A BASIC UNDERSTANDING OF THE CHEMISTRY AND CHARACTERISTICS OF NATURAL GAS ODORANTS

Introduction

Modern industry conducts itself much differently than it did at the turn of the century. Public safety and care for the environment has gone from the bottom of the list of goals, right to the very top.

This has come about for a variety of reasons, including increased knowledge of the products, processes and services offered together with the hazards associated with them, greater awareness of the effects on the population and environment, and the introduction of legislation to ensure compliance with the standard practices necessary to ensure these goals are met.

For the gas industry, one essential way of providing this service to their customers is by odorization of natural gas.

Odorization of natural gas has evolved from a fragmented, unregulated practice, into the current highly regulated and monitored practice we see today. The primary focus of odorization is safety, and this must be kept in mind as we develop, maintain and improve our odorization techniques and processes in a changing regulatory environment.

This paper will focus on the chemistry and characteristics of gas odorants and will discuss related topics including odor-fade, blend rationalization and questions odorant suppliers are frequently asked.

History

Odorization of gas was first proposed in Germany in the 1880s' by Von Quaglios' use of ethyl mercaptan as a means of leak detecting the escape of blue water gas.

The manufactured gas used at the turn of the century contained by-products which are the source of the term gassy odor. As high quality natural gas displaced lower quality manufactured gas, the by-products that caused the gassy odor in the lower quality gas were no longer present.

Without these by-products, natural gas had little if any detectable smell to warn of leaks or accumulation. This undetectable gas caused the disaster at the New London Elementary school in 1937 that leveled the school, killing many children.

The gassy odor of manufactured gas was originally duplicated in natural gas by cheap refinery by-product streams. However, these by-product streams were unreliable and varied in quality. The growth of the chemical industry during World War II resulted in the availability of high quality synthetic chemicals that proved well suited for natural gas odorization. These chemicals are the low molecular weight (C3-C4), branched chained alkyl mercaptans, alkyl sulfides and a cyclic sulfide. By 1960, virtually all natural gas odorization was done with blends of these synthetic chemicals.The use of synthetic blend components was a big step forward. However, it also had its downside.

Consider the following:

1. A large number of blends were developed, often based largely on personal preference rather

than sound technical reasons. Many blends were created in which the only differences were minor variations in the ratio of the same components. Advantages were perceived rather than real.

2. When first manufactured, these blend components often contained significant levels of impurities. These impurities became part of the blend specifications. Today, with improved technology, components with a much higher purity are manufactured. Capabilities changed, specifications did not.
For example, secondary butyl mercaptan (SBM) was an impurity of the original tertiary butyl mercaptan (TBM) process. So if you request 1 -3% of SBM in a TBM based blend today, the SBM must be made separately, then added to the blend.
Also, there is a greater understanding today of ways in which pipeline conditions and gas quality affects odorant performance. If this knowledge had been available at the time synthetic blends started to be manufactured, no doubt fewer blends would have been developed.

Odor Fade

Odor Fade can be a major problem. Gas may be satisfactorily odorized at source, but if it no longer has the necessary odor impact and intensity by the time it reaches the customer, escaping gas can go undetected and result in a serious fire or explosion hazard.

To understand why it occurs and what can be done to overcome the problem, we have to consider the following:

1. Odorant blend types and the chemistry of the various components
2. Pipeline conditions
3. The quality of the gas to be odorized

Odorant Blends and Their Components

Odorant blends are extremely odorous, volatile, flammable liquids. Acceptable odorants must possess certain physical and chemical characteristics. These include a gassy odor, low odor threshold, high odor impact, resistance to pipeline oxidation and good soil penetrability. Vapor pressure of blend components used in vaporization type odorizers is also a very important consideration.

