

Monitoring Flammable Vapors and Gases in Industrial Processes

Flammability Hazards

Industrial fires and explosions happen more frequently than most people think. They cause downtime, property damage, injury and sometimes death. These fires and explosions result from a dangerous mixture of flammable vapors with air and a source of ignition.



Flammable vapors

Solvents, chemicals and other sources of flammable vapors and gases are present in many manufacturing, production and converting processes and act as the fuel in process fires or explosions.

Combustion air

In most industrial processes, enough oxygen is present to support combustion. But even in inert or purged processes, a sudden accidental introduction of air can mix with process vapors to produce a flammable mixture.

Ignition

There are many potential sources of ignition which can trigger a fire or explosion: electrical sparks; friction; static discharge; hot surfaces; air streams; and direct-fired burners in ovens and thermal oxidizers.

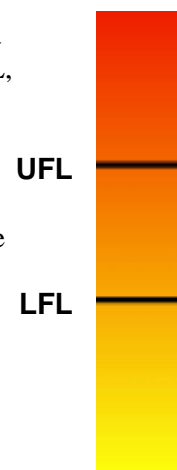
Since we can never be guaranteed that an environment will remain completely free of air or of a source of ignition, the most reliable means of preventing fire or explosion is to measure and limit the amount of flammable vapors to a safe level.

Flammability Measurement

For each flammable substance there is a level of concentration in air, usually expressed as a percent by volume, that is known as its Lower Flammable Limit, or LFL⁽¹⁾. Below the LFL, the mixture of fuel and air is too lean to support combustion. For example, a mixture of 1.1 percent Hexane in air is equal to 100% of its LFL—just rich enough to burn.

As the amount of fuel continues to increase, the mixture will eventually become too rich to burn—there will be too much fuel and not enough air. This concentration is known as the Upper Flammable Limit, or UFL⁽²⁾.

Between the LFL and the UFL lies the flammable range where, given a source of ignition, the mixture will readily ignite. While it may be theoretically possible to operate safely at concentrations up to 100% of the LFL, authorities world-wide have established safety regulations which require operation well below this point.



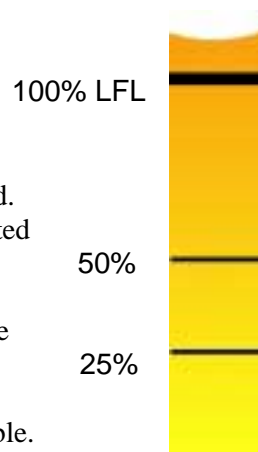
^{(1) (2)} The terms LFL and UFL are used interchangeably with the older terms, LEL (Lower Explosive Limit) and UEL (Upper Explosive Limit)

Safety Margins

Almost all safety authorities require a 4:1 margin of safety below the LFL, based on worst-case conditions. This means that enough dilution air must be used to always maintain a concentration of less than 25% of the LFL⁽³⁾.

However, a process oven or oxidizer is allowed to operate with only a 2:1 safety margin (up to 50% of the LFL), when continuous flammability analyzers are used. The requirements stipulate real-time, fast-response, *continuous* analyzers connected in such a manner as to trigger corrective action at predetermined alarm points.

So unprotected processes, which may normally run at only 10 or 12 percent of the LFL to avoid reaching 25 percent in case of accidental upset, can operate at much higher vapor concentrations when LFL analyzers are used. The resulting cost savings due to reduced ventilation or increased throughput can be considerable.



How Accurate Are Published LFL Values?

Because Lower Flammable Limits are determined empirically, there are variations in the values published by different authorities at different times. These variations may be due to small inaccuracies in test procedures such as sample preparation, vessel size, air flow, temperature, observation methods, and monitoring instruments—nevertheless, they do exist. Measurement results are usually rounded-off to the nearest 0.1 percent by volume.

You may be surprised to learn that a comparison of the LFL value for fifty common solvents, published by six different authorities, shows that one-third of the solvents compared disagree by a standard deviation of more than ten percent. Given these differences, the LFL of a substance is certainly not an absolute value and ample allowances should be made to ensure safe operation.

