

Devils in the Details:

Air Emissions of Volatile Organic Compounds

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To what extent do regulators and environmental managers need to pay attention to detail when it comes to VOCs?

All too often, people who deal with the “big picture” issues (e.g., policy, regulatory compliance) assume that technical details are not their concern (i.e., these are things that should be addressed by laboratories, technicians, or contractors). This is true in many cases; however, it is also important to be aware of the extent to which the technical details can have an impact on the larger issues.

Those involved with the field of air pollution in the United States are familiar with the regulatory term volatile organic compounds (VOCs), and that these chemicals are regulated as an aggregate because of their reactions with oxides of nitrogen (NO_x) to form tropospheric ozone (which can have detrimental effects on human health and vegetation). The overall purpose of VOC reduction policies is to reduce levels of tropospheric ozone, and many facilities have numerical permit limits restricting their VOC emissions. This article first identifies the fact that these policies are inexact, given that different chemicals in the VOC category can have very different reactivities. Then, this article identifies issues related

to emissions quantification, including (1) factors that can systematically bias results from one of the more common methods for measuring VOCs, and problems associated with using this method or any other methods to attempt to quantify all of the chemicals in the VOC category, and (2) common problems encountered when estimating the volatilization of VOCs.

THE INEXACT NATURE OF VOC POLICY

The U.S. Environmental Protection Agency (EPA) defines the term VOC broadly: “...(VOC) means any compound of carbon, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate, which participates in atmospheric photochemical reactions.... This includes any such organic compound other than the following, which have been determined to have negligible photochemical activity...”¹

The definition then continues to exclude dozens of chemicals and chemical classes, most of which are regulated under

Title VI of the Clean Air Act (CAA) as stratospheric ozone-depleting substances, in part because of their lack of reactivity in the troposphere. (Despite the term “volatile organic compound,” no chemicals are excluded based on their volatility; perhaps a more appropriate term that has been used by some regulatory agencies is “reactive organic gases,” or ROGs.) This leaves an essentially infinite number of chemicals in the VOC category.

Different organic chemicals have significantly different reactivities with respect to ozone formation (“ozone reactivity”), and studies have been conducted to tabulate the reactivities of some of these chemicals.² However, relative reactivities also differ with respect to the ratio of VOC to NO_x in the air; therefore, it is virtually impossible to conduct ozone reactivity experiments on all the VOCs in existence at all the possible VOC-to-NO_x ratios. EPA has adopted a step-function approach to regulation: chemicals with reactivities above a certain point are regulated as VOCs, and those with reactivities below that point are excluded from the category. Currently, the number of excluded organics are relatively few in number, and in most practical measurement situations, the only excluded chemical present in significant quantities (and the only excluded chemical that can be identified and quantified relatively easily in the typical measurement process) is methane (CH₄). The terms “non-methane organic compounds” (NMOCs), “non-methane organic gases” (NMOG), and “non-methane hydrocarbons” (NMHCs) are therefore often used as surrogates for the term VOCs. At the federal level (and in most states), there is no requirement to weight total VOC emissions by the ozone reactivities of the VOCs being emitted (e.g., in the same manner that emissions of various dioxins and furans are weighted to determine a “toxicity equivalent” relative to a specific dioxin). Total VOC is strictly, at least in theory, a total weight of all chemicals falling into the VOC category.

It is well documented that at some VOC-to-NO_x ratios, VOC emissions reduction does little to reduce tropospheric ozone, and that tropospheric ozone formation is primarily only a concern during the warmer months,³ so there are certainly several situations in which VOC emissions reductions are doing little if anything to reduce tropospheric ozone formation. It is therefore apparent that the current policies of reducing VOCs for the purpose of reducing tropospheric ozone are imprecise and inexact means of accomplishing the goal. Determining the “total weight of VOCs” is also not possible within most budgets, and a typical measurement methodology for approximating total VOCs is subject to biases due to differences in procedures, which can affect compliance with emissions limits.

