces with carbon dioxide, too.

- ▶ In 80% of confined space fatalities, that exact confined space had been entered before without any problems *by the same person who died*.
- ▶ Of fatal confined space accidents, only 7% had signs on them indicating that they were confined spaces.
- ▶ In 40% of fatal atmosphere accidents, the hazard was not present at the time of initial entry.
- ▶ 89% of confined space fatalities were jobs authorized by supervisors.
- ▶ 35% of the fatalities were the supervisors.*

The fuel ethanol industry has many, many various types of confined spaces in every production facility. This industry has recognized since its inception that having a strong confined space entry program, including a comprehensive written program; an entry permit process, an enforced lock-out/tag-out program; specialized monitoring, ventilation, fall arrest and retrieval equipment; and thorough employee training for entry workers, attendants, and supervisors are all crucial to maintaining a safe work environment.

In this industry, carbon dioxide accumulation is one of the biggest atmospheric hazards, especially in confined spaces. Ensure that your facility has a comprehensive confined space program, including written compliance program, the mandatory confined space inventory with hazards of each space listed, and a complete entry permit. Ensure you have up-to-date, comprehensive confined space training for your confined space entry workers, attendants and entry supervisors. Remember: OSHA minimum compliance mandates annual refresher training for all confined space entry workers as well as audits and necessary updates to your program. Lastly, ensure that any contractors working on your site that are working in confined spaces or in support of confined space entry operations, comply with local and federal rules as well.

² From the statistics of the 10-year study of nitrogen asphyxiation accidents commissioned by the National Chemical Safety and Hazard Investigation Board, Mary C. DeVany, DeVany Industrial Consultants, Vancouver, WA.

Take a Fresh Look at Standard Operating Procedures and JHA's (Job Hazard Analyses)

- ▶ Evaluate standard operating procedures that allow employees to be routinely exposed to carbon dioxide and design new ways to eliminate or at least reduce these exposures. Resist complacency in workers and supervisors that push against change. Also, resist being proud of what has already been done and be open to additional suggestions for ways to improve protections. For example, the worker who has to open the top hatch (manway) to pour yeast into a propagator can be exposed to high levels of CO₂ whenever doing this job. Consider installing an eductor system to eliminate this need for exposure. Also consider that workers risk other injuries carrying the yeast up many flights of stairs.
- ▶ Critically evaluate procedures for preparing process vessels for entry. For example, drain, wash, and drain again then repeat, steam then cool twice with air escaping out the bottom and make-up air coming in from the top; open the top and blow in air via forced draft ventilation and with the bottom open to release air out the bottom; during the course of the work open the top to provide make-up air and put an exhaust fan in the bottom pulling air out. Run ductwork from the fan's exhaust side away, to discharge the "air" to a safer area for dispersal. Caustic cleaning with spray nozzles is another effective method to remove CO₂ from the air space prior to opening vessels containing CO₂. See the chapter below entitled, "Ventilation Principles; with Illustrations Demonstrating Specific Techniques" for examples of safe confined space entry ventilation methods.
- ▶ Establish a procedure with equipment to ensure continuous voice, visual or signal monitoring of employees working in or inspecting areas where the possibility, however remote, of CO₂ collecting can occur.
- ▶ Identify work areas and job tasks that may not be routine, that could present great exposures, or that present a higher risk of hazard to workers. Develop special procedures and oversight to ensure that in these unusual or hazardous situations, workers are required to take the additional precautions necessary to ensure their safety.
- ▶ Evaluate and ensure that increased levels of illumination are available in all process areas where operating personnel, mechanics and millwrights will need to conduct work.

Provide Education, Information and Resources

- ▶ Conducting mandatory, comprehensive, and specific training on CO₂ safe handling and hazard minimization for all employees that work anywhere outside the office. For those workers that are inside offices only, hazard awareness training should be conducted.
- ▶ Ensure that carbon dioxide is included in the Chemical Hazard Communication Program and included labeling, worker training, exposure evaluation, and an (M)SDS for CO₂ (see the appendix for a CO₂ (Material) Safety Data Sheet).
- ▶ Provide training in proper use and limitations, and make readily available, appropriate employee personal protective equipment, including breathing-quality, supplied-air respiratory protection.
- ▶ Install CO₂ warning signs or barricade off areas where CO₂ is present or can collect. Train employees on the warning techniques and how to avoid these areas of elevated CO₂. Label all piping systems and process vessels that could contain CO₂ elevated levels.
- ▶ Educate employees on all aspects of the carbon dioxide detection systems, whether that be fixed CO₂ monitors, hand held devices, or personal CO₂ detector that can be worn. Identify the various types of alarms when going out into unmonitored and non-ventilated production areas. Some of these work areas and tasks include: working on the tops of fermenters; in or around the CO₂ scrubber or the baghouse; whenever a system is opened – valves, slurry/mash, steep tanks, propagators, wastewater treatment, containment areas around fermenters inside and outside; any space where CO₂ or water can collect and organic material can decompose in the water (pools of “beer”); sump pump pits; drain lines in floors – trenches; any kind of tank; grain storage areas; unloading areas; and hoppers. These are examples of areas where monitors should be worn as a minimum. Also, wear monitors when evaluating individual processes for unique situations where exposures could occur, such as when conducting confined space entry or work around fermentation or yeast propagation vessels.
- ▶ Evaluate the facility for situations where exposures could occur, including low-lying areas and during sub-freezing weather. Pay special attention to low wind situations which can cause accumulation of CO₂ in outside areas from CO₂ stacks. Train workers on these potential hazards and mitigate hazards as needed to manage process safety risks. Some examples include placing warning signs here, having workers wear a direct-reading CO₂ monitor with an audible alarm, and immediately leaving the area if the alarm should activate.
- ▶ Protect, warn and train outside contractors, vendors, and visitors regarding the hazards of possible CO₂ exposure and necessary precautionary measures. This is mandatory if contractors are doing confined space entry.
- ▶ As a minimum, the OSHA safety and health standards must be followed to prevent worker injuries, illnesses, and fatalities. *It is the employer's responsibility to know the relevant standards, then abide by them.*

Federal OSHA requires that employers institute control measures to protect workers from hazardous materials using a three-tiered approach, in this order:

1

First, employers must implement engineering controls. Many examples are listed above, including special procedures for construction, process design changes, and process location; use of **CO₂** electronic monitors; diverted venting of **CO₂** from process vessels pressure relief devices; eliminating job tasks that cause exposures; and mechanical ventilation to keep employees from being exposed.

2

Second, employers must institute and enforce administrative controls to protect workers. Examples of such controls include rotating workers so that the exposures to any single individual is reduced, routine inspection programs, and preventive maintenance schedules.

3

Third, personal protective equipment designed to limit employee exposures are to be made available at no cost to employees.

Although it is beyond the scope of this document to develop specific safety and health procedures and other policies that apply broadly to the safety and health of workers and the protection of property and assets, **because of their critical importance and relevance to the control of carbon dioxide exposures, some of the recommended safe practices listed above will be explained in more depth below.** Please see this section below for information on specific safe practices, equipment and procedures.

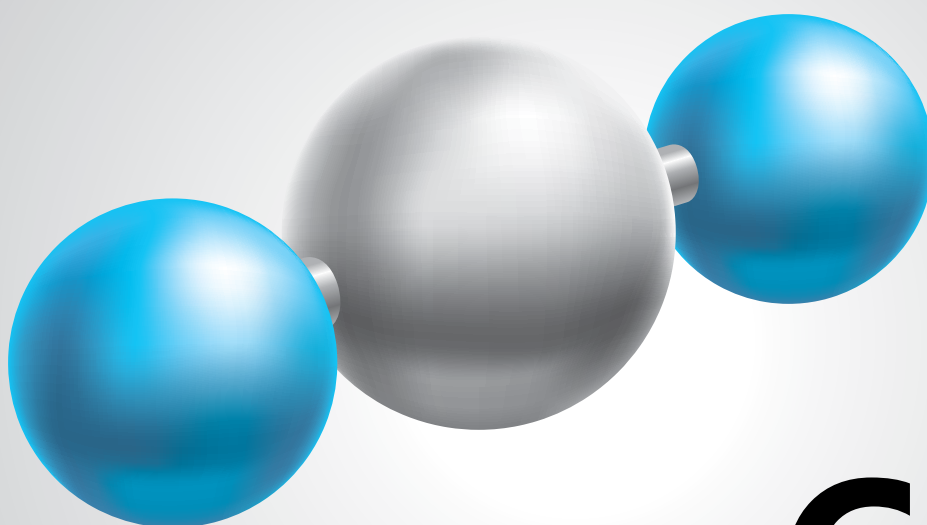
Managers must keep in mind their paramount responsibilities for the protection of the safety and health of people, and the control of property damage and assets at their facilities.

2

CHAPTER 2: What Is Carbon Dioxide? An Overview of Its Properties

The molecule carbon dioxide has the chemical formula CO_2 and is made of one atom of carbon covalently bonded to two atoms of oxygen. At the normal range of temperatures on earth (from -60°F to 140°F), carbon dioxide is a gas. It is colorless and odorless, and because of these characteristics, it is considered to have no “warning properties.” That is, an individual being exposed is unable to detect it without doing chemical testing; in other words, humans have no way to detect its presence.

Other names for carbon dioxide are carbon (IV) oxide, carbonic anhydride, carbon oxide, dry ice (solid phase), carbonic acid, and carbonic acid gas.



CO_2
Carbon dioxide

Carbon dioxide is non-flammable and will not burn, and it is not considered to be an oxidizer in a fire. Carbon dioxide is a common and abundant gas on earth. As of 2015, carbon dioxide had a concentration of approximately 0.04%, or 400 ppm (part per million) in the atmosphere. It is relatively stable and non-reactive in the air.

Its concentration is far below the three most common gases in the atmosphere, which are nitrogen (78%), oxygen (20.9%) and Argon (0.8%). It is heavier than air, with a density of ~1.53 times the air mixture of nitrogen, oxygen and argon. Because of this, it tends to collect in low lying areas and can remain there for long periods of time if there is little ventilation.

The solid form of carbon dioxide is also commonly known as “dry ice.” Solid carbon dioxide typically does not melt into liquid CO₂

before it evaporates into a gas. At normal room temperature, it goes from the solid form directly into a gas – this process of going directly from a solid to a gas is called sublimation. In fact, when CO₂ is at or above -109°F (-78°C), it will sublime. Above 87.9°F (31°C) (its critical temperature), carbon dioxide cannot exist as a liquid, regardless of the pressure.

CO₂ can only be solid when temperatures are below -104°F (-76°C). Carbon dioxide is most commonly found in solution, when carbon dioxide is dissolved in water. “Carbon dioxide is only water-soluble when pressure is maintained. After pressure drops, the CO₂ gas will try to escape to air. This event is characterized by the CO₂ bubbles forming in water.”³ It is commonly shipped as a liquefied compressed gas, and the solid form is shipped as “dry ice.”

Incompatible Materials/Reactivity

Dusts of a number of metals can ignite and are explosive when suspended in CO₂. These include aluminum, chromium, magnesium, manganese, titanium, and zirconium. In addition, CO₂ is incompatible with oxidizers, including permanganates, perchlorates, peroxides, chlorates, nitrates, fluorine, chlorine, and bromine; reducers, including lithium sodium and aluminum and their hydrides; metal carbides, metal salts, and strong bases, including sodium hydroxide and potassium hydroxide.

When shipped in steel cylinders, CO₂ is in the form of gas over liquid and at 68°F (19°C) exerts a pressure of 830 psi. Carbon dioxide dissolves in water and reacts to form carbonic acid (see dissociation factor, H₂CO₃ is a weak acid). CO₂ dissolves to a lesser extent in alcohol and other neutral organic solvents.

³ “Carbon Dioxide – Lenntech”, www.lenntech.com/carbon-dioxide.html

Other Chemical and Physical Properties of Carbon Dioxide*

Characteristic	Common Property
Molecular Mass	44.01
CAS Registry Number	124-38-9
UN (United Nations) Number	UN 1013 (compressed gas); UN 2187 (refrigerated liquid); UN 1845 (solid)
DOT Classification	Non-flammable gas
DOT Label	Non-flammable gas
Transport Canada Classification	2.2
Latent Heat of Fusion at -56.6 °C (-69.9 °F), 518kPa	7.95 kJ/mol; 190 kJ/kg; 43.17 kcal/kg; 85 btu/lb
Thermal Conductivity, gas at 101.325 kPa at 26.85 °C	0.166W/(m·K); 39.6 X 10 ⁻⁶ cal/(s·cm·°C)
Vapor Pressure at 70 °F	56.5 atm./42,946mm Hg; 5801 kPa; 844 psia; 58 bar
UEL/LEL	Nonflammable, non-combustible
Liquid Density, at 21.1°C (70°F), 6430 kPa	762 kg/m ³ ; 0.713 kg/l; 47.6 lb/ft ³
Vapor Density relative to air; 70°F and 1 atm.	1.833 kg/m ³ ; 0.115lb/ft ³
Specific Gravity, gas (air =1), 70°F & 1 atm.; at 32 °F & 1 atm.	1.522; 1.524
Specific Volume, at 70°F and 1 atm.; at 32 °F	8.75 ft ³ /lb; 1.976 g/l at 760 mm; 0.546 m ³ /kg; at 32°F= 8.104 ft ³ /lb/0.546 m ³ /kg
Surface Tension at -52.2 °C	16.54 mN/m; 16.54 dyn/cm
Ionizing Potential	13.77 eV
Water Solubility	.90vol/vol at 68°F/0.759cm ³ /1cm ³ at 0°C
Henry's constant for solubility	298.15 moles/kg * bar
Critical Density	29.2 lb/ft ³ ; 468 kg/m ³
Concentration in the atmosphere	400 ppm (0.04%)
Sublimation point at 1 atm (101.325 kPa)	-109 °F, -78.4 °C
Critical Temperature	87.9 °F, 31.1 °C
Critical Pressure	1,070.6 psia, 72.9 atm., 7382 kPa abs
Critical Volume	2.137dm ³ /kg
Triple Point: Temperature	-56.6°C at 5.11 atm; -69.9°F at 60.4psig
Triple Point: Pressure	75.13 psia; 5.112 atm.; 5.18 bar; 517.97kPa
Heat of Formation	94.05 kcal/mol
Latent Heat of Vaporization at 32 °F (0 °C)	100.8 btu/lb; 234.5 kJ/kg
Viscosity, gas at 26.85 °C, 101.325kPa	0.01501 mPa·s; 0.01501 mN·s/m ² ; 0.01501cP
Viscosity of saturated liquid at 2 °F/-16.7°C	0.287 lb/(ft)(hr); 0.000119 Pa·s

*(Handbook of Compressed Gases, Compressed Gas Association, Arlington, VA, 1990; Van Nostrand Reinhold, NY, NY), pp. 284-285; and Braker, William and Allen L. Mossman, Matheson Gas Data Book, Matheson Gas Products, Secaucus, NJ, 1980, p. 120).