The Effects Of Process Temperature On Flammability

Most published LFL values are calculated at room temperature. But as a given mixture is heated, its flammability increases and thus the concentration required to achieve 100% of its LFL is less. This source of increased danger is often overlooked.

Consider the adjacent diagram. The yellow band indicates 100% of the LFL of a sample mixture, given the degree of uncertainty in published values as previously mentioned. Note how the red area of danger becomes greater as the temperature increases. Note also the green "safe" area. What was safe at 75° becomes dangerous at 200° or 400°.



⁽³⁾ National Fire Protection Association. Standard # NFPA 86

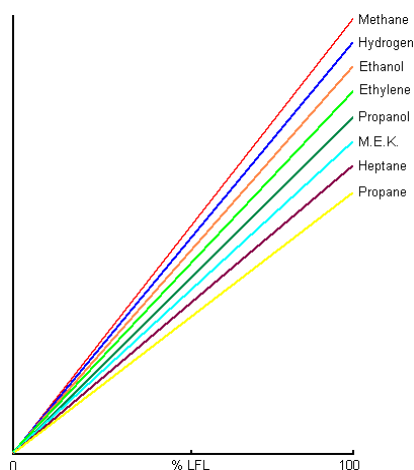
Comparison Of Sensors Typically Used For LFL Measurement

The sensor must be appropriate for the application

Although several different types of sensors are employed as LFL monitors, each has an appropriate application to which it is best suited. Fires and explosions in what was thought to be “protected” equipment can occur without warning when a sensor is not capable of doing the job that had been assigned to it. This is most often caused by a misunderstanding of the different available technologies.

Catalytic combustion sensors

Catalytic-bead sensors are constructed of two small wire coils covered with a catalyst. One coil is “active” while the other is rendered inert and acts as a reference. A flow of electrical current through the internal coils heats the catalytic coating to a temperature at which the active coil will react with many flammable vapors and gases. This reaction occurs in the form of surface combustion which in turn causes an increase in the sensor's temperature. The resulting electrical change is measured on a companion monitor instrument.

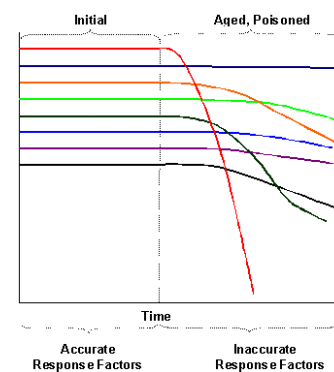


The intensity of the catalytic reaction varies for different flammable substances and with their concentration. Therefore, the sensor needs to be calibrated for use with a specific substance or group of closely related substances. Like most reactive compounds, the response of the catalyst will change over time. How quickly it changes depends upon the particular flammable substance to which it has been exposed and upon the concentration of that substance. Calibration correction may be required for each different solvent or solvent mixture used in the process. Catalytic sensors are also susceptible to poisoning, coating and etching caused by compounds in the sample.

Since a hot surface itself can act as a source of ignition, catalytic-bead sensors are shielded by a sintered-metal cap or a series of fine-mesh wire screens. These flame arrestors slow the ability of a flammable gas to reach the catalytic sensing element. That slow response alone may eliminate a catalytic sensor from consideration as a process monitoring device. The fine passages of the flame arrestors are also susceptible to clogging by condensate and particulate matter, blinding the sensor.

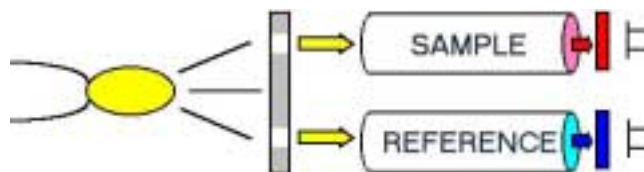
Catalytic sensors will exhibit considerable response drift when exposed to constant levels of flammable vapors. There is no way to ensure that they are responding accurately—or even responding at all—other than by injecting a known concentration of test gas through the flame arrestor. This calibration test should be done frequently, as this type of sensor gives no notice of failure.

