Method 21 Monitors Fugitive Emissions

This EPA method provides the framework to discover the best available technology for detecting leaks at pumps, valves, compressors and other components.

By Susan Hennigan

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While the Clean Air Act Amendments propose fugitive emission leak rates from 10,000 parts per million (ppm) to 500 ppm,[1] some facilities consider a component that emits as low as 100 ppm volatile organic compounds (VOCs) a problem.

The emphasis now is on compliance in a cost-effective and reliable manner to ensure a cleaner environment and greater efficiency at the plant.

Method 21 is the process specified by EPA for monitoring fugitive emissions at valves, pumps, compressors and other components. The method is designed as a screening procedure and in some cases provides a wide range of instrument specifications. The intent of these specifications is to standardize the test procedure while not limiting the method to only one type of detection method or analyzer.

Variable results have been obtained by different instruments that fall at either end, but within the stated design criteria. For example, the distance between the component and the analyzer probe tip, the strength of the analyzer internal sampling pump and ambient wind velocity will affect the level of leaker status. Again, the intent is not to limit the choice of analyzer employed, but to offer to the user the "Best Available Technology" for a particular product/plant monitoring program.

The Code of Federal Regulations (40 CFR Part 60) outlines EPA's Standards of Performance for New Stationary Sources.[2] Appendix A, Method 21 — Determination of Volatile Organic Compound Leaks — outlines the procedure to be followed to measure fugitive emission leaks.

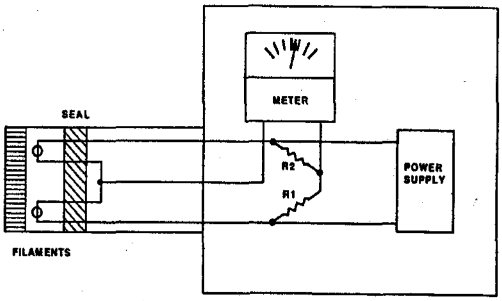


Figure 1. Catalytic Oxidation Detection

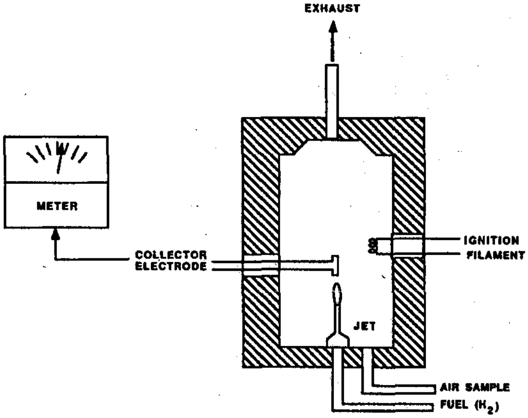


Figure 2. Flame Ionization Detection

EPA defines fugitive emissions as those emis-

continued on page 26

continued from page 22

sions that do not occur as part of the normal operation of plants. They result from an equipment leak and are characterized by a diffuse release of VOCs or hydrocarbons into the atmosphere. VOCs are any organic compound that participates in atmospheric photochemical reactions, generally non-methane hydrocarbons in the C_2 through C_6 range; or which is measured by a reference method, equivalent method, alternative method or determined by procedures specified under any subpart.

Analyzer manufacturers try to make sure they are meeting all the instrument specifications; however, some instruments lend themselves to certain applications better than others and it is important to know the limitations of each.

Instrument Specifications

The agency's Method 21 specifies that the VOC instrument detector shall respond to the compounds being processed. Detector types that may meet this requirement include, but are not limited to, catalytic oxidation, flame ionization, infrared absorption and photo ionization.

Catalytic oxidation detection (See Figure 1, page 22) employs a Wheatstone bridge circuit with an active element (normally a platinum wire) with an inactive or sealed element of similar material to balance ambient variations. Liberation of the heat of combustion causes an increase in filament temperature, and therefore an imbalance in the bridge. This response increases with gas concentration through the lower explosive limit, but falls when the gas concentration reaches 100 percent, since there is no combustion.

