



PROCEDURES FOR HEADSPACE ANALYSIS OF GASOLINE CONTAMINATED SOILS

North Dakota Department of Environmental Quality

Division of Waste Management – Underground Storage Tank Program

4201 Normandy St., 2nd Fl., Bismarck, ND 58503-1324

Telephone: 701-328-5166 ● Fax: 701-328-5200 ● Email: ndust@nd.gov

Website: <https://deq.nd.gov/wm>

Updated 2-2021

This document provides general guidance on the procedures for conducting analytical screening of gasoline contaminated soils using a portable photoionization detector (PID), portable flame ionization detector (FID), portable gas chromatograph (GC), or colorimetric detector tubes.

I. Sample Collection (soils)

- A. The appropriate method for obtaining a soil sample is determined by site conditions. Soil samples can be collected using any of the following types of equipment:
 - 1. A hand auger or trowel can be used for collecting surface samples and composite samples of stockpiled soils;
 - 2. A split spoon sampler can be used when drilling well boreholes and constructing depth profiles; and
 - 3. A backhoe can be used for collecting samples from the excavation area.
- B. The sample should be placed in a glass container such as a Mason jar or laboratory vial. Sample containers should be cleaned prior to use and decontaminated between samples if they are reused (as described in step D. below). After placing the sample in the container, the container is quickly covered and sealed with one or more sheets of aluminum foil or Teflon sheeting (approximately 2 mm thick) and an air-tight, screw-on lid.

Containers typically vary in size from 8 to 32 ounces (approximately 250 to 1000 ml). Polyvinyl chloride or acrylic bottles can be used; however, glass containers are preferred. The type and size of sample containers and the amount of sample placed in the containers should be consistent for all samples taken at a particular site.

- C. One-half to two-thirds of the container volume should be filled with sample. The amount of sample can be visually estimated.
- D. Sample containers can be decontaminated by cleaning with detergent, then rinsing with water or methanol, followed by single or multiple rinses with distilled water.

II. Sample Collection (water)

- A. Groundwater samples should be obtained from monitoring wells using a clean bailer. Samples may also be obtained directly from well pumps. If a bailer is used to collect groundwater samples, it should be securely attached to clean nylon cord and slowly lowered into the well. Care must be taken to avoid creating additional turbulence in the well when sampling. When the bailer is filled with water, it is removed from the well and the contents are poured into the sample container.

Bailers are decontaminated before reuse. Surface water samples can be obtained using a glass container.

- B. The water sample should be placed in a glass container such as a volatile organic acid (VOA) bottle with a Teflon-lined lid containing a septum, or a Mason jar. Containers can range in size from 40 ml VOA vials, to 8 to 32 ounce (approximately 250 to 1000 ml) glass containers. Containers are thoroughly cleaned (as described in step D. below) prior to use. After the sample is placed in the container, the container is sealed with one or more sheets of aluminum foil or Teflon sheeting, and a snap-on or screw-on, air-tight lid. Containers can be designed with a stopcock attached to the cap. The analytical instrument probe is connected to the stopcock with tubing to allow direct measurement of headspace vapors from the container. Sample containers constructed of polyvinyl chloride (PVC) or an acrylic compound can also be used; however, glass is preferred because it is more inert than PVC or acrylic materials, which reduces the risk of sample carryover if containers are reused.
- C. The sample container should be filled one-half to two-thirds full with water sample. The volume of water sample used will vary with different container sizes. The type and size of the sample container and the amount of sample placed in the container should be consistent for samples collected at the sample site.
- D. Sample collection equipment and containers can be decontaminated by a methanol rinse followed by single or multiple rinses of distilled water.

III. Sample Preparation and Analysis (static analysis)

- A. Prior to analysis, the sample should be allowed to sit for 5 to 10 minutes to reach ambient temperature. Samples should not be allowed to sit so long that condensation forms in the container. Samples may be placed in a 70°F (21°C) water bath for 5 minutes.
- B. The aluminum foil or Teflon sheet covering the sample container is pierced with the instrument probe. Sample analysis is conducted just long enough for the instrument to respond to volatile organic vapors, but not so long as to draw in ambient air from outside of the container.

IV. Sample Preparation and Analysis (dynamic analysis)

- A. Prior to analysis, the sample should be manually shaken or agitated for 15 to 20 seconds. The agitation period should be consistent for samples collected at the sample site. If the ambient temperature is below 32°F (0°C), the sample should be placed in a heated vehicle or a building during agitation and analysis. A hot water bath, 75° - 80°F (24° - 27°C), can also be used to warm the sample prior to analysis.
- B. The sample can be analyzed immediately following agitation or after allowing a period of time for development of headspace vapors. The practice selected should be consistent for all samples taken at a particular site.

- C. After sample agitation and the headspace development period, the screw-cap is removed to expose the aluminum foil or Teflon seal. When the field instrument (PID or FID) is ready for conducting measurements, quickly puncture the foil seal with the tip of the instrument sampling probe and insert it to a point about one-half of the headspace depth. Exercise care to avoid uptake of soil particles or water into the instrument probe. The instrument probe should not be allowed to directly contact the soil or water sample.
- D. If VOA bottles are used, obtain a vapor sample by inserting a syringe through the vial septum, withdrawing the sample from the bottle headspace, and injecting it into a portable GC for analysis.

V. Method Results and Calibration

- A. Instrument readings should be recorded using one of two methods: the highest meter response observed within the first 5 to 10 seconds on the analytical field instrument is recorded; or instrument readings are taken at certain time intervals over a set time period (usually 2 to 5 minutes), and then the recorded instrument measurements are averaged. Results obtained from portable field instruments are reported as total organic volatiles (TOV) in either ppm levels or as "instrument units." If outside air is inadvertently drawn into the sample container, vapors in the headspace will be diluted and instrument readings will not accurately represent the contaminant concentration.
- B. Instruments should be calibrated at least once a day prior to beginning sample analysis, or no less than once every ten (10) analyses, whichever is greater.
- C. The time that it takes to collect a headspace sample depends on the technique used but, generally, is in the range of 5 to 15 minutes. An additional 5 to 10 minutes is needed to perform each analysis. Sample analysis using a portable PID or portable FID can be completed in under 5 minutes. GC sample analysis usually takes less than 10 minutes, depending on the compounds being identified.

VI. Environmental Influences

Environmental factors that adversely influence the performance of this method include:

1. High soil moisture;
2. High organic and clay levels in soil;
3. Dissolved organics in water; and
4. Age or degree of weathering of the contaminant.

These factors all affect partitioning of volatile constituents from the sample into the headspace. These factors influence sample analysis by producing low readings on field instruments.

High soil moisture and high organic and clay levels in soil can limit the amount of volatile contaminants that will volatilize into the container headspace. The presence of dissolved organics in water can also reduce volatilization of contaminants. Contaminants that are weathered contain fewer volatile constituents because they have already volatilized to varying degrees over time and, therefore, volatile contaminant concentrations will be lower than would be