Because of these characteristics, catalytic sensors are typically used only as leak detectors. They are generally well suited to area-monitoring applications where response times of ten to twenty seconds are acceptable; where the atmosphere does not contain condensate, dirt or dust; and where the atmosphere is normally free of flammable vapors.



Infrared absorption

Combustible gases absorb infrared radiation at certain characteristic wavelengths. A typical non-dispersive infrared (NDIR) detector passes a source of infrared energy through the sample and measures the energy received by one of two detectors. The active detector responds to wavelengths in the same band as the sample gas, while the other detector measures a reference to compensate for changes within the instrument.



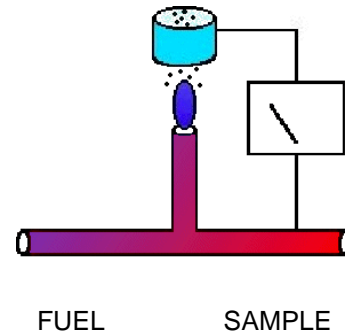
When combustible gases are present, they absorb some of the infrared energy and produce a signal in the active detector relative to the reference detector. Energy absorbed by the combustible gas for a given wavelength varies exponentially with the particular gas's absorptivity, the concentration, and the path length. This means that infrared detectors must be specifically calibrated for a particular gas, and can have very high variations in response factors and linearity for other gases.

Infrared detectors are usually limited to detecting a single combustible gas. Like catalytic-bead sensors, they are best suited to area monitoring applications.

Flame ionization

Flame ionization is a well-established measurement technique. A well designed FID completely burns the sample by pre-mixing a small quantity of sample with hydrogen fuel and injecting it into a burner. Combustible gases burned in a hydrogen flame will produce ions that can be measured as a weak current through an imposed electrical field. The resulting electrical signal is proportional to the amount of carbon present in the sample.

Some combustible gases contain oxygen, halogens or other electro-negative species which, in general, tend to inhibit the formation of ions. Because of its principle of operation, the FID is often referred to as a carbon-counter.



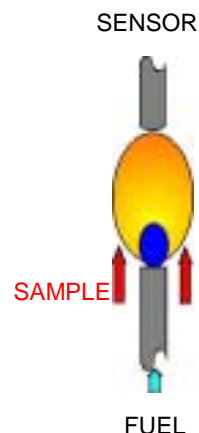
The response time of this detector is very fast but its measurement of flammability is indirect. To measure flammability, the substance being sampled must be known. The number of carbon ions in the sample must be converted to the number of specific molecules for that substance and then that concentration must then be expressed as a percentage of the LFL. While this technique works well for single substances, a FID's wide variation in response factors can sometimes make it impossible to accurately measure the flammability of other substances or of mixtures.

Flame temperature

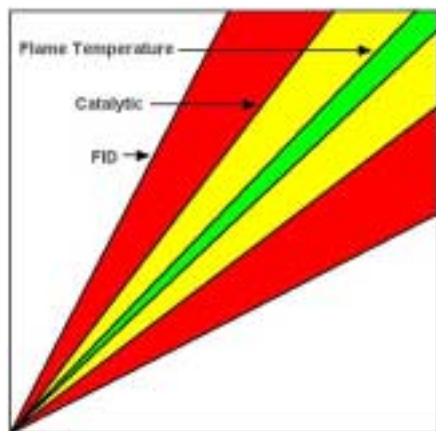
The flame temperature analyzer measures the amount of heat given off by a pilot flame as it burns in an explosion-proof measuring chamber. The small, well-regulated flame heats the tip of a temperature sensor suspended directly above it. The signal produced by the sensor when no flammable vapors are present drives the LFL indicator up to 0% LFL. This failsafe technique is known as a "live" zero because a weakening or loss of flame caused by lack of fuel will generate a downscale malfunction alarm.

