Scott Technical Note 101

PIDs for Continuous Monitoring of VOC's

Toxic Gases and Vapors

Four-Gas monitors make up the bulk of real-time gas monitoring in industry today. However, because four-gas monitors typically only measure oxygen (O2), the lower explosive limit (LEL) of combustible gases, carbon monoxide (CO) and hydrogen sulfide (H2S), they miss many common toxic gases and vapors that are major constituent sor by-products of industrial processes. Therefore, workers are often underprotected, with negative health consequences, or overprotected, with loss of worker productivity.

Though written specifically for sewer entries, OSHA recognizes this shortcoming in gas detection in its publication 1910.146, appendix E:

> *"where the employer has not been able to identify the specific atmospheric hazards present or potentially present in the sewer, broad range sensors are preferable because they indicate that the hazardous threshold of a class (or classes) of contaminants (i.e., hydrocarbons) in the sewer have been exceeded."*

PIDs: Accurate Broad-Band Sensors

Photoionization detectors (PIDs) measure low levels (0 to 10,000 ppm) of VOCs (volatile organic compounds) and other toxic gases. A PID provides a compact, accurate, affordable and reliable real-time gas monitoring alternative for measuring many of the common toxic gases and vapors in industry such as VOCs that four-gas monitors miss.

What Are Some Common VOCs?

VOCs are the chemical compounds that keep industry going, and include:

- Fuels
- Oils, degreasers, heat transfer fluids
- Solvents, paints
- Plastics, resins and their precursors

VOCs are found throughout industry, from the obvious applications in the petrochemical industry to not-so-obvious applications such as sausage manufacturing.

Why Not Use an LEL Monitor?

Many VOCs are flammable and may be detected by the LEL (lower explosive limit) or combustible gas sensors found in virtually every multi-gas monitor. However, LEL sensors are not particularly useful in measuring toxicity because they do not have enough sensitivity.

Why Not Use Colorimetric Tubes?

Colorimetric tubes (often referred to as "Dräger" tubes) have been the foundation of gas detection for years. They provide an accepted and proven means of measuring many toxic gases and vapors at ppm levels. Colorimetric tubes are inexpensive, but have limitations:

- Tubes only provide "snapshots," like a Polaroid camera. They cannot provide quality analysis or continuous monitoring with alarms. A tube cannot be put on personnel and be expected to alarm when conditions become dangerous.
- The "spot check" nature of tubes also makes them more prone to sample errors. Continuous monitors, sampling at 100 to 500 cc/min, are less likely to be fooled by a false high or low reading due to small sample volume, air currents, or bad sampling technique.
- Tubes are slow to respond. They give readings in minutes rather than seconds.
- Bellows-type tube pumps provide 25% accuracy at best, and piston/syringe style tubes provide 15% accuracy, so if the true concentration of a gas is 100 ppm, a bellows-type tube can read between 75 and 125 ppm.
- Tube readings are subject to interpretation.
- Tubes generate glass splinters and chemical waste.
- A large stock of tubes can be expensive.
- Tubes expire.
- There is a limited number of tube chemistries, so tubes are not as specific as many would want to believe.

Why Not Use a MOS Sensor?

Semiconductor or Metal Oxide Sensors (MOS) are one of the oldest and least expensive measurement technologies used in portable instruments. While MOS sensors can detect a very wide range of contaminants, they have number of shortcomings that limit their effective.

- They have limited sensitivity, with detection limits usually in the tens of ppm.
- They produce a non-linear output, so they are not particularly accurate. MOS sensors at best gross indicators for toxic gases and vapors. Making go/no-go decisions based on their output can be dangerous because their non-linear output is like trying to measure paper with a rubber ruler.
- They are slow to react (relative to a PID).
- They respond positively to moisture and temperature.
- They can be poisoned and dirtied and are not easily cleaned.
- MOS sensors are the first true broad-band sensors, so they respond to a wide variety of compounds.

Adsorbent Media Followed By GC/MS Lab Analysis

Low-flow pumps are used to pull a sample through an adsorbent tube to provide continuous monitoring over an entire workday. These adsorbent tubes are sent to a lab where they are desorbed. After analysis with gas chromatography/mass spectrostrophy (GC/MS), one can tell exactly what the average concentration of chemical exposure was for the worker who wore a pump. To approximate the concentration versus the time of exposure, multiple tubes must be run through the pump during the working day. This leads to greater complication and cost. Specific, adsorbent tubes are reactive rather than proactive, and results can take days or weeks to return from the lab. By the time that the results are available, workers may have often forgotten what they were doing when they were exposed. The delay in feedback makes it difficult for workers to modify their work patterns in real time to reduce or eliminate exposures. Because the exposure data is often interpreted and delivered to the worker by a trained safety professional, the nature of the presentation of the data can be of a disciplinary nature.

If a Colorimetric Tube is like a Polaroid snapshot, then adsorbent media is like a 35mm camera. Adsorbent media provide excellent results, but you must wait for the film to be developed! In addition, lab analysis is expensive.

Portable GC/MS

Gas chromatography/mass spectrometry has the ability to be selective but not continuous. It can only take "snapshots" and is unable to provide continuous monitoring with alarms. The spot-check nature of GC/MS also makes it prone to sample error. Continuous monitors, sampling at 100 to 500 cc/min, are less likely to be fooled by a false high or low reading due to small sample volume, air currents, or bad sampling technique.

In addition, no GC/MS is portable or rugged enough to be worn continuously by a worker. Therefore, a GC/MS is also a reactive rather than a proactive form of protection. It can only report intermittently on what happens. A GC/MS can tell a story in snapshots rather than continuous, instantaneous data. Finally, GC/MS tends to be prohibitively expensive.

Flame Ionization Detectors (FIDs)

Flame Ionization Detectors (FIDs) respond to a broad range of organic compounds but are non-selective. While their linearity is excellent, their use is limited by their large size and weight, including the need to carry a hydrogen cylinder. FIDs are relatively expensive and maintenance-intensive, and this limits their use in most industries. PIDs and FIDs are often referred to generically as organic vapor analyzers, or OVAs. Many people want to know the difference between the two techniques, and the difference is really one of preference. The difference between an FID and a PID is like the difference between a meterstick and a yardstick. They effectively measure the same things, but because PIDs are smaller, easier to use, and significantly less expensive, their usefulness in industry is potentially greater than FIDs.

Photoionization Detectors (PIDs)

A PID is essentially a gas chromatograph without its separation column. Therefore, a PID can provide excellent accuracy. Some say that while the PID is

clearly sensitive and accurate to many toxic gases and vapors at ppm levels, its lack of selectivity reduces its usefulness. However, most of the other methods also have limited selectivity, including colorimetric tubes, MOS and FIDs. The advantage of the PID is that while it is not selective, it is a small, continuous monitor that can provide instantaneous feedback to workers. This lets them take control of their actions and allows them to perform their job tasks with confidence that they are not being exposed to hazardous chemicals. Like a VCR, the PID measures continuously and its results can be datalogged and "played back" instantly.

References

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