Headspace Vapor Screening with a Photoionization Detector

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Approval Signatures:

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REVISION HISTORY

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ER-SOP-20025, R0	8/27/15	New procedure	New document control number assigned; Supersedes SOP-06.33

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1. PURPOSE

This standard operating procedure (SOP) states the responsibilities and describes the process for screening headspace vapor for volatile organic compounds (VOC) in soil samples with a photoionization detector (PID) for the Los Alamos National Laboratory.

Work performed using this procedure shall help fulfill the requirements of applicable work plans required by the NMED/DOE 1, 2005, *Compliance Order on Consent*, EP-DIR-AP-10008, *ADEP Roles, Responsibilities, Authorities, and Accountabilities*, DOE Order 458.1 *Radiation Protection of the Public and the Environment*, and LANL P315, *Conduct of Operations Manual.* This SOP integrates the criteria of EP-DIR-QAP-0001, *Los Alamos National Laboratory Environmental Programs Directorate Quality Assurance Program (QAP) Implementation Plan*, hereinafter referred to as the Quality Assurance Plan.

2. SCOPE

This procedure applies to all personnel assigned to perform headspace vapor screening on soil samples using a PID. A PID is capable of detecting and measuring real-time concentrations of many organic vapors in air. This field screening technique can be used to provide evidence of the potential presence of contaminants and to aid in the selection of soil samples for laboratory analysis of VOCs. This vapor screening SOP is **NOT** for health and safely purposes.

2.1 Background

As with any field instrument, accurate results depend on the operator being completely familiar with the operator's manual. The instructions in the operating manual should be followed explicitly in order to obtain accurate results, while taking care to prevent the PID from being exposed to excessive moisture, dirt, or contamination.

The PID employs the principle of photoionization. Volatile organics present in the soil sample will volatilize into the headspace gas where they can be detected using a PID or other vapor analyzer. Limitations of the headspace method are listed below in Subsection 5.2.

The analyzer will respond to most vapors that have an ionization potential less than or equal to that supplied by the ionization source, which is an ultraviolet (UV) lamp. Photoionization occurs when an atom or molecule absorbs a photon of sufficient energy to release an electron and form a positive ion. This will occur when the ionization potential of the molecule in electron volts (eV) is less than the energy of the photon. The sensor is housed in a probe and consists of a sealed ultraviolet light source that emits photons with an energy level high enough to ionize many trace organics, but not enough to ionize the major components of air (e.g., nitrogen, oxygen, carbon

Background, cont.

dioxide). The ionization chamber exposed to the light source contains a pair of electrodes, one a bias electrode, and the second the collector electrode. When a positive potential is applied to the bias electrode, an electro-magnetic field is created in the chamber. Ions formed by the adsorption of photons are driven to the collector electrode. The current produced is then measured and the corresponding concentration displayed on a meter, directly, in units above background [usually part per million volume (ppmv)]. Four probes, each having a different eV lamp and a different ionization potential, are available for use with the PID; the light energies are 9.5, 10.2, 10.6 and 11.7 eV. All four probes detect various aromatic and large molecular hydrocarbons. The 10.2 eV and 11.7 eV probes, in addition, detect some smaller organic molecules and halogenated hydrocarbons. The 10.2 and 10.6 eV probes are the most useful for environmental response work where VOCs are suspected, as they are more durable than the 11.7 eV probe and detects more compounds than the 9.5 eV probe. The Consent Order requires LANL to, at a minimum, use a PID equipped with a 10.6 or higher eV probe. Gases with ionization potentials near or less than that of the lamp will be ionized. These gases will thus be detected and measured by the analyzer. Gases with ionization potentials higher than that of the lamp will not be detected. The selection of the appropriate probe is essential in obtaining useful field results. Though it can be calibrated to a particular compound, the instrument cannot distinguish between detectable compounds in a mixture of gases and, therefore, indicates an integrated response to the mixture. A PID is similar to a flame ionization detector (FID) in application. However, the PID is unable to respond to certain low molecular weight hydrocarbons, such as methane and ethane that are readily detected by FID instruments. See Tables 1 and 2 of Appendix A of the EPA ERT SOP website SOP 2114 Photoionization Detector (PID) HNU website www.ert.org/products/2114.PDF for: a list of ionization potentials for a large number of individual species, Table 1; and, relative photoionization sensitivities for gases, Table 2.

