BIAR Sampling Systems

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WHITEPAPER

FUGITIVE EMMISSIONS AND GRAB SAMPLING

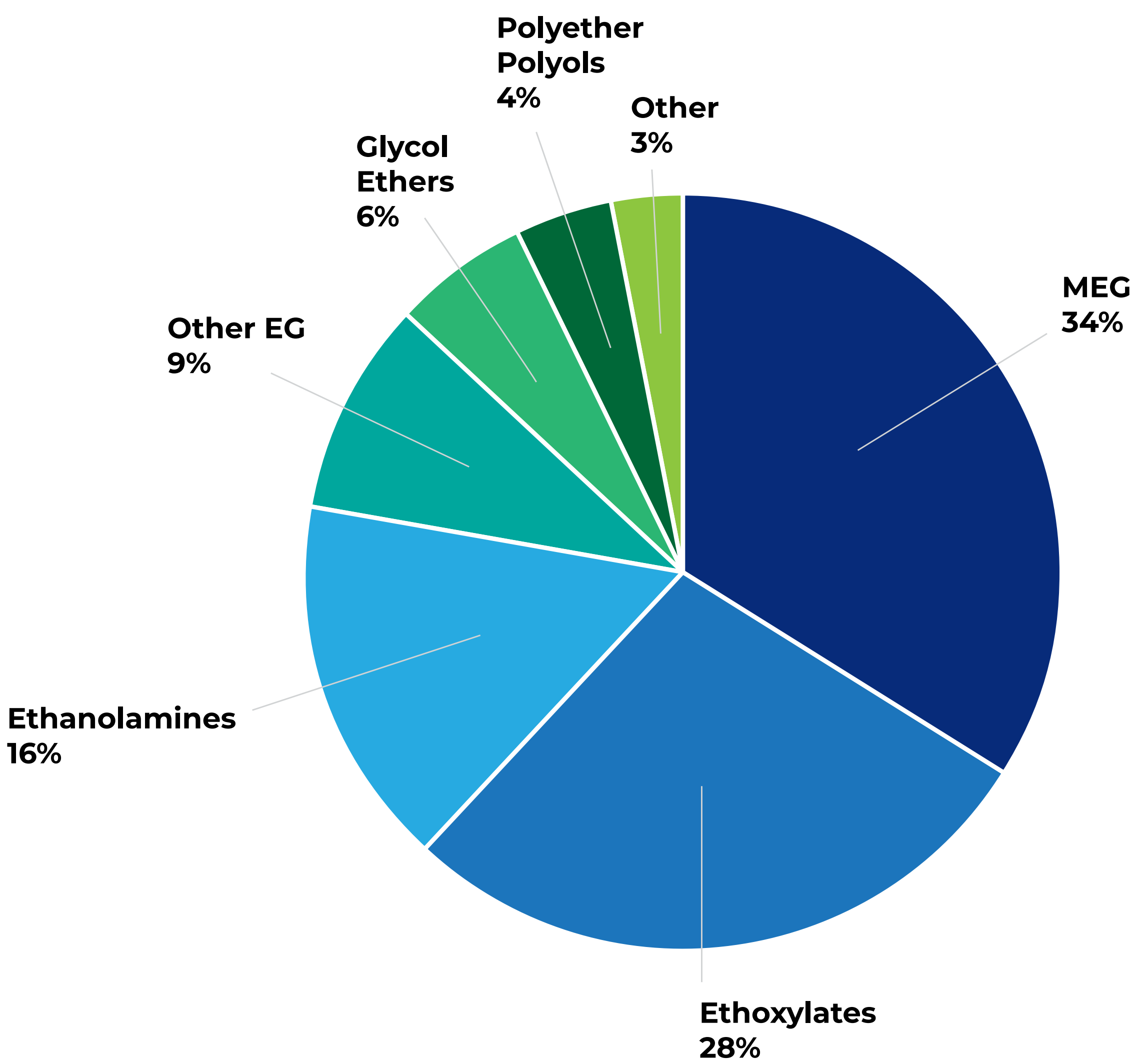
The complex case of Ethylene Oxide

Abstract

The primary aim of this document is to discuss the fundamental challenges which manufacturers and chemical plants are presented with when grab sampling EO. We outline some of the processes and systems currently employed in the industry and discuss methods which may offer an alternative to traditional sampling methods. We need to present new engineered solutions to reducing emissions in the sampling process, not only to comply with ever more stringent regulations, but to make sampling and subsequent analysis safer for those involved. This article may be of particular interest to Operations Managers, Safety Management, EHS and Lab personnel, Process Engineers, Engineering Managers and those in Continuous Improvement. Chemical plants interested in looking at improvements in their sampling process, whether it be for reducing exposure risk, eliminating emissions, getting better quality samples or complying with ever changing federal and state regulations will find it informative. It may be particularly relevant while conducting a Process Hazard Analysis (PHA), hazard and operability study (HAZOP) or Safety Audit. It may also serve as a good reference for plants considering different types of sample systems for an expansion, new installation, new product lines, or to replace antiquated or homemade systems which may fall foul of new regulations.

Ethylene Oxide (EO, EtO), also known as Oxirane, has the chemical formula C_2H_4O and is a chemical derived from natural gas or petroleum. It is a colorless gas or liquid and has an ether-like odor. A colorless gas when at room temperature and atmospheric pressure, at higher pressures it becomes a highly volatile liquid. Simply put, EO is industrially produced by the oxidation of ethylene (ET) in the presence of a silver catalyst.

Current Ethylene Oxide consumption in the U.S. (2019)[1]



[1] (Swift, Moore, Rose-Glowacki, & Sanchez, 2019)