With flame ionization detection (FID) (See Figure 2, page 22), hydrocarbons are introduced into a flame and ionization takes place in strict proportion to the amount of compound. The reaction is:

$$RH + O = RHO^+ + e^- = H_2O + CO_2$$

The positive ions generated are collected on an electrode and the resulting current is amplified to a readout device.

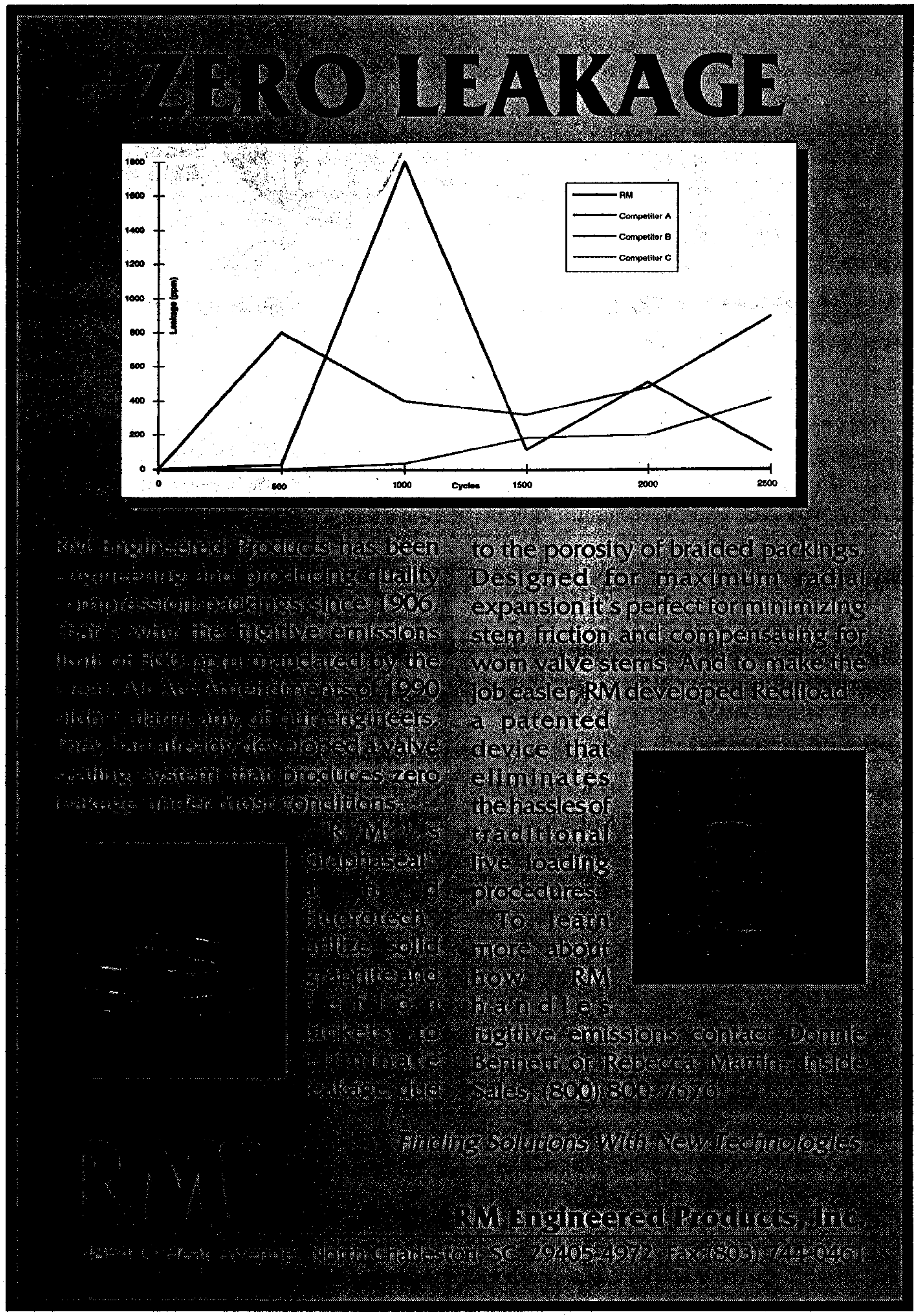
Photo ionization detection (PID) (See Figure 3, page 28) occurs when a molecular species absorbs a photon of light energy and disassociates into positive ions and an electron:

$$R + hv = R^+ + e^-$$

The energy of the photon is dependent on the ultraviolet lamp used; higher energy lamps (11.7/11.8ev) are more universal than the more selective lower-energy lamps. The PID is one of the most versatile nonradioactive ionization detectors.

