Am. Ind. Hyg. Assoc. J. 51(6):326-330 (1990)

J. Forbes

(5)

59099

4201

Decreased Sensitivity of Photoionization Detector Total Organic Vapor Detectors in the Presence of Methane*

Received by ER-RPF
SEP 04 1998
MA

JONATHAN E. NYQUIST, DAVID L. WILSON,
LORI A. NORMAN, AND RICHARD B. GAMMAGE
Health and Safety Research Division, Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, TN 37831

The reduction in sensitivity of the Photovac TIP, TIP-1, and the H-NU101 total organic vapor analyzers equipped with photoionization detectors (PID) to toluene and gasoline in the presence of methane (0.5–5.0% v/v) was examined. The results showed an exponential decrease in detector sensitivity, with a reduction of about 30% for 0.5% methane and 90% for 5% methane. A Photovac TIP (PID), a Century OVA equipped with a flame ionization detector (FID), and a Photovac 10S50 portable gas chromatograph (PID) were used in a soil gas survey to map the areal extent of gasoline contamination. The survey area was paved, and comparison of FID and PID response showed that methane was widespread under the asphalt, including areas where gas chromatography showed no gasoline contamination. Two soil gas samples analyzed in the laboratory showed concentrations of 0.23% and 0.99% methane by volume. Because high concentrations of biogenic methane are found in the environment, this loss of sensitivity may be important when PID organic vapor analyzers are used in the field.

Small, portable, total organic vapor analyzers are commercially available and have been used to screen for volatile organic compounds for purposes of industrial hygiene,[1] soil gas surveying,[2,3] and screening soil and water samples in the field.[4] Most of these instruments use either a flame ionization detector (FID) or a photoionization detector (PID). Flame ionization instruments combine the air sample with hydrogen gas and ignite the mixture to produce ions. The response to a given compound for the FID is roughly proportional to the number of carbon atoms. Photoionization detectors use an ultraviolet (UV) light source instead of a flame to ionize the sample. Early work at H-NU[5] showed that PIDs are more sensitive than FIDs to aromatic compounds such as benzene, toluene, and xylene (BTX), commonly found at sites with gasoline contamination.[6,7] This increased sensitivity and the freedom from a source of hydrogen has made PID instruments enormously popular.

An additional advantage is claimed by proponents of PID instruments—insensitivity to biogenic methane, which is frequently present in high concentrations under landfills, in sewer lines, and in the soil. Using an FID instrument, the large signal produced by methane can obscure the signal produced by other volatile organics unless a chromatographic column is first used to separate the compounds, making it difficult to distinguish contamination hot spots and decaying vegetation (particularly where a diffusion barrier, such as clayey soil or asphalt pavement, allows the biogenic methane levels in the soil to build). Although methane cannot be ionized by a PID, methane is a UV absorber. Senum[8] observed a reduction of PID response by methane in a study of potential carrier gases for PID gas chromatographs. In the present study, the reduction in PID response to volatile organic compounds for instruments that lack a chromatographic column to separate compounds was measured. The ability of the Photovac TIP, TIP-1, and the H-NU model 101 (Photovac, Toronto, Canada) to detect toluene and gasoline standards in mixtures of methane and air was tested.

EXPERIMENTAL MATERIALS AND METHODS

Generating the Mixtures

The gas mixtures tested consisted of hydrocarbon-free (HCF) air, methane and 102.5 ppm toluene, 10.19 ppm toluene, and 10 ppm gasoline, all in HCF air (Scott Specialty Gases, volumetric standards, Plumsteadille, Pa.). The desired mixtures were generated by running copper tubing from the tank regulators through a mass flow controller and to a three-way solenoid switch (Matheson, Secaucus, N.J.). When the switch is off, the gas is directed out to a fume hood. When the switch is on, the gas passes through the solenoid to a flow tube (calibrated using a primary flow calibrator [Gilian, Orlando, Fla.]) until the flow has stabilized in the calibrated line. The solenoid is then switched off and a Tedlar® gas-tight bag is attached to the flow tube with rubber tubing. The solenoid is then switched on for a timed interval.