VOC MEASUREMENT ISSUES

There are many different means of measuring VOCs in vents and stacks, including handheld analyzers, rack-mounted on-site instruments, and sample collection and laboratory

analysis. Issues associated with which measurement to choose can be further complicated by the extent to which individual chemical species need to be identified (e.g., for identification of hazardous air pollutants, or HAPs). For simplicity's sake, however, this discussion will focus primarily on one of the least expensive and most common means of measuring VOCs in stack tests for regulatory compliance purposes: a flame ionization detector (FID) used in accordance with EPA Method 25A.⁴ Specifically, this section presents an understanding of what the FID is measuring, and identifies potential biases associated with the calibration gases used, oxygen concentrations, the different ways that results are reported, the detector's sensitivity to different types of VOC, and shortcomings of current alternatives to this method.

The principle of Method 25A is as follows: a probe inserted into the stack is connected to the FID by a heated sampling line to avoid moisture condensation in the line. This “wet” sample is then passed through the FID's hydrogen-fueled flame, which cracks the hydrocarbon molecules and generates charged particles; an electrostatic field is then used to generate a current, which is correlated to the amount of carbon present. In standard analyzers, there is no means of subtracting out influences from chemicals that have been exempted from the VOC category on the basis of ozone reactivity, so the results are instead referred to as total hydrocarbons (THCs). Newer analyzers, such as the Thermo Environmental Instruments Inc. Model 55C Direct Methane, Non-Methane Analyzer and the J.U.M. Engineering GmbH Model 109A Non-Methane Hydrocarbon/Total Hydrocarbon Analyzer, are capable of providing continuous or semicontinuous measurements of non-methane hydrocarbons (NMHCs).

Though the principle of Method 25A is relatively simple, there can still be misunderstandings as to what the results from a Method 25A analysis mean. Method 25A allows for different calibration gases to be used; methane (CH₄) and propane (C₃H₈) are the most common (some state regulatory agencies prefer methane, some prefer propane, and many allow either to be used). Concentrations (read as “ppm,” or parts per million, on the analyzer readout) should therefore be reported as either ppmvC₁ (ppm by volume, wet basis, where a readout of 100 ppm corresponds to 100 ppm of methane) or ppmvC₃ (where 100 ppm corresponds to 100 ppm of propane). Because propane has three times as many carbon atoms as methane, not identifying the calibration gas can lead to errors of a factor of 3. Unfortunately, many equipment vendors still state specifications in terms of ppm or ppmv, which can leave considerable room for misunderstanding. For example, emissions of “120 ppm THC, 50% benzene (C₆H₆)/50% hexane (C₆H₁₄)” might be construed as 10 ppm each of benzene and hexane (if the 120 ppm was measured as ppmvC₁), 30 ppm each of benzene and hexane (if the 120 ppm was measured as ppmvC₃), or 60 ppm of benzene molecules and

60 ppm of hexane molecules (e.g., measured by a methodology other than Method 25A).

This example brings up another point: The FID is in actuality not a perfect counter of carbon atoms and, therefore, in many cases, 10 ppm of hexane would not register as exactly 20 ppmvwC₃ or 60 ppmvwC₁. Response factors for one popular analyzer are such that 10 ppmvw hexane would actually result in a reading of 16 ppmvC₃ if propane were used as a calibration gas, and 40 ppmvC₁ if methane were used.⁵ This example illustrates two important points. First, if the person conducting the test did not know the instrument's response factor for hexane, they would underpredict the concentration of carbon atoms in the exhaust (by 20% if propane were used as a calibration gas, or by 33% if methane were used). Second, the calibration gas itself makes a difference in the end result: the degree of underprediction is more significant if methane is used than if propane is used, because the response for propane is not three times the response for methane (as would be predicted by using the "carbon equivalent correction factors" listed in Section 12 of Method 25A). Sources using this particular analyzer to quantify unknown VOCs would therefore appear to have lower exhaust concentrations if propane, rather than methane, is used as a calibration gas.