3

CHAPTER 3: Where Does Carbon Dioxide Come from? How Is Carbon Dioxide Formed in the Earth's Atmosphere?

Many various natural and man-made processes cause carbon dioxide to be formed or given off. These include geothermal, biological, combustion, and industrial processes. The ethanol production process is a biological process that produces carbon dioxide.

Life on Earth as we know it would not exist without carbon dioxide. This essential gas is a critical component of the **carbon cycle**, "...A biogeochemical cycle in which carbon is exchanged between the Earth's oceans, soil, rocks and biosphere." The carbon cycle has two main components. One, the fast carbon cycle, involves, "the movements of carbon between the environment and living things", and the other, the slow carbon cycle, is the "movement of carbon between the atmosphere, oceans, soil, rocks and volcanism." Both are completely dependent upon atmospheric carbon dioxide. (http://en.wikipedia.org/wiki/Carbon_dioxide_in_Earth's_atmosphere).

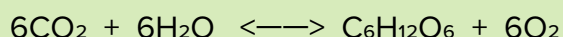


"Carbon dioxide occurs in the atmosphere of many planets. In our solar system, the optical layer thickness due to CO₂ is 100,000 cm/atm., but is only 220 cm/atm. on Earth."⁴

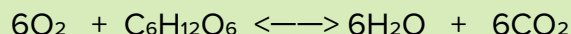
⁴ Handbook of Chemistry and Physics, page 293, #1809, 2013

Biological Production of CO₂

The main *biological* processes that give off or use carbon dioxide are varied and many but all are linked to basic cellular metabolism. In the presence of sunlight, all green plants (including algae), cyanobacteria and other organisms that contain chlorophyll are able to manufacture simple glucose, (a sugar/carbohydrate) and oxygen from carbon dioxide and water. This process is called photosynthesis, since light is used to synthesize energy in the form of sugar. This is the reaction:



All aerobic (“oxygen loving”) organisms without chlorophyll, including animals, fungi, molds, yeasts, and most bacteria, and all photosynthetic organisms at night or in the dark, take in oxygen and give off carbon dioxide – a reverse of photosynthesis – during metabolism. This reaction is the opposite of photosynthesis and is called respiration (breathing):



This is considered a “combustion” process, since organic materials are used up along with oxygen and heat is given off. This heat that is generated is moderated metabolically in animals, and is controlled to a fine degree in “warm-blood” animals to maintain a consistent body temperature.

The details of the fermentation process that converts sugar to ethanol and gives off carbon dioxide is so critical to this document that this whole section is devoted to it

Decaying vegetation can also produce CO₂, resulting in local areas where large concentrations of carbon dioxide can collect for indefinite lengths of time. This includes many types of relevant process areas, including wastewater treatment systems, sewers, landfills, manure collection areas, culverts, generation, biological waste collection points, and agriculture process residues.⁵ Since grain also undergoes respiration as it sits in grain silos, carbon dioxide concentrations as high as 90% can be reached. These sources of carbon dioxide will be explored further in the safe handling sections of this document, where specific procedures and techniques for recognizing, evaluating and controlling CO₂ levels for protecting workers are reviewed.

⁵ “Carbon Dioxide Emissions Associated with Bioenergy and Other Biogenic Processes”, EPS, September 9, 2013; www.epa.gov/climatechange/ghgemissions/biogenic-emissions.html.

The Basic Biological Fermentation Process

The process of ethanol production is based upon the fermentation of sugar by yeast. It is a biological process in which starches that are broken down into sugars, such as glucose, fructose, and sucrose, which are then fermented by yeast into ethanol and carbon dioxide. Approximately equal pounds of CO₂ and ethanol can be produced from one bushel of corn.

This process must take place in some type of container that not only keeps air out but is able to let carbon dioxide escape as it is produced. The by-products of this process that are organic – contain carbon in some form, such as DDGS (distillers dried grains with solubles)—also form carbon dioxide when they decompose. In addition, grain is living and gives off carbon dioxide. This can make CO₂ accumulate anywhere grain is stored or handled, such as in rail cars, in grain elevators,

in bucket elevators, and in conveyor systems. The only unknown is just how much CO₂ will be given off. In the production of fuel ethanol there are two main types of milling processes, the dry and wet mill processes. They both yield equal amounts of ethanol.

In addition, ethyl alcohol (ethanol) is also manufactured using cellulosic biomass. This is based upon the principle mentioned above that what is normally considered as organic by-products can be broken down by fermentation, yielding ethanol. CO₂ is given off here as well.

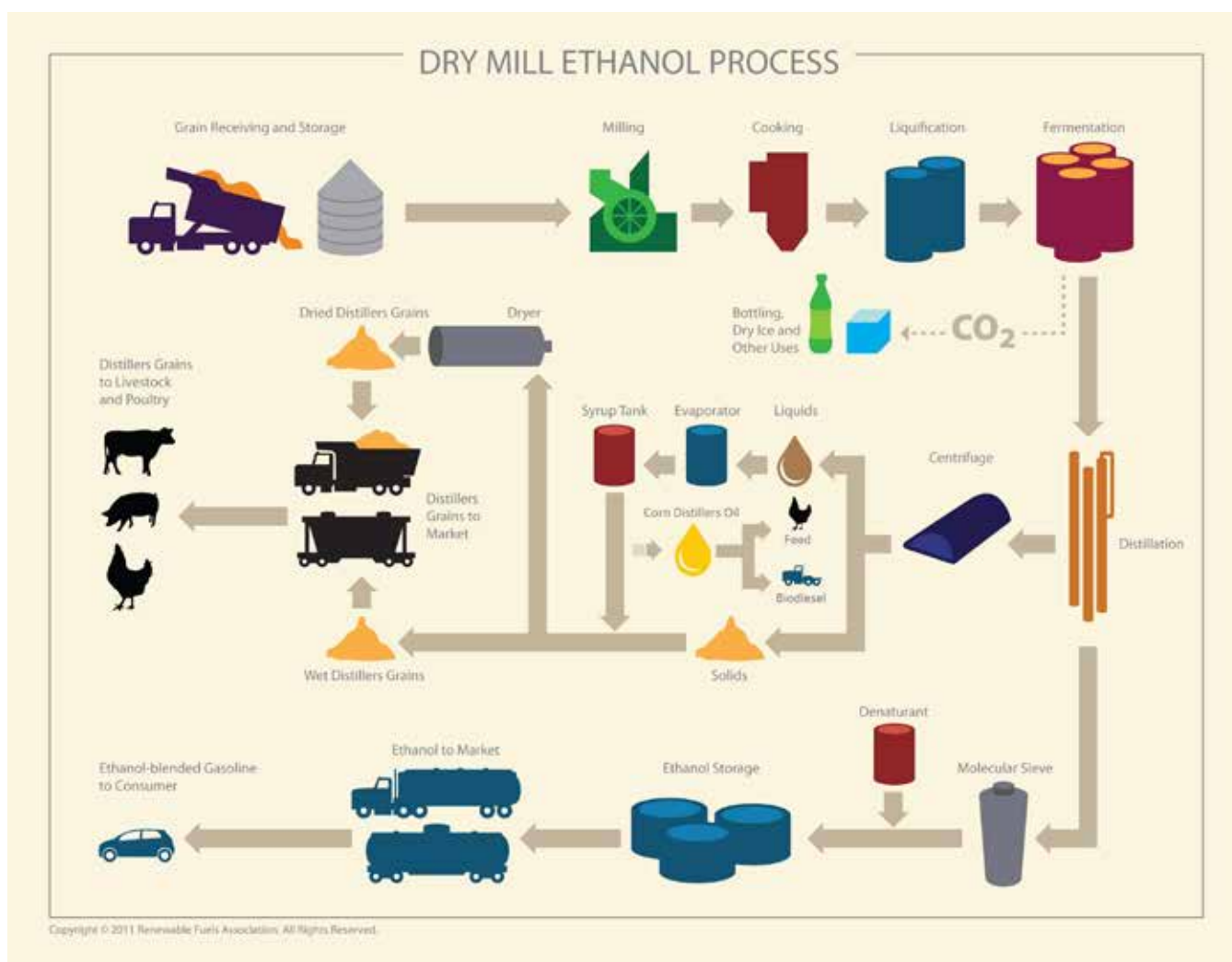
Below these three processes are explained using a graphic diagram as well as a written explanation. As can be seen for all ethanol production processes, CO₂ is mainly given off as a by-product of fermentation, but it is also released in smaller quantities throughout the production process.

Dry Milling Ethanol Production

In dry milling, the entire corn kernel or other starchy grain is first ground into flour, which is referred to in the industry as "meal" and processed without separating out the various component parts of the grain. The meal is slurried with water to form a "mash." Enzymes are added to the mash to convert the starch to dextrose, a simple sugar. Ammonia is added for pH control and as a nutrient to the yeast.

The mash is processed in a high-temperature cooker to reduce bacteria levels ahead of fermentation. The mash is cooled and transferred to fermenters where yeast is added and the conversion of sugar to ethanol

and carbon dioxide (CO₂) begins. This fermentation process generally takes about 40 to 50 hours. During this part of the process, heat is generated, and the mash is agitated and kept cool to facilitate the activity of the yeast. After fermentation, the resulting "beer" is transferred to distillation columns where the ethanol is separated from the remaining "stillage." The ethanol is concentrated to 190 proof using conventional distillation and then is dehydrated to approximately 200 proof in a molecular sieve system.



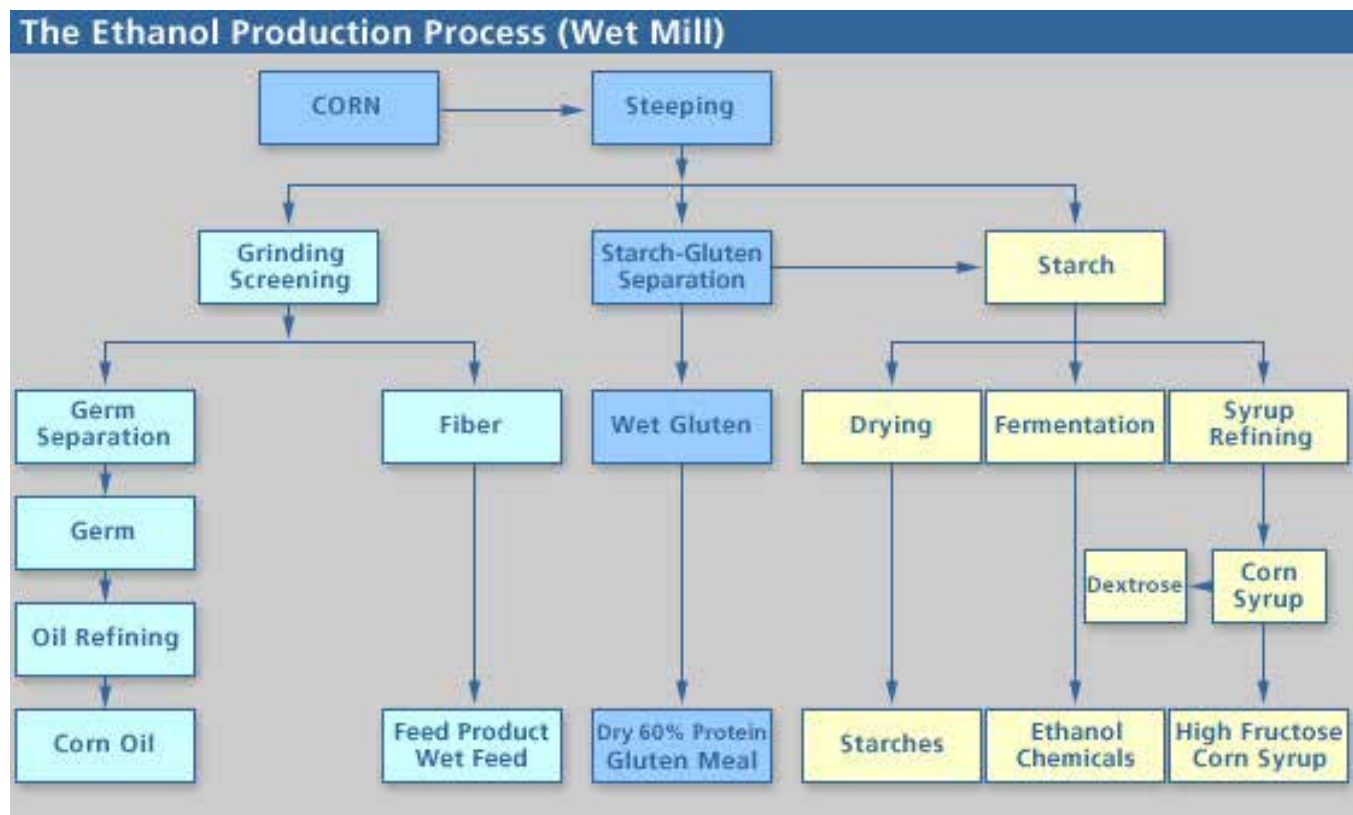
www.ethanolrfa.org/pages/how-ethanol-is-made (2015)

The anhydrous ethanol is then blended with 2 - 5% denaturant (such as natural gasoline) to render it undrinkable and thus not subject to beverage alcohol tax. It is then ready for shipment to gasoline terminals or retailers.

The stillage is sent through a centrifuge that separates the coarse grain from the solubles. The solubles are then concentrated to about 30% solids by evaporation, resulting in Condensed Distillers Solubles (CDS) or "syrup." The coarse grain and the syrup are then dried together to produce dried distillers' grains with solubles (DDGS), a high quality, nutritious livestock feed. The CO₂ released during fermentation can be captured and sold for use in carbonating soft drinks and other beverages and in the manufacture of dry ice. Approximately 85% of fuel ethanol manufacturing processes use dry milling.

Wet Milling Ethanol Production

In wet milling, the grain is soaked or "steeped" in water and dilute sulfurous acid for 24 to 48 hours. This steeping facilitates the separation of the grain into its many component parts. After steeping, the corn slurry is processed through a series of grinders to separate the corn germ. The corn oil from the germ is either extracted on-site or sold to crushers who extract the corn oil. The remaining fiber, gluten and starch components are further segregated using centrifugal, screen and hydroclonic separators.



www.ethanolrfa.org/pages/how-ethanol-is-made (2015)

The steeping liquor is concentrated in an evaporator. This concentrated product, heavy steep water, is co-dried with the fiber component and is then sold as corn gluten feed to the livestock industry. Heavy steep water is also sold by itself as a feed ingredient and is used as a component in Ice Ban, an environmentally friendly alternative to salt for removing ice from roads. The gluten component (protein) is filtered and dried to produce the corn gluten meal co-product. This product is highly sought after as a feed ingredient in poultry broiler operations.