3. REFERENCES

ANSI/NCSL Z540-1-1994, American National Standards for Calibration.

EP-DIR-QAP-0001, Quality Assurance Plan for the Environmental Programs Directorate.

EP-DIR-AP-10003, *Records Management Procedure for ADEP Employees.*

EP-DIR-AP-10007 *Environmental Programs Procedure Preparation, Revision, Review, Approval and Use.*

"Expedited Site Assessment Tools for Underground Storage Tank Sites, A Guide for Regulators," EPA 510-B-97-001, US Environmental Protection Agency, Office of Solid Waste and Emergency Response, Washington, DC. March 1997.

HNU Systems, Inc. 1975. "Instruction Manual for Model PI-101 Photoionization Analyzer".

"New Mexico Environment Order on Consent", 2005 with revision in 2011.

3. REFERENCES, cont.

Section 7.2.3, Documentation of Field Activities, of EPA's RCRA Waste Sampling Draft Technical Guidance

US EPA Photoionization Detector (PID) HNU SOP#: 2114 DATE: 10/06/94
REV. #: 0.0.

U.S. Code of Federal Regulations, 49 CFR Parts 100 to 177, Transportation, revised November 1, 1985. U.S. Environmental Protection Agency.

"Characterization of Hazardous Waste Sites – A Methods Manual: Volume II, Available Sampling Methods, Second Edition, EPA-600/4-84-076, Environmental Monitoring Systems Laboratory, Office of Research and Development, Las Vegas, Nevada.

4. DEFINITIONS AND ACRONYMS

4.1 Definitions

*Integrated work document (IWD***)**— Hazard control documentation that integrates work definition, hazards, and controls for work authorization and user-friendly communication to the workers. The IWD may be a subset of a larger "work package" such as the field readiness review package, that includes other documents and information relating to an activity but not addressing hazard controls.

Photoionization Detector (PID)— The PID is a portable, single piece, hand-held unit for the measurement of organic and inorganic species that can be ionized by the ultraviolet (UV) lamp contained within the unit.

4.2 Abbreviations

EP	Environmental Program
eV	Electron Volt
FID	Flame ionizing detector
FTL	Field Team Lead

4.2 Abbreviations, cont.

IWD	Integrated Work Document

LANL	Los Alamos National Laboratory
NMED	New Mexico Environment Department
PID	Photoionization Detector
PPMV	Parts per million volume
RPF	Records Processing Facility
SOP	Standard Operating Procedure
STL	Site Technical Lead
STR	Site Technical Representative
UV	Ultraviolet
VOC	Volatile Organic Compound
M&TE	Measuring and Test Equipment

5.0 PRECAUTIONS AND LIMITATIONS

5.1 Precautions

In all instances, the ultimate procedures employed should be documented and associated with the final report. Mention of trade names or commercial products does not imply LANL endorsement or recommendation for use.

Use this procedure in conjunction with an approved IWD to familiarize personnel to hazards of reagents or calibration gas handling and use.

5.2 Limitations

The PID is a nonspecific total vapor detector. It cannot be used to identify unknown substances; it can only roughly quantify them.

The PID must be calibrated to a specific compound.

5.2 Limitations, cont.

The PID does not respond to certain low molecular weight hydrocarbons, such as methane and ethane.

The PID does not detect a compound if the probe has a lower energy than the compound's ionization.

Certain toxic gases and vapors, such as carbon tetrachloride and hydrogen cyanide, have high ionization potentials and cannot be detected with a PID.

Certain models of PID instruments are not intrinsically safe and should be used in conjunction with a Combustible Gas Indicator.

Electrical power lines or power transformers may cause interference with the instrument and thus cause measurement errors. Static voltage sources such a power lines, radio transmissions, or transformers may also interfere with measurements.