A further complication is that Method 25A measurements do not quantify the mass of the VOC; they only quantify the amount of carbon present. Mass emissions results are typically reported in terms of the calibration gases used. Mass emissions "as methane (CH₄)" assign a molecular weight of 16 to each carbon (equivalent to assuming that there are four hydrogen atoms present per carbon atom), whereas mass emissions "as propane (C₃H₈)" assign a molecular weight of 14.7 to each carbon (i.e., the molecular weight of propane divided by three, equivalent to assuming eight hydrogen atoms for every three carbon atoms). The difference is 9% in the weight assigned per carbon, and may make a relatively small difference at the highest levels of public policy-making, but can be significant for those trading VOC emissions credits in market-based programs, or for plants complying with an emissions limit. Of course, this is still not truly the mass of the VOC, since any other atoms present in the organic chemicals, such as oxygen, nitrogen, sulfur, and chlorine, are not accounted for at all.

FID responses can also sometimes be significantly affected by oxygen concentrations, particularly when stack oxygen concentrations are low (e.g., in boiler and incinerator stacks, or in exhaust from inert environments). The diluent gas used in calibration gas cylinders is often chosen to have an oxygen concentration similar to that in the stack (e.g., using nitrogen as the diluent gas when testing boilers, or using air as the diluent gas when testing process sources such as paint spray booths). This is not, however, specifically required by Method 25A. Method 25A recommends that a 40% hydrogen/60%

inert gas mixture be used to fuel the FID flame (rather than 100% hydrogen) to alleviate an "oxygen synergism effect"; however, this is often not required in practice, due to concerns of increased gas usage and problems keeping the FID's flame lit.

Another issue that is often overlooked is that Method 25A cannot capture all of the substances in the VOC classification. The method's applicability is identified as being "the determination of total gaseous organic concentration of vapors consisting primarily of alkanes, alkenes, and/or arenes (aromatic hydrocarbons)." It is known that formaldehyde—which, incidentally, has a very high ozone reactivity—can be almost invisible to FIDs, and that the response of the FID to carbon compounds containing electronegative atoms (e.g., nitrogen, oxygen, phosphorous, sulfur, and halogens) is diminished.⁶ For these reasons, the term total hydrocarbons (THCs) is sometimes used to refer to the results of Method 25A, rather than total organic compounds (TOCs).

One EPA guidance document states that "Method 25A can only be used in situations where an appropriate response factor for the stack gas can be determined. In gas streams that cannot be characterized or which have changing composition, the response factor of the stream cannot be determined; Method 25A is not applicable for such a gas stream."⁷ In most cases, however, this guidance is not followed, partly because of issues related to the available alternatives. A casual observer might assume that a "volatile organic" sampling train (VOST) specified by EPA Method 0030⁸ (which incorporates condensers, Tenax/charcoal sorbent traps, and impingers) should be used to capture "volatile organic" compounds. However, this method—which is onerous to implement, requiring a complex setup and offsite chemical analysis—was designed for chemicals with boiling points between 30 and 100 °C only. There are many compounds with boiling points outside this range that are still considered VOCs.

Another alternative for measuring VOCs is EPA's guidance for quantifying "total organics,"⁹ which specifies that samples of stack gas be collected in bags, separated by gas chromatography (GC) and quantified by FID to quantify chemicals with boiling points less than 100 °C; that a semivolatile sampling train be used to determine chemicals with boiling points between 100 and 300 °C (e.g., as specified by EPA Method 0010,⁸ another relatively complex method, which requires isokinetic sampling, a specially designed packed bed of porous polymeric absorbent resin, and methylene chloride and methanol for sample recovery); and that chemicals with higher boiling points are determined gravimetrically (i.e., collection in solid form, followed by weighing). However, this method still misses the light aldehydes, that is, formaldehyde and acetaldehyde (boiling points < 30 °C), which will not be accurately quantified by the "purge and trap" GC/FID methodology identified for the other high-volatility organics

(and which, as mentioned previously, have high ozone reactivities). To quantify these compounds, yet another sampling train needs to be run (e.g., as per EPA Method 0011,⁸ which requires isokinetic sampling, a specially prepared reagent for derivatizing the aldehydes in impingers, and the use of methylene chloride for sample recovery). Another alternative for VOC measurement is EPA Method 18,⁴ which incorporates several different methodologies (including sorbent tubes); however, this methodology also has limitations with respect to sample recovery.

