Guidance Document for the Use of Periodic Volatile Organic Compound (VOC) Monitors at Small NJ Sources.

Disclaimer: This document provides the technical background and guidance information for facilities and consultants to develop a VOC monitoring protocol that would meet the minimum technical requirements at small sites where the permit allows the use of periodic monitors. It is designed to address questions regarding the use and operation of periodic VOC monitors but does not outline all the components in a full monitoring protocol. The protocol outline is in a separate guidance document. This is considered a "living" document and may be changed at any time as regulations and/or periodic monitoring technology change. In keeping with the spirit of a guidance document, the technical evaluation and final approval of a monitoring protocol rests with the BTS staff.

Summary: Some of the standard methods for VOC emissions determination for stack tests with a control device are Reference Methods 25, 25A, or 18. Because of high variability, short operation, or limited emissions potential at a site, periodic equipment is more practical than continuous monitoring equipment. These instruments may be used as surrogates for the reference methods. The overall objective should be that they provide comparable emission numbers. If a periodic equipment monitoring protocol is required it must be prescriptive in nature because the instruments are often not used regularly, the response factors vary from site to site, and the technician operating the equipment may not operate the equipment on a regular basis. The submittal of a standard operating procedure (SOP) for the operation of the periodic equipment is not currently required; however, the use of a SOP is strongly recommended.

The commercially available periodic VOC instruments operate on various principles that are rarely the same as the reference methods. These differences produce results that may underreport the VOC emissions in uncorrected periodic instruments. The procedures described in the periodic equipment protocol must address this discrepancy and correct the values to approximate the result from a reference method.

Emission limits expressed in lbs/hr must be calculated in the classical manner using the equation in NJAC 7:27B-3.7 section (f)5 and include a response factor to correct the concentration value that is due to the response difference in periodic instruments versus the reference method. Emission limits expressed in concentration units (ppm) must take into consideration the compound or mix of compounds measured and the instrument response factor(s) to convert to the permitted parameter, e.g. "as methane". If the permit requires the control device to operate at some removal efficiency then the inlet measurement must use the same units as the outlet measurement.

When the permit requires several conditions or allows for any of several conditions, the facility must fully describe the sampling and analytical method, and show example calculations that will be used to satisfy each condition. In addition, if options are available the protocol or Standard Operating Procedure (SOP) must outline the hierarchy that will be used to satisfy each condition.

There are two common types of periodic VOC monitoring instruments typically used in the field. One is a Photo Ionization Detector (PID) that ionizes the molecules using an UV lamp and is most sensitive to compounds containing double bonds (π electrons). The other is a Flame Ionization Detector (FID) that in a typical periodic instrument measures the number of molecules ionized in a flame. Please note that most currently available periodic FID instruments do not respond to organics in the same manner as the reference methods and operate on a different principle. This is often confusing and the source of errors. PID and FID instruments from different manufacturers will have different responses to the same chemicals even when the same calibration gas is used. Therefore the make and model must be specified in the protocol or SOP.

Underlying assumptions regarding the use of periodic monitors.
The standard to which all equipment shall be referenced: When periodic monitors are used for VOC emissions the Bureau of Technical Services interprets the term "as methane" to mean equivalent to the results from the analysis by a Method 25A FID to measure organic content in VOC samples. The principle of operation that Method 25A uses is described in the article "Methane Formation by Flame-Generated Hydrogen Atoms in the Flame Ionization Detector", Analytical Chemistry 1996, 68, 3607-3611. Most of the periodic FID instruments do not operate on

this principle and cannot provide a direct "as methane" measurement even when they are calibrated with methane, and the results need to be corrected. Commercially available periodic instruments that operate on the reference method (Method 25A) principle may be used as per Method 25A and the results reported directly.

Correcting the VOC instrument direct readout to "as methane" will typically yield 2 to 10-fold change in the concentration even after calibrating the FID with methane. The use of periodic monitors may only be used if the proper correction factor between the periodic instrument and the reference method is determined. There are two ways to determine a correction (response) factor.

