

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

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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,<sup>(1)</sup> soil gas surveying,<sup>(2-3)</sup> and screening soil and water samples in the field.<sup>(4)</sup> 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<sup>(5)</sup> 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.<sup>(6-7)</sup> This increased sensitivity and the freedom from a source of hydrogen has made PID instruments enormously popular.

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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<sup>(8)</sup> 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, Plumsteadville, 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<sup>®</sup> 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

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.<sup>(9)</sup> 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,<sup>(10)</sup>

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

where  $I$  is the absorption intensity,  $I^0$  is the initial photon flux,  $\alpha$  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-

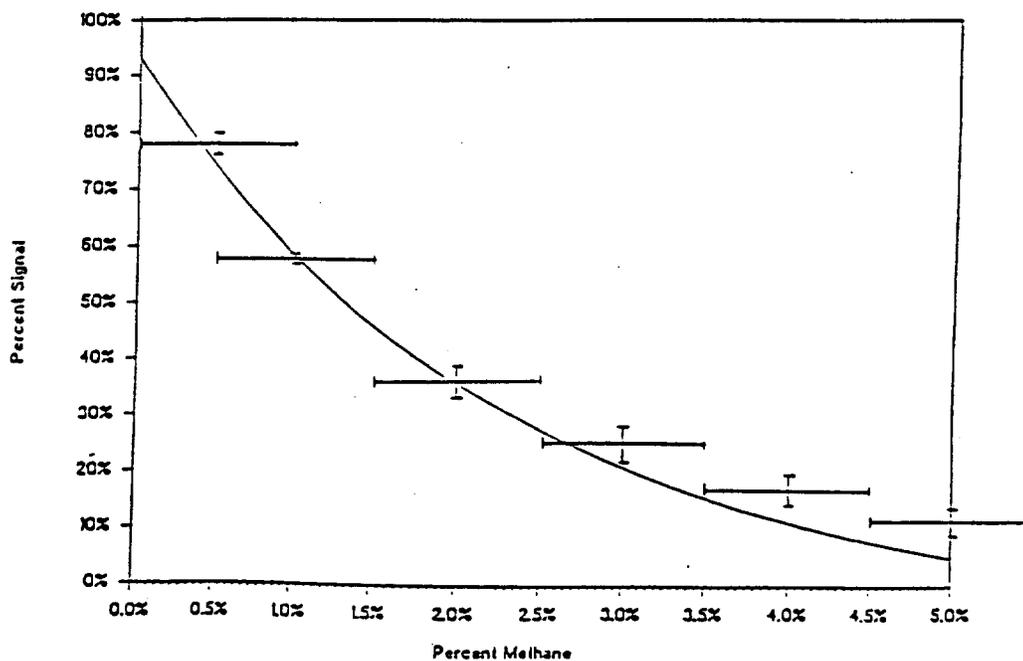


Figure 1—Percent reduction in the Photovac TIP response to 102 ppm toluene diluted by increasing amounts of methane compared with the TIP response to 102 ppm toluene diluted by the same amount of hydrocarbon-free air. The error bars represent one-standard-deviation uncertainties in the methane concentrations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

