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PULP & PAPER: MEASURING TURPENTINE & CLO_2

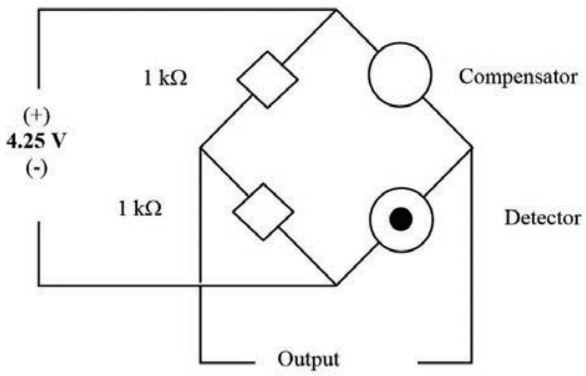
Like many industries, Pulp & Paper manufacturing facilities have many confined spaces that may require atmospheric gas measurement to ensure employee safety. However, turpentine vapors and chlorine Dioxide (ClO_2) gas tend to be specific to the Pulp & Paper industry and present their own gas monitoring challenges. Understanding these gases and vapors and the means of measuring them can help raise workers confidence in their gas monitors.

TURPENTINE

The pulping process produces two major product streams. One stream is the fiber used to produce paper; the other stream is the chemicals derived from wood products that have applications as diverse as paints and foods. Turpentine is one of these chemicals, and it is unusual because it has a low LEL (Lower Explosive Limit) of 0.8% by volume (8,000 ppm) and it is a cool-burning vapor with a low ignition temperature of just 488°F compared to 999°F for methane. These characteristics make it very difficult to measure turpentine vapors with a conventional LEL sensor. To understand why turpentine is difficult to measure with most LEL monitors, one must understand the operation of an LEL sensor.

LEL SENSORS WERE DESIGNED TO MEASURE METHANE

LEL sensors were originally designed to solve the problem of measuring methane levels in coal mines. Most LEL sensors use a Wheatstone bridge to measure the heat released when a flammable gas burns on a catalyst bead. The temperature rise causes a change in resistance, which is measured and converted to % LEL.



LEL Sensors Simplified

A Wheatstone bridge sensor is simply a tiny electric stove with two burner elements. One element has a catalyst (such as platinum) and one doesn't. Both elements are heated to a temperature that normally would not support combustion. However, the element with the catalyst "burns" gas at a low level and heats up relative to the element without the catalyst. The hotter element has more resistance and the Wheatstone bridge measures the difference in resistance between the two elements. Effectively, this sensor measures the temperature at which gas burns.

LEL Sensor Limitations

Two mechanisims affect the performance of Wheatstone bridge LEL sensors and reduce their effectiveness when applied to all but methane:

1. Gases burn with different heat outputs at their respective LELs. Some gases burn hot and some burn relatively cool. These differing physical characteristics lead to difficulties when using LEL sensors. For example, 100% of LEL methane (5% methane by volume) produces much more heat than 100% of LEL turpentine (0.8% turpen tine by volume). Because LEL sensors actually measure the heat at which a gas or vapor burns, they can be "fooled" by vapors like turpentine that burn cool relative to methane.

2. "Heavier" hydrocarbon vapors have difficulty diffusing into the LEL sensor, reducing its output. Some "heavier" hydrocarbon vapors like turpentine have difficulty diffusing through the sintered metal flame arrester on LEL sensors. This flame arrestor is necessary to prevent the sensor itself from starting a fire, but it doesn't prevent "light" gases like methane, propane, and ethane from reaching the Wheatstone bridge. However, "heavy" hydrocarbon vapors like turpentine, gasoline, diesel, etc., have difficulty diffusing through the flame arrestor, so less vapor reaches the Wheatstone bridge and the sensor gives less output.

Wheatstone bridge LEL Sensor Sensitivity Relative to Methane

According to the following chart, turpentine produces about one-third (34%) of the response of methane on a Wheatstone bridge sensor.

Gas/Vapor	LEL (%vol)	Sensitivity (%)
Diesel	0.8	30
Hexane	1.1	47
Methane	**5.0**	**100**
Pentane	1.5	45
Propane	2.0	53
Turpentine	0.8	34

For example: After calibration on methane, if an LEL sensor displays 34% of LEL in a mixture of turpentine and air, the actual LEL is approximately 100% because turpentine only produces 34% of the sensor output compared to methane. LEL readings can be corrected by choosing calibration gases that are more appropriate to the gas that you are measuring. Some manufacturers calibrate their LEL sensors to hexane, pentane or propane for this reason.

Correction Factors (response factors) can also be used during calibration or electronically applied by the gas monitor to correct the reading to the intended target gas while still calibrating on methane. However, even with the appropriate correction factor, LEL sensors lack the sensitivity for accurately measuring the LEL of turpentine.