For infrared detection (IR) (See Figure 4, page 31), infrared energy, emitted from a wire source, is directed to a filter wheel that allows energy at the selected wavelength to be collected by a light pipe assembly and to pass through the gas cell to the detector. The sample absorbs infrared energy from the beam and the amount of absorption is measured by the detector, amplified and sent to the display. The amount of infrared radiation absorbed by a sample is directly related to the concentration of the sample according to Beer's Law:

$$A = a \times b \times c$$



The analyzer must be able to read the leak defined and therefore the user should consider the upper dynamic range of the detector and its saturation point for each VOC monitored.

where A = absorbance, a = absorptivity constant, b = pathlength and c = concentration.

It is imperative to choose an analyzer that will respond to the compounds being processed to meet instrument specification "a" in 40 CFR 60 Method 21.

The method also requires that "both the linear response range and the measurable range of the instrument for each of the VOCs to be measured, and for the VOC/gas that is used for calibration, shall encompass the leak definition concentration specified in the regulation. A dilution probe assembly may be used to bring the VOC concentration within both ranges; however, the specifications for instrument response time and sample probe diameter shall still be met."

Careful Selection

The leak definition concentrations can vary depending on the compound and type of leak being monitored. The analyzer must be able to read the leak defined and therefore the user should consider the upper dynamic range of the detector and its saturation point for each VOC monitored. Instruments are not necessarily linear for all compounds over the entire range. Detectors should be carefully selected to ensure the analyzer is linear over the range for the specific compound.

Method 21 indicates that the instrument must measure the leak definition, (generally 500 to 10,000 ppm) in a linear fashion. Should a dilution accessory be employed, the response time must still be less than 30 seconds and the sample probe outside diameter less than 1/4 inch.

In addition, Method 21 requires that:

- The scale of the instrument meter shall be readable to +2.5 percent of the specified leak definition concentration when performing a no detectable emission survey.
- The instrument shall be equipped with an electrically driven pump to ensure that a sample is provided to the detector at a constant flow rate. The nominal sample flow shall be 0.10 to 3.0 liters per minute when the probe is fitted with a glass wool plug or filter that may be used to prevent plugging of the instrument.
- The instrument shall be intrin-