The starch and any remaining water from the mash can then be processed in one of three ways: fermented into ethanol, dried and sold as dried or modified corn starch, or processed into corn syrup. The fermentation process for ethanol is very similar to the dry mill process described above.

Cellulosic Biomass Ethanol Production

The process flow diagram below shows the basic steps in production of ethanol from cellulosic biomass. Note that there are a variety of options for pretreatment and other steps in the process and that several technologies combine two or all three of the hydrolysis and fermentation steps within the shaded box. Chart courtesy of the National Renewable Energy Lab. (Renewable Fuels Assc., www.ethanolrfa.org/pages/how-ethanol-is-made, 2015)

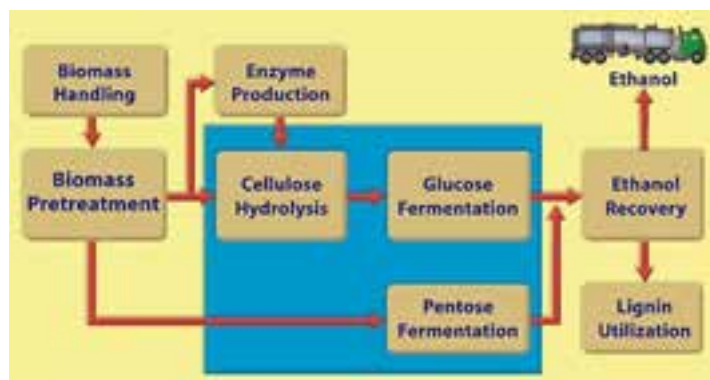


Chart courtesy of the National Renewable Energy Lab

Geothermal, Industrial and Combustion Process Emissions of CO₂

In addition to biological processes, geothermal emissions, combustion processes, and industrial manufacturing also give off extensive amounts of carbon dioxide. Surface soils can sometimes contain high concentrations of this gas, from decaying vegetation or chemicals changes in bedrock.⁶

Carbon dioxide is widely known for being given off during the combustion process, including the burning of diesel, wood, peat, coal, gasoline, propane, natural gas (methane), and other flammable and combustible organic materials. This combustion is mainly used for energy generation and transportation. Along with forest burning and land clearing these are the main sources of carbon dioxide generation outside of biological processes.

Other important but minor sources of carbon dioxide also exist. CO₂ is a by-product of steam reforming of methane, propane and naphtha. The production of lime (calcium oxide or CaO), and sodium phosphate generate carbon dioxide as well. In addition, the industrial production of hydrogen and ammonia, cement manufacturing, as well as iron and steel emit CO₂.⁷ Iron begins as iron oxide ore. In a blast furnace, along with coke, iron is reduced to pig iron and carbon dioxide.

Lastly, when rocks containing carbonates, limestone, and dolomite are dissolved by rain and bodies of water, carbon dioxide is dissolved in this water, making it acidic. It is also given off geothermally during from geysers, hot springs, and volcanic eruptions.

⁶ "Carbon Dioxide," Chemical Fact Sheets, www.h-dhs.wisconsin.gov/eh/chemfs/fs/carbondioxide.html

⁷ www.airproducts.com/company/Sustainability/environment-health-and-safety/~media/files/PDF/company/safetygram-18.pdf

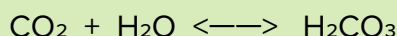
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CHAPTER 4: How is Carbon Dioxide Used?

Carbon dioxide is in demand around the world because it has many varied uses. CO₂ is used around the world as a non-flammable propellant, and is *the* ingredient in dry ice manufacturing. Dry ice is widely used to, “refrigerate dairy products, meat products, frozen fruits and vegetables, poultry, and other perishable foods while in transit.”⁸

It is extensively used for decaffeinating coffee, being a propellant in paint ball markers, for quick-inflating life jackets, in air guns, and in cans used for inflating tires. It is even used in scanning electron microscopy to preparing specimens.⁹ One of its most common uses is for “carbonated” beverage dispensing. It is the gas that makes the bubbles in carbonated soft drinks. Here is how this happens:

Carbon dioxide is soluble in water and forms carbonic acid, a weak acid. See below.



This reaction is not complete however, and the carbonic acid readily reverts back to carbon dioxide. Although it is this reaction that makes the bubbles in carbonated beverages, this reaction also explains why, when the carbon dioxide escapes back into the air, is the reason soft drinks “go flat.”

Because of the weakly acidic nature of carbon dioxide, it is a common water treatment used to neutralize basic (alkaline) water. Carbon dioxide is a critical ingredient in beer and sparkling wine. Besides the food industry, it is also commonly used in agriculture, especially in greenhouses to promote plant growth. CO₂ is the component in one type of fire extinguisher, for use on electrical and flammable liquid fires. Because it is heavier than air, it prevents oxygen from further contact with the fire, helping to smother the fire and put it out. Carbon dioxide is sometimes used by welding fabricators to replace the moisture brittleness of the weld is not critical, such as common mild steel welds.

⁸ Handbook of Compressed Gases, Compressed Gas Association, Arlington, VA, 1990; Van Nostrand Reinhold, NY, NY

⁹ http://en.wikipedia.org/wiki/Carbon_dioxide

It is also used, “as an expendable refrigerant for freezing and chilling of food products; for low temperature testing of aviation, missile, and electronic components; for stimulation of, or increased recovery from, oil and gas wells; for rubber tumbling; and for controlling chemical reactions.”¹⁰

Carbon dioxide has many uses in medical applications as well. It is commonly mixed with ethylene oxide, usually in a mixture of 80% ethylene oxide and 20% carbon dioxide, and used as a cold sterilant gas mixture. Thousands of materials, from plastic syringes to I.V. tubing, are made of plastics and other disposable materials and cannot be sterilized using heat. This mixture is an extremely effective means for sterilizing materials at ambient or cooler temperatures. Carbon dioxide has many other medical applications too, including its use for testing acidity of the blood, some lung function tests, and for other medical tests.

It is used in plastics and rubber production, and is also used in the process of electronic component manufacturing. (www.airproducts.com/company/Sustainability/environment-health-and-safety/~media/files/PDF/company/safetygram-18.pdf). In the chemical industry, carbon dioxide is used in the manufacture of methanol, urea, and is also a main ingredient in other chemicals and intermediaries, including carboxylic acid, metal carbonates and bicarbonates. Historically, it has been used as a cloud-seeding agent.

CO₂ in the form of dry ice is sometimes used on the stage and in live theatre productions to make fog. Lastly, one of the first lasers ever made used carbon dioxide.



¹⁰ Handbook of Compressed Gases, Compressed Gas Association, Arlington, VA, 1990; Van Nostrand Reinhold, NY, NY, p. 287

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CHAPTER 5: Health Effects from Overexposure to Carbon Dioxide

Accidental Overexposures to Carbon Dioxide

- ▶ People that manufacture dry ice and transport it are sometimes in situations where the dry ice off-gases and there is not enough air movement to keep the concentration at safe levels. Closed vehicles, unventilated rooms, tight work spaces that have little fresh air exchange, and enclosed areas are all places where people inadvertently find themselves in high concentrations without realizing it because there is no warning.
- ▶ People have died from carbon dioxide being used on stage as a “special effects” fog.
- ▶ All over the world, people have died when faulty manifold systems or piping from beverage dispensing machines (where CO₂ is used to make the “fizz” in soft drinks) leak, and the concentration builds up.
- ▶ Food processing facilities and freezers; filling and handling CO₂ cylinders, tank trucks and rail cars; and piping systems in refrigeration units have all leaked, resulting in exposures that have killed many people.

- ▶ People have even been overexposed in their basement from an abandoned coal mine under their house; and hundreds of people at a time have been killed when an eruption from underground releases CO₂ into the low-lying area surrounding a lake where they lived.

In the beer manufacturing as well as the ethanol production industries, because CO₂ is a natural by-product of the processes, people can routinely be exposed to carbon dioxide. And without constant vigilance, overexposures can occur that can be serious.



Symptoms of Overexposure

Research has shown that carbon dioxide is far more hazardous than previously thought. In 2012, it was conclusively demonstrated that even concentrations as low as 1,000 ppm impair thinking, concentration and logical thought processes.¹¹ This is quite serious, especially when considering how critical it is for employees to be able to make quick process decisions unimpaired.

Acute toxicity data from the National Institute of Occupational Safety and Health (NIOSH) and other studies show that *even in the presence of normal concentrations of oxygen, death will occur at exposures of 7% carbon dioxide in only 5 minutes.*

Other studies also dispel the myth that carbon dioxide is an asphyxiant gas and only causes adverse health effects when it displaces oxygen. "Several studies have demonstrated that breathing concentrations of 30% carbon dioxide, even with 70% oxygen, leads to unconsciousness in 30 seconds. Some patients exhibited seizures that were characterized as decerebrate (no cerebral functioning)."¹²

According to the EPA, "Exposure of humans to carbon dioxide concentrations ranging from 17% to 30% quickly (within one minute) leads to the loss of controlled and purposeful activity, unconsciousness, coma, convulsions, and death... Exposure to concentrations from greater than 10% to 15% carbon dioxide leads to dizziness, drowsiness, severe muscle twitching, and unconsciousness within a few minutes... Exposure to a concentration of 6% carbon dioxide can produce hearing and visual disturbances within 1 to 2 minutes."¹³

Symptoms of overexposure by inhalation include but are not limited to dizziness, headache, nausea, rapid breathing, shortness of breath, deeper breathing, increased heart rate (tachycardia), eye and extremity twitching, cardiac arrhythmia, memory disturbances, lack of concentration, visual and hearing disturbances (including photophobia, blurred vision, transient blindness, hearing loss and ringing in the ears), sweating, restlessness, vomiting, shaking, confusion, flushed skin, panic, parathesis (a sensation of numbness in the extremities), disorientation, convulsions, unconsciousness, coma, and death. These adverse health effects have been known for more than forty years. (NIOSH, 1976).

Even in the presence of normal concentrations of oxygen, death will occur in only 5 minutes at exposures of 7% carbon dioxide. (NIOSH)

¹¹ Stish U., Mendell M.J., et al 2012. "Is CO₂ and Indoor Pollutant? Direct Effects of Low-to-Moderate CO₂ Concentrations on Human Decision-Making Performance." (<http://ehp.niehs.nih.gov/wp-content/uploads/2012/09/ehp.1104789.pdf>). *Environmental Health Perspectives* 120 (12).

¹² www.netl.doe.gov/publications/proceedings/04/carbon-seq/169.pdf

¹³ www.epa.gov/ozone/snap/fire/co2/appendixb.pdf

At a concentration of 5,000 ppm (0.5%), the International Space Station crew experienced headaches, lethargy, mental slowness, emotional irritation, and sleep disruption, even though oxygen concentrations were maintained at 20.9%.¹⁴

A recent study in the United States of humans exposed in only 2.5 hour sessions showed serious decreases in cognitive abilities at only 1,000 ppm (0.1%). At a concentration of only 2,500 ppm for 2.5 hours, most measured cognitive functions were impaired to the extent that the individuals were *rendered cognitively marginal or dysfunctional*. The functions measured included task orientation, initiative, information usage, and use of basic strategy.¹⁵

Carbon dioxide can also cause injury in the liquid and solid (dry ice) forms. This is mainly because under pressure it is very cold/ as the gas is released from a steel cylinder or is released from a fire extinguisher or a pipe break, CO₂ can cause serious burns, blisters, and frostbite.¹⁶

At an exposure of only 2,500 ppm for 2.5 hours, most measured cognitive functions were impaired to the extent that the individuals were rendered cognitively marginal or dysfunctional.

Fortunately, during the past decade, great strides have been made in developing accurate, rugged, and dependable carbon dioxide sensors at a reasonable cost. These sensors can now be part of a multi-gas monitor, such as those used for confined space entry, or be a single gas monitor that is hand-held or worn by the worker. The industry is poised to embrace this technology and train workers to use them as a routine part of production work.



¹⁴ http://en.wikipedia.org/wiki/Carbon_Dioxide

¹⁵ Stish U., Mendell M.J., et al 2012. "Is CO₂ and Indoor Pollutant? Direct Effects of Low-to-Moderate CO₂ Concentrations on Human Decision-Making Performance." (<http://ehp.niehs.nih.gov/wp-content/uploads/2012/09/ehp.1104789.pdf>). *Environmental Health Perspectives* 120 (12).

¹⁶ Carbon Dioxide - Lenntech, www.lenntech.com/carbon-dioxide.html

How Inhaled Carbon Dioxide Affects the Body

Normally, humans breathe in air that is approximately 20.9% oxygen, 78% nitrogen, 0.8% argon, and 0.04% (400 ppm) of carbon dioxide. Like CO₂, oxygen also dissolves in the lungs and is transported to the blood via diffusion across the lung tissue (alveoli). Once in the blood, oxygen is carried throughout the body by the arteries, and is used in cell metabolism throughout the body.

Carbon dioxide is given off as a by-product of cell metabolism and is carried by the blood through the venous system (veins) to the lungs. Here it is exhaled. The concentration of CO₂ in each breath is ~3.8%, and the “average” person produces approximately two pounds of carbon dioxide each day. More CO₂ is given off by strenuous activity.

Hypercapnia, hypercarbia, or hypercapnea, is the physiological term for the condition of, and the body’s response to, excessive carbon dioxide. The CO₂ is breathed into the lungs, dissolves in the water there, diffuses across the alveolar-capillary membrane, and enters the bloodstream. As it combines with water, it forms carbonic acid, making the blood acidic. So CO₂ in the bloodstream lowers the blood pH.

When CO₂ levels become excessive, a condition known as acidosis occurs. This is defined as the pH of the blood becoming less than 7.35. The body maintains the balance mainly by using bicarbonate ions in the blood. As the body responds to neutralize this condition, an electrolyte imbalance – an increase of plasma chloride, potassium, calcium and sodium, can occur. In the blood stream, CO₂ concentration is also controlled by reversible reactions with two major blood components, plasma proteins and hemoglobin.

In addition, the body uses other specific mechanisms to compensate for the excess carbon dioxide. Breathing rate and breathing volume increase, the blood pressure increases, the heart rate increases, and kidney bicarbonate production (in order to buffer the effects of blood acidosis), occur. Blood vessels in the extremities constrict, restricting blood flow to these body parts. At the same time, arteries in the brain, spinal cord, and heart dilate, so that more blood flows is diverted to maintain the function of these critical organs.