Due to the combination of sensor drift and the Wheatstone bridge's inability to accurately measure turpentine, LEL monitors using a Wheatstone bridge sensors may give workers a false sense of security when the atmosphere really is potentially flammable. In extreme cases this has resulted in injuries where hot work was performed in atmospheres containing flammable levels of turpentine vapors.

Using a PID to Measure Turpentine

Photoionization detectors (PIDs) are sensitive hydrocarbon sensors originally designed to measure ppm levels of hydrocarbons for the environmental industry. PIDs have excellent sensitivity to turpentine and can be used for reliable measurement in the range of 0-2000 ppm. 10% of LEL turpentine is 800 ppm (the LEL = 0.8% by volume or 8000 ppm). So if a PID is set to alarm at 800 ppm turpentine that is the same as a 10% of LEL alarm. Based upon the following chart, one can see that PIDs will provide the most consistent readings at 10% of LEL Turpentine (800 ppm).

	Display	Actual (ppm)
PID Display	800	800
PID low (-10%)	720	720
PID high (+10%)	880	880
LEL Display	10	800
LEL low (-3%)	7	***560***
LEL High (+3%)	**13**	***1040***

Sensor accuracy affects user confidence. At 10% of LEL, a PID is clearly the more accurate sensor:

- PID range of uncertainty: 160 ppm
- LEL Sensor range of uncertainty: 480 ppm

So a Wheatstone bridge LEL sensor has three times the range of uncertainty relative to a PID. To learn more about PIDs please read the AP-211: PIDs for Continuous Monitoring of VOCs.

RAE PID CHOICES FOR PULP & PAPER

ToxiRAE Pocket PID
An affordable "personal" PID that fits into a shirt pocket.

MultiRAE PID & Multi-gas Monitor
The PID detector, in addition to oxygen, LEL, two toxic gas sensors and an internal pump, makes it a versatile instrument for all confined space entries in Pulp & Paper industries:

- Internal pump to remotely sample confined spaces.
- Case sealed for the damp, dusty environments found in Pulp & Paper industries.
- Durable composite case for rugged use.

CHLORINE DIOXIDE

In the pulping process it is often necessary to bleach the wood fibers to make them white. For years this was accomplished by using chlorine (Cl_2). However, one of the by-products of chlorine bleaching is the production of toxic dioxins that enter the environment through bleaching waste streams. Therefore, more environmentally friendly means of bleaching pulp have been pursued.

One of the most common substitutes for chlorine is to use chlorine dioxide (ClO_2). It whitens pulp even better than chlorine, and it does not produce the toxic dioxin waste streams produced by elemental chlorine bleaching. Both Cl_2 and ClO_2 are carcinogens and are toxic in low quantities, but ClO_2 is less stable and more toxic. Therefore, it must be handled in the working environment with extreme care.

Comparison of elemental chlorine and chlorine dioxide

Threshold	Cl_2	ClO_2
Odor	0.08 ppm	0.1 ppm
TWA (NIOSH)	0.5 ppm	0.1 ppm
TWA (OSHA)	1.0 ppm	0.1 ppm
IDLH	10 ppm	5 ppm
STEL		0.3 ppm

Chlorine (Cl_2) is a greenish yellow gas with a pungent, irritating odor. It has an advantage in that it can easily be smelled at 0.08 ppm, which is well below its toxic threshold (1.0 ppm OSHA, 0.5 ppm NIOSH). It is virtually impossible for workers to remain in a chlorine-contaminated atmosphere without proper respiratory protection.

Chlorine dioxide is a yellowish gas with a sweet odor similar to chlorine and nitric acid. However, its odor threshold is the same as its toxic threshold, so that once you can smell ClO_2 you are already in potential trouble. In addition, ClO_2 deadens the olfactory nerve, so prolonged exposure desensitizes people to ClO_2. Because of this it is desirable to have a monitor to measure exposure to ClO_2 gas in the working environment.

CHLORINE DIOXIDE SENSOR SENSITIVITY AND RESOLUTION

Developments in sensor technology have yielded sensors that can be highly sensitive and specific to chlorine dioxide. RAE Systems has developed a monitor with the resolution necessary to accurately measure chlorine dioxide. Most chlorine monitors only offer 0.1 ppm resolution. This is appropriate because chlorine's toxic threshold (OSHA) is 1.0 ppm. However, chlorine dioxide has a toxic threshold that is 10% of chlorine's. So a monitor with just 0.1 ppm resolution would go into alarm as soon as it came across chlorine dioxide. This can lead to too many false alarms. Therefore, a chlorine dioxide monitor needs to have 0.01 ppm resolution. The RAE Systems ToxiRAE II (ClO_2) provides this necessary resolution. When turned on, it displays 0.00 ppm in a clean environment.