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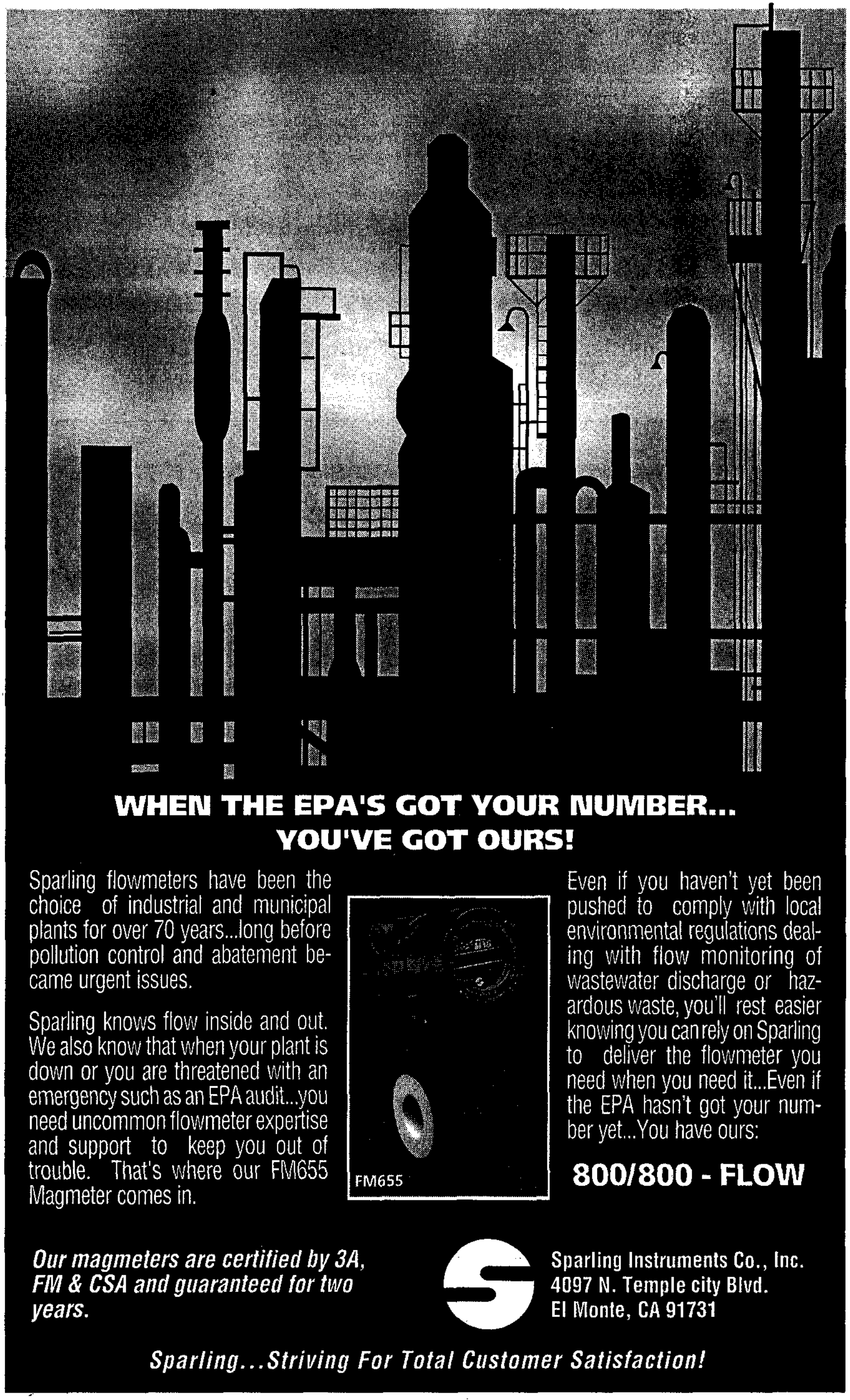

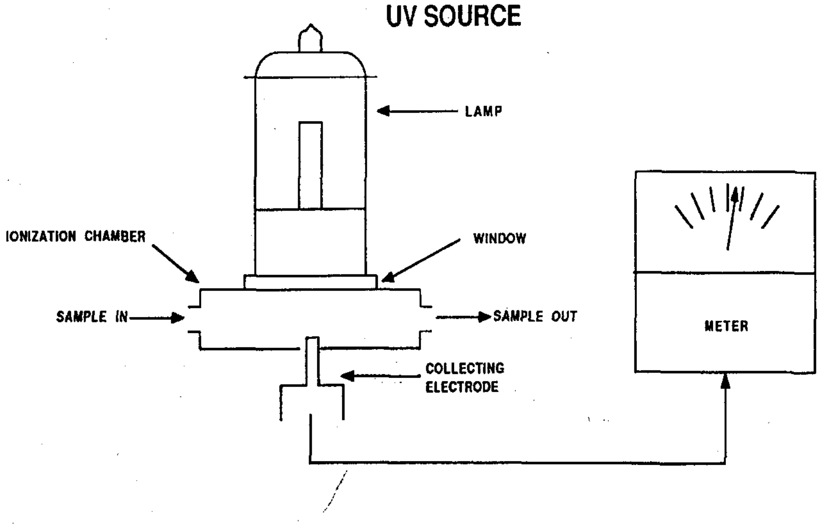

Figure 3. Photo Ionization Detector

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sically safe as defined by the applicable U.S. standards (for example, National Electric Code by the National Fire Prevention Association) for operation in any explosive atmospheres that may be encountered in its use. The instrument shall, at a minimum, be intrinsically safe for Class I, Division 1 and Class II, Division 1 conditions, as defined by the example code. The instrument shall not be operated with any safety device, such as an exhaust flame arrestor, removed.