A total volume of 5 L was always generated. For example, a mixture of 102 ppm in HCF air and 1% methane by volume was

*This work was performed at Oak Ridge National Laboratory operated by Martin Marietta Energy Systems, Inc., for the U.S. Department of Energy under contract DE-AC05-84OR21400.

Copyright 1990, American Industrial Hygiene Association

7193

generated by adding methane for 15.4 sec at 0.00325 L/sec and 102.5 ppm toluene in HCF air for 188 sec at 0.0421 L/sec. This dilutes the concentration of toluene in this 5-L sample to 102 ppm. To compare the instrument's response to the two organic mixtures with and without methane, a 5-L control sample was generated substituting HCF air for methane to achieve the same dilution. A sample of each mixture was also analyzed on a Photovac, Model 10A10 to verify that the diluted toluene or gasoline concentrations in the control and sample bags were as calculated. The Photovac GC was operated with a 0.61-m SE30 column, at ambient temperature, using hydrocarbon-free air as the carrier gas. This column separates the compounds sufficiently before they are detected that methane has negligible effect on the other peaks.

As a direct test of the accuracy of the methane concentrations generated, samples from a complete set—0.5%, 1.0%, 2.0%, 3.0%, 4.0% and 5.0% methane—were analyzed on a Perkin-Elmer (Norwalk, Conn.) model 3910 laboratory GC equipped with a Supelco (Bellefonte, Pa.) 5A molecular sieve and a thermal conductivity detector.

Instruments Tested

The instruments tested were a Photovac TIP, the newer Photovac TIP-1, and the H-NU model 101. The TIP's lamp energy is 10.6 eV and the H-NU's is 10.2 eV, although the emission is probably not monochromatic.[9] Each day the instruments were checked with HCF air and toluene or gasoline standards to determine a two-point calibration. According to instrument specifications, the response of all three instruments is linear over the range of concentrations used in this study.

RESULTS AND DISCUSSION

Figures 1 and 2 show the response of the TIP, TIP-1, and H-NU 101 to 102 ppm toluene as a function of the percentage of methane present. The solid line shows the best exponential fit, which in both cases had an r^2 of better than 0.99. Note that 5% methane was sufficient to reduce the signal 90%. The results for 10.19 ppm toluene and 10 ppm gasoline were more difficult to quantify, but all cases showed a signal reduction by methane. The H-NU 101 was less sensitive to toluene than either TIP, and hence, the results are subject to greater uncertainty, but the reduction of signal strength with increasing methane is apparent. Figure 3 is typical; a concentration of 5% methane was sufficient to drop the signal below baseline (which is always present because of photoionizable compounds outgassing in the detector cell and background impurities in the carrier gas). This reduction below baseline produces a negative peak on a PID chromatograph.

The probability of photon absorption is given by the Beer-Lambert law,[10]

$$I = I^0 \exp(-\alpha CL)$$

where I is the absorption intensity, I^0 is the initial photon flux, α is the absorption coefficient, C is the concentration of the compound of interest, and L is the path length. Table I gives absorption coefficients for some selected gases. Methane's absorption coefficient for the incident energy is very high even though the UV energy is below the methane ionization potential. The Beer-Lambert law predicts an exponential increase in UV absorption by methane as the concentration increases and, con-