Odorant Components

The odorants used today are usually blends of two or more components, which achieve the desirable characteristics.
Therefore, it is important to understand the characteristics of the components. Basically there are three chemical groups from which odorants are blended:

1. Alkyl Mercaptans
2. Alkyl Sulfides
3. Cyclic Sulfide

Mercaptan Components

Tertiary Butyl Mercaptan (TBM)

```
         CH3
          |
  CH3 - C - SH
          |
         CH3
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TBM is the leading single component used in natural gas odorants. Its low odor threshold, gassy odor, good soil penetration, and highest resistance to oxidation of the mercaptans, makes TBM very desirable. However, the high freezing point of TBM (34F) results in the need for blending with other components to prevent freezing. Otherwise, TBM would be an excellent "stand alone" odorant.

Isopropyl Mercaptan (IPM)

$$
\begin{array}{c}
CH_3 \\
| \\
CH_3 - C - SH \\
| \\
H
\end{array}
$$

IPM has a strong, gassy odor and low freezing point (-202°F). Of the mercaptans it is the second most resistant to oxidation. IPM is commonly blended with TBM to depress the freezing point while enhancing the odor impact. IPM is also a stand-alone odorant, but rarely, if ever, used as such.

Normal Propyl Mercaptan (NPM)

$$CH_3 - CH_2 - CH_2 - SH$$

NPM is not a major component in odorant blends, typically 2-6%. It is more easily oxidized than other mercaptans. However, NPM has a low freezing point (-171°F) and a strong odor. NPM was originally a co-product in the IPM manufacturing process. It is not a good stand-alone odorant due to low oxidative stability.

Secondary Butyl Mercaptan (SBM)

$$
\begin{array}{c}
CH_3 \\
| \\
CH_3 - C - CH_2 - SH \\
| \\
H
\end{array}
$$

SBM, originally an impurity in TBM manufacture, is probably the least used component in odorant blends. On the rare occasions it is used, it is typically in the 2 – 4% range. It is a branched chain mercaptan, which resists oxidation. SBM has a strong odor, low freezing point, but high boiling point and low vapor pressure. Sometimes used at 100% in evaporative systems.

Alkyl Sulfide Components

Alkyl sulfides are resistant to oxidation but they do not have the odor impact of the mercaptans. **They are not considered "stand alone" odorants. Their primary function is to lower the freezing point of TBM.**

Dimethyl Sulfide (DMS)

$$CH_3 - S - CH_3$$

DMS has been widely used as a blend component, particularly with TBM. DMS will not oxidize in the pipeline and has good soil penetrability. DMS has a much higher vapor pressure than TBM; thus TBM/DMS blends are not suitable for vaporization type odorizers.

Methyl Ethyl Sulfide (MES)

$$CH_3 - S - CH_2 - CH_3$$

MES is the latest addition to odorant blends with TBM. MES will not oxidize in pipelines. MES has a vapor pressure similar to TBM; therefore TBM/MES blends are suitable for injection or vaporization type odorizers.

Cyclic Sulfide

Tetrahydrothiophene (THT) or Thiophane

$$
\begin{array}{ccc}
H_2C & - & CH_2 \\
| & & | \\
H_2C & & CH_2 \\
\backslash & & / \\
 & S &
\end{array}
$$

THT is the most resistant to pipeline oxidation. It has a gassy odor but low odor impact and poor soil penetrability. The low odor impact makes it difficult to over-odorize with THT. THT may be used in pure form or as part of a blend with TBM. THT is a "stand alone" odorant.

Blend Composition

The odorant blends in use today fall into one of three main categories, which are:

1. All mercaptan blends
2. Mercaptan/alkyl sulfide blends
3. Tetrahydrothiophene (THT) /mercaptan blends.

The following compositions (and minor variations thereon) are the most common blend types in use today. Also listed is the type of odorizing equipment that can be used.

All Mercaptan Blends

Component	Blend 1(%)
TBM	79
IPM	15-19
NPM	2-6
Odorization Method	Vaporization or Liquid Injection

Mercaptan/Sulfide Blends

Component	1(%)	2(%)	3(%)
TBM	75	80	10
DMS	25	0	10
MES	0	20	0
IPM	0	0	70
NPM	0	0	10
Odorization Method	Liquid Injection	Vaporization or Liquid Injection	

Tetrahydrothiophene (THT)/Mercaptan Blends

Component	Blend 1(%)	Blend 2(%)
THT	100	50
TBM	0	50
Odorization Method	Vaporization or Liquid Injection	Liquid Injection

Blend Rationalization

The gas industry today is in a state of flux with companies merging, consolidating and rationalizing. Consider the merger of five utilities to form one new company. As the dust starts to settle, someone suddenly realizes that each utility uses a different odorant blend - so now we have one company using five different blends, and the question is - - Why? More often than not the answer from each utility will be "We have always used this blend and it works, and moreover, we do not want to change". .

Some of you may know there were about 20 different odorant blends in use in the industry. However it has been estimated that at least 80-90% of natural gas is currently being odorized by no more than 8 blends. It can be argued that that number is greater than required.