EO is one of the most important raw materials in the chemical industry today, 99% of which is used as an intermediate in the production of other chemicals.

It is a key ingredient in the manufacture of mono-ethylene glycol (MEG), which accounts for a large proportion of total world EO production.

MEG in turn is a major intermediate in the production of polyethylene terephthalate (PET) which is found in most food grade containers and water bottles, and for the manufacture of fiberglass, polyester and antifreeze. EO is also a major component in detergents, cleaners and antifreeze and an important raw material in the production of polyester resins, solvents and adhesives.

While its use as a sterilant accounts for a very small proportion of its use in volume, it has become one of the most important sterilizers currently in use today, particularly for medical equipment which cannot be sterilized using heat. EO's unique properties mean that it can penetrate packaging and tubing which cannot be sterilized effectively by other means. Currently, EO in its gaseous form is used to sterilize roughly 50% of all the hospital equipment in the U.S., and a very small proportion is used as a fumigant for spices.

EO is an extremely flammable and volatile substance and is considered an occupational carcinogen by NIOSH and the EPA.

Sources of Emissions and Exposure

The main sources of environmental emissions are those from controlled venting in an industrial facility or chemical plant, fugitive emissions from leaking tanks, valves, and other process equipment, grab sampling and in its capacity as a medical sterilizer and fumigant. In chemical plants, exposure is highest for employees 'during the loading or unloading of transport tanks, product sampling procedures, and equipment maintenance and repair'.[2] Concerns about EO emissions and the general public are currently a hot topic of debate with the EPA, who issued stricter guidelines on EO emissions in 2020.

IN CHEMICAL PLANTS, EXPOSURE IS HIGHEST FOR EMPLOYEES 'DURING THE LOADING OR UNLOADING OF TRANSPORT TANKS, PRODUCT SAMPLING PROCEDURES, AND EQUIPMENT MAINTENANCE AND REPAIR'.