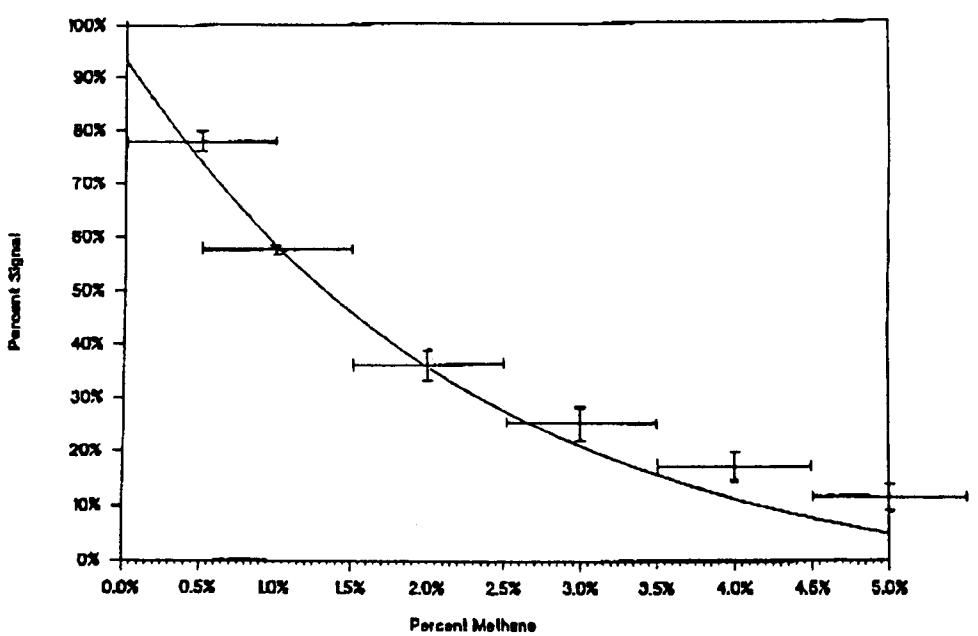

Figure 1—Percent reduction in the Photovac TIP response to 102 ppm toluene diluted by increasing amounts of methane compared with the TIP response to 102 ppm toluene diluted by the same amount of hydrocarbon-free air. The error bars represent one-standard-deviation uncertainties in the methane concentrations and the TIP readings. The solid line is the best fit exponential; the r^2 is better than 0.99.