Consider the following example:-

The most common TBM/DMS blend has a 75/25 component ratio. There is also a TBM/DMS blend with an 80/20 ratio. Hardly a significant difference in the % of TBM.
Add to that, spec limits of $\pm$ 2%, so for blend 1 we could have a TBM content in the range 73-77% and for blend 2 it could be 78-82%
This means that a blend with 77% TBM and one with 78% TBM are considered different!!!

Pipeline Conditions and Gas Quality

Odorization, especially by an injection system, is an accurate way of verifying that you have added the required ratio of odorant to gas. However, there are circumstances that occur within distribution systems that can mask the odorant level in the gas stream or cause the odorant to fade. There are basically three causes for this phenomenon and they are the following:

Oxidation - formation of di-sulfides in the presence of iron oxide (rust) and air (oxygen)

New pipe -

- Adsorption/absorption of odorant onto/into the surface of synthetic (plastic) pipe
- Formation of patina layer inside steel pipe

Gas Quality -

- Absorption, masking, or reaction of odorant components with impurities in the gas stream.

Some of the causes of odorant fade are chemical reactions whereas the others are physical phenomena. Let us explore the possible causes of odor fade mentioned above.

Oxidation

The presence of rust and air within a pipeline will act as a catalyst on mercaptans causing them to oxidize into compounds that have virtually no detectable odor. Of the common mercaptan odorants, the following list represents how they will react in the presence of a rust/oxygen environment:

TBM Most resistant to Oxidation
IPM ↕
NPM Least resistant to Oxidation

All of the sulfide components (DMS, MES, & THT) used in odorant blends are resistant to oxidation.

The solution: **temporary increase in the odorant dosage rate**

New Pipe

Plastic- the other potential cause for odor fade is a physical reaction caused in the presence of new plastic pipe. In this case, the odorant is being adsorbed and/or absorbed onto and into the plastic pipe. However, once equilibrium is achieved, the amount of odorant going onto and into the surface of the pipe wall equals the amount coming back out. When this point is finally attained, odor detection with normal dosage levels should resume.
The solution: **temporary increase in the odorant dosage rate**

Steel - this same principle exists, to some extent, in the presence of new steel pipe although a chemical reaction, not physical. However, introducing larger than normal quantities of odorant into the pipe at the start can pickle new steel pipe. Eventually an iron sulfide layer forms (patina) on the inside surface of the pipe and the conditions that would cause odor fade will diminish.
The solution: **temporary increase in the odorant dosage rate**

Gas Quality

The gas quality must also be considered when investigating causes of odor fade. Is your gas supply?

1. Dry - Not Naturally Odorized?
2. Wet - Not Naturally Odorized?
3. Dry - Naturally Odorized?
4. Wet - Naturally Odorized?
5. Peak Shaved Gas?

Dry Gas - Not Naturally Odorized

Dry Gas, not naturally odorized is the easiest to odorize and does not cause odor fade. Any of the defined commonly used odorant blends will perform satisfactorily provided that continuous odorization is practiced. Low flow absorption may be an issue

Wet Gas - Not Naturally Odorized

Condensed liquids in the pipeline absorb odorant components. Some odor masking may also occur due to the odor imparted by the impurities in the gas. Both give rise to odor fade.

Odorants with the highest vapor pressure and lowest threshold values work best. Blends high in IPM (with its high vapor pressure) are considered best in this situation. TBM blends work well in overcoming masking but are not recommended where liquid levels are high.

Do not use THT or THT blends. Their low vapor pressure and low K_d values results in a higher degree of absorption in pools of condensate resulting in more rapid odor fade. Also, if drier gas is later introduced, condensates with a high level of dissolved odorant can rapidly evaporate, resulting in overodorization of the gas stream.

Dry Gas - Naturally Odorized

Dry, naturally odorized gas can cause odor fade because it contains among others; methyl and ethyl mercaptan, which can cause oxidation of TBM to disulfides, which have low vapor pressure and low odor impact. As the levels of natural mercaptans increase, it is best to use sulfide blends, which are oxidation resistant. THT blends are best. DMS is oxidatively stable but lacks odor impact, and is not considered a "stand alone" odorant.

Wet Gas - Naturally Odorized

It is almost impossible to satisfactorily odorize this type of gas. IPM based blends may work if liquids are the main problem. THT blends may work if natural mercaptans are the major contaminants. The best solution is not to purchase this quality of gas.