Environmental Concerns

EO emissions have come under increased scrutiny in recent years, and the EPA is working closely with industry, state and local agencies to dramatically reduce emissions from manufacturers and chemical facilities which use EO in their chemical processes. 'Controlling fugitive emissions is also an important consideration in valve design and selection'.[3] The EPA defines "fugitive emissions" in the regulations promulgated under title V as "those emissions which could not reasonably pass through a stack, chimney, vent, or other functionally-equivalent opening" in title 40 of the Code of Federal Regulations, sections 70.2 and 71.2. In other words, they are uncontrolled releases into the environment from storage equipment, flanges, pumps or valves which can add significantly to total releases from a chemical facility.

2 NIOSH Publications and Products - Ethylene Oxide (EtO): Evidence of Carcinogenicity (81-130)
3 (Ethylene Oxide Panel/ Ethylene Oxide Safety Task Group, 2007)

Ethylene Oxide sampling

Chemical plants that need to sample EO to determine product integrity during the manufacturing process are faced with the challenge of obtaining a sample that is representative of the batch. They must also ensure that the process is safe so that the Operator is not exposed and that no EO is released into the environment. It is widely accepted that an engineered solution to tackle these challenges is the best way forward. This means that sampling systems must be robust and designed to a standard which minimizes the exposure risk to the Operator and emissions into the environment.

Properties of EO that pose challenges for sample system design.

1. Product expansion: EO has a high rate of thermal expansion, which can result in higher pressure when exposed to ambient temperatures. Sampling receptacles must be designed to allow for product expansion.
2. Sample valve design must also take into consideration that EO liquid trapped in systems where 'dead space' is present may not only compromise the valve[4], but affect the integrity of the next sample.
3. Due to its toxicity and ever-more stringent regulations, no exposure to EO is allowed and no releases are allowed into the environment.

Many plants have opted for the traditional 'sample panel' system which features a cylinder positioned vertically on a bypass loop and which feature 'quick connectors' and flexi tubing. These cylinders may also feature a dip tube to allow for product expansion within the sample cylinder. While these systems are widely used for the sampling of liquified gas, they present some issues which are worthy of further discussion and are outlined below.

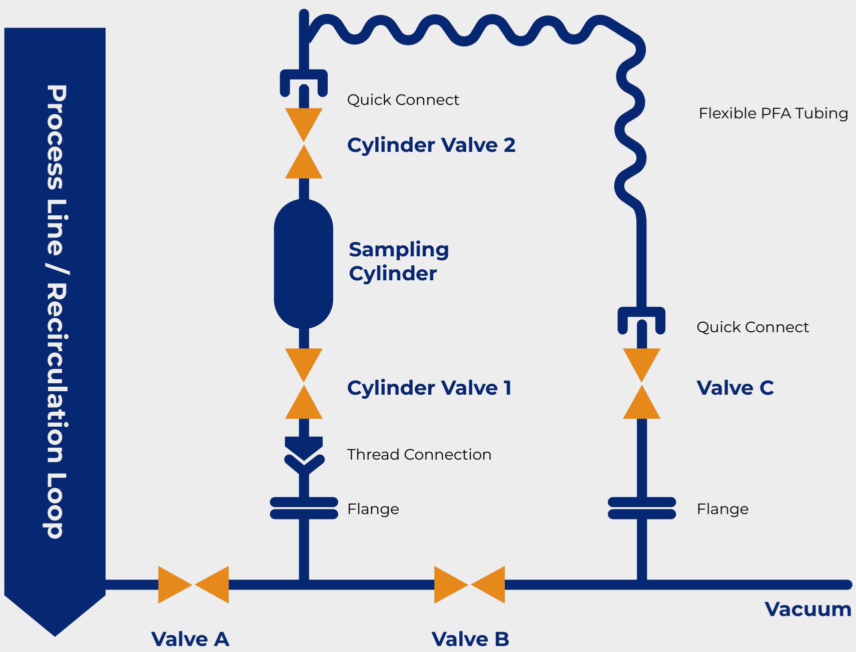
4 (Ethylene Oxide Panel/ Ethylene Oxide Safety Task Group, 2007), p.58

Traditional Sample Panel features.

