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Technical Note #104

Do PIDs Detect CWAs?

How well do Photoionization Detectors Detect and Warn of Unknown Chemical Warfare Agents?

Photoionization detectors (PIDs) are non-specific detectors capable of simultaneously detecting numerous different gases, vapors, and particulates. The PID's advantage of being able to simultaneously respond to a myriad of different gases, vapors, and particulates in low concentrations is offset by two things: not knowing the specific gas, vapor, or particulate that generated a positive response in the detector and not knowing the concentration of the unknown gas, vapor, or particulate. The concentration of the chemical is unknown because the PID's sensitivity varies depending upon the specific chemical detected. Unless the detected chemical is known, the concentration of the chemical cannot be determined by the PID's response. As one PID manufacturer stated in its literature:

> "The PID is not a selective monitor. It has very little ability to differentiate between chemicals."

Because of its lack of selectivity, PIDs are well suited for the detection and monitoring of a single, gas, vapor, or particulate that is known to be present in an environment where other detectable gases, vapors, and particulates are not present. Without the addition of a chromatographic column or a selective filter, PIDs are not well suited for identifying unknown gases, vapors, or particulates.

It is true that in cases where lamps with lower ionization potential are used, the PID may not be able to ionize some specific gases, vapors, or particulates. Therefore, when using the lower powered lamp approach to improve selectivity, it may be possible to exclude from the hundreds of detectable gases, vapors, and particulates that generate a positive response the specific gases, vapors, and particulates that cannot be ionized with the lower powered lamp. However, this approach does not identify the specific chemical that is present, or its concentration. It merely identifies what is not present. Likewise, when using this lower powered lamp approach to achieve some broad discrimination among possible unknown chemicals that are present, the same non-ionized gases, vapors, and particulates that cannot be ionized could be present and the PID would not detect these chemicals nor their concentrations. Therefore, this lower powered lamp approach for identifying unknowns is of no practical benefit in identifying unknown vapors, gases, or particulates. In other situations, common substances such as high humidity may be present that depress a PID's signal. Additionally, chemicals that could be used in explosives or to cause an explosion such as hydrogen peroxide, methane, ethane, and hydrogen chloride or hydrogen fluoride cannot be detected by a PID. The problems and risks created by such non-specific PID measurements are greatly increased when PIDs are used at spills of unknown hazardous materials to detect and warn of the presence of unknown concentrations of highly toxic and corrosive chemical warfare agents.

At terrorist attack sites where chemical warfare agents (CWA) are suspected, PIDs may not be able to differentiate CWAs from particulates formed due to burning materials or even from safe levels of industrial gases or vapors. Not knowing the types of the gases, vapors, or particulates that are present or the concentration of each gas, vapor, or particulate prevents knowing the optimum type and extent of effective response that is appropriate.

This problem with a lack of specificity for some instruments is one of the major reasons colorimetric detector tubes are selected for detection of CWAs. The hundreds of different applications available as well as the tubes' specificity and low detection limits (ppb) are additional reasons for using colorimetric detector tubes over PIDs. Logic charts associated with colorimetric detector tubes can be used to lead users through an analysis in order to determine the unknown gas and vapor and its concentrations, allowing for rapid and appropriate corrective action.

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The belief in using colorimetric detector tubes over PIDs is confirmed by the U.S. government's testing of PIDs for detection of CWAs. The following information and quotations were taken from the Soldiers and Biological Chemical Command AMSSB-REN, Aberdeen Proving Ground Summary Report titled, "Testing of Commercially Available Detectors Against Chemical Warfare Agents: Summary Report" dated February 1999 (hereafter referred to as "summary report").

Discussion Points

Some of the relevant points stressed in the summary report concerning the use of PIDs for the detection of CWAs are as follows:

[1] Photoionization Detectors give false positives when exposed to common interferents.

As seen in the summary report (page 8, Table 5) and in Table 1 below, both the RAE Systems PID and the MSA Passport II PID responded to commonly found interferents by generating false positive alarms. All of the interferences listed in Table 1 could readily be found at a terrorist attack site where CWAs are suspected.

Table 1: Interferents Causing False Positives in PIDs*

		Does Interferent Cause False Positive when Testing for CWAs?	
No.	Interferent	RAE PID	MSA PID
1	Gasoline Exhaust (Engine Revved)	Yes	Yes
2	Gasoline Vapor	Yes	Yes
3	JP8 Vapor (Jet Fuel)	Yes	Yes
4	Burning Wood Fire Smoke	Yes	Yes
5	Doused Wood Fire Smoke	Yes	Yes
6	Kerosene Vapor	Yes	Yes
7	Burning Cardboard Smoke	Yes	No
8	Burning Clothing Smoke	Yes	Yes

* This table is condensed from Table 5 on page 8 of the Soldiers and Biological Chemical Command AMSSB-REN, Aberdeen Proving Ground Summary Report titled, "Testing of Commercially Available Detectors Against Chemical Warfare Agents: Summary Report" (dated February 1999).