These are only some of the issues related to VOC emissions measurement, but they help demonstrate that VOC emissions are imperfectly measured (and will probably never be perfectly measured), and that the term “VOC” is, in turn, imperfectly defined (as a class, with respect to the goal of tropospheric ozone reduction). To go even deeper into the realm of imperfection, however, it should be noted that many VOC emissions are not measured directly at all—they are instead calculated.

EMISSIONS CALCULATIONS AND THE QUESTION OF VOLATILITY

As stated previously, no chemicals are exempted from the EPA definition of “volatile organic compound” based on their volatility, but there remains the question of what proportion of the low-volatility substances are emitted to air. Attention is usually focused on liquids; organic solids (including items such as plastic bottles and countertops) are not technically exempt from the definition of VOC, but most regulatory agencies are comfortable with their being excluded from inventories of VOC usage (except for solids that sublime, such as naphthalene). Aside from using EPA emission factors when available,¹⁰ the three basic types of methodologies for estimating air emissions include (1) the assumption that everything volatilizes; (2) mass balance; and (3) calculations based on scientific principles (e.g., mass transfer, equilibrium, diffusion).

The assumption that “everything” volatilizes is only a reasonable assumption for highly volatile materials, and is sometimes not even a very good assumption for these, for example, in cases of dilute solutions of highly soluble chemicals. This is the simplest methodology for estimating emissions, and provides an upper bound, but it often yields very unrealistic results. For instance, in the case of wastewater, regulators have sometimes assumed that all VOCs in wastewater streams will be emitted somewhere in the sewer system between the facility and the public treatment works. Although it has been shown that sewer systems can emit significant amounts of some VOCs,¹¹ the assumption of 100% emission is usually far too inaccurate, and for certain HAPs, EPA has published estimates of the fraction of material that is emitted¹² (though these are also based on “typical” models of treatment systems, and are far from exact).

Mass balance techniques are popular—again, due to their simplicity—but are inappropriate for estimating air emissions when the amount of material emitted to air is a small fraction of the amount used. In these cases, errors calculating the major pathways (e.g., material usage and amounts sent off-site) are usually significant enough that attempts to calculate air emissions by mass balance result in highly variable results. Among the most straightforward calculations are supposed to be those for paints and coatings; that is, manufacturers identify the VOC content of the paint or coating (often by mass-balance methods such as EPA Method 24 or 24A), and VOC emissions are determined by multiplying this factor by the number of gallons used. Even then, mistakes are often made. Sometimes paint thinner is inadvertently not considered; other times, VOC is assumed to be the same as the “% volatile” specification, which, in fact, includes water as well as VOCs. A somewhat subtler mistake is made when VOC emissions are overestimated by multiplying a “lb VOC/gal less exempt solvents” specification by the gallons of paint used (when, in fact, “less exempt solvents” means that the specification was determined by removing exempt solvents such as water, and determining the lb VOC per gallon of the remaining material; the lb VOC per gallon of coating is a significantly lower number).



Scientific principles are useful for calculating emissions in some cases, but are frequently subject to errors, require technical data that are not available, or are applied incorrectly. For example, the "flat-plate" equation of mass transfer¹³ has been applied on more than one occasion to situations that lie outside its applicability, even in court cases. For example, in one court case, the flat-plate equation was used to argue that evaporative emissions in a 5-mph wind were 2 orders of magnitude higher than those under still conditions. Two of the more popular models that have been used for compliance demonstrations, EPA's WATER model and Enviromega's TOXCHEM model, are complex, yet have been shown to yield results that differ by as much as an order of magnitude.¹⁴ Results from both models depend upon Henry's law coefficients for the chemicals of interest; however, although such coefficients have been measured for several chemicals at temperatures of 20 to 25 °C, the coefficients vary exponentially with temperature, and relatively little data are available at other temperatures. The models can theoretically be "tuned" through the use of flux chamber measurements of evaporation (i.e., floating an enclosure over a surface and measuring emissions inside the enclosure), but it is difficult to correct for radiant heating underneath the flux chamber, there is no validated reference methodology for this technique, and published methodologies for this technique differ.^{15,16}