- Numerous steps require the operator to handle multiple valves in a precise sequence in order to prevent exposure and guarantee a representative sample.
- There are numerous potential leak points.
- The nature of some fittings (i.e. Quick-connect flexible tubing) present potential exposure risks.
- A robust design is difficult to achieve due to small tubing and different materials involved.
- Residue is likely to remain in the system due to numerous tubing and valves which may need to be purged out.
- Possible additional waste if flushed/ purged product cannot be recycled.
- Operators could be exposed to ‘puffs’ when disconnecting some parts of the system. At the very least the product is released into the environment.

Typical sample panel system used for ethylene oxide sampling. (Ethylene Oxide Panel/ Ethylene Oxide Safety Task Group, 2007, p.67)

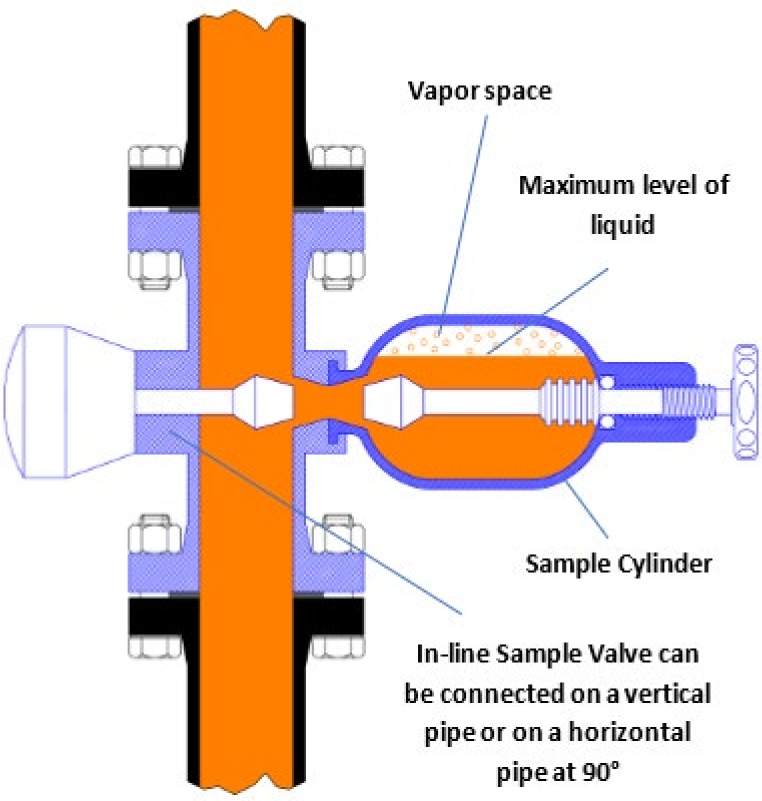
To illustrate the complexity of the traditional sample panel above, below is an example of some of the steps the operator may have to follow in order to grab a representative sample in a safe way:



1. **Remove the safety cap from the thread connection**
2. **Remove the safety cap from the sample cylinder**
3. **Screw the sample cylinder to the thread connection**
4. **Connect the quick-connect on the sample cylinder**
5. **Make sure Valve B is closed**
6. **Open Valve C**
7. **Open Cylinder Valve 2**
8. **Open Cylinder Valve 1**
9. **Open valve A**
10. **Wait a defined period of time**
11. **Close Cylinder Valve 2**
12. **Close Cylinder Valve 1**
13. **Close Valve A**
14. **Wait a defined period of time to make sure the flexible PFA tubing has been entirely flushed**
15. **Close Valve C**
16. **Open Valve B**
17. **Wait a defined period of time to make sure the thread connection and tubing between Valve A and Valve B have been entirely flushed**
18. **Close valve B**
19. **Disconnect the quick-connect on the sample cylinder**
20. **Unscrew the sample cylinder from the thread connection**
21. **Put the safety cap back on the thread connection**
22. **Put the safety cap back on the sample cylinder**

One option to tackle these challenges is to use a BIAR inline sample system with sample cylinder. This not only simplifies the process, it also reduces the amount of potential leak points.