When there is exposure to very high levels of CO₂, in excess of 5% (50,000 ppm), the body’s compensatory mechanisms can become overwhelmed, and the central nervous system (brain and spinal cord) functions are depressed, and then fail. Death soon follows.¹⁷

¹⁷ Farrar et al. 1999; IVHHN 2005; Nelson 2000; NIOSH 1975 and 1996



Even though oxygen is necessary to carry out cell functions, it is not the lack of oxygen that stimulates breathing. Breathing is stimulated by an excess of CO₂. If an individual breathes too slowly (bradypnea, does not breathe deeply enough, as in emphysema), or is exposed to excessive CO₂ levels, too much CO₂ can build up. This causes increased breathing and the other physiological responses discussed above. Hyperventilation (rapid breathing) can cause too little CO₂ and result in alkalosis (pH of the blood becomes elevated).

People at high altitudes that are not acclimated (pilots without supplemental oxygen, travelers to high altitudes), because there is less available oxygen to breathe (lower partial pressure of oxygen because the air is “thinner”), can become unconscious due to lack of oxygen without ever having a sensation of “air hunger.”

Concentrated CO₂ conditions also impact most living organisms. Plant roots can actually be suffocated, which inhibits the uptake of nutrients and subsequently kills the plants ⁽¹⁸⁾.

The Maximum Legal Workplace Exposure Limit

The legal exposure limit set by OSHA has not been updated since 1970, and is 5,000 ppm averaged over an 8-hour workday, with the subsequent 16 hour having no exposures above fresh air concentrations and exposures totaling 40 hours per week. However, at that concentration of 5,000 ppm, the International Space Station crew experienced headaches, lethargy, mental slowness, emotional irritation, and sleep disruption, even though oxygen concentrations were maintained at 20.9%. (http://en.wikipedia.org/wiki/Carbon_Dioxide).

A recent study in the United States of humans exposed in only 2.5 hour sessions showed serious decreases in cognitive abilities at only 1,000 ppm. At a concentration of only 2,500 ppm for 2.5 hours, most measured cognitive functions were impaired to the extent that the *individuals were rendered cognitively marginal or dysfunctional*. The functions measured included task orientation, initiative, information usage, and use of basic strategy.¹⁹ This study demonstrates that exposure levels as low as 1,000 ppm adversely impacts judgement, decision-making ability, and thinking skills on a short-term basis, even for healthy individuals.

¹⁸ Ferrar et al. 1999; NIOSH 1976

¹⁹ Stish U., Mendell M.J., et al 2012. "Is CO₂ and Indoor Pollutant? Direct Effects of Low-to-Moderate CO₂ Concentrations on Human Decision-Making Performance." (<http://ehp.niehs.nih.gov/wp-content/uploads/2012/09/ehp.1104789.pdf>). *Environmental Health Perspectives* 120 (12).

CO₂ Exposures in Ethanol Production

Since yeast releases CO₂ as a fermentation by-product, workers in the ethanol production industry are at special risk to areas in the production facilities collecting pockets of high concentrations of carbon dioxide. In addition, since CO₂ is a byproduct of metabolic activity of grain, workers in grain elevators, silos, and rail cars, where stored grain can produce an atmosphere of 37% CO₂ during oxidation of carbohydrates, are at extreme risk for high CO₂ levels of exposure.²⁰

Workers and others who handle CO₂ must remember: it is a toxic waste product given off by the body as a gas, just as other waste products are given off by the body in liquid and solid form. They must work to dispel the

pervasive belief that since we exhale carbon dioxide – and therefore are exposed to it with every breath – it is not toxic.

Everyone must stay alert for any of these symptoms in themselves or others when working in areas where elevations in carbon dioxide could possible occur. These physiological effects caused by excess carbon dioxide are usually reversible if exposure is brief. For longer or very high exposures, damage can be permanent.

Many countries have legal exposure limits that are significantly lower than the United States, and others are reviewing carbon dioxide studies and re-evaluating their legal exposure limits.

Immediate First Aid

No safety manual would be complete without addressing first aid in cases of overexposures. What follows are only general methods to immediately assist people that are suffering from symptoms of overexposure to CO₂ while waiting for emergency response personnel to arrive. These suggestions are only offered for immediate response. It is not to be construed as replacing professional assistance and emergency medical treatment and consultation.

In cases of overexposure to gaseous carbon dioxide, immediate first aid includes removing the exposed worker from the exposure

area to fresh air and restoring breathing by trained personnel. (NIOSH, 1976) Other appropriate first aid measures should be taken immediately, depending upon the nature of the condition of the person, followed by prompt medical evaluation and assistance.

In cases of overexposure to liquid or solid carbon dioxide, quickly remove contaminated clothing and rinse contaminated skin gently with lukewarm, not hot, water. Do NOT rub any skin or affected areas. Transfer promptly to a medical facility for evaluation and treatment.

²⁰ Nelson 2000, NIOSH 1976

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CHAPTER 6: Carbon Dioxide Exposures: Examples

Historic CO₂ Exposures

For centuries, since before scientists recognized that there was a gas that we now know as carbon dioxide, overexposure to CO₂ was known to be hazardous, and potentially fatal. In coal and other mining operations, miners called this gas, “black damp,” and used mice and canaries to give a warning when too much was present (they became unconscious or died).

Candles were also used – and when the flame flickered and went out, miners knew the air was not safe and they had to leave. Even so, many people died as a result of overexposures to carbon dioxide. Too often, a little bird keeling over or a candle going out was not enough of a warning to escape.

Present Day CO₂ Exposures

Unfortunately, in modern times, people are still experiencing overexposures on the job and adverse health effects from breathing carbon dioxide; fatalities are still way too common. Yet carbon dioxide now has so many uses and is present in so many processes, protecting people from overexposures can be difficult, especially since high concentrations of CO₂ give no warning to the person breathing it.

*Part of this problem is the pervasive belief that since we exhale carbon dioxide – and therefore are exposed to it with every breath – it is not toxic. This belief has been hard to dispel. Even public health professionals, industrial hygienists, and doctors persist in believing that carbon dioxide is little more than a simple asphyxiant. Many also believe that even when someone experiences nausea, severe headaches, seizures, and unconsciousness, once someone is re-exposed to fresh air, they will recover fully. **They are wrong on both counts.***

In this section we are going to review some of the ways that people become sick, ill, or die from their exposures to CO₂. We will also look at some of the subtle adverse effects that low-level overexposures to carbon dioxide can cause. This is important, because people that work with and around CO₂ need to be able to recognize these symptoms in themselves and others before they the symptoms become serious.

Specific Cases of Accidental Injuries and Fatalities Involving Exposures to Carbon Dioxide in Ethanol and Beer Production

Beer Production

In October 2012, a beer manufacturer in Houston received multiple citations from OSHA for failing to protect workers from exposure to CO₂ and other workplace hazards while working in brewery cellars. This company was issued a proposed penalty of \$88,000 and was required to implement many engineering, equipment, training and program changes to reduce the probability of a recurrence, along with paying the hefty fine.

Ethanol Production

In January 2013, two men were found unconscious as they did maintenance in an ethanol production facility. One died and one has residual neurological damage from the CO₂ overexposures. We are going to explore this accident in detail. Later, possible changes that the ethanol industry could make to protect its workers from a similar accident will be explored.

Four large fermenters stood adjacent to each other in a “4-pack” arrangement. A small 2-story interstice building was located in between the 4 vessels, with ¼ of the curve of each vessel inside the building. The interstice building housed pumps, piping, and heat exchangers that needed to be protected from freezing during cold weather.

The base of the fermenters together with the bottom part of the interstice building were located within a containment dike, and there were multiple points at which to go over the dike and down to the base of the fermenters on the first floor of the building.



The top of the interstice building

Each fermenter had a small D-shaped manway inside the building. The flange for the flat part of the D extended slightly below the bottom of each fermenter, so that by removing the D manway, residual mash could drain out of the fermenter onto the floor, where it flowed to a sump pump to allow it to be reclaimed. This allowed for the complete draining of each fermenter.



D-shaped manway (inside the building)

Each fermenter also had a larger round manway outside of the building, and each of these manways was the entry point for its respective fermenter if there was a need to make an entry.



Round manway (outside of the building)

Preparations were being made to drain and sterilize one of the fermenters. The fermenter had been emptied as far as the normal discharge piping and associated pump would allow, and the next step was to open up the D manway to allow the residual mash in the bottom to drain out, and also open the outside manway to begin to ventilate the vessel. Historically the maintenance workers would either open the D manway inside the building, then go outside, open the outside manway, then exit out of the diked area; or they would open the outside manway, go into the building and open the D manway, then walk out of the building and go up over the dike.

On the morning of the incident, the maintenance workers opened the D manway inside the building, then went outside and opened the outside manway, then went back into the building.

Tragically, during the time that they were opening the outside manway, enough carbon dioxide had migrated out of the fermenter through the D manway that an Immediate Danger to Life and Health (IDLH) atmosphere now existed inside the interstice building. Both workers passed out, one on the floor and the other in a seated position leaning back against a set of steps. While exact times cannot be pinpointed, it is believed that they may have been exposed to high carbon dioxide levels for as long as 45 minutes. They were discovered by two other employees who entered the building to start another job, and who then immediately initiated emergency procedures. By that time, there was no longer an IDLH atmosphere in the building.

The worker found on the floor did not survive. The other worker survived but continues to suffer from neurological damage done by the extended exposure to high levels of carbon dioxide.

After a thorough investigation and input from many experts, the lessons learned resulted in both engineering and procedural changes that now allow for the carbon dioxide to be evacuated from the fermenters before either manway is removed.

7

CHAPTER 7: Overview of Carbon Dioxide Exposure Standards and Guidelines

The mission of the U.S. Federal Occupational Safety and Health Administration (OSHA), a division of the Department of Labor, is to assure the safety and health of America's workers by setting and enforcing standards; providing training, outreach, and education; establishing partnerships; and encouraging continual improvement in workplace safety and health.

Individual states and territories are allowed to have their own safety and health plans that must be reviewed and approved by Federal OSHA. Each state plan must demonstrate that it is at least as comprehensive and effective as Federal OSHA. At this time, 27 states and one territory have their own approved workplace safety and health plans. A list of these states, key personnel in each state, and contact information is contained in the Appendix B.

Note that these state plan-approved states and territories may adopt different exposures limits, more stringent ones, than Federal OSHA's.

The National Institute of Occupational Safety and Health, (NIOSH), is part of the Center for Disease Control (CDC), US Department of Health & Human Services (US DHHS). NIOSH is responsible for conducting research and making recommendations for the prevention of work-related illnesses and injuries.

OSHA and NIOSH also review and publish specific methods for testing and analyzing chemical contaminants in the air, including carbon dioxide.

The American Conference of Governmental Industrial Hygienists, ACGIH® is a member-based organization that advances occupational and environmental health. This scientific-based organization reviews available research and studies on airborne contaminants as well as other workplace stressors and establishes exposure levels that are designed to protect most normal, healthy adults in the workplace.

Agency	Work Day Exposure Limit	Short-Term Exposure Limit	IDLH
OSHA	5,000 ppm, TWA ₈	30,000 ppm	30,000 ppm
NIOSH	5,000 ppm, TWA ₁₀ , up to 40 hours/week	30,000 ppm	
ACGIH	5,000 ppm TWA ₈	30,000 ppm	

TABLE OF WORKPLACE EXPOSURES

ppm = parts per million

IDLH = Immediately Dangerous to Life and Health

STEL = Short Term Exposure Limit (workplace allowable exposure for 15 minutes followed by 1.75 hours of no exposure)

PEL = Permissible Exposure Limit

TWA = Time Weighted Average

REL = Recommended Exposure Limit

NIOSH = National Institute for Occupational Health and Safety (Federal Agency)

OSHA = Occupational Safety & Health Administration (Federal Agency)

ACGIH = American Conference of Governmental Industrial Hygienists (Professional Association)

NOTE: These workplace exposure limits are for 8- or 10-hour work days, up to 40 hours per week. They are established with the intent that the exposed workers will not be exposed to carbon dioxide outside of these work hours except for background levels in fresh air.

Other nations have more protective limits, including:

- ▶ Germany - PEL = 5,000 ppm, STEL = 10,000 ppm for 60 min.
- ▶ Sweden - PEL = 5,000 ppm, STEL = 10,000 ppm for 15 min.
- ▶ United Kingdom - PEL = 5,000 ppm, STEL = 15,000 ppm for 10 min.

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CHAPTER 8: Physical Hazards and Including Bulk Shipment of Liquefied Carbon Dioxide

Physical Hazards of Carbon Dioxide

The physical hazards of carbon dioxide are centered around its pressure and temperature. It can be routinely handled safely by keeping in mind a few important characteristics of this gas:

- ▶ **Carbon dioxide is approximately 50% heavier than air** and tends to sink. Limited ventilation can allow carbon dioxide to reach very hazardous concentrations. *NOTE: Although it is heavier than air, warm carbon dioxide will float away and not sink. It can then travel to remote locations as it cools, collecting in areas that are unsuspected*
- ▶ **When handling or working around piping systems**, escaping carbon dioxide gas becomes **very cold**. The longer the gas release and the higher the initial pressure, the colder it becomes. Therefore, the piping, manifolds, valves (including control valves and check valves), pressure relief devices, hoses, regulators, flowmeters, mass flow controllers, and other components of the mechanical systems can become extremely cold.
- ▶ **In the presence of moisture, carbon dioxide forms carbonic acid**, a weak acid.
- ▶ **Pressurized CO₂ can cause severe injuries** to the eyes, face, hands, and other exposed parts of the body when released.

Using materials of construction and personal protective equipment specifically designed to be compatible with these physical and chemical properties are essential to its safe handling.

Materials of construction must be designed to withstand the elevated pressures, very low temperatures, and acidic conditions. Piping systems and vessels should be designed to have a working pressure as specified by competent engineers using a safety factor conforming to the ASME code for pressure piping and vessels.²¹ See “Safe Handling” for materials recommendations.

²¹ Matheson Gas Data Book, Matheson Gas Products, Secaucus, NJ, 1980, p. 120-124

Routine inspection and testing of equipment, and maintaining records of these inspections and tests, especially of hoses, piping systems, relief devices and other service equipment (including but not limited to specific equipment states above) to ensure it is adequate to continue in carbon dioxide service. Establish a procedure for inspecting and maintaining at regular intervals all piping, tubing, hoses, fittings and other equipment in CO₂ service. The entire system should be maintained by qualified personnel in accordance with the manufacturer's instructions and recommendations.

Leak testing is also important, **and** in addition to this, area **continuously monitoring CO₂ detectors** should be installed (with battery back-up in case of a power failure) that give an audible alarm and a flashing light when carbon dioxide concentrations exceed their set point. This set point should be no higher than 5,000 ppm. It is also highly recommended that the remote sensors are tied to control panels so that operating personnel are warned electronically when the levels are high.