In short, many estimation techniques are either limited in applicability or have potentially high uncertainties. Yet, when there is not an opportunity to make a measurement (e.g., when filing a preconstruction permit application), estimation methods are the only means available for quantifying emissions.

CONCLUSIONS

In this article, it has been shown that policies to reduce tropospheric ozone through VOC emissions reduction are imprecise and inexact means of accomplishing that goal; that there are several means by which Method 25A results can be biased high or low; that Method 25A does not truly measure total VOC (and that no method truly does); and that techniques for estimating VOC volatilization are often misused, or are subject to large errors. The sheer number of chemicals that fall into the VOC category will always require that some assumptions be made with respect to identification and quantification; however, the law can be relatively inflexible with respect to these assumptions. It is clear that the biases that are associated with Method 25A, and the inherent limitations of what the method is measuring (and what other methods for quantifying VOCs are measuring), can have significant implications with regard to regulatory compliance.

One of the best means of eliminating risks associated with variable methodologies is to include more specific permit language. For instance, if measurements are being made using Method 25A, the permit should include a limit for THC's, not

VOC's, and specifically state that Method 25A will be used as a compliance method, rather than making a generic reference to EPA stack testing methods located in Appendix A of 40 CFR 60. Concentration limits for THC's should be expressed as "ppmvwC₁" or "ppmvwC₃" instead of simply "ppm," and mass emissions limits should specifically be identified as being on a "methane basis" or "propane basis." If emissions were based on test data that used a certain type of calibration gas diluent, or were based on using 40% hydrogen/60% inert gas in the FID, it may be worthwhile even mentioning this level of detail. If emissions are being estimated from wastewater using a model such as WATER or TOXCHEM, permits should identify which model is being used to make these estimates.

Those sources with existing permits that are not specific must recognize the extent to which the technical details matter when it comes to overall compliance. For example, sources that have historically demonstrated compliance with VOC limits using Method 25A may foresee having to test for specific organics through different test methods in the future (e.g., as a result of EPA initiatives with respect to HAP's), and should recognize the extent to which these methods might potentially result in larger VOC concentrations or mass emissions.

Progress will continue to be made toward improving measurement and estimation techniques, and possibly even in providing a better metric for relative impacts on tropospheric ozone than total mass. For example, researchers are already beginning to look at means of directly measuring the ozone reactivity of VOC emissions, by mixing samples with NO_x and measuring the degree of ozone production.¹⁷ With respect to calculational techniques, more data can always be obtained and more complex computer-based tools will be developed. But, hopefully, more science will also emerge to help organize knowledge and allow for more educated assumptions or approximations with respect to classes of chemicals, rather than simply looking up numbers in larger and larger tables of information.

However, there will likely never be a solution that eliminates all of the problems associated with VOC emissions quantification and estimation. Assumptions will always need to be made when choosing a methodology for measuring or estimating VOC's, and the desire to obtain perfect information (i.e., the total mass of all chemicals that meet the definition of VOC) will therefore need to be tempered by the reality of methodology limitations, costs, and the realization that total mass emissions of VOC's is a crude metric with respect to ozone reactivity. For example, although Method 25A does not detect formaldehyde (and formaldehyde is known to be a common byproduct of combustion) the amount of formaldehyde may be relatively low compared to emissions of other VOC's that are quantifiable by Method 25A, in which case, Method 25A might still be an appropriate methodology for measuring those

emissions. The key to making these assumptions is for both regulators and the regulated community to exercise professional judgement regarding what chemicals are reasonable to expect in an emissions stream, and what calculational results make sense. ☺

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