Class I, Division 1 — Areas where flammable gases or vapors exist under normal conditions may exist due to repair, maintenance or leakage, or released because of breakdown or failure of operation. Class II, Division 1 are areas where combustible dust exists.

- The instrument shall be equipped with a probe or probe extension for sampling not to exceed 1/4-inch in outside diameter, with a single end opening for admission of sample.

Performance Criteria

A response factor must be determined for each compound that is to be measured, either by testing or from reference sources. The response factor tests are required before placing the

The calibration precision test must be completed prior to placing the analyzer into service, and at subsequent intervals or at the next use, whichever is later.

analyzer into service, but do not have to be repeated at subsequent intervals.

The instrument response factors for each of the VOCs to be measured shall be less than 10. When no instrument is available that meets this specification when calibrated with the reference VOC specified in the applicable regulation, the available instrument may be calibrated with one of the VOCs to be measured, or any other VOC, so long as the instrument then has a response factor of less than 10 for each of the compounds to be measured.

Not only is it important to know that the response factor is less than 10, but the concentration at which the response factor is applied also must be considered. The relative response is not necessarily a linear function, is compound dependent and can differ significantly between 500 ppm and 10,000 ppm. A response factor should be applied that has been generated at the same concentration as the leak rate defined.

If a response factor has been published for the compound of interest for the instrument or the detector type, the response factor determination is not required and existing results may be referenced. If the response factor is less than 3 for a volatile hazardous air pollutant that accounts for 90 percent or more by weight of the process stream, then direct instrument readings may be used without adjustment for response factors.

Several studies have provided a large database of analytical response factor information (see Other Resources at end of article).

The response time test is required prior to placing the instrument into service. The instrument response time shall be equal to or less than 30 seconds. The instrument pump, dilution probe (if any), sample probe and probe filter that will be used during testing shall be in place during the response time determination.

To check the instrument response time, introduce zero gas into the instrument sample probe. When the meter reading has stabilized, switch quickly to the specified calibration gas. Measure the time from switching to 90 percent of the final stable reading. Perform this test sequence three times and record the results. Calculate the average response time.

The calibration precision must be equal to or less than 10 percent of the calibration gas value. This calibration precision test must be completed prior to placing the analyzer into service, and at subsequent three-month inter-

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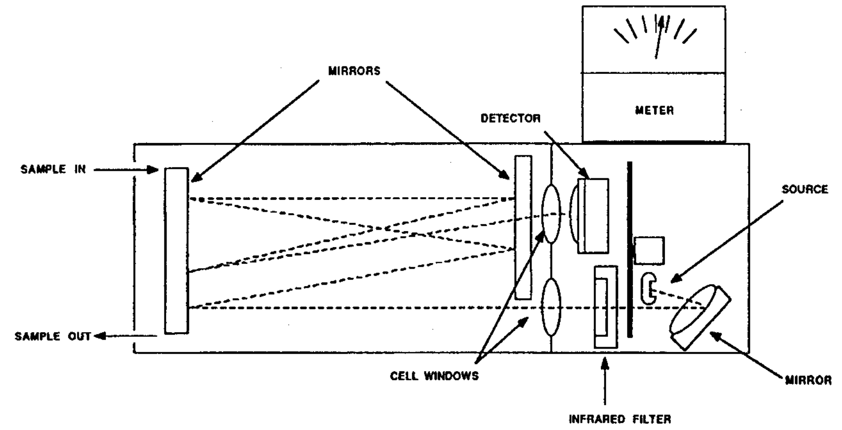

Figure 4. Infrared Detector

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vals or at the next use, whichever is later.

Conclusion

Many portable detectors are available for compliance with EPA Method 21.

Selection should be based on the instrument's ability to measure the compounds present over the defined leak rate concentration range in a safe, accurate and linear fashion. EP

References

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