Peak Shaving

This practice which involves addition of propane diluted with air to natural gas results in a similar situation to that of naturally odorized gas in which the ethyl mercaptan used to odorize the propane promotes oxidation of mercaptan based odorants resulting in odor fade. Also the addition of oxygen and moisture increases the possibility of mercaptan oxidation. So even if unodorized propane is purchased conditions for oxidation, albeit reduced, still exist. THT blends are considered best if conditions are severe.

NOTE:

Sulfides Oxidative Resistance As previously mentioned, alkyl sulfides (DMS, MES) and the cyclic sulfide (THT) are resistant to oxidation. However, THT is the only sulfide that will act as an effective stand-alone gas odorant. Both DMS and MES do not possess the required gassy odor and are therefore ineffective as stand-alone gas odorants. Additionally, both DMS and MES are typically used in minor concentrations (20%-30%) further reducing the chances of odor detection should 100% of the mercaptan in the blend be oxidized.

Frequently Asked Questions

Q. What type of odorant blends can be used in injection systems?
A. Any odorant blend can used since it is being injected directly into the gas flow Differences in component vapor pressures do not affect performance

Q. What type of odorant blends can be used in evaporative systems?
A. Single component odorants, e.g., THT, or blends where components have similar vapor pressures, e.g., all mercaptan blends or blends

with TBM and MES, can be used in evaporative systems. Do not use mercaptan/DMS or mercaptan/THT blends. The components in these blends have widely differing vapor pressures, which results in inconsistent odorization of your gas.

Q. Am I using the odorant blend best suited to my needs?
A. Consult your supplier for advice.

Q. If I change my blend, will I experience any compatibility problems mixing the new blend with the blend currently in my storage tank?
A. No. All blend components are soluble in each other.

Q. Will they react?
A. No. Mixing will not diminish their effectiveness as odorants. There will be no reaction.

Q. Will a different blend be compatible with the materials of construction used in my storage tanks and injection equipment?
A. Yes. The same materials of construction are recommended for all odorant blends.

Q. We are installing a new odorant storage tank at one of our stations and our old tank is half full of odorant. Can you help?
A. During an odorant delivery to a number of your stations, your supplier can transfer the odorant from the old tank to the new tank on site or to another tank off site if the old tank is not being replaced.

Q. What is a "closed loop" delivery? Are there any advantages over the traditional flare delivery?
A. In a flared delivery, a liquid hose is connected to a liquid line on the tank, which is preferably fitted with a dip-tube. The vapor line on the tank which is connected to the flare is opened to vent off any pressure. Pressure is applied to the odorant trailer and the liquid valves are opened to allow flow to the storage tank. The displaced vapors from the tank are vented to the flare until the delivery is complete. These vapors burn in the flare and are emitted as sulfur dioxide, which raises environmental issues. Additionally, if the tank has a faulty level gauge, it is possible to overfill the tank with odorant, which will cause overflow through the flare resulting in odorant spillage. This is an environmental problem and also results in false leak complaints.
In a "closed loop" delivery, a vapor hose is connected to a vapor line on the tank in addition to the liquid hose. This is done through the truck manifold which is connected to a compressor, which pulls pressure off the tank and supplies it to the trailer to allow flow by differential pressure. This allows the delivery to take place without venting to the flare. Also, when performed correctly, a closed loop delivery removes the chance of tank overfill, and the overall result is a safer, "odor free" delivery.

Q. We have installed a new storage tank. What do we need to do prior to receiving our first odorant delivery?
A. The first thing to do is to ensure that the tank and fittings have been properly installed according to the design blue-print, ensuring safe storage of your odorant. Ensure that the tank is clean and dry. Pressure test the tank and check for any leaks at flange connections, valves etc.
Finally, purge the tank with nitrogen or gas to remove any oxygen. Odorant vapors and oxygen can form explosive mixtures.

Frozen Injection Lines

When winter comes around, this phenomenon sometimes happens. The question then arises. . . "Why is this happening, and what can I do to overcome the problem?" What we want to do is consider the possible causes and suggest remedies for overcoming them. .

Possible Causes

There are only two possible causes:

1. Frozen t-Butyl Mercaptan (TBM) or