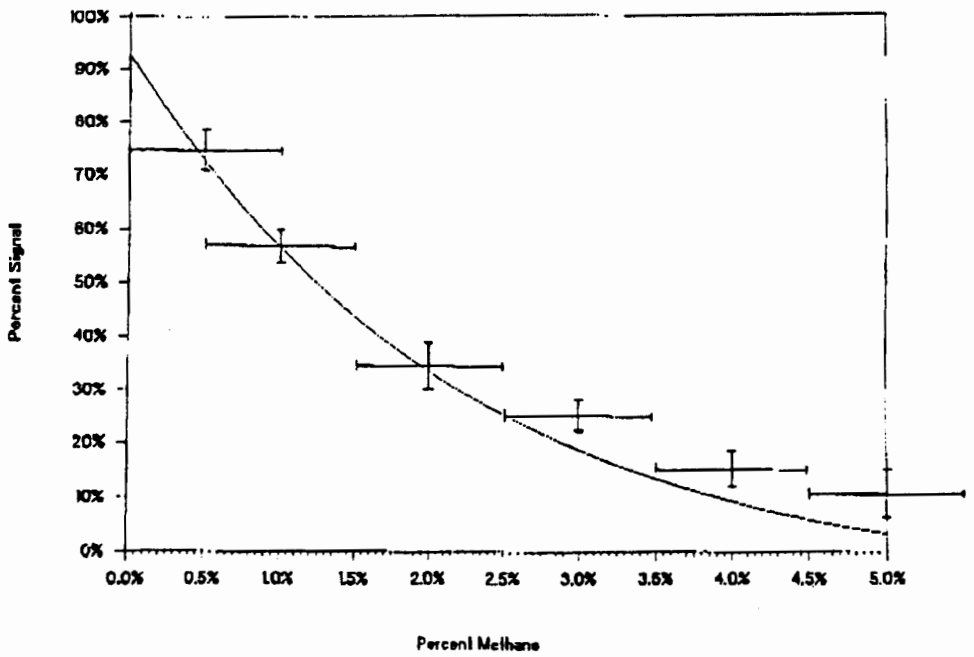

Figure 2—Percent reduction in the Photovac TIP-1 response to 102 ppm toluene diluted by increasing amounts of methane compared with the TIP-1 response to 102 ppm toluene diluted by the same amount of hydrocarbon-free air. The error bars represent one-standard-deviation uncertainties in the methane concentrations and the TIP readings. The solid line is the best fit exponential; the r^2 is better than 0.99.

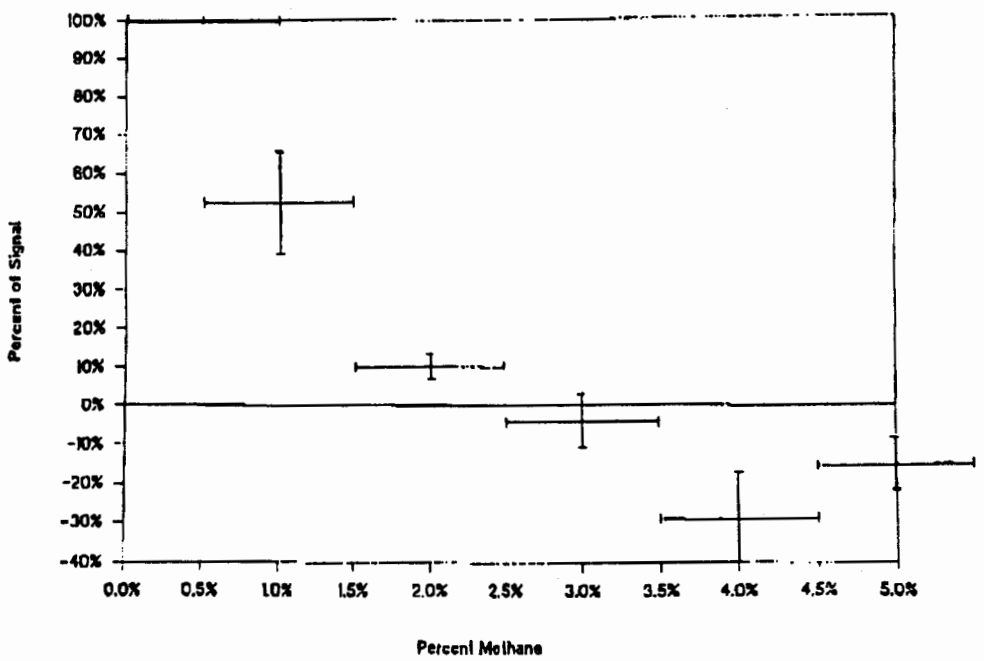

Figure 3—Percent reduction in the H-NU 101 response to 102 ppm toluene diluted by increasing amounts of methane compared with the H-NU 101 response to 102 ppm toluene diluted by the same amount of hydrocarbon-free air. The error bars represent one-standard-deviation uncertainties in the methane concentrations and H-NU 101 readings.

TABLE I
Selected Gas Absorption Coefficients[A]

Gas	Absorption Coefficient at 10.2 eV (m^{-1})
Oxygen	27
Nitrous oxide	10 000
Carbon dioxide	200
Methane	40 000
Carbon tetrafluoride	negligible
Carbon monoxide	300
Argon	negligible
Helium	negligible

[A]From Reference 8.

sequently, a decline in the number of photons available to ionize other compounds simultaneously present in the mixture, producing an exponential reduction in PID response for the non-methane compounds.