Bulk Shipments of Carbon Dioxide

Carbon dioxide is one of the most common liquefied compressed gases shipped by rail car or over-the-road tank trucks. "Typical shipping containers for bulk shipments of liquefied compressed gases are single-unit tank cars, multi-unit tank cars (TMUs), and cargo tanks."²²

General principles²³ that need to be addressed for safely handling liquefied carbon dioxide in railcars and tank trucks include:

- ▶ Understanding the physical and chemical properties.
- ▶ Using equipment specifically designed to be compatible with these physical and chemical properties.
- ▶ Fully complying with the regulations and standards governing their handling.
- ▶ Implementing appropriate procedures designed to minimize accidents which could result from human failure.



²² Handbook of Compressed Gases, The Compressed Gas Assc., Inc., Chantilly, VA; 5th ed., 2013

²³ Handbook of Compressed Gases, The Compressed Gas Assc., Inc., Chantilly, VA; 5th ed., 2013

Carbon Dioxide Shipping Information Chart ²⁴	
DOT Proper Shipping Name	Carbon Dioxide Carbon Dioxide, refrigerated liquid Carbon Dioxide, solid or dry ice
Dot Hazard Class	2.2 (Non-flammable gas) 9 (Dry ice)
DOT Label	NON-FLAMMABLE GAS (no label required for Carbon Dioxide as solid or dry ice)
TC Shipping Name	Carbon Dioxide Carbon Dioxide, refrigerated liquid Carbon Dioxide, solid or dry ice
TC Classification	2.2 9 (dry ice)
UN Number	UN 1013 (for compressed gas) UN 2187 (for refrigerated liquid) UN 1845 (for solid)

Current U.S. DOT regulations as well as any state and local rules and standards that may apply need to be consulted in addition to this industry standard when handling bulk shipments of liquefied carbon dioxide. This safety manual is only meant to supplement the regulations and standards and provide safe handling information. Note that all local, state and DOT regulation in place in the jurisdiction supersedes these recommendations.

Since it is not possible to delineate all the safe handling practices to be used when handling carbon dioxide at any particular facility, it is the intent of this Carbon Dioxide Safety Program to establish and highlight the more important principles to be considered and implemented. It is designed to assist Managers with their paramount responsibilities for the protection of the safety and health of people, and the control of property damage and assets at their facilities.

This information follows.

²⁴ Handbook of Compressed Gases, The Compressed Gas Assc., Inc., Chantilly, VA; 5th ed., 2013

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CHAPTER 9: Process Controls

Materials of Construction

According to the recommendations of the Compressed Gas Association, Inc.:

Common commercially available metals can be used for carbon dioxide installations (those not handling carbon dioxide in aqueous solutions). Any carbon dioxide system at the user's site must be designed to safely contain the pressures involved and must conform with all state and local regulations. See also CGA G-6.1, Standard for Low Pressure Carbon Dioxide Systems at Consumer Sites. For low-pressure carbon dioxide systems (up to 400 psig or 2758 kPa), containers and related equipment should have design pressures rated at least 10% above the normal maximum operating pressure.

For such systems, Schedule 80 threaded pipe with forged steel fittings rated at 2,000 psi (13,790 kPa) or seamless Schedule 40 steel pipe with welded joints is recommended; alternate recommendations include stainless steel, copper, or brass pipe and stainless steel or copper tubing. Special materials and construction are required for containers operating at temperatures below -20°F (-28.9°C).

Since carbon dioxide forms carbonic acid when dissolved in water, systems handling carbon dioxide in aqueous solutions must be fabricated from such acid-resistant materials as certain stainless steels, Hastelloy metals, or Monel metal.²⁵ During the design phase of a carbon dioxide generation facility, the location should be chosen to be above grade so that dangerous levels of carbon dioxide have more chance of dissipating rather than accumulating. According to recommendations of Federal OSHA, “even when carbon dioxide is delivered in enclosed areas or below grade locations that are not confined spaces, it is necessary to ventilate such areas adequately to maintain a safe working environment for personnel.” And because CO₂ is 1.5 times heavier than air, it is generally found concentrated at lower levels and areas where there is limited air movement. When designing ventilation systems, exhaust from the lowest level and allow make-up air to enter at a higher point.²⁶

²⁵ *Handbook of Compressed Gases*, Compressed Gas Association, Arlington, VA, 2013; Van Nostrand Reinhold, NY, NY

²⁶ OSHA Hazard Information Bulletins, Potential Carbon Dioxide (CO₂) Asphyxiation Hazard When Filling Stationary Low Pressure CO₂ Supply Systems”, http://www.osha.gov/dts/hib/hib_data/hib19969605.html

It is critical that the atmosphere is monitored for CO₂ and local exhaust ventilation is installed where the levels may exceed 2,500 (1/2 the PEL). **NEVER depend upon measuring the oxygen levels instead**, because CO₂ can be lethal, even when oxygen concentrations are 20.9% (normal concentration in outside fresh air).

Warning Signs

Informative warning signs should be strategically placed at entry points to areas where it is possible for carbon dioxide to accumulate. The following language is an example:

WARNING! CARBON DIOXIDE GAS!
Ventilate the Area
A High CO₂ Gas Concentration May Occur in This Area and
May Be Hazardous or Even Cause Death!

Personal Protective Equipment

Personal protective equipment, or PPE, is considered the last line of defense to protect the health and safety of workers. PPE needs to be worn as part of a complete CO₂ exposure safety and health plan, and is designed to supplement engineering and administrative controls. It is not legal to use PPE as a substitute for these controls unless they are impossible or not feasible to implement. Legally, cost is not allowed to be considered a factor.

Training on the proper use and limitations of all appropriate employee personal protective equipment, including breathing-quality, supplied-air respiratory protection, must be done before the initial use. A separate PPE program and Respiratory Protection Program that each, at the least, complies to the relevant OSHA standards needs to also be written, trained on, and made readily available to workers.



Working with or around gaseous CO₂ at or above 2 atmospheres, or 44.3psig

Specific PPE needs to be worn in areas where overexposure to pressurized CO₂ can occur, or when working on process lines or equipment that were once under pressure, (even if lines are bled off). The minimum necessary PPE for workers making, breaking or working on or near pressurized CO₂ lines or equipment that do not contained liquefied CO₂ include:

- ▶ Hard hat,
- ▶ Goggles (to protect the eyes),
- ▶ Full face shield (to protect the face and neck),
- ▶ Leather or heavy insulated gloves with gauntlets reaching to mid-forearm,
- ▶ Shirts with full length sleeves,
- ▶ Long pants,
- ▶ Resistant apron or body protection (coveralls are fine),
- ▶ Sturdy work boots,
- ▶ A direct-reading electronic CO₂ monitor should be running continuously in the worker's immediate (within 2 feet) work area.

All equipment and lines must be bled down, blocked, and properly locked and tagged out of service before the work begins. Consider having a second worker serving as a safety watch during the initial phases, especially the line breaking, of this work.

Working with or around liquid or solid CO₂

Because of its very cold properties and elevated pressures, liquefied CO₂ can cause freezing burns, frostbite, and extreme eye damage including blindness. Clothing must be resistant to temperatures below 109°F (47°C). Leaks of liquefied gas can cause life-threatening concentrations of CO₂ to occur within seconds. Therefore, in addition to the equipment listed below, supplied air must be provided.

The potential concentration of CO₂, the projected duration of the job, and the ease of use are all factors that must be considered when deciding what kind of supplied air is most appropriate. A full face, airline respirator supplied from a breathing air source or a breathing air (ONLY) compressor, as well as a 5 or 10 minute escape bottle of breathing air (in case of failure of the supplied air system) are minimum requirements. However, an SCBA (Self Contained Breathing Apparatus) that is pressure demand or one that maintains positive pressure may be easier for jobs of short duration in more remote areas of the facility.

In addition to supplying a full face respirator supplied with breathing-quality air (see above paragraph), other PPE necessary include:

- ▶ Hard hat,
- ▶ Heavy insulated gloves with gauntlets reaching to the elbow, gloves worn under the body suit, and gloves cuffed. Gloves must be impermeable to liquid carbon dioxide,
- ▶ Long pants and long-sleeved shirt under a resistant, impervious body suit,
- ▶ Work boots, with body suit worn OVER the boots, not tucked into the boots,
- ▶ Full body protection – coveralls are not good enough; must be resistant to liquid,
- ▶ A direct-reading electronic CO₂ monitor should be running continuously in the worker's immediate (within two feet) work area.

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CHAPTER 10: Ventilation Principles; with Illustrations Demonstrating Specific Techniques

The single greatest hazard of carbon dioxide occurs when people are exposed to excessive concentrations and experience adverse health effects as a result. Areas needing special consideration include:

- ▶ Confined areas and confined spaces, including diked areas around any kind of tank;
- ▶ Ground floor locations and other low-lying areas, including those outdoors and water treatment (including anaerobic and aerobic tanks);
- ▶ Locations with restricted or limited ventilation whatever the elevation, especially those areas where people rarely need to go;
- ▶ Locations where carbon dioxide is given off from processes, including inside the buildings that house the fermentation tanks, yeast propagation, grain unloading, hoppers, slurry/mash “steep” tanks, drains that collect liquid materials and pump it out, and
- ▶ Areas where carbon dioxide is collected and discharged, especially the carbon dioxide scrubber.
- ▶ Consider your unique facility and try to evaluate/locate other areas that may have high CO₂ levels by using a direct-reading monitor.

Forced draft or mechanical ventilation is generally divided into two broad categories: **supply ventilation** – blowing fresh air into the area; and **exhaust ventilation** – pulling air out by negative pressure and exhausting it in a safe area, away from the air intake. When there is little air flow, carbon dioxide tends to collect in low lying areas since it is 50% more dense than air. Because of this, exhausting (pulling) air through ductwork from a low point to the outside where it can be discharged safely – away from the air intake – and bringing in make-up air coming from above, is generally considered most efficient.

In confined spaces, either continuous mechanical ventilation or continuous air monitoring is required. In practice, most organizations do both whenever possible. Exhaust systems are most effective when the air intake is located as close as possible to the immediate area where workers are present. This results in the workers being in the path of the incoming fresh air. See illustration numbers 1, 2, 3, and 4 on the following pages.

Supply ventilation is the process of blowing fresh air into the space and exhausting it outside. This is often a useful practice, especially when fresh air is used to push contaminated air out of the space. This is because blowing air into the space moves contaminants up to 30 times the distance that exhaust air can. In addition, supply ventilation is helpful when air movement is provided for the comfort of the workers inside, and to ensure fresh breathing air so that air does not become stagnant during the course of the job. If done properly, mechanical ventilation may sometimes eliminate the need for workers to wear respiratory protection.

There are however, disadvantages to using mechanical ventilation. It is noisy, ductwork can restrict entry to/exit from the space, the air flow can blow up dust and other contaminants causing irritation to those inside, and the air movement generates static electricity. Precautions including grounding and bonding, hearing protection, goggles and other measures for safe egress need to be considered during the job planning.

No matter how good the intention, if ventilation is not set up properly, air movement can be short-circuited. This means that air only circulates in a small area of the confined space, leaving the rest of the space unventilated. See the illustrations of poor and good ventilation techniques below.²⁷

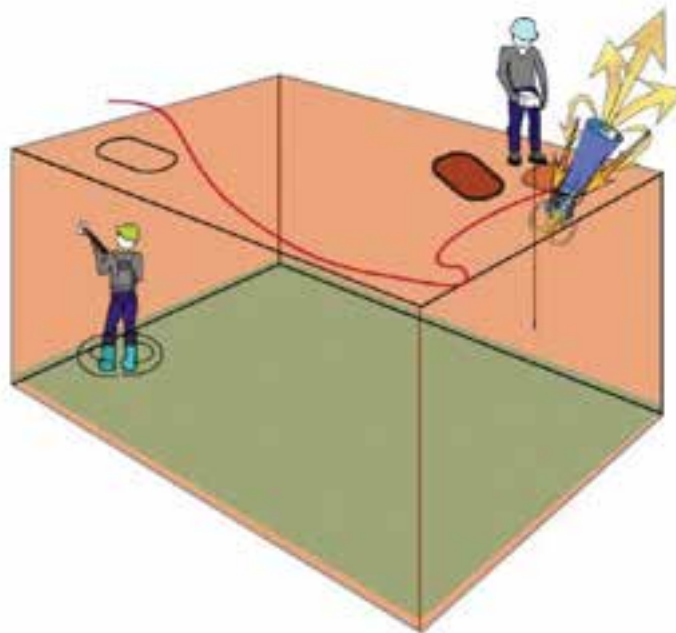


Illustration 1 — Shows exhaust ventilation being short-circuited; the space is not being ventilated as necessary. Also, note other issues, including that the atmosphere is not being monitored where the entrant is working.

Source: Edward J. Willwerth, Atlantic Environmental & Marine Services

²⁷ US Federal OSHA, OSHA publication 3639-04 2013, *Ventilation in Shipyard Employment*, 2013

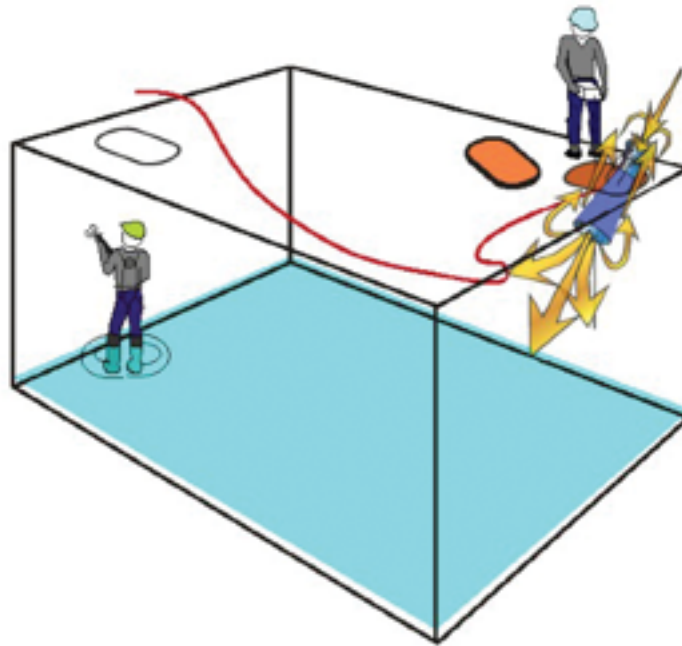


Illustration 2 — Shows supplied ventilation being short-circuited.
 Source: Edward J. Willwerth, Atlantic Environmental & Marine Services