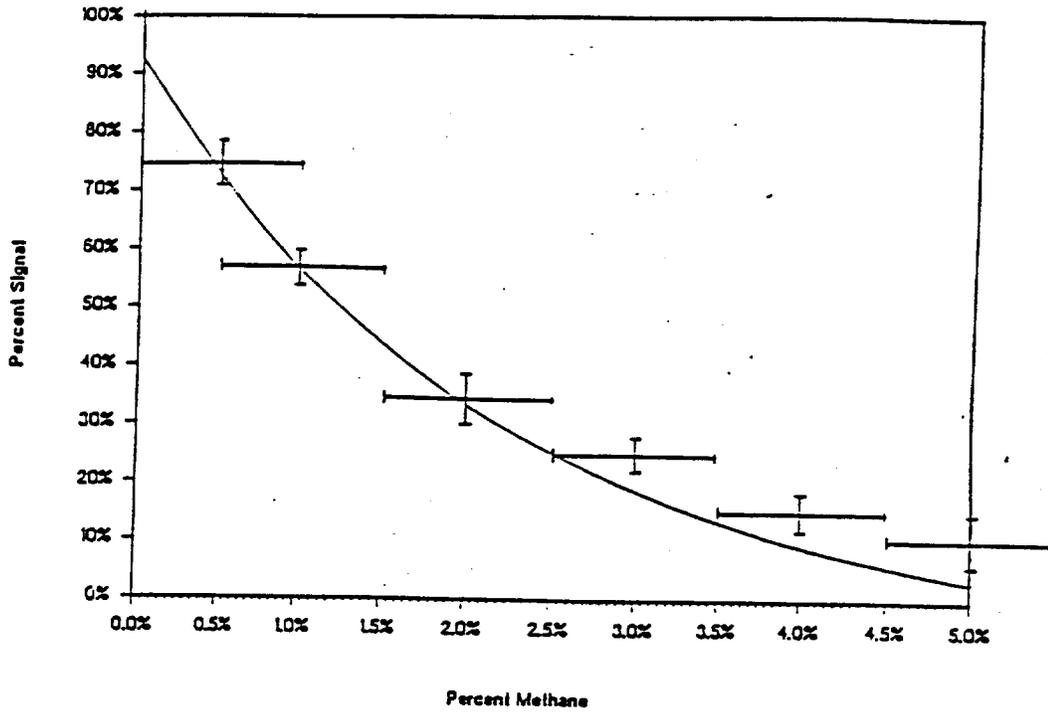


Figure 2—Percent reduction in the Photovac TIP-1 response to 102 ppm toluene diluted by increasing amounts of methane compared with the TIP-1 response to 102 ppm toluene diluted by the same amount of hydrocarbon-free air. The error bars represent one-standard-deviation uncertainties in the methane concentrations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

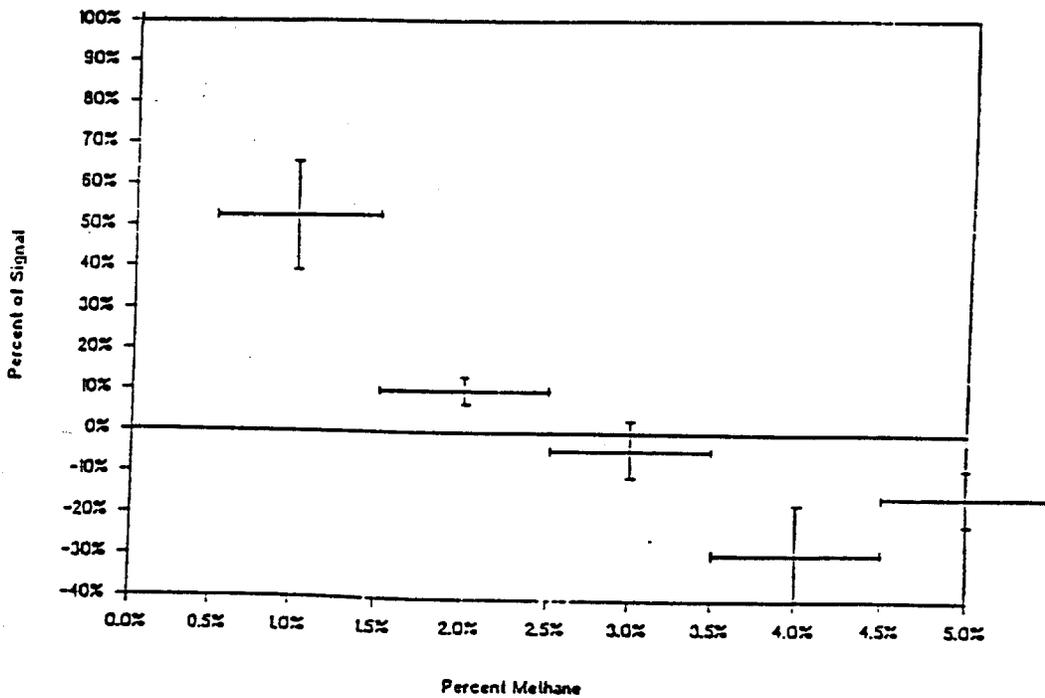


Figure 3—Percent reduction in the H-NU 101 response to 102 ppm toluene diluted by increasing amounts of methane compared with the H-NU 101 response to 102 ppm toluene diluted by the same amount of hydrocarbon-free air. The error bars represent one-standard-deviation uncertainties in the methane concentrations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