MEASURING HEAT TRANSFER FLUIDS WITH A PID

Heat transfer fluids are used in many processing applications to carry heat from a source, such as a boiler, to a target process, such as a chemical processing vessel. While hardly volatile at room temperature, some heat transfer fluids contain highly toxic substances that can become volatile when heated. Heat transfer fluids typically are contained in a closed-loop system so that they do not come in contact with personnel or the process. However, leaks can and do occur. Because of the high toxicity of some heat transfer fluids, it is desirable to measure them for leak detection and to assure that levels are low enough to allow workers to operate safely. photoionization detectors (PIDs) are very sensitive to the compounds that make up many heat transfer fluids and offer an effective means of providing real-time measurement for worker health and safety and for leak detection.

WHY MEASURE HEAT TRANSFER FLUIDS?

Some heat transfer fluids, but not all, have toxicity issues (for example: DowTherm® A, Therminol VP-1®). Users must check the material safety data sheet (MSDS) of a fluid to ascertain its toxicity. To understand why a PID is necessary to measure heat transfer fluids, one needs to understand their chemical properties and toxicity.

DowTherm A is made up of 73% diphenyl oxide (phenyl ether) and 27% diphenyl (biphenyl). Both of these constituents have relatively low exposure limits:

Threshold	Diphenyl Oxide	Diphenyl	DowTherm® A	DowTherm® A (Calc.)
Odor	0.001-0.01 ppm	0.0095 ppm	0.0095 ppm	<0.001 ppm
PEL (OSHA)	1 ppm (7 mg/m^3)	0.2 ppm (1 mg/m^3)	1 ppm (OSHA)	0.48 ppm
IDLH	100 ppm	20 ppm (100 mg/m^3)	10 ppm (NIOSH)	48 ppm

DowTherm A has a characteristic sweet odor. It can be readily detected by smell well below its exposure limits. But because of its relatively low exposure limits, the only way to accurately know how much DowTherm A is too much is through measurement. Grab samples and lab analysis provide accuracy, but they take too long for the results. This does not allow workers to make timely decisions on leak detection or personal protection equipment (PPE). PIDs provide immediate, accurate measurement of DowTherm A to allow workers to immediately make these decisions.

The Calculated TLV for DowTherm A is given by the following formula:

$$TLV_{mix} = 1 / (X_1/TLV_1 + X_2/TLV_2)$$

where X_i and TLV_i are the mole fraction (percentage) of total VOCs, TLVs, of the individual components, respectively (reference RAE Systems publication TN-106: Correction Factors, Ionization Energies and Calibration Characteristics). Therefore, the calculated limits for DowTherm A are:

$$TLV = 1 / (0.73/1 + 0.27/0.2) = 0.48$$

$$IDLH = 1 / (0.73/100 + 0.27/20) = 48$$

HOW DOES A PID MEASURE DOWTHERM A?

PIDs can measure vapors that have an ionization energy (IE) that is less than the output of the PID lamp. (For more information on how PIDs work and what they measure, refer to RAE Systems publication AP-211: Continuous Monitoring of VOCs). Diphenyl oxide (phenyl ether) has an IE of 8.09 eV, and diphenyl (biphenyl) has an IE of 7.95 eV. Both of these ionization energies are less than the 10.6 eV output of the standard PID lamp, so both diphenyl oxide and diphenyl, and therefore DowTherm A, can be measured with a PID. PIDs are very sensitive to these compounds and can provide accurate, reliable and affordable real-time measurement of DowTherm A.

Measuring at Lower Temperatures

DowTherm A's high boiling temperature of 495°F (257°C) and vapor pressure of 0.025 mm Hg at 25°C means that at normal ambient temperatures few DowTherm A vapors are produced. For example, sampling the vapors above a bucket of DowTherm A well below room temperature (41°F, 5°C) should produce little or no reading on a PID. At room temperature (68°F, 20°C) the staturated air space above a bucket of DowTherm A could be expected to contain 33 ppm. However, because DowTherm A is used as a heat transfer fluid, it is often found at elevated temperatures that can produce significant vapors.