High winds and high humidity will affect measurement readings. The PID may become unusable under foggy or humid conditions. An indication of this is the needle dropping below zero, or a slow constant climb on the read-out dial.

The lamp window must be periodically cleaned to ensure ionization of the new compounds by the probe (i.e., new air contaminants).

The PID measures concentrations from about 1-2000 ppm, although the response is not linear over this entire range. For example, if calibrated to benzene, the response is linear from about 0-600 units (ppm) above background. This means the PID reads a true concentration of benzene only between 0 and 600 ppm. Greater concentrations are detected at a lower level than the true value.

This instrument is not to be exposed to precipitation (rain). The units are not designed for operation under wet conditions.

Do **NOT** use this instrument for headspace analysis where liquids can inadvertently be drawn into the probe.

6.0 PREREQUISITE ACTIONS

6.1 Planning and Coordination

[1] Ensure the required equipment and supplies are available for the PID to be used according to the Equipment and Supplies Checklist (Attachment 1).

6.2 Performance Documents

[1] **ENSURE** field the notebook(s) are available and prepared in accordance with section 7.2.3, Documentation of Field Activities, of EPA's RCRA Waste Sampling Draft Technical Guidance.

[2] **ENSURE** manufacture's operating manual is available and the make, model, and year of PID is covered in it.

6.3 Tools and Equipment, Parts, and Supplies

Field Team Leader

[1] Ensure the equipment and supplies identified in Attachment 1 are correct, available and approved by the site technical lead (STL) and field team leader (FTL) with direction from the Site Technical Representative (STR), as appropriate. Additional items may be added to the checklist, as appropriate.

Field Team Members

[2] Use only the equipment and supplies authorized by the FTL and included on the equipment and supply checklist for this procedure.

[3] Report to the FTL any equipment or supply item listed on the checklist that is not available for use and the need for equipment or supply items in addition to or different from the equipment and supplies listed on the checklist.

7.0 STEP – BY - STEP PROCESS DECRIPTION

7.1 Perform Field Calibration

Field Team Leader

[1] **VERIFY** the Integrated Work Document (IWD) is complete and evaluates the hazards associated with using the PID.

7.1 Perform Field Calibration, cont.

Field Team Member

[2] **FOLLOW** the start-up procedure in manufacturer's operations manual. The monitoring instruments shall be calibrated each day to the manufacturer's standard for instrument operation.

[3] **RECORD** the following information in the site logbook in accordance with section 7.2.3, Documentation of Field Activities, of EPA's RCRA Waste Sampling Draft Technical Guidance: the instrument ID number (U.S. EPA decal or serial number if the instrument is a rental), the initial and final span settings, the date and time, the concentration and type of calibration gas used, and the name of the person who field-checked the calibrated instrument.

[4] **IMPLEMENT** the field calibration in accordance with the manufacturer's operations manual, which will be similar to the following example of calibration:

[1] **SET** the FUNCTION switch to the range setting, which includes the concentration of the calibration gas.

[2] **ATTACH** a regulator to a disposable cylinder of calibration gas. Record make, model, and serial number of cylinder. Connect the regulator to the probe of the PID with a piece of clean Tygon tubing. Open the valve on the regulator.

[3] **READ** the PID meter after 15 seconds: the meter reading should equal the response value as indicated on the calibration gas cylinder use,

[4] **IF** the reading is within ±15% of the response value,
THEN the instrument can be field calibrated to the response value using the external SPAN ADJUSTMENT control. The SPAN ADJUSTMENT control should be adjusted to a lower setting until the correct reading has been obtained. The lower the number on the SPAN ADJUSTMENT control, the greater the instrument sensitivity. If the SPAN ADJUSTMENT control has to be adjusted below a setting of 4.00, the unit should be red-tagged and returned to the manufacturer for repairs.

[5] **IF** the meter reading is greater than ±15% of the response value of the calibration gas used,
THEN the instrument should be **RED TAGGED** and **RE-CALIBRATED** according to the manufacturer's instructions, prior to use.

[6] **IF** the PID does not start up, check out, or calibrate properly, the instrument should not be used. The instrument should be red tagged and returned to the manufacturer for repair and recertification.