The most direct method is to conduct side by side (duplicate) analysis of the gaseous emissions using the reference method and the periodic instrument. If this method is chosen then a minimum of 7 samples taken on 6 different days must be used to develop the correction factor. Correction factors developed by this method are only applicable to the make and model used in the duplicate analysis, and are specific to the site from where the samples were taken. When this approach is used the protocol or SOP must fully describe the sampling method, type of sample container and the means of determining the total organic (VOC) concentration.

If the character of the gaseous emissions is known then a weighted response factor may be developed from the instrument manufacturers' response factor table. For example if 30% of the VOC is known to be toluene and 70% is known to be trichloroethylene and the response factors are 0.6 and 1.1 respectively; then the weighted response factor is;

(0.6 x 30%/100) + (1.1 x 70%/100) = 0.95 (response factor for mixture)

Other assumptions:

One is permitted to assume the character of the VOC gaseous emissions does not change as the air passes through carbon adsorption units. In other words, if the mix of two substances is 60%/40% on the inlet side the relative concentrations are the same on the outlet. The practical value of this assumption is that for removal efficiency the absolute value of the concentration is not required. Therefore a response factor is not required. Any instrument that meets the minimum specifications and can be calibrated for both the inlet and outlet concentrations can be used to show removal efficiency without using a response factor. However if the permit expresses an emission limit in either lbs/hr or in ppm then a correction factor must be determined and applied.

For oxidixers in general, the character of the gases change as the VOC is oxidized in the control device. Although some material may pass unchanged most is changed and generally the transformation is to smaller molecules. These smaller molecules may contain significant concentrations of carbonyls that are poorly detected by PIDs. Therefore PIDs are not permitted to be used at the outlets of oxidizers. PIDs are not permitted at the inlet side of oxidizers because the inlet VOC concentration is usually high and PIDs are not linear at high (>5000 ppm) ranges. FIDs have a wider dynamic range and are permitted at both the inlet and outlet of the oxidizer. Internal combustion engines require the use of FIDs.

The qualitative character of VOC at landfills, groundwater remediation sites, lagoons, and soil remediation sites does not change over time. If it is 60%/40%, toluene/trichloroethylene at the beginning of the monitoring program then it remains 60%/40%. If the facility determines the character of the emissions changes the protocol or SOP must include language that will accommodate the change. As an alternative the worst case scenario may be assumed.

For Soil Vapor Extraction (SVE) operations the character of the vapor may be assumed to be identical to the character of the volatiles in the water or soil. If water/soil analysis shows a 60%/40%, mass toluene/trichloroethylene ratio then one may assume the vapor is 60%/40%, mass toluene/trichloroethylene. Where there is uncertainty in a value or parameter at the facility, the worst case may be assumed. For example; if one is uncertain about the exact molecular weight of a gaseous mix due to changing operating scenarios, but is certain that the heaviest substance is PERC (tetrachloroethylene), with a molecular weight of 166, then one is permitted to use 166 as the molecular weight of the mix of gases when calculating emissions.

One may assume the molecular weight of gasoline is 100, unless one has data and can demonstrate that the molecular weight is different.

When Charcoal/Carbon traps are used prior to the instrument to measure methane slip, one may assume only non-VOC (methane et. at.) is measured by the instrument. Typically there is some methane slip through thermal oxidizers that is picked up by the FID. Several manufacturers allow for the use of a "methane monitor" to be used on the inlet of the FID and lets methane only (non-VOCs) into the instrument. Subtracting this measurement from the total is an acceptable method of determining the VOC concentration. In some other non-oxidizer applications where the ambient concentration of methane may be significant, one is permitted to subtract it out when determining non-methane VOC.

When Tedlar bags are used to collect a sample, all VOCs are assumed to remain in a gaseous state as long as there is no condensed moisture visible in the bag. If moisture is observed in the bags, then prior to analysis one must re-heat the bags to a temperature that vaporizes all the moisture prior to analyzing the contents with an FID. PIDs are not allowed to be used for analysis on re-heated bags because PIDs are not to be used in condensing environments. Please be reminded that the assumptions described in this document are sweeping in scope and may not be applicable to all VOC tests. For example; when light polar organics are known to be present with nonpolar heavy organics then assumption #1 and 6 may not apply. Also, when dealing with non-toxics and non-HAPs the measurements must be able to account for 95% of all the VOC. Protocols and SOPs containing deviations from the above guidance must include an explanation of why the change should be permitted and data supporting the variance.