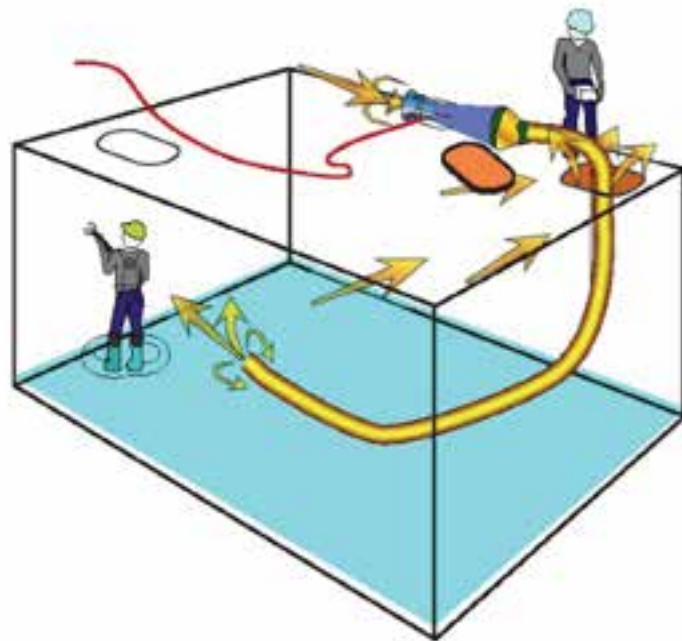


Illustration 3 — Shows efficient method of supplied ventilation (forced air) with system away from tank opening.
 Source: Edward J. Willwerth, Atlantic Environmental & Marine Services

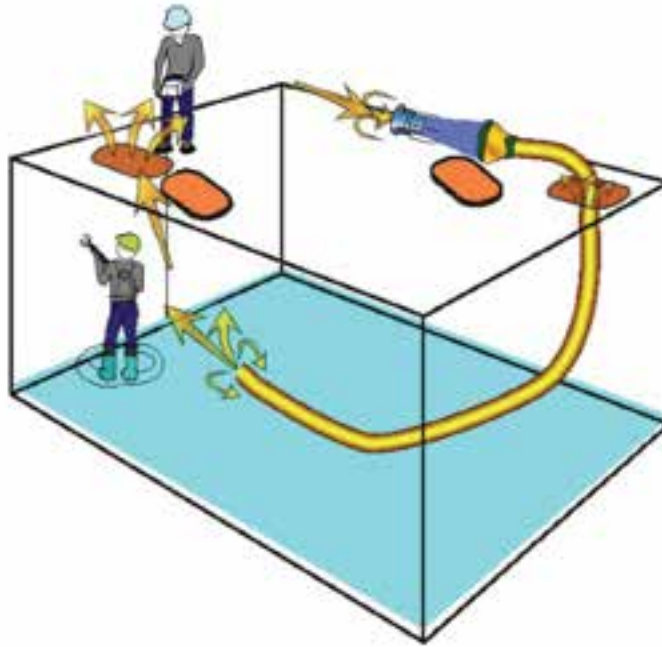


Illustration 4 — Shows enhanced method of supplied ventilation (forced air) when two accesses are available.

Source: Edward J. Willwerth, Atlantic Environmental & Marine Services

Providing safe breathing air to workers requires significant pre-planning when workers are doing hot work (cutting, welding, burning), working with solvents, sanitation agents, or other chemicals in a confined spaces, or when spray-painting or spray-applying any surface coating. Since this is beyond the scope of this Carbon Dioxide Safety Program, refer to specialized references and to the equipment manufacturer for technical support. In these cases, supplied air respirators in addition to forced-draft/mechanical ventilation may be necessary, not only to protect the worker but to keep flammable atmospheres from developing.

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CHAPTER 11: Carbon Dioxide Sampling Equipment

Overview

Many different types of equipment are available to detect the presence of carbon dioxide, from levels that exceed background up to levels that exceed life-threatening concentrations. The broad types of equipment available and described below all measure carbon dioxide without needing to have samples analyzed by a laboratory and thus waiting for their analysis to get the results – which can often exceed a week or more. The equipment described below all give CO₂ concentrations immediately, within minutes, or by the end of the workshift.

The electronic monitors are the fastest, the most reliable and the most accurate. These include portable single gas monitors that can be worn or hand held, portable multi-gas monitors that are excellent for confined space entry and other uses, and single-gas, stationary CO₂ monitors that can give an audible alarm, flashing lights and also be tied in to a computer remotely to inform workers when an area of the facility exceeds a set threshold level of CO₂.

An explanation of the theory of operation of each of these types of equipment follows.

NOTE: Examples of the types of equipment described in this section and the brands shown in the Appendices A through C are for demonstration purposes only. Their use in this document is not to be construed as an endorsement of any of these specific products by the RFA.

Lastly, OSHA and NIOSH also have sampling methods that have been reviewed and these include the equipment types described below as well as methods that need to be analyzed by a laboratory. Consult the Appendices for equipment examples as well as OSHA sampling methods. Specifically, see **Appendix D: Additional OSHA CO₂ Sampling Methods**, for these government-approved methods.

Portable and Stationary Electronic Carbon Dioxide Gas Monitors

Theory of Operation NDIR Sensors

According to Robert Henderson, MBA, President of GFG Instrumentation, Inc., Ann Arbor, MI., a recognized technical expert in direct-reading monitoring equipment, this is the theory of how these sensors work:

The most widely used technique for real-time measurement of carbon dioxide is by means of non-dispersive infrared (NDIR) sensors that measure CO₂ as a function of the absorbance of infrared light at a specified wavelength.

Molecules can be conceptualized as balls (atoms) held together by flexible springs (bonds) that can vibrate (stretch, bend, or rotate) in three dimensions. Each molecule has certain fixed modes in which this vibratory motion can occur. Vibrational modes are dictated by the nature of the specific bonds that hold the molecule together. The larger the molecule, the greater the number of modes of movement. Each mode represents vibrational motion at a specific frequency. The modes are always the same for a specific molecule. Chemical bonds absorb infrared radiation. The bond continues to vibrate at the same frequency but with greater amplitude after the transfer of energy. For infrared energy to be absorbed (that is, for vibrational energy to be transferred to the molecule), the frequency must match the frequency of the mode of vibration.

Specific molecules absorb infrared radiation at precise wavelengths. When infrared radiation passes through a sensing chamber containing a specific contaminant, only those wavelengths that match one of the vibration modes are absorbed. The rest of the light is transmitted through the chamber without hindrance. The presence of a particular chemical group within a molecule thus gives rise to characteristic absorption bands. Because most chemical compounds absorb at a number of different frequencies, IR absorbance can provide a “fingerprint” for use in identification of unknown contaminants.

Alternatively, for some molecules it may be possible to find an absorbance peak at a specific wavelength that is not shared by other molecules likely to be present. In this case, absorbance at a particular wavelength can be used to provide substance-specific measurement for a specific molecule. Carbon dioxide has such an absorbance peak at a wavelength of 4.26 microns (μm).

Absorbance of infrared light at this wavelength is proportional to the concentration of CO₂ present in the sensor’s sensing chamber. The absorbance is not linear per concentration unit but is mathematically predictable and easily calculated by microprocessor-equipped portable gas detectors.

How the Electronic CO₂ Sensor Works

Miniaturized NDIR CO₂ sensors include an infrared light source (typically a tungsten filament lamp) capable of emitting light in the desired wavelengths. Optical filters are used to limit the light transmitted through the sensing chamber to a narrow range of wavelengths. Most NDIR CO₂ sensors are dual detector systems that provide both a reference and an active signal. Pyroelectric detectors capable of measuring absorbance at the specific wavelengths of interest are used to provide the measurement and reference signals. The active detector in a CO₂ sensor measures the amount of light in the 4.26 microns (μm) range that reaches the detector after passing through the sensing chamber. The reference detector measures the amount of light at another wavelength (or range of wavelengths) where there is no absorbance for the gas of interest. The greater the concentration of CO₂, the greater the reduction in the amount of light that reaches the active detector when compared to the reference signal.²⁸

NDIR equipment is now very commonly used in portable gas monitors and CO₂ is a readily available gas for detectors. Many wineries, breweries, fuel ethanol manufacturers, coal mines, fracking operations, grain handlers, shipyards, municipalities, sewage treatment facilities, concrete producers, contractors, and a wide variety of other industries that have the potential for carbon dioxide exposures use these instruments because they are rugged, easy to calibrate, and a relatively inexpensive way to keep workers safe.

See **Appendix C: Direct Reading Portable and Stationery Electronic Instruments, Including for Multi-Gas Monitors**, for equipment examples.

²⁸ http://oshonline.com/Articles/2006/07/Carbon-Dioxide-measures_up-as-a-Real-Hazard.aspx

Direct-Reading Detector Tubes

These inexpensive, simple-to-use instruments have been available for many decades to do spot checks for the presence of hazardous air-borne gases and vapors in the immediate area. Detector tubes usually get a usable reading within 5-10 minutes. They are not used to measure personal exposures, only the air in a specific area.

Theory of Operation of Detector Tubes

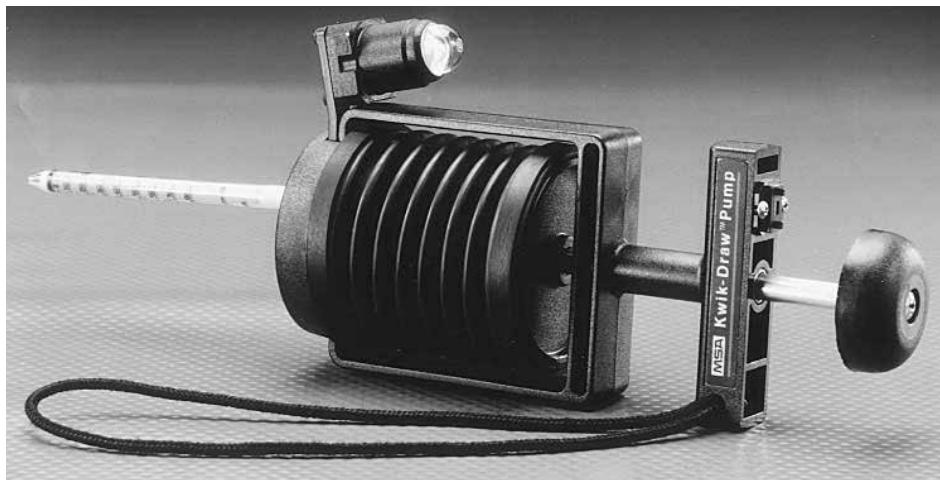
Detector tubes work on the principle that each airborne substance can react chemically with a specific material. The reaction is designed to cause a color change in the tube.



Examples of MSA Detector Tubes

Note: no air can reach the chemical inside the tube until the glass tip on each end is broken off

The tubes are made of glass with sealed ends. Inside each tube is a particular chemical designed to react with a specific airborne contaminant to be tested for.



MSA Detector Tube Pump

To perform the air test, the tip of each end is broken off and the tip of the tube that is marked as the end is inserted into a hand pump. The pump pulls precisely 100 ml of air through the tube with each stroke. As the air is drawn through the tube, the contaminant of interest reacts with the chemical in the tube, causing it to change color. The side of the tube is calibrated so that the user can read directly how much of the contaminant is present by how long the color change inside the tube is and how many pump strokes it took for the color change to reach that point.

Many manufacturers make these detector tubes and pumps, and most sell a wide variety of detector tubes, since every air contaminant has a different and specific tube (with a specific chemical inside) for its detection.

Each type of detector tube has specific chemicals that interfere with accurate readings. This information, as well as more details regarding operation, readings, and limitations, is contained in the box. Detector tubes have a listed accuracy of 25%.

The tubes need to be read immediately and are discarded after one use. These tubes have a marked shelf life, usually from six months to three years. The life of these detector tubes is usually best maintained by keeping them refrigerated, although most manufacturers state that this is not required. See **Appendix A: Direct Reading Carbon Dioxide Detector Tubes**, for other equipment examples.

Dosimeter Tubes

Dosimeter tubes look a little like detector tubes, because they are glass tubes with a particular chemical inside that reacts with the specific airborne contaminant to be measured. These tubes are different, though, because they do not work with a pump; instead, they work on the principle of air diffusion.

Dosimeter tubes can be used to measure personal worker exposures to CO₂ over a specified time period, usually 4-8 hours. They can also be placed in work areas to measure exposures over the course of hours in a specific place. The dosimeter tube is placed in a tube holder, then clipped to the worker's collar or other location in his/her breathing zone, or taped to a wall or similar location for an area sample.

For pictures and an example of a CO₂ dosimeter tube, see **Appendix B: Example Direct-Reading Dosimeter Tubes (for Personal and Area Exposure Monitoring)**.

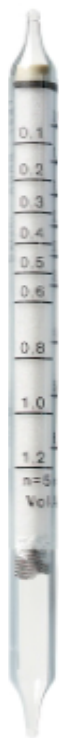
A

APPENDIX A: Direct Reading Carbon Dioxide Detector Tubes

For other detectors tube examples, see the photos in the theory of operation in previous section.

NOTE: The instrumentation shown in these Appendices is for demonstration purposes only. Their use in this document is not to be construed as an endorsement of any of these products by the RFA.

Detector Tube: GASTEC Carbon Dioxide 0.1%/a CH 23501



Order No. CH 23501

Standard Measuring Range : 0.5 to 6 / 0.1 to 1.2 Vol.-%

Number of Strokes (n) : 1 / 5

Time for Measurement : app. 30 s / app. 2.5 min

Standard Deviation : ± 5 to 10 %

Colour Change : white to pale violet \rightarrow

blue violet

Ambient Operating Conditions

Temperature : 0° to 30° C

Absolute Humidity : max. 30 mg H₂O / L

Reaction Principle

CO₂ + Amine \rightarrow blue violet reaction product

Cross Sensitivity

Hydrogen sulphide and sulphur dioxide in the TLV range do not interfere.

B

APPENDIX B: Example Direct-Reading Dosimeter Tubes (for Personal and Area Exposure Monitoring)

GASTEC No.2D Instructions for Carbon Dioxide Passive Dosi-Tube

FOR SAFE OPERATION :

Read this manual carefully before use.

⚠ CAUTION : If not observed, injuries to the operator or damage to the product may result.

1. When breaking the Passive Dosi-Tube, keep away from eyes
2. Do not touch the broken glass tubes, pieces and reagent with bare hand(s).
3. Keep tubes out of Direct Sunlight. The sunlight fades the discoloration of the tube.

△ NOTES : For maintaining performance and reliability of the test result

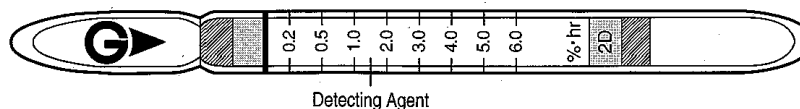
1. Use this tube within the temperature range of 0 - 40°C (32 - 104°F).
2. Use this tube within the relative humidity range of 0 - 90%.
3. This tube may be interfered by the coexisting gases. Please refer to the "INTERFERENCES".
4. Shelf life and storage conditions of the Passive dosi-tube are marked on the label of the box of tube.

APPLICATION OF THE TUBE :

Use this tube for the detection of Carbon Dioxide in air or the industrial areas and environmental atmospheric condition.