Case History

At an industrial construction site near Oak Ridge, Tennessee, an underground gasoline tank failed a recent pressure test. An area where gasoline and water seeped through the asphalt after heavy rains was observed by workers. To determine the extent of the leak, soil gas samples were collected through tubes driven to a depth of 0.5 m throughout the suspected zone of contamination, and the samples were analyzed using a Photovac 10S50 portable gas chromatograph and two total organic vapor detectors: the Photovac TIP and the Foxborough OVA (Norwalk, Conn.) (Figure 4). The OVA (FID) data were divided, somewhat arbitrarily, into high (>100 ppm), medium (100–10 ppm), and low (<10 ppm). The results showed elevated readings for all soil gas samples taken where the ground was paved, whereas the TIP analyses categorized the same way showed an elevated region only near the filling station.

A mixture 102.5 ppm toluene in air was used to calibrate the TIP and the OVA, thus the response of these total organic vapor detectors to a mixture of volatile organics is expressed in units of equivalent ppm toluene. To express the GC results in the same units, the GC chromatogram peak areas were summed and the total area renormalized using the GC response to toluene. A 0.1 m SE30 screening column was used for all the field GC analyses. With this short column, all volatile organic compounds elute in less than about 5 min so that the contribution from the heavier volatiles is included. The GC and TIP results agree reasonably well (Figure 4). In two cases the TIP reading was high and the GC was medium. This was probably because the TIP reading was always taken first at a sample point and the vapors in the hole had not reached equilibrium when the GC sample was drawn.

The presence of methane almost everywhere under the asphalt was inferred from the high FID readings in areas where there was little PID response and from the characteristic negative peaks on most of the chromatograms. Two soil gas samples were analyzed in the laboratory and had methane concentrations of 0.28% and 0.99%.

Relying solely on the OVA to map fuel contamination would have been a mistake at this site, as biogenic methane produced false positives. Relying on the TIP data would have produced roughly the same map of the lateral extent of soil and groundwater contamination in this case as using data from a gas chromatograph. When the contaminant is known, and present in relatively high concentrations, the selectivity and additional sensitivity of the gas chromatograph may not be required. In an area where the contamination has spread out further, however, high levels of methane associated with fuel degradation will reduce all the readings, shifting the soil gas contours, possibly causing the extent of the plume to be underestimated when TIP data are used.

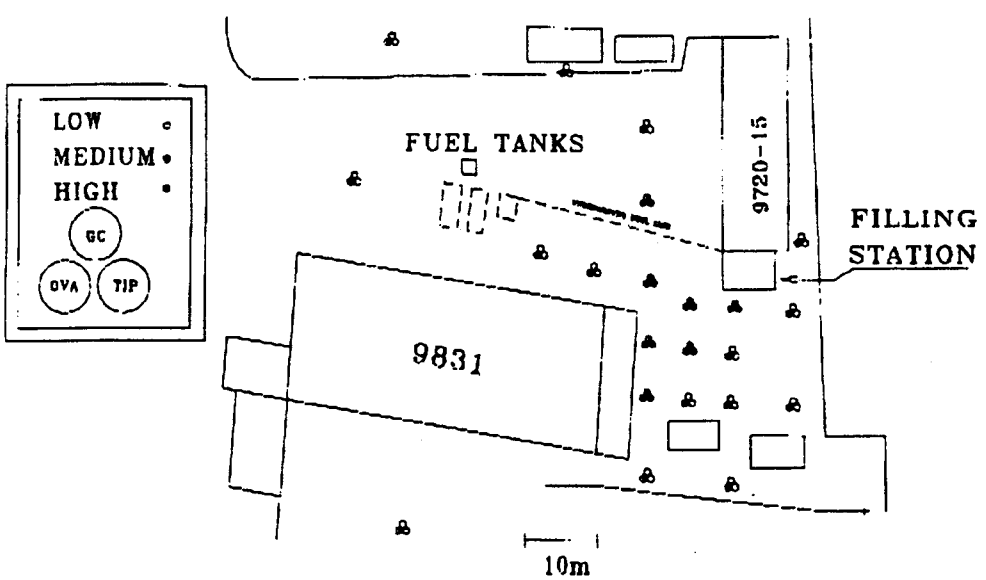

Figure 4—Comparison of results of soil gas analyses made with a Photovac TIP, OVA, and Photovac 10S50 GC equipped with a 0.1-m SE30 screening column. The readings have been divided into high (>100 ppm), medium (100–10 ppm), and low (<10 ppm).