Calibrating a PID to DowTherm A

Because DowTherm A has a high boiling point, it is impossible to make a compressed gas standard for it. Therefore, it is recommended that a "surrogate" calibration method be used to calibrate the PID to DowTherm A. This type of calibration is used

quite often with PIDs and provides for reliable, repeatable and affordable calibration. RAE Systems testing has shown that our PIDs are 2.5 times as sensitive to DowTherm A than to the surrogate calibration gas isobutylene. That means that if a PID is calibrated on isobutylene and then is used to measure DowTherm A, it reads too high by a factor of 2.5 times. Therefore, if the reading is multiplied by the reciprocal value of 2.5 (0.4), then the reading will be corrected to "ppm units of DowTherm A":

(2.5 ppm of DowTherm A in Isobutylene Units)
x
(0.4 Correction Factor for DowTherm A)
=
(1.0 ppm of DowTherm A Actual)

Because the target concentrations of DowTherm A are low, it is recommended that users calibrate with our lowest range of Isobutylene cal gas for greatest accuracy. RAE Systems recommends calibrating with 10 ppm Isobutylene (p/n 600-0069-000).

Unusual Characteristics of DowTherm A

DowTherm A's high boiling temperature means that it has a "sticky" nature. It tends to remain on surfaces that it has touched and is readily absorbed by some materials. Therefore, when using a PID for sampling for leaks, it is recommended that the probe be protected by slipping a drinking straw over it. If liquid DowTherm A comes in contact with the straw, the straw can be thrown away. If DowTherm A comes in contact with the sample probe of a PID, it must be thoroughly solvent cleaned before further sampling.

Never Use Tygon Tubing with DowTherm A

Because Tygon® sample tubing quickly absorbs heat transfer fluids, it should never be used when sampling for them. Long sample lines can cause heat transfer fluid vapors to condense. Therefore, it is recommended that all sampling be conducted without additional sampling hose. Inline filters can also promote condensation of heat transfer fluid, so they should be eliminated or reduced.

Sampling High Concentrations of DowTherm A

When DowTherm A can be seen in plumes, this is an indication that high concentrations (25 to 100 ppm) are present, which can lead to condensation in the sampling train. High hits of DowTherm A may condense in the sampling train of a PID. If the PID does not clear with a 5-minute exposure to fresh air, then clean the components of the PID using a methanol wash in the following order:

1. Sample probe
2. Clean/replace filters
3. Clean Sensor and PID lamp

For further information on PID cleaning, refer to your RAE Systems instrument manual.

RAE SYSTEMS PIDS FOR MEASURING HEAT TRANSFER FLUIDS

While any RAE Systems PID can measure heat transfer fluids, two are particularly recommended for routine monitoring.

ppbRAE Plus PID. Breakthrough technology to measure VOCs and other ionizable compounds in parts per billion (ppb). The ppbRAE provides unsurpassed accuracy, capable of continuous detection down to 1 ppb. Advanced comparitor circuitry in the ppbRAE Plus' sensor allows it to be set to zero out background VOCs so that the operator can see the rise in VOCs above the current background level.

MiniRAE 2000 PID. The MiniRAE 2000 is our best detection, or survey, instrument.

- Its strong pump (>400 cc/min) provides quick response and clears out overexposures quickly.
- The MiniRAE 2000's sensor is in front of its pump, and this keeps the length of sample line to a minimum.
- The quick response of the MiniRAE 2000 makes it uniquely suited as a Detector. The "Geiger counter" feature of our MiniRAE 2000 means that it beeps at a higher frequency as the concentration increases. This is particularly useful when checking pump seals for leaks.
- Quick Lamp and Sensor Access. Access the lamp and sensor in seconds without tools. Other PIDs have quick lamp access, but what is the point if you can't clean the sensor. Cleaning the lamp without cleaning the sensor is like taking a shower and then putting on the same sweaty clothes!

REFERENCES

NIOSH: *Pocket Guide to Chemical Hazards*, NIOSH Publications, Cincinnati, OH 1994

RAE Systems: Correction Factors, Ionization Energies and Calibration Characteristics (Technical Note TN-106)

RAE Systems: Setting Alarm Limits for Mixtures (Technical Note TN-130)

RAE Systems: Continuous Monitoring of VOCs (Applications Note AP-211)

TRADEMARKS