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When compared to detector tubes, the summary report states on page 10 that none of the detector tubes tested for interferents at the same time as the PID detectors indicated the presence of CWAs when exposed to the interferents.

[2] Exposing the PIDs to common interferents results in serious loss of sensitivity.

As seen in the summary report (page 8), PIDs requires cleaning and recalibration before reuse and even then have a loss of sensitivity:

"None of the detectors would calibrate correctly after the field test. All detectors required disassembling and cleaning before they could be properly calibrated in order to continue laboratory testing. However, after the first series of Laboratory Interference testing, they failed the routine calibration once again. The interferents appear to adversely affect the sensitivity of the detectors."

[3] PID sensors lose sensitivity when exposed to CWAs.

As seen in the summary report (page 9), PIDs are less sensitive after exposure to CWAs:

"Occasionally, the detectors were rechecked with the calibration gas after the agent challenges to observe residual effects and/or calibration drift. The responses usually were somewhat lower than the initial calibration values. This suggests that the detection sensitivity may have been degraded by exposure to the CW agent vapors."

[4] Dirty UV lamps in PIDs cause low detector sensitivity.

The problem with low detector sensitivity from dirty lamps was mentioned repeatedly in the summary report (page 10):

"The fact that these detectors require frequent cleaning even when operated in the clean laboratory environment indicates that the detectors would require more frequent cleanings when operated in the damp, dusty, and smoky field environments common during emergency response situations such as highway spills, railroad accidents, fires and explosions. Detection capability if CW agents were also present would be questionable."

The summary report (page 10) further details the effect of dirty lamps on PID readings:

"It appears that CW agent vapors in combination with the humidity also coated the lamp surfaces…Test results confirmed what was stated in the operational manuals provided by the manufacturers that many compounds, as well as, moisture and oxygen will quench the PID signal causing the instrument to under report the vapor concentration."

[5] PIDs are poor detectors of CWAs.

Based upon the results of the PIDs when exposed to CWAs and the effect of exposure to common interferents, the summary report (page 10) concluded the following:

"The failure of the detectors in the calibration process after the agent sensitivity test, field interference tests, and interference testing in the laboratory, plus the wide range of response factors and the low CW agent detection sensitivity, suggests that these detectors cannot be relied upon for CW agent vapor detection. Detection of the CW agent vapor was unreliable even when the detectors were calibrated successfully."

The summary report (page 10) stressed the poor detection capabilities of these products:

"Of the PID/FID detectors tested, the results of CW agent challenge can be summarized as follows:

· MiniRAE Plus responded to GA and HD, but failed to detect GB.

· TVA 1000B PID responded to GA and HD, but failed to detect GB.

· TVA 1000B FID responded to GB and GA, but not as well for HD.

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· HNU units responded to GB, GA and HD, however, they frequently had trouble achieving proper span adjustments during calibrations.

· Passport II responded to HD only.

· The quantitative effects of interferent contamination on CW agent detection could not be determined with useful precision."

Conclusion

The Soldiers and Biological Chemical Command AMSSB-REN, Aberdeen Proving Ground Summary Report titled, "Testing of Commercially Available Detectors Against Chemical Warfare Agents: Summary Report" (dated February 1999) made the following conclusions on page 11:

[1] "*The UV lamps used by the photoionization detectors (PIDs) to ionize the vapor samples for detection become contaminated easily by dust, dirt, moisture, and residue during use.*"

[2] "*The frequent lamp cleaning required to retain performance is impractical.*"

[3] "*There was no assurance that the response to CW agent would remain the same even when they were calibrated with the calibration gas successfully.*"

[4] "*Neither the PID nor the FID detectors tested can be relied upon for CW agent detection and warning. Exposure to vapors of CW agents and many other substances significantly degrades the overall performance of the detectors.*"

[5] "*Neither the Mini RAE Plus, the HNU, the Passport II, the TVA PID, nor the TVA FID could detect any of the agents at the JSOR level, even under ideal conditions."*

NOTE: Please contact Nextteq if you would like a PDF of the Soldiers and Biological Chemical Command AMSSB-REN, Aberdeen Proving Ground Summary Report titled, "Testing of Commercially Available Detectors Against Chemical Warfare Agents: Summary Report" (dated February 1999).

*** To get the document directly, go to the following website:**
http://www.ecbc.army.mil/hld/ip/detectors_summary_download.htm

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