



Using RAE Systems PIDs For Measuring Soil Headspace And In Soil Vapor Extractions

Introduction

Photoionization detectors (PIDs) are often employed to measure VOC concentrations in water or soil. For example, hydrologists and environmental engineers often use PIDs to monitor chlorinated solvents (e.g., perchloroethylene) and fuels (e.g., gasoline, diesel) in soil or groundwater during clean-up operations such as excavations and soil vapor extractions. PIDs can also be used to monitor water stripper effluents and off-gases from wastewaters. Although PIDs cannot measure directly in these media, they can indirectly measure the vapors emitted from them. For example, Hewitt and Lukash* reported linear correlations between headspace PID response and soil concentrations of benzene, toluene, xylenes, dichloroethylenes, trichloroethylene and perchloroethylene. The concentration in the headspace, measured in ppmv, does not equal the soil or water concentration, measured in mg/kg or mg/L. The vapor concentration depends on such factors as soil-to-headspace weight and volume ratio, soil permeability, affinity of the compound to the soil, temperature, equilibration time, and dilution during the measurement procedure. Therefore, it is important that these factors are controlled as closely as possible if quantitative soil or water concentrations are desired.

Soil and Water Headspace Screening

In a typical procedure, a sample of soil or water is filled approximately halfway into a mason jar with a ring-type lid. Enough air space ("headspace") above the sample is allowed for sampling. A piece of aluminum foil is placed over the mouth of the jar and held in place with the lid ring. The jar and its contents are brought to room temperature and shaken to mix the soil sample with the air in the headspace. The influent probe and effluent line of the portable PID are then poked through the foil and the VOC concentration measured in the headspace of the jar. A similar procedure can be performed using a plastic bag instead of a jar, but the headspace volume is not as reproducible, and thus the results are less quantitative. A sampling septum can be made easily for virtually any hard container with aluminum foil held in place by a rubber band around the rim of the vessel. When sampling with the PID, ensure that dirt and water are not sucked into the PID probe.

Procedures for Optimum Performance of PIDs

Measuring organic compounds emitted from potentially contaminated soil and water requires special attention beyond that needed for typical ambient air monitoring. Stripper effluents and soil vapor extraction streams are typically near 100% relative humidity (RH), and soil samples are often dusty and humid. Such conditions can cause high, drifting readings on many PIDs, if not properly maintained. Interferences are usually traceable to condensation in the sensor, causing a current leakage across the electrodes and thus a false positive signal. This situation is exacerbated when the sensor is contaminated by soil dust or condensed, high-boiling organic compounds.

1. Keep the sensor clean by using high-purity methanol, preferably using an ultrasound bath. A low-cost (less than \$150) ultrasonic cleaner can be obtained from Cole-Parmer (part number H-08849-00; phone number: 800-323-4340; www.coleparmer.com), or use a jewelry cleaner from a local department store. Flush the residual solvent from the sensor with a rapid stream of clean air, and clean the lamp housing area that contacts the sensor when it is in place.
2. On sensors with inter-digital fingers, check that the metal electrode fingers are straight, parallel, and do not contact the Teflon sensor walls. Bend them carefully if necessary. Replace the sensor if the electrodes are corroded.
3. Keep the lamp surface clean by using high-purity methanol. Never use acetone on 11.7 eV lamps.
4. Use the 4.5 cm "water trap" filters as an extra precaution, especially in dusty or moist environments where water mist may be present. Change filters frequently.
5. Avoid situations in which the PID is colder than the soil being sampled, such as heating the soil samples to increase the headspace organic concentration, or bringing a cold PID into a warm room without allowing time for temperature equilibration. If anything, try to keep the PID warmer than the soil samples.



6. To obtain more stable readings, plumb the effluent flow from the MiniRAE 3000 or ppbRAE 3000 back into the sample container to reduce the losses. Use Teflon or metal tubing for this purpose so as to prevent adsorption to Tygon or other plastic tubing. Losses will not be stopped altogether, but will be greatly reduced.
7. If humidity problems persist, use a Humidity Filtering II tube (p/n 025-2002-010) to absorb moisture. These tubes allow many organic vapors such as TCE and gasoline to pass almost unaffected, but they may absorb some heavy or polar compounds. (See Technical Note TN-178). A lower cost but less effective means is to use the C-Filter to absorb dust and some moisture. (See Technical Note TN-162). Perform frequent changes of the C-Filter (daily to weekly, depending on usage and dirtiness).

Response of PIDs to Semi-volatiles on Soils

Often repeated is the statement that PIDs do not respond to semi-volatile organic compounds. This statement seems to be an old piece of "common knowledge" that may have been true at one time for an old PID used for soil headspace measurements, but is no longer true in general. The larger the organic molecule (and thus less volatile), the lower the ionization energy and the greater the PID sensitivity. However, there is a point of diminishing sensitivity when adsorption losses in the instrument sample lines

and filters begin to dominate over this sensitivity increase. This is true for any instrument including FIDs (flame ionization detectors) and PIDs if they are not specifically designed to handle semi-volatile compounds. New PIDs have higher flowrates and better sensor designs that reduce such losses, and therefore most compounds up to a boiling point of about 300° C can be detected on the MiniRAE 3000 or ppbRAE 3000. Boiling points for fuel oils, diesels, and kerosenes range from about 170° C for #2 Fuel Oil to 260° C for #5 or #6 fuel oils. As the oil weathers and the light ends evaporate, the response time increases and the overall response drops because less organic vapor is present. The response may drop to zero before all the oil is removed from a soil sample, because only non-volatile components remain. Again, this effect is the same for FIDs and PIDs. In such cases, a direct measurement of the oil contamination on the soil may be needed—for example, using a solvent-extraction procedure followed by laboratory gas chromatography. For such high-boiling compounds, it is also important not to use any rubber or Tygon tubing to draw in samples, as several inches of such tubing can completely absorb heavy fuels. Teflon or metal tubing is preferred.

* Hewitt, A.D. and J.E. Lukash: PID-based estimation of the concentration of aromatic and chlorinated VOCs in soil. *Field Analyt. Chem. Technol.* 1999, 3(3):193-200.