When a flammable sample is drawn into the measurement chamber it is seen by the pilot flame as an additional source of fuel. This causes the temperature in the area of the pilot flame to increase. Since the meter knows that the increased temperature can only be caused by added fuel (the sample), it rises above zero in direct proportion to the flammability of the sample.

The dynamics of the flame temperature analyzer give it highly uniform response factors for a wide variety of combustible gases.



Analyzer Accuracy and Relative Response



Broad-band response

Few analyzers react the same way to all substances. A catalytic sensor calibrated to accurately read Methane will be wildly inaccurate when exposed to Hydrogen gas. A FID calibrated for Heptane might not measure Alcohol accurately. Both of these sensors are broad-banded and will react indiscriminately with most flammable vapors to which they are exposed.

Narrow-band response

An infrared sensor is a narrow-band instrument. It can usually discriminate between the substance of interest and background gases but it does not respond to gases outside of its narrow range of vision.

These variations in infrared sensor response may not pose a significant problem when measuring an atmosphere containing a single substance. But when asked to measure a mixture of different vapors, catalytic, FID and infrared instruments will usually fail miserably.

Universal response

Flame temperature analyzers will react accurately to most flammable substances and will usually measure both single substances and mixtures with the same high degree of accuracy. Unlike some sensors, flame temperature analyzers were developed for one specific purpose—to directly measure flammability.

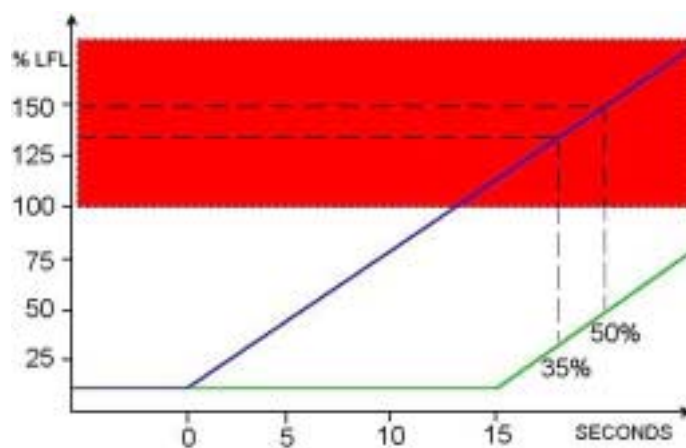
Speed Of Response

While accuracy is certainly a prime concern when selecting a flammability analyzer, consideration must also be given to how quickly a process might get out of control. The analyzer must be able to produce an alarm and initiate corrective actions in time to prevent a disaster. An analyzer with a stated response time of 10 seconds T_{63} , means that the analyzer will take ten seconds to reach 63 percent of it's final reading. An analyzer with a stated response time of 13 seconds T_{90} may actually be faster than the one rated 10 seconds T_{63} .

It's also important to calculate the time it will take for the sample to reach the analyzer. An analyzer designed to mount directly on a process wall or duct may have a sample delivery delay of only a fraction of a second but a remotely-mounted analyzer with a fifty foot sample line could have a sample delivery delay of 10 seconds or more. Add this to the analyzer response time and the total time to trigger an alarm may be unacceptable.

In the example illustrated here, the combined sample line delay and the response time of the analyzer produce a 15 second total delay. In other words, the response of the analyzer is fifteen seconds behind the real event. By the time the analyzer activates it's warning alarm set at 35% LFL, the true concentration in the process is already above 130% LFL.

Think about the corrective action that the analyzer's alarm relays will control. How long will it take for that damper, fan or e-stop to have an effect on the process? Only after you have calculated the reaction time of all these elements will you know the true response time of the system upon which you will depend for the protection of your product, equipment and people.



