

**COMMONWEALTH OF VIRGINIA  
DEPARTMENT OF ENVIRONMENTAL QUALITY**

**FIELD OPERATIONS MANUAL FOR AIR INSPECTORS**  
**Air Standard Operating Procedures (ASOPs)**

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**ASOP - 7  
VOC TESTING**

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I. PURPOSE:

The purpose of these guidelines are to aid regional personnel in the observation of VOC stack testing. The material presented will be from an enforcement point of view.

II. VOC Testing

Generally VOC test methods are method 18, method 25, and method 25A (EPA Reference Methods found in 40 CFR 60, Appendix A). Depending on the nature of the pollutant being tested, the testing company will choose one of the afore mentioned methods to measure concentrations. The methods and their basic uses are as follows:

A. Method 18 This method was designed for the synthetic Organic Chemical Manufacturing Industry (SOCMI). The philosophy behind the method was to standardize monitoring equipment (Gas chromatograph) to analyze several "known" organic chemicals and to quantify those known constituents. It cannot quantify a constituent unless it is "known".

B. Method 25 was designed for measuring the VOC destruction efficiency from primarily thermal incineration control devices. It converts all carbon constituents to make a comparison to methane (a one carbon compound) and then makes a "total" carbon analysis as compared to methane.

C. Method 25A was designed for non-destructive VOC control devices and compares the carbon analysis to a standard gaseous organic, usually propane. Propane is a three carbon compound, so the sample comparison is to straight carbon/hydrogen organic but is not well suited for picking up organic alcohols or chlorinated organic (C-OH or C-CL compounds) because the flame ionization detector has a hard time oxidizing these compounds. Therefore, this method will be biased low if these compounds are present, especially if low carbon chlorinated compounds

are present.

### III. Testing Protocol

In the protocol submitted by the source tester, the tester should justify why a particular method has been chosen. In Gaseous pollutant testing the tester will assume the gas stream is saturated with the pollutant being tested. Two methods should always be run in a gaseous test to ensure accuracy, Method 2 to determine velocity and Method 4 to determine moisture.

Once these methods are run the tester will be able to convert the ppm readings to a mass rate that is applicable to the regulations and permit conditions.

With the exception of method 25A gas testing requires testing in the field and then taking samples to a lab to have analyzed. The inspector should take care to insure that all of the field work performed is quality assured and that samples taken in the field are analyzed quickly.

### IV. Method 18

#### A. Principle

The major organic components of a gas mixture are separated by gas chromatography (GC) and individually quantified by flame ionization, photoionization, electron capture or other appropriate detection principles.

Basically the retention times of each separated component are compared (in a lab) with those of known compounds under identical conditions. The analyst confirms the identity and approximate concentrations of the organic emission components. With this information, the analyst then prepares or purchases commercially available standard mixtures to calibrate the GC under conditions identical to those samples.

#### B. Sampling

Prior to the test several samples may be drawn to determine the concentrations of the particular pollutant in the gas stream being sampled. This will enable the tester to determine what tubes are needed to accurately record concentrations in the stack.

Collection of samples during the test and during preliminary test can be from several different methods ranging from Glass Sampling Flask, Tedlar or Aluminized Mylar Bags, or an Evacuated Flask. The sample is drawn into one of the approved containers from a single point in the stack (the gas stream is assumed to be saturated with a mixture of the gasses).

During the actual compliance test a sample is obtained using a sample train as pictured in attachment 1. A leak check of both the bag and container should be performed. The tester will: Connect the vacuum line from the needle valve to the teflon sample line from the probe. Place the end of the probe at the centroid of the stack, or at a point no closer to the walls than 1m, and start the pump with the needle valve adjusted to yield a flow of 0.5 liter/minute. After allowing sufficient time to purge the line several times, connect the vacuum line to the bag, and evacuate until the rotameter indicates no flow.

Once accomplished, position the sample and vacuum lines and begin sampling. When the sample has been collected the tester will shut off the pump, secure the bag and deliver for testing.

The bag should be protected from sunlight and whenever possible the analysis of the bag should be performed within 2 hours of the sample collection.

Once the sample is drawn the gas is returned to the lab, then fed into a GC to determine the concentration of the gas in the container. Calculations for the conversion of the concentration to PPM of each organic in the diluted gas can be found in the method 18 procedures. A calibration of the unit should have been done before and immediately after each day's testing.

#### C. Special Conditions to Look for

Attention should be given to the tester's equipment and recent calibration of each machine. The tester should be able to provide a certification of the GC. In addition, the tester is required to calibrate the instrument before and after each day's sampling using NIOSH approved methods. For the GC, the tester must use a minimum of three different standards; selecting the concentration to bracket the expected average sample concentration.