CONCLUSIONS

In summary, the objective of this study was to determine the reduction in PID response to volatile organic compounds for instruments that lack a chromatographic column to separate compounds. The ability of the Photovac TIP, TIP-1, and the H-NU model 101 to detect toluene and gasoline standards in mixtures of methane and air was tested. The laboratory results showed an exponential decrease in detector response, with about a 90% reduction in the response to 102 ppm toluene in the presence of 5% methane. The results for lower concentrations were less easily quantified but consistently showed decreasing detector sensitivity as the amount of methane in the mixture was increased. The instruments were used in a soil gas survey in which methane in excess of 0.5% at multiple locations under an asphalt parking lot, including sites far from the gasoline contamination, was being mapped.

The decrease of PID response by methane was reported previously by Senum[8] in a study of potential PID carrier gases. Senum suggests that methane would be a poor choice for a PID GC carrier gas. The results of this study confirm this, and show that when large concentrations of methane are present in the sample, and no chromatographic column is used, methane becomes part of the carrier gas. High concentrations of methane may be found in landfills, sewer lines, during well drilling, and under pavement.

Users of PID total organic vapors analyzers should be aware of the danger of false negatives when using these instruments in an environment where methane may be present. It is suggested that an FID total organic vapor analyzer should be used to screen for methane or a chromatographic column be used to separate the compounds before users should rely on PID data.

REFERENCES

1. **Barsky, J.B., S.S. Que Hee, and C.S. Clark:** An Evaluation of the Response of Some Portable, Direct-Reading 10.2 eV and 11.8 eV Photoionization Detectors, and a Flame Ionization Gas Chromatograph for Organic Vapors in High Humidity Atmospheres. *Am. Ind. Hyg. Assoc. J. 46*:9–14 (1985).
2. **Marrin, D.L. and H.B. Kerfoot:** Soil-Gas Surveying Techniques. *Environ. Sci. Technol. 22*:740–745 (1986).
3. **Nyquist, J.E.:** Soil Gas on a Shoestring. *Eos, Trans. Am. Geophys. Union. 69*:353 (1988).
4. **Clay, P.F. and T.M. Spittler:** The Use of Portable Instruments in Hazardous Waste Site Characterizations. In *Proceedings of Management of Uncontrolled Hazardous Waste Sites*, Silver Springs, Md.: HMCRI, 1980. pp. 40–44.
5. **Driscoll, J.N.:** Evaluation of a New Photoionization Detector for Organic Compounds. *J. Chromatogr. 134*:49–55 (1977).
6. **Barker, J.F., G.C. Patrick, and D. Major:** Natural Attenuation of Aromatic Hydrocarbons in a Shallow Sand Aquifer. *Groundwater Monit. Rev. Winter*: 64–71 (1987).
7. **Senn, R.B. and M.S. Johnson:** Interpretation of Gas Chromatographic Data in Subsurface Hydrocarbon Investigations. *Groundwater Monit. Rev. Winter*: 58–63 (1987).
8. **Senum, G.I.:** Quenching or Enhancement of the Response of the Photoionization Detector. *J. Chromatogr. 205*:412–418 (1981).
9. **Cassida, M.E. and K.C. Cassida:** Application of a Unified Theory of Gas Chromatographic Photoionization Detector Response to a 10.2-eV Detector. *J. Chromatogr. 200*:35–45 (1980).
10. **Freedman, A.N.:** The Photoionization Detector: Theory, Performance and Application as a Low-Level Monitor of Oil Vapour. *J. Chromatogr. 236*:11–15 (1982).