Sample Conditioning

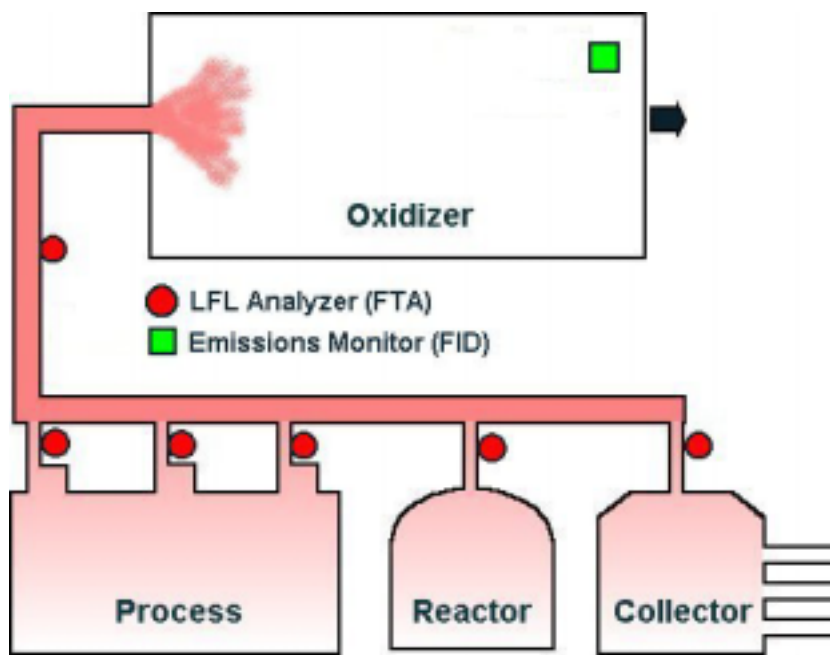
To ensure that the vapor concentration reaching the analyzer is exactly the same as the concentration at the point of origin, the sample must always be kept in a vapor state. The analyzer, the sample line and any other elements of the sample train may have to be heated to keep the sample above it's dew point. If allowed to cool, the sample will condense, causing drop-out and possible clogging.

Light condensation will coat the walls of the sample line, reducing the concentration that reaches the analyzer and causing false readings. Heavier condensation may clog the sample line, causing the analyzer to shut down the process.

When determining the operating temperature required for the analyzer and sample line, remember to calculate the flash point or condensation temperature of *all* substances in the sample atmosphere, even those that are not flammable. *Any substance can clog the sample line or analyzer if it is allowed to condense.*

Application Examples

Consider an oxidizer which may have to destroy a VOC stream from one or more sources. Danger is present when the inlet stream suddenly gets rich enough to ignite or explode. Some possible sources of this unexpected increase in flammability are shown in the sketch below.



- Most modern process lines re-circulate heated ventilation air to reduce fuel usage and lower the air flow through the oxidizer. Their exhaust streams tend to be highly concentrated.
- Reactors may run out of control, raising the VOC concentration in the vessel and associated ducts above 100% of the LFL.
- Collection vats can accumulate a dangerous concentration of vapors from various inlet ducts.

LFL monitors are typically used on the exhaust ducts of these sources, allowing them to operate at high vapor concentrations while protecting the system from fire and explosion.

An LFL analyzer on the inlet duct to an oxidizer protects it from dangerous concentrations produced by rich vapor streams.

A FID at the outlet of the oxidizer ensures that it does not exceed emission levels into the atmosphere. Depending on the type of operating permit, the use of a FID may also allow the oxidizer's operating temperatures to be reduced to more economical levels.

Summary

When selecting a flammability analyzer, it's always a good idea to enlist the advice of a specialist in the field. That specialist may be a co-worker, a “for-hire” expert or an impartial instrument manufacturer that makes not just one but several of the analyzers mentioned in this document.

Do not assume that “one size fits all” or that the analyzer which was correct for a previous job will also be the right choice for another application. Whether new or similar, the specific details of each application need to be examined closely to prevent disaster. The application survey that a manufacturer's technical sales representative or engineer asks you to fill out is a critical part of this selection process.

Choosing the right kind of instrument can be a detailed task, even for those familiar with the process. The instrument of choice may vary from one application to the next, but *the correct process flammability analyzer will always be fast, accurate, and fail-safe*. In most cases, it will also be able to read a wide range of flammable substances.

This document provides a simplified overview of flammability monitoring in processes applications. For in-depth information, please contact:

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