The following illustration shows how a BIAR Columbia-LY container can provide sufficient vapor space when mounted horizontally to prevent overpressure from volumetric expansion. The increase in temperature causes the internal cylinder pressure to rise by the combined volumetric expansion of the liquid (compressing the vapor space) and an increase in the vapor pressure of the contents. Outage is the vapor space in the cylinder expressed as a percentage of the total volume of the cylinder.



Procedure

1. Take safety cap off the cylinder
2. Take safety plug off valve
3. Connect cylinder to the valve
4. Open the cylinder
5. Open the valve
6. Close the cylinder
7. Close the valve
8. Disconnect the cylinder
9. Put safety cap back ón cylinder
10. Put safety plug back ón the valve

Another option to tackle these issues is a piston-injector with expansion ring sampling set-up. This is an enclosed container that, like the cylinder, fits directly onto the sample valve but features a spring fitted behind the piston to allow expansion of the ethylene oxide as the temperature increases. Thoroughly emptying and cleaning the container is easy using this set-up. However, because there are moving parts involved, the risk of leakage is increased, and there is appreciably more maintenance required. A good preventative maintenance regime can ensure that leaks are kept to a minimum.

Both the sampling valve and the piston injector are designed with no dead space to prevent any entrapment of the ethylene oxide gas which could influence the next sample. The piston injector can also be fitted with a sight glass which allows for a more accurate sample volume.

The optimal sampling vessel is ultimately determined by the sampling conditions and customer preference. For instance, the piston injector would be more compatible with processes with lower pressure conditions while the cylinder would have a much higher pressure rating.

Summary

EO is a good example of a chemical which poses significant challenges and hazard risk to those that need to sample it. We have identified the complexities related to sampling EO using traditional sample panels and offered some simple solutions which would make the process of sampling EO safer while also minimizing releases into the environment.

Traditional Sample Panel	Inline System
Complicated design	Simple to operate
Many valves and connections	One connection between valve and receptacle
Flushing to get a representative sample	Representative sample first time every time
Fragile connections and quick-connects	Robust valve and accessory
Many potential leak points	Certified Low Leak Technology
Increased exposure risk	Minimized exposure risk
More waste generated	No waste: Improved Industrial Hygiene

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Customers

About Us

BIAR Sampling Systems was established in the early 80's by Guy Masson, a chemical engineer working with hazardous chemicals in Switzerland. Tasked with finding a solution to safely sample hazardous chemicals, Guy invented the PRISEMASSON® sampling system which became the first sample system to feature a hand Wheel and conical seat. Now, nearly 40 years later, we continue to pioneer innovations in the field of chemical sampling and produce a range of valve configurations with unmatched quality and precision. There is simply no shortcut when the health and safety of operators and the surrounding environment are at stake.

All our valves are fitted with a spring-to-close system to prevent any spillage should the operator suddenly step away from the valve. This may be in the form of a hand-wheel, lever, or pneumatic actuator, depending on the nature of the system. For example, for viscous liquids that are not under extreme pressure, the spring-to-close lever actuator will provide a better solution than our standard spring-to-close hand-wheel. By taking the time to thoroughly characterize the specific details of a customers' application, we can provide them with the optimal sampling system tailored for their sampling needs.

Our valves are used in a myriad of challenging applications; liquids that pose thermal or toxic hazards, applications that demand an aseptic sampling environment or are atmosphere sensitive, to extremely toxic liquefied gases such as phosgene and chlorine. To meet such a wide-ranging array of needs, we have established a strong global network that consists of a knowledgeable sales staff and distributors who work to customize each sampling valve to meet the customer's application. Aspects such as the chemical in question as well as the temperature, pressure, and pipe size of the given process system must be established in order to specify the correct valve type and its receptacle.

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