SPECIFICATION :

(As a result of Gastec's commitment to continued improvement, specifications are subject to change without notice.)



Detecting Agent

Measuring Range	0.02 - 12 %
Sampling Time	0.5 - 10 hours
Detecting Limit	0.02 % (10 hours)
Color Change	Orange → Yellow
Reaction Principle	Carbon Dioxide neutralizes analyzing agent to produce yellow stain.

**** Shelf Life :** Please refer to the Validity Date printed on the box of tube.

**** Store the tubes in dark and cool place.**

CORRECTION FOR TEMPERATURE, HUMIDITY AND PRESSURE :

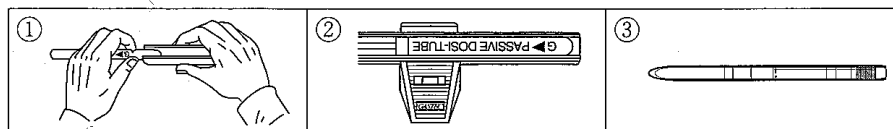
Temperature : For tube temperature other than 20°C, tube reading must be corrected the tube reading according to the correction factor below:

Temperature °C (°F)	0 (32)	10 (50)	20 (68)	30 (86)	40 (104)
Correction Factor	1.3	1.2	1.0	1.0	0.9

Humidity : Humidity correction is not required.

Pressure : Pressure correction is not required.

MEASUREMENT PROCEDURE :



NOTE: The instrumentation shown in these Appendices is for demonstration purposes only. Their use in this document is not to be construed as an endorsement of any of these products by the RFA.

1. Break the tube at the score of the tube with Gastec Passive Dosi-Tube Holder No. 710.
2. Set the Dosi-tube in the Tube Holder firmly inside the holder so the broken part is not appeared from the edge of the holder. Record the measurement starting time on the peel off numbered label in each box of the tube and put the label on the tube.
3. For personal sampling, put the dosi-tube holder to the shirt collar of the personnel or workplace where the measurement is required. When the sampling is finished, record the time on the label of the tube.
4. Average gas concentration can be obtained from an hour sampling. 4 - 10 hours sampling term is recommended. Calculate actual sampling time and obtain the average gas concentration can be obtained by the following formula :

$$\text{Average Concentration} = \frac{\text{Dosi-Tube Reading (\% hour)}}{\text{Actual Sampling Time (hour)}}$$

5. To protect the tube holder of shirt collar from dropping during operation, support the tube holder with string through a small hole of the tube holder.

INTERFERENCES :

Substance	Concentration	Interference	Change color by itself
Ammonia	500 ppm or lower	No effect	No discoloration up to 500ppm
Hydrogen chloride	500 ppm or lower	No effect	No discoloration up to 500ppm
Chlorine	10 ppm or lower	No effect	No discoloration up to 5ppm
Hydrogen cyanide	50 ppm or lower	No effect	No discoloration up to 30ppm
Sulfur dioxide	15 ppm or lower	No effect	No discoloration up to 15ppm
Nitrogen dioxide	10 ppm or lower	No effect	No discoloration up to 10ppm
Hydrogen sulfide	50 ppm or lower	No effect	No discoloration up to 30ppm

DANGEROUS AND HAZARDOUS PROPERTIES :

Threshold Limit Value-Time Weighted Average by ACGIH (1999) : 5000 ppm (7 - 8 hours)

DISPOSAL INSTRUCTION :

Reagent of the tube does not use toxic substances. On disposing the tube regardless of whether used or unused, follow the rules and regulations of the local government.

WARRANTY :

If you have any questions regarding gas detection and quality of the tubes, please feel free to contact your Gstec representatives.

Manufacturer : Gastec Corporation
6431 Fukaya, Ayase-City, 252-1103, Japan

IM012DE1
Printed in Japan
00A1Z

C

APPENDIX C: Direct Reading Portable and Stationery Electronic Instruments, Including for Multi-Gas Monitors

NOTE: The instrumentation shown in these Appendices are for demonstration purposes only. Their use in this document is not to be construed as an endorsement of any of these products by the RFA.

Single CO₂ Gas Detector

Product # 36F313

Item # 36D915

Mfr. Model # 8318975

UNSPSC # 46171613

Technical Specs

Item: Single Gas Detector

Gas Type: CO₂

Detects Carbon Dioxide

Sensor Range: 0 to 5 Vol %

Resolution: 0.1 Vol % (1000 ppm)

Operating Temp. Range: 20 to 120 Degrees F

Alarm Setting A1 - 0.5 Vol %, A2 - 1 Vol %

Alarm Type: Audible, Visual, Vibrating

Battery Type: Alkaline Lithium

Battery Life: 13 mos.

Display: LCD

Interchangeable Sensors: No

Height: 3-3/8"

Width: 2-1/2"

Depth: 7/8"

Standards Rated Intrinsically Safe by UL, CSA, and ATEX

Features: simple two-button operation, integral rubber over mold for durability, large display with bright backlight, loud audible, bright visual and robust vibrating alarms

Includes Instrument, Lithium Alkaline Battery

Details: Small, robust personal monitor has user-friendly features including a large LCD with backlight and 1-handed operation, even when wearing gloves. Automatic bump tests.

Adjustable intervals for tests and calibration, reminders, and "out of order" message if overdue or failed. 120-hr. data logger has date and time stamp.



- Adjustable TWA and STEL alarms
- IP65 dust and water ingress protection

Direct Reading Portable Electronic Multi-Gas Monitors

NOTE: The instrumentation shown in these Appendices are for demonstration purposes only. Their use in this document is not to be construed as an endorsement of any of these products by the RFA.

GfG G460 Multi-Gas Detector

G460 Multi-gas Detector with optional built-in flashlight

Exceptional Confined Space Performance

- ▶ Compact and robust 1-to-6 gas design
- ▶ Full 3-year warranty on O₂, LEL, H₂S, CO and COSH sensors
- ▶ Direct reading sensors for CO₂, NH₃, SO₂, Cl₂, ClO₂, NO₂, NO, PH₃, HF, O₃ and PID for VOC measurement
- ▶ Optional motorized pump operates in diffusion or sample-draw mode
- ▶ Highly water resistant (IP 67)
- ▶ Top-mounted, back-lit, three color graphic display
- ▶ Bright, flashing 360° LED alarms and loud 103 dB buzzer
- ▶ Optional built-in “flash light” LEDs
- ▶ Event and datalogging standard



Direct Reading Stationary Instruments

NOTE: The instrumentation shown in these Appendices are for demonstration purposes only. Their use in this document is not to be construed as an endorsement of any of these products by the RFA.



131 Business Center Drive, Unit A-3, Ormond Beach, FL 32174
TEL: 877.678.4259 | FAX: 866.422.2356

EMAIL: sales@co2meter.com | www.co2meter.com

Datasheet: CO2 Transmitter with Display

The Tongdy CO₂ Transmitter lets you transmit, control and monitor indoor air quality. Use it to transmit ambient carbon dioxide levels to an HVAC or demand controlled ventilation system. CO₂ levels can be sent as industry standard 4-20mA or 0-10V signals back to a control panel. Use it to monitor air quality with its easy-to-read backlit LCD display that quickly changes from green to yellow to red as air quality declines. You can also read the CO₂ level directly from the display. With its single-button ease of use and industry-standard 24V power requirements, the Tongdy CO₂ Transmitter with Display is perfect for anywhere monitoring and controlling indoor air quality is important.

Real-time Carbon Level Transmitter and Monitor
3-Color backlit LCD to Easily Check IAQ
Industry-Standard Wall-Mount

CO₂ Sensor

Measurement Range 0 - 5,000 ppm
Sensing Method non-dispersive infrared (NDIR) waveguide technology with ABC automatic background calibration algorithm
Sampling Method Diffusion
Response Time (T_{1/4}) < 2 minutes for 90% step change
Signal update Every 2 seconds
Warm up time 2 hours after initial power up for ABC calibration, 2 minutes on subsequent use

General Performance

Operating Temperature Range 32 - 122°F (0 to 50 °C), 0 - 95% RH non condensing
Storage Temperature Range 14 - 140°F (-10 to +60 °C), 5 - 95% RH non condensing
Sensor Life Expectancy > 15 years
Maintenance Interval no maintenance required
Self-Diagnostics complete function check of the sensor module
Warm-up Time ≤ 5 minutes
Conformance with the standards..... CE-Approval
Operating Environment Residential & business indoor spaces

Electrical/Mechanical

Power Input..... 24 VAC/VDC
Current Consumption 2.8 W average, 3.5 W Max.
Signal Output 4-20mA or 0-10V Standard
Housing PC/ABS fireproof plastic material; protection class IP30
Dimensions 130mm (H) × 85mm (W) × 36.5mm (D), 200g

Warranty

Model TON-0002 1 Year

D

APPENDIX D: Additional OSHA CO₂ Sampling Methods

Monitoring Methods Used by OSHA

https://www.osha.gov/dts/chemicalsampling/data/CH_225400.html

Primary Laboratory Sampling/Analytical Method (SLC1):

sampling media: Five Layer Aluminized Gas Sampling Bag (5 liter)

maximum volume: 5.0 Liters

maximum flow rate: 0.05 L/min (TWA)

maximum volume: 4.5 Liters

maximum flow rate: 0.3 L/min (STEL)

minimum volume: 2.0 Liters

current analytical method: Gas Chromatography; GC/TCD

method reference: 2 ([OSHA ID-172](#))

sampling analytical error: 0.11

method classification: Fully Validated

note: Use Detector tubes for screening. If greater than PEL call lab+ for gas sampling bags.

Secondary Laboratory Sampling/Analytical Method (SAM2):

► **device:** Detector Tube

company: Gastec

part #: 2L

range: 0.13-6.0 %v

class: SEI certified

► **device:** Detector Tube

company: Draeger

part #: CH 23501

range: 0.5-6 %v

class: SEI certified

► **device:** Detector Tube

company: Matheson/Kitagawa

part #: 8014-126SA

range: 0.1-2.6 %

class: SEI certified

► **device:** Instrumentation

company: Infrared Spectrophotometer

part #: MIRAN 1A & 1B

range: 0.4 ppm @ 4.3 µm

class: Mfg

► **device:** Instrumentation

company: Infrared Spectrophotometer

part #: MIRAN 103

range: 2% @ 4.45 µm

class: Mfg

Laboratory Sampling/Analytical Method (Wisconsin OHL):

sampling media: Evacuated Cans - Back Filled with Nitrogen (Hold button down for a full 10 seconds)

maximum volume: 120 mLiters

current analytical method: Gas Chromatography; GC/TCD

method reference: (WOHL In-House File)

method classification: Not Validated

note: Use Detector tubes for screening. If greater than PEL call Wisconsin Occupational Health Laboratory (WOHL) for evacuated cans. If a TWA determination is desired collect a 5 liter sample in gas sampling bag. A grab sample can then be collected from the bag using the evacuated cans.

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E

APPENDIX E: (M)SDS for CO₂



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Print Date 10/27/2014

1. PRODUCT AND COMPANY IDENTIFICATION

Product name	: Carbon Dioxide
Chemical formula	: CO ₂
Synonyms	: Carbon dioxide, Carbonic Anhydride, Carbonic Acid Gas, Carbon Anhydride
Product Use Description	: General Industrial
Manufacturer/Importer/Distributor	: Air Products and Chemicals, Inc 7201 Hamilton Blvd. Allentown, PA 18195-1501 GST No. 123600835 RT0001 QST No. 102753981 TQ0001
Telephone	: 1-610-481-4911 Corporate 1-800-345-3148 Chemicals Cust Serv 1-800-752-1597 Gases/Electronics Cust Serv
Emergency telephone number (24h)	: 800-523-9374 USA +1 610 481 7711 International

2. HAZARDS IDENTIFICATION

GHS classification

Gases under pressure - Liquefied gas.
Simple Asphyxiant

GHS label elements

Hazard pictograms/symbols



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Signal Word: Warning

Hazard Statements:

H280: Contains gas under pressure; may explode if heated.
May displace oxygen and cause rapid suffocation.
May cause frostbite.
May increase respiration and heartrate.

Precautionary Statements:

Storage : P410+P403: Protect from sunlight. Store in a well-ventilated place.

Hazards not otherwise classified

Can cause rapid suffocation.
Compressed liquefied gas.
Avoid breathing gas.
Direct contact with liquid can cause frostbite.
Self contained breathing apparatus (SCBA) may be required.

3. COMPOSITION/INFORMATION ON INGREDIENTS

Components	CAS Number	Concentration (Volume)
Carbon dioxide	124-38-9	100 %

Concentration is nominal. For the exact product composition, please refer to Air Products technical specifications.

4. FIRST AID MEASURES

General advice	: Remove victim to uncontaminated area wearing self contained breathing apparatus. Keep victim warm and rested. Call a doctor. Apply artificial respiration if breathing stopped.
Eye contact	: In the case of contact with eyes, rinse immediately with plenty of water and seek medical advice. Keep eye wide open while rinsing. Seek medical advice.
Skin contact	: Wash frost-bitten areas with plenty of water. Do not remove clothing. Cover wound with sterile dressing.
Ingestion	: Ingestion is not considered a potential route of exposure.
Inhalation	: Move to fresh air. If breathing has stopped or is labored, give assisted respirations. Supplemental oxygen may be indicated. If the heart has stopped, trained personnel should begin cardiopulmonary resuscitation immediately. In

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case of shortness of breath, give oxygen.

Most important symptoms/effects - acute and delayed : Exposure to oxygen deficient atmosphere may cause the following symptoms: Dizziness. Salivation. Nausea. Vomiting. Loss of mobility/consciousness. Shivering fit. Sweating. Blurred vision. Headache. Increased pulse rate. Shortness of breath. Rapid respiration.

5. FIRE-FIGHTING MEASURES

Suitable extinguishing media : All known extinguishing media can be used.

Specific hazards : Upon exposure to intense heat or flame, cylinder will vent rapidly and or rupture violently. Product is nonflammable and does not support combustion. Move away from container and cool with water from a protected position. If possible, stop flow of product. Keep adjacent cylinders cool by spraying with large amounts of water until the fire burns itself out. Most cylinders are designed to vent contents when exposed to elevated temperatures.

Special protective equipment for fire-fighters : Wear self contained breathing apparatus for fire fighting if necessary.

6. ACCIDENTAL RELEASE MEASURES

Personal Precautions, Protective Equipment, and Emergency Procedures : Monitor carbon dioxide level. Evacuate personnel to safe areas. Wear self-contained breathing apparatus when entering area unless atmosphere is proved to be safe. Ventilate the area. Monitor oxygen level.

Environmental precautions : Should not be released into the environment. Do not discharge into any place where its accumulation could be dangerous. Prevent further leakage or spillage. Prevent from entering sewers, basements and workpits, or any place where its accumulation can be dangerous.