2, Ice Formation (from water in your system)

TBM, the most common of all odorant components, has a freezing point of 34F. It is always blended with other components to depress the freezing point to less than -50F. Could your supplier deliver an odorant blend with insufficient diluents to ensure TBM does not freeze in winter conditions? This is highly unlikely. Why? Odorant blends are carefully analyzed by Gas Chromatography to ensure the ratio of blend components is within specification. Furthermore, a Cloud Point test is also conducted. The main purpose of this test, which must meet a specification of less than -50'F, is to detect the presence of moisture. However, it also ensures that the blend does not freeze above this specification temperature limit.
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The only situation in which TBM is likely to freeze is in by-pass odorizers. This can only happen if the wrong blend is used. For example, the use of a blend where Dimethyl Sulfide (DMS) is used as the diluent for TBM. DMS, which has a much higher vapor pressure than TBM, will evaporate more quickly, leaving concentrated TBM in the by-pass odorizer, which can then freeze when the temperature drops below 34F.

If frozen TBM is not the culprit, then the only other possible cause is freezing of water present in your system, almost certainly in your odorant storage tank.

Causes and remedies.

1. Cause – Wet Pad Gas

If the tank pad gas used contains traces of moisture, over a period of time (often several years), water, which is virtually insoluble in odorant, can condense out and fall to the bottom of the tank. NOTE: Water is more dense than odorant blends.

Normally, the feed line to your injection system is above the bottom of the storage tank, albeit very slightly. Eventually, the water layer can build up and find its way into your injection lines, and in severe weather, can freeze up.

Remedies

Short Term

A. Carefully apply heat to your injection lines to thaw the ice build up.
B. Add a small quantity of methanol to the storage tank contents to dissolve the water layer
Note: Normally, a gallon of methanol added to 500 gallons of odorant will do the job. However, up to 0.5% of methanol can be added without adversely affecting the odorant performance

Long Term

Use dry pad gas

2. Cause - Supplier delivers Wet Odorant

This is possible, but highly unlikely, as previously stated, suppliers carry Out a Cloud Point Test to ensure that the odorant you receive is essentially "dry".

Remedy

This is the responsibility of your supplier who must ensure that properly documented systems are in place to ensure accuracy of sampling and accuracy and frequency of testing. Certificates of analysis are provided with each shipment. Products are not shipped unless they meet all specification limits which includes Cloud Point.

3. Cause New Tank Contains Water Residues

New tanks are often delivered in a "wet" condition. Always ensure any newly installed tank is clean and dry before receipt of its first batch of odorant. **We find that failure to ensure that the new tank is dry is probably the most common cause of water in the injection lines.**

One customer experienced this problem of water in the injection lines despite the fact that the Certificate of Analysis showed the Cloud Point to be within specification. This was the first delivery to a new tank. It was accepted that residual water from failure to dry the tank properly caused the problem.

The same problem occurred during the next delivery. We were blamed for supplying wet odorant.

He was surprised to hear me agree with him that the problem was associated with the delivery, and even more surprised, even skeptical, when I said water in the new batch of odorant was almost certainly not the culprit.

The answer is actually quite simple. The water causing the problem were residues from the original failure to dry out the tank.
This is not a problem under normal operating conditions, as long as the water level is below the level of the feed Iine to the injection system.

Deliveries are usually made through a dip tube which goes to the bottom of the tank. Addition of new odorant causes agitation of the tank contents, resulting in suspension of water droplets which can find their way into the injection lines, and if the temperature drops, can freeze up.

Water in your system can cause serious freezing problems. In order to overcome the problem suppliers must ensure that odorant blends are "dry" and you the end-user must ensure that it remains so.

Conclusion

Hopefully, the information in this paper will increase your knowledge of odorant behavior.

Always remember that **safety of the public** is our prime concern. Proper odorization allows your customers to safely use natural gas by providing an adequate warning level allowing them to recognize a leak, should one exist, prior to the gas reaching an explosive level.

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