7.2 Perform Operation

Field Team Member

[1] **VERIFY** a PID equipped with an appropriate eV lamp (in most cases with VOCs, 10.6 eV), combustible gas indicator is applicable to the VOC species being monitored.

[2] **CONDUCT** headspace vapor screening by placing a sample in a plastic sample bag or a foil-sealed container allowing space (the container should be one-half to two-thirds full) for ambient air.

[A] **SEAL** the container and then shake gently to expose the sample to the air trapped in the container.

[B] **REST** the sealed container for a minimum of five minutes while vapors equilibrate.

[C] **MEASURE** the vapors present within the sample bag headspace by inserting the probe of the PID instrument in a small opening in the bag or through the foil.

[3] **RECORD** all readings in the site logbook according section 7.2.3, Documentation of Field Activities, of EPA's RCRA Waste Sampling Draft Technical Guidance. The maximum value and the ambient air temperature of the headspace air shall be recorded in the field sample log for each sample. Readings should be recorded as ppm, following background readings, also listed as ppm (i.e., background = 0 ppm; sample = 10 ppm).

- The background reading is the reading of ambient air outside the sample container.
- Under no circumstances should the probe tip assembly be immersed in fluid. In some field applications, with the exception of the probe's inlet and exhaust, the PID should be wrapped in clear plastic to prevent it from becoming contaminated and to prevent water from getting inside in the event of precipitation.

7.3 Perform General Post Operation Tasks

Field Team Member

[1] **FOLLOW** the PID shut-down procedure in the manufacturer's operations manual.

[a] **TURN** the FUNCTION Switch to OFF.
[b] **RETURN** the PID to a secure area and check the calibration before charging.

7.3 Perform General Post Operation Tasks, cont.

[c] **CONNECT** the instrument to the charger and plug in the charger

[d] The probe must be connected to the readout unit to charge the PID.

[2] **COMPLETE** logbook entries, per section 7.2.3, Documentation of Field Activities, of EPA's RCRA Waste Sampling Draft Technical Guidance. Ensure the site logbook information specified above in Section 7.1, Step 2, is complete.

[3] **CHECK** the equipment, repair or replace damaged equipment, and charge the batteries.

[4] **VERIFY** the instrument is working, following completion of a series of "0" readings.

8.0 RECORDS

Field Team Member

[1] **MAINTAIN** and **SUBMIT** the following records to the Records Processing Facility according to EP-DIR-AP-10003, *Records Management Procedure for ADEP Employees*:

- Completed Logbook
- Completed calibration records

9.0 ATTACHMENTS

Locate the form associated with this procedure on the ADEP SharePoint Site/Document Control System/Procedures, Policies/Standard Operating.

Attachment 1 Equipment and Supplies Checklist

ATTACHMENT 1
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Equipment and Supplies Checklist

Attachment 1: Equipment and Supplies Checklist		
	ITEM	**QUANTITY**
☐	PID (HNU) with probe-10.6 eV or higher (as appropriate for best ionization potential)	
☐	Operating manual	
☐	PID lamp cleaning kit	
☐	Battery charger for PID	
☐	Spare batteries	
☐	Jeweler's screwdriver for adjustments	
☐	Tygon tubing	
☐	NBS traceable calibration gas	
☐	"T" valve for calibration	
☐	Field Data Sheets/Site Logbook	
☐	Intake assembly extension	
☐	Strap for carrying PID	
☐	Teflon tubing	
☐	Sample containers (plastic baggies or glass jars)	
☐	Aluminum foil to cover mouth of sample jar	
☐	Plastic bags for protecting the PID from moisture and dirt	
	REAGENTS (some may require special handling/waste disposal, Refer to site IWD)	**QUANTITY**
☐	Isobutylene standards for calibration	
☐	Benzene reference standard	
☐	Methanol for cleaning ionization chamber (GC grade)	
☐	Mild soap solution for cleaning unit surfaces	
☐	Specific gas standards when calibrating to a specific compound	
☐	Light source cleaning compound Cat. No. PA101534-A1 (For use only with 9.5 and 10.2 lamps)	
☐		