

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
REGION 4
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Issue: Inconsistency in the Reporting of Volatile Organic Compound (VOC) Test Results Using Methods 25 and 25A

Executive Summary:

Region 4 recently became aware of the fact that there have been inconsistencies in the way state and local air pollution control agencies have used U.S. Environmental Protection Agency (EPA) Method 25 and 25A results to calculate VOC emission rates. Method 25 measures total gaseous nonmethane organic compound (TGNMO) concentrations in terms of carbon and Method 25A measures total hydrocarbon concentrations in terms of the gas used to calibrate the analyzer. Therefore, Method 25 and 25A results must be converted to an "as VOC" basis if emission rates are being calculated in order to determine compliance, determine rule applicability, or establish fees based upon VOC emission rates.

Background:

The majority of VOC testing is conducted using one of three EPA methods. Method 18 is a gas chromatography based method that reports results in terms of the concentration of specific organic compounds. Method 25 is a method for measuring TGNMO concentrations, and it also involves the use of gas chromatography during the analysis phase. The purpose of the chromatography step in this method, however, is to separate methane, carbon monoxide, and carbon dioxide from the nonmethane organic compounds in the sample, rather than to separate all of the organic compounds in the sample so that their concentrations can be determined individually. Method 25 results are expressed in terms of carbon because all of the VOC in the sample is converted to methane prior to being quantified with a flame ionization detector (FID). Because of this conversion to methane during the analysis, Method 25 provides a one-to-one response for all the carbon atoms in the sample. Method 25A involves determining total hydrocarbon concentrations by introducing samples directly to a FID without a gas chromatography step to separate the compounds in the sample, and results are expressed in terms of the gas used to calibrate the FID (usually methane or propane). Because some organic compounds containing atoms such as chlorine or oxygen may cause a depressed or an elevated response on an FID, Method 25A does not necessarily provide a one-to-one response for all of the carbon atoms present in the sample.

Based upon a survey conducted by the North Carolina Department of Environment and Natural Resources (NCDENR), it is clear that there has been inconsistency regarding how the results obtained with Methods 18, 25, and 25A have been used to calculate VOC mass emission rates. It is relatively easy to convert Method 18 results to mass emission rates since this method

reports concentrations in terms of the actual organic compounds in the sample. Once the concentrations of the specific organic compounds are known, the molecular weight of the compounds and the volumetric flow rate of the gas stream tested can be used to calculate VOC mass flow rates. The major area of inconsistency identified by the NCDENR survey involves the calculation of VOC emission rates when either Method 25 or 25A is used to conduct the testing.

In order to convert Method 25 results to a VOC mass flow rate, it is necessary to know the VOC-to-carbon weight ratio for the mixture of organic compounds in the gas stream tested. For example, methanol has a molecular weight of 32, and each methanol molecule contains one carbon atom, yielding a VOC-to-carbon weight ratio of 2.67 (i.e., 32 divided by 12). Therefore, if Method 25 is used to measure the VOC concentration of a gas stream that contains only methanol, the carbon mass flow rate calculated from the Method 25 results and gas flow rate data must be multiplied by 2.67 to express the results in terms of VOC.

Converting Method 25A results to a VOC mass flow rate is similar to converting Method 25 results, but an additional factor that must be taken into account is the relative response factor between the organic compounds in the gas stream and the gas used to calibrate the Method 25A analyzer. In cases where the organics present in the gas stream have either a depressed or an elevated response relative to the calibration gas, it would be necessary to multiply the Method 25A results by both the VOC-to-carbon weight ratio for the mixture of organic compounds in the gas stream and a response factor in order to accurately calculate the VOC mass emission rate.

The NCDENR sent letters to state air pollution agencies in Regions 1, 2, 3, 4, 5, and 6 asking how the reporting of Method 25 and 25A results is addressed in other states. The number of states responding to these letters was relatively small, but based upon the responses received, it is clear there is no consistency at the state level with respect to the reporting of VOC emission rates when Methods 25 and 25A are used to conduct testing. Of the seven agencies responding, four indicated results should be reported as VOC, two indicated that the results should be reported as carbon, and one indicated that results should be reported in terms of the calibration gas used for the Method 25A analyzer.

In order to convert Method 25 or 25A results to an “as VOC” basis it is necessary to have some knowledge regarding the relative concentration of the various organic compounds in the gas phase. Obviously, in situations where a complex mixture of organics is present in a gas stream, calculating an average VOC-to-carbon weight ratio can be a difficult task itself. In the case of coating operations, it may be possible to calculate a concentration-weighted average VOC-to-carbon weight ratio using manufacturer data regarding the solvents contained in the coating(s) applied. In cases where such information is not available, it may be necessary to conduct the VOC testing with Method 18 in order to determine the concentration of specific organic compounds directly.

In some situations, there are potential ways of simplifying or streamlining the calculation of VOC mass flow rates for gas streams that contain a complex mixture of organic compounds. For

example, some gas streams may contain compounds whose VOC-to-carbon weight ratios are similar enough that a representative average ratio can be chosen for use in the calculation without actually knowing the precise concentration of each compound in the gas stream. In other circumstances, it may be possible to show that emissions are below a relevant emission rate standard or rule applicability threshold even if the “worst case” VOC-to-carbon weight ratio for all of the compounds in the gas stream is used to convert carbon emission rates to VOC emission rates. In such situations, therefore, it would not be necessary to know the exact concentration of each compound in the gas stream.

EPA position:

Since Method 18 measures concentrations of specific organic compounds, concentrations and mass emission rates should be reported on an “as VOC” basis when this method is used. The end use of the VOC data is an issue that must be considered when deciding on the reporting format for Method 25 or 25A test results. If testing is conducted at the inlet and outlet of a control device to determine its efficiency, the calculated efficiency results will be the same regardless of whether the results are reported on an “as carbon” or on an “as VOC” basis. Therefore, if the sole purpose of a test is to determine control device efficiency, results may be expressed as either carbon or as VOC.

If the test data will be used to determine whether a source is subject to a regulation whose applicability is based upon VOC emission rates, to determine compliance with VOC emission rate standards, or to set permit fees, however, the results must be reported as VOC, rather than as carbon. The basis for this position is that reporting the results as carbon in such circumstances will understate the impact of the emissions on the environment and, thereby, may lead to incorrect conclusions regarding compliance or rule applicability.

This Regional position regarding the proper reporting of VOC test results was previously explained in a February 7, 1996, letter from the Region to the South Carolina Department of Health and Environment, and a copy of this letter is included as an attachment to this issue paper.

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