Attention should be given to calibration gas used.

Calibration gas must be certified.

Attention should be given to expected spikes for test. The detector should never become saturated.

V. Method 25

A. Principle

An emission sample is withdrawn from the stack at a constant rate through a heated filter and a chilled condensate trap by means of an evacuated sample tank. After sampling is completed, the TGNMO (total gaseous nonmethane organics) are determined by independently analyzing the condensate trap and sample tank fractions and combining the analytical results. The organic content of the condensate trap fraction is determined by oxidizing the NMO to CO<sub>2</sub> and quantitatively collecting the effluent in an evacuated vessel, then a portion of the CO<sub>2</sub> is reduced to CH<sub>4</sub> and measured by the FID. The organic content of the sample tank fraction is measured by injecting a portion of the sample gas into a gas chromatographic column to separate the NMO from carbon monoxide (CO), CO<sub>2</sub> and CH<sub>4</sub>; the NMO are oxidized to CO<sub>2</sub>, reduced to CH<sub>4</sub> and measured by an FID. In this manner the variable response of the FID associated with different types of organics is eliminated.

B. Sampling

Prior to any test a leak check is required. This leak check should be run in accordance with section 4.1.4 of Method 25 as outlined in the federal register. When ready to begin testing the tester will place the probe in the stack pointing AWAY from the direction of the gas flow. At that point the tester will set the probe temperature controllers to 129°C and the filter temperature controller to 121°C. The probe and filter will be allowed to heat up for about 30 minutes before purging the sample train.

Following that heatup cycle the tester will close the sample valve, open the purge valve and start the vacuum pump. The flow rate will be set between 60 and 100 cc/min and he will purge the train for approximately 10 minutes. This will continue until the temperature at the exit ends of the probe and filter are within their ranges. Once this is accomplished the Sampling may begin.

During the test the tester will constantly check the dry ice in the trap and record the vacuum in the sample tank and flowmeter setting at 5 minute intervals. The sampling will continue until the correct amount of gas has been sampled according to the figure 25.8 (attached).

Following the field test a post test leak check should be performed. The inspector should document the results of the leak check as well as note any unusual occurrences that occurred during the test.

C. Analysis

Like method 18, the samples run in the field will be analyzed in the lab. The inspector when documenting the field work should document that all startup, field test, and cleanup procedures outlined in the method are followed.

VI. Method 25A

A. Principle

A gas sample is extracted from a source through a heated sample line if necessary and glass fiber filter (optional) to a flame ionization analyzer (FID). Results are reported as volume concentration equivalents of the calibration gas or as a carbon equivalent.

B. Calibration gases

This method requires the monitoring unit to be calibrated in the field. To do this calibration gases are used in accordance with the procedure in Protocol No. 1 listed in Citation 2 of the Bibliography of the CFR. Additionally the manufacturer of the cylinder of gas should provide a shelf life for the cylinder of cal gas.

Calibrations error should be checked no more than 2 hours before the start of the first run. Zero and high level cylinder gasses are introduced and the instrument is adjusted, then the low and mid level responses are predicted assuming a linear response. If the actual responses are within 5% of the predicted responses, the calibration error test passes.

C. Pretest Preparation

Sight selection, location of the sample probe, and response time testing, should all be performed in accordance with the part 60, App.A, method 25A.

D. Emission Measurement Test Procedure

During the test, record time and process information as required. In particular, the tester and the DEQ observer should note any process interruption or cyclic operation during the test.

E. Drift determination

Immediately following completion of the test period and hourly during the test period, reintroduce the zero and mid level calibration gases, one at a time, to the measurement system at the calibration valve assembly. (The tester should make no adjustments to the measurement system until after both the zero and calibration drift checks are made). The analyzer response should be recorded. If the drift values exceed the specified limits, invalidate the test results preceding the check and have the test repeated following corrections to the measurement system.

Analysis of the three test procedures outlined above for gaseous pollutants, method 25A is the only one where testing and results are obtained in the field. The DEQ observer should pay particular attention to calibration checks, cal gas certifications and process upsets. If the observer feels that testing is not in compliance with the methods outlined in the CFR, documentation will be crucial when the department accepts or denies the test.

VII. Applicability Of VOC Methods

Method	18	25	25A
Speciation?	yes	no	no
Combustion Source?	No	yes	no
Lb/Hr Reg?	yes	no	no

Measure <50ppm?        yes                                no                                no

Method 18                Known gaseous organics except polymerics (high MW  
compounds) very low vapor pressure.

Method 25                TGNMO Total gaseous non-methane organice as carbon.

Method 25A                Designed for non destructive VOC control devices.