Methods for cleaning up : Ventilate the area.

Additional advice : If possible, stop flow of product. Increase ventilation to the release area and monitor oxygen level. If leak is from cylinder or cylinder valve, call the Air Products emergency telephone number. If the leak is in the user's system, close the cylinder valve, safely vent the pressure, and purge with an inert gas before attempting repairs.

7. HANDLING AND STORAGE

Handling

Only experienced and properly instructed persons should handle compressed gases/cryogenic liquids. Protect cylinders from physical damage; do not drag, roll, slide or drop. Do not allow storage area temperature to exceed 50°C (122°F). Before using the product, determine its identity by reading the label. Know and understand the properties and hazards of the product before use. When doubt exists as to the correct handling procedure for a particular gas, contact the supplier. Do not remove or deface labels provided by the supplier for

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the identification of the cylinder contents. When moving cylinders, even for short distances, use a cart (trolley, hand truck, etc.) designed to transport cylinders. Leave valve protection caps in place until the container has been secured against either a wall or bench or placed in a container stand and is ready for use. Use an adjustable strap wrench to remove over-tight or rusted caps. Before connecting the container, check the complete gas system for suitability, particularly for pressure rating and materials. Before connecting the container for use, ensure that back feed from the system into the container is prevented. Ensure the complete gas system is compatible for pressure rating and materials of construction. Ensure the complete gas system has been checked for leaks before use. Employ suitable pressure regulating devices on all containers when the gas is being emitted to systems with lower pressure rating than that of the container. Never insert an object (e.g. wrench, screwdriver, pry bar, etc.) into valve cap openings. Doing so may damage valve, causing a leak to occur. Open valve slowly. If user experiences any difficulty operating cylinder valve discontinue use and contact supplier. Close container valve after each use and when empty, even if still connected to equipment. Never attempt to repair or modify container valves or safety relief devices. Damaged valves should be reported immediately to the supplier. Close valve after each use and when empty. Replace outlet caps or plugs and container caps as soon as container is disconnected from equipment. Do not subject containers to abnormal mechanical shock. Never attempt to lift a cylinder by its valve protection cap or guard. Always use backflow protective device in piping. When returning cylinder install valve outlet cap or plug leak tight. Never use direct flame or electrical heating devices to raise the pressure of a container. Containers should not be subjected to temperatures above 50°C (122°F). Never attempt to increase liquid withdrawal rate by pressurizing the container without first checking with the supplier. Never permit liquefied gas to become trapped in parts of the system as this may result in hydraulic rupture.

Storage

Open/close valve slowly. Close when not in use. Wear Safety Eye Protection. Check Safety Data Sheet before use. Use a back flow preventative device in the piping. Use only with equipment rated for cylinder pressure. Read and follow the Safety Data Sheet (SDS) before use. May increase respiration and heart rate. Full containers should be stored so that oldest stock is used first. Containers should be stored in the vertical position and properly secured to prevent toppling. The container valves should be tightly closed and where appropriate valve outlets should be capped or plugged. Container valve guards or caps should be in place. Observe all regulations and local requirements regarding storage of containers. Stored containers should be periodically checked for general condition and leakage. Protect containers stored in the open against rusting and extremes of weather. Containers should not be stored in conditions likely to encourage corrosion. Containers should be stored in a purpose built compound which should be well ventilated, preferably in the open air. Keep containers tightly closed in a cool, well-ventilated place. Store containers in location free from fire risk and away from sources of heat and ignition. Full and empty cylinders should be segregated. Do not allow storage temperature to exceed 50°C (122°F). Return empty containers in a timely manner.

Technical measures/Precautions

Containers should be segregated in the storage area according to the various categories (e.g. flammable, toxic, etc.) and in accordance with local regulations. Keep away from combustible material.

8. EXPOSURE CONTROLS / PERSONAL PROTECTION

Engineering measures

Provide natural or mechanical ventilation to prevent accumulation above exposure limits.
Provide natural or mechanical ventilation to prevent oxygen deficient atmospheres below 19.5% oxygen.

Personal protective equipment

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- Respiratory protection : Self contained breathing apparatus (SCBA) or positive pressure airline with mask are to be used in oxygen-deficient atmosphere. Air purifying respirators will not provide protection. Users of breathing apparatus must be trained.
- Hand protection : Wear working gloves when handling gas containers. Chemical-resistant, impervious gloves complying with an approved standard should be worn at all times when handling chemical products if a risk assessment indicates this is necessary.
- Eye protection : Safety glasses recommended when handling cylinders.
- Skin and body protection : Safety shoes are recommended when handling cylinders.
- Special instructions for protection and hygiene : Ensure adequate ventilation, especially in confined areas.

Exposure limit(s)

Carbon dioxide	Time Weighted Average (TWA): ACGIH	5,000 ppm	-
Carbon dioxide	Short Term Exposure Limit (STEL): ACGIH	30,000 ppm	-
Carbon dioxide	Recommended exposure limit (REL): NIOSH	5,000 ppm	9,000 mg/m3
Carbon dioxide	Short Term Exposure Limit (STEL): NIOSH	30,000 ppm	54,000 mg/m3
Carbon dioxide	Permissible exposure limit: OSHA Z1	5,000 ppm	9,000 mg/m3
Carbon dioxide	Time Weighted Average (TWA): OSHA Z1A	10,000 ppm	18,000 mg/m3
Carbon dioxide	Short Term Exposure Limit (STEL): OSHA Z1A	30,000 ppm	54,000 mg/m3
Carbon dioxide	Time Weighted Average (TWA) Permissible Exposure Limit (PEL): US CA OEL	5,000 ppm	9,000 mg/m3
Carbon dioxide	Short Term Exposure Limit (STEL): US CA OEL	30,000 ppm	54,000 mg/m3
Carbon dioxide	Time Weighted Average (TWA): TN OEL	10,000 ppm	18,000 mg/m3
Carbon dioxide	Short Term Exposure Limit (STEL): TN OEL	30,000 ppm	54,000 mg/m3

9. PHYSICAL AND CHEMICAL PROPERTIES

- Appearance : Liquefied gas. Colorless gas
- Odor : No odor warning properties.
- Odor threshold : No data available.
- pH : Not applicable.
- Melting point/range : -70 °F (-56.6 °C)
- Boiling point/range : -127 °F (-88.1 °C)
- Flash point : Not applicable.

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Evaporation rate	: Not applicable.
Flammability (solid, gas)	: Refer to product classification in Section 2
Upper/lower explosion/flammability limit	: No data available.
Vapor pressure	: 831.04 psia (57.30 bara) at 68 °F (20 °C)
Water solubility	: 2.000 g/l
Relative vapor density	: 1.519 (air = 1) Heavier than air.
Relative density	: 0.82 (water = 1)
Partition coefficient (n-octanol/water)	: Not applicable.
Auto-ignition temperature	: No data available.
Decomposition temperature	: No data available.
Viscosity	: Not applicable.
Molecular Weight	: 44.01 g/mol
Density	: 0.112 lb/ft ³ (0.0018 g/cm ³) at 70 °F (21 °C) Note: (as vapor)
Specific Volume	: 8.74 ft ³ /lb (0.5456 m ³ /kg) at 70 °F (21 °C)

10. STABILITY AND REACTIVITY

Chemical Stability	: Stable under normal conditions.
Conditions to avoid	: No data available.
Materials to avoid	: No data available.
Hazardous decomposition products	: No data available.
Possibility of hazardous Reactions/Reactivity	: No data available.

11. TOXICOLOGICAL INFORMATION

11.1 Information on toxicological effects

Likely routes of exposure

Effects on Eye	: Contact with liquid may cause cold burns/frostbite.
----------------	---

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Effects on Skin	: Contact with liquid may cause cold burns/frostbite.
Inhalation Effects	: Concentrations of 10% CO ₂ or more can produce unconsciousness or death. Unlike simple asphyxiants, carbon dioxide has the ability to cause death even when normal oxygen levels (20-21%) are maintained. Carbon Dioxide is physiologically active, affecting circulation and breathing. At concentrations between 2 and 10%, carbon dioxide can cause nausea, dizziness, headache, mental confusion, increased blood pressure and respiratory rate. In high concentrations may cause asphyxiation. Symptoms may include loss of mobility/consciousness. Victim may not be aware of asphyxiation. Asphyxiation may bring about unconsciousness without warning and so rapidly that victim may be unable to protect themselves.
Ingestion Effects	: Ingestion is not considered a potential route of exposure.
Symptoms	: Exposure to oxygen deficient atmosphere may cause the following symptoms: Dizziness. Salivation. Nausea. Vomiting. Loss of mobility/consciousness. Shivering fit. Sweating. Blurred vision. Headache. Increased pulse rate. Shortness of breath. Rapid respiration.
Acute toxicity	
Acute Oral Toxicity	: No data is available on the product itself.
Inhalation	: Unlike simple asphyxiants, carbon dioxide has the ability to cause death even when normal oxygen levels (20-21%) are maintained. 5% CO ₂ has been found to act synergistically to increase the toxicity of certain other gases (CO, NO ₂). CO ₂ has been shown to enhance the production of carboxy- or met-hemoglobin by these gases possibly due to carbon dioxide's stimulatory effects on the respiratory and circulatory systems.
Acute Dermal Toxicity	: No data is available on the product itself.
Skin corrosion/irritation	: No data available.
Serious eye damage/eye irritation	: No data available.
Sensitization.	: No data available.
Chronic toxicity or effects from long term exposures	
Carcinogenicity	: No data available.
Reproductive toxicity	: No data is available on the product itself.
Germ cell mutagenicity	: No data is available on the product itself.
Specific target organ systemic	: No data available.

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toxicity (single exposure)

Specific target organ systemic toxicity (repeated exposure) : No data available.

Aspiration hazard : No data available.

Delayed and Immediate Effects and Chronic Effects from Short and Long Term Exposure

Not applicable.

12. ECOLOGICAL INFORMATION

Ecotoxicity effects

Aquatic toxicity : No data is available on the product itself.

Toxicity to fish - Components

Carbon dioxide

LC50 (1 h) : 240 mg/l

Species : Rainbow trout (Oncorhynchus mykiss).

Carbon dioxide

LC50 (96 h) : 35 mg/l

Species : Rainbow trout (Oncorhynchus mykiss).

Toxicity to other organisms : No data available.

Persistence and degradability

Biodegradability : No data is available on the product itself.

Mobility : No data available.

Bioaccumulation : No data is available on the product itself.

Further information

When discharged in large quantities may contribute to the greenhouse effect.

13. DISPOSAL CONSIDERATIONS

Waste from residues / unused products : Contact supplier if guidance is required.

Contaminated packaging : Return cylinder to supplier.

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14. TRANSPORT INFORMATION

DOT

UN/ID No. : UN1013
Proper shipping name : Carbon dioxide
Class or Division : 2.2
Label(s) : 2.2
Marine Pollutant : No

IATA

UN/ID No. : UN1013
Proper shipping name : Carbon dioxide
Class or Division : 2.2
Label(s) : 2.2
Marine Pollutant : No

IMDG

UN/ID No. : UN1013
Proper shipping name : CARBON DIOXIDE
Class or Division : 2.2
Label(s) : 2.2
Marine Pollutant : No

TDG

UN/ID No. : UN1013
Proper shipping name : CARBON DIOXIDE
Class or Division : 2.2
Label(s) : 2.2
Marine Pollutant : No

Further Information

Avoid transport on vehicles where the load space is not separated from the driver's compartment.
Ensure vehicle driver is aware of the potential hazards of the load and knows what to do in the event of an accident or an emergency. The transportation information is not intended to convey all specific regulatory data relating to this material. For complete transportation information, contact an Air Products customer service representative.

15. REGULATORY INFORMATION

Toxic Substance Control Act (TSCA) 12(b) Component(s):

None.

Country	Regulatory list	Notification
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USA	TSCA	Included on Inventory.
EU	EINECS	Included on Inventory.
Canada	DSL	Included on Inventory.
Australia	AICS	Included on Inventory.
Japan	ENCS	Included on Inventory.
South Korea	ECL	Included on Inventory.
China	SEPA	Included on Inventory.
Philippines	PICCS	Included on Inventory.

EPA SARA Title III Section 312 (40 CFR 370) Hazard Classification
Sudden Release of Pressure Hazard.

Sudden Release of Pressure Hazard.

US. California Safe Drinking Water & Toxic Enforcement Act (Proposition 65)

This product does not contain any chemicals known to State of California to cause cancer, birth defects or any other harm.

16. OTHER INFORMATION

NFPA Rating

Health : 1
Fire : 0
Instability : 0

HMIS Rating

Health : 1
Flammability : 0
Physical hazard : 3

Prepared by : Air Products and Chemicals, Inc. Global EH&S Product Safety Department

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For additional information, please visit our Product Stewardship web site at
<http://www.airproducts.com/productstewardship/>

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About the RFA

The Renewable Fuels Association (RFA) is the national trade association for the U.S. fuel ethanol industry. Membership is comprised of numerous ethanol producers, both large and small, as well as suppliers to the industry and other interested parties. Founded in 1981, the RFA's primary objective is to promote public policy initiatives that increase the market for fuel grade ethanol produced from a variety of feedstocks including grains, agricultural wastes, and various biomass feedstock sources.

As the ethanol industry has grown, so too has the Renewable Fuels Association's areas of responsibility to its membership. Today, the RFA not only focuses on legislative/regulatory and public policy type issues but also maintains several committees and task groups to address industry needs. These committees include a technical committee to address various technical issues and to assist with technical industry publications (such as this one). In addition, there are plant and employee safety, environmental, and cellulosic committees monitoring efforts in each of these respective areas. Other committees utilize standing and ad hoc task forces and work groups as well. These committees and task forces are comprised of representatives of our member companies, staff, and, when necessary, technical consultants and other interested stakeholders. The RFA provides support for educational outreach programs through its research and education arm, the Renewable Fuels Foundation.

The RFA promotes the use of fuel grade ethanol in all its legal applications. Fuel ethanol is blended in nearly all of the nation's gasoline. This includes not only conventional E10 (90% gasoline/10% ethanol), E15 (85% gasoline/ 15% ethanol), reformulated gasoline (RFG) and fuels that are considered primarily gasoline, but all developing markets such as E85 and mid-level ethanol fuel blends for use in flexible fuel vehicles (FFV's). This document focuses on the safe handling and production of carbon dioxide (CO₂) to promote the important safety procedures and discusses other important documents such RFA's "Implementing an Effective Safety and Health Program for a Fuel Ethanol Facility" which list numerous OSHA guidelines and other information. The purpose of this document is to serve as a condensed technical reference for manufacturers and retailers of CO₂ and other interested parties who need such information. All RFA Technical Publications and other RFA Reference materials are available on the RFA website at: www.EthanolRFA.org.



