

Measurement

by Kevin Crosby

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Recent federal regulations have set air quality standards for fine particulate matter (PM_{2.5}) and require by January 2011 an improved method for measuring “smokestack” emissions of condensable PM from stationary sources. The U.S. Environmental Protection Agency (EPA) proposed a new method in 2009 and is currently responding to public comments.



of $PM_{2.5}$ Emissions and the Proposed Method for Condensables

The new method may provide results different from older methods employed in some parts of the United States and for past development of the emission factors for use in permitting. Tests are being conducted to determine how effective the new method might be in providing improved measurements. The limited results currently available may provide some indication whether the method works as expected.

NSR Implementation Rule

The $PM_{2.5}$ new source review (NSR) Implementation Rule¹ passed in 2008 applies to new or modified stationary sources in $PM_{2.5}$ nonattainment areas with more than 100 tons per year of direct $PM_{2.5}$ emissions. It also applies to certain sources in areas subject to regulations for the prevention of significant deterioration (PSD). The overall objective is for all areas to attain the National Ambient Air Quality Standards (NAAQS) for $PM_{2.5}$ and for states to develop plans to bring any nonattainment areas into attainment status.

The new rule provides a regulatory link between PM emissions, atmospheric processes, and $PM_{2.5}$ that is measured in the ambient air. While the measurement technique for ambient air $PM_{2.5}$ is well established and standardized, the measurement of $PM_{2.5}$ emissions is not, and this creates confusion and uncertainty in NSR and PSD calculations.

$PM_{2.5}$ in the Ambient Air

Ambient $PM_{2.5}$ includes primary and secondary particles. Primary particles are directly emitted (i.e., particles in the stack and gases that condense into particles immediately after release from the stack into the atmosphere); and secondary particles are formed from precursor gases, such as sulfur dioxide (SO_2) and nitrogen oxides (NO_x). These gases

are not particles immediately after emission from the stack, but rather are subject to a complex set of particle-forming chemical reactions over time in the atmosphere.²

Ambient air quality monitoring stations typically measure primary and secondary particles together. In some areas of the United States, ambient $PM_{2.5}$ is often comprised of mostly secondary particles such as sulfate and nitrate salts.

The new rule requires air quality professionals and agency personnel to calculate the impact of new and existing emission sources on the ambient air quality, as part of their NSR and PSD evaluations. The computer models used for air quality impact analysis handle primary emissions well, and those used for regional air quality prediction also account for the formation of secondary $PM_{2.5}$. However, the $PM_{2.5}$ emission data, or emission factors used for input to those models, are typically of poor quality because they are often based on limited

Figure 1. A typical PM emission testing apparatus.

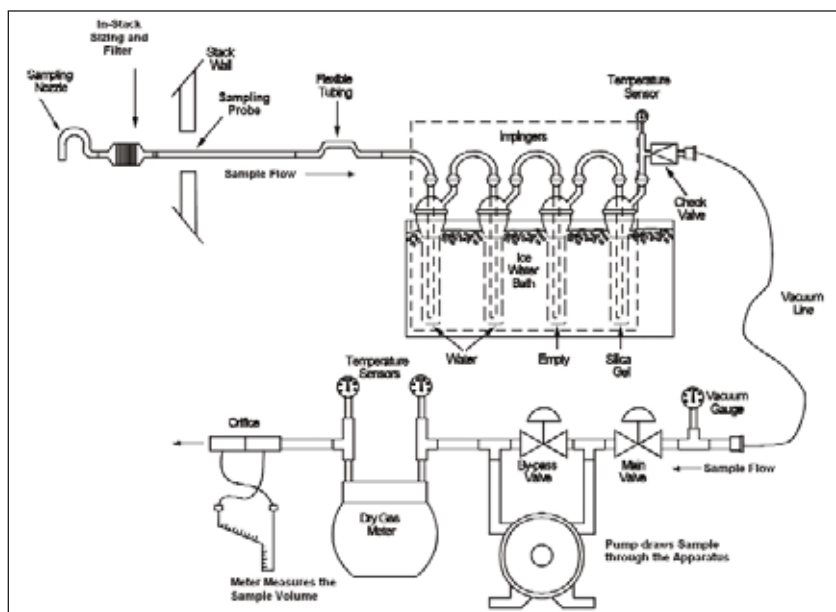




Figure 2. A typical set of impingers, which stand about 18 in. The first three are shown containing water and the fourth with granular silica gel to completely dry the sample gas. The impingers are immersed in an ice-water bath during sampling.



Figure 3. Sample being bubbled through impingers. Gas-to-liquid contact is maximized by this technique.

data from outdated measurement methods.² Currently published emission factors for condensables can be grossly inaccurate by an order of magnitude or more due largely to problems with those existing test methods.³ The old axiom “garbage in, garbage out” applies in many cases.

Problems with Existing Methods

Existing test methods provide for the sampling of filterable and condensable PM. Filterable PM includes particles that exist at stack temperature and pressure, or at least at the temperature of the sampling filter. The test methods for the filterable fraction of PM or PM_{2.5} are relatively straightforward and are not an issue. The methods for the condensable fraction, however, have inconsistencies that must be addressed.

Testing of condensable emissions is nothing new. Condensable PM emissions have been regulated for decades by state and local agencies that developed test methods long ago. Common problems with existing stack testing procedures for condensables include the poor reproducibility or precision of the method results and the artifact biases that vary with the specific method used, the duration of each test run, and the stack parameters (e.g., the matrix of gases in the stack emissions and stack temperature).³

A diagram of a typical test method is shown in Figure 1. The pump draws the sample through the nozzle, filter, and probe, out of the stack, and through the impingers where the condensables are collected. The filtered, dried stack gas then flows through a calibrated dry gas meter to measure the precise volume of the sample. The mass of the condensable PM collected is determined by drying the impinger contents and weighing the residue, so that results can be provided in concentration units of mass per volume of stack gas (i.e., grains per dry standard cubic foot, or milligrams per dry standard cubic meter).

The reproducibility problem is caused, in part, by “small” differences in technique among the various methods used (e.g., Washington and Oregon,^{4,5}

California,⁶ and local agencies within California⁷). When EPA promulgated the existing Method 202⁸ for condensable PM in the 1990s, the agency included several choices in technique so that testers could tailor the method to the type of emission source. Unfortunately, choices made by different testers at different times have added variations in technique that contribute to the poor reproducibility of the results from EPA Method 202.

All of the existing test methods draw the sample through a set of impingers, and this leads to the formation of an artifact or “pseudo” particulate. A typical set of impingers is shown in Figure 2, and Figure 3 illustrates the sample being drawn through the impingers. This method maximizes the gas-liquid contact, which does a very good job of collecting condensable PM. Unfortunately, non-condensable gases such as ammonia and SO₂ dissolve in the water as well.

When the water is evaporated away in the laboratory to measure the weight of the residue, those dissolved gases form salts such as ammonium sulfate. SO₂ gas can be oxidized in the impinger water to form sulfuric acid. These noncondensable gases are therefore counted by the method as if they were primary, condensable emissions. While some of the acid or the salts may be actual primary PM_{2.5} emissions, much can be an artifact; a feature that is not naturally present but is a product of an extrinsic agent, method, or the like.

The most studied, common artifact bias comes from SO₂ dissolved in the impinger water.³ The formation of artifact residue from SO₂ has been found to be a function of the test run duration and the stack gas composition (e.g., the SO₂ concentration).³ EPA has developed newer methods to eliminate or reduce the artifact bias and to improve the consistency of the results.

New Improved Methods

EPA has been working on improved methods for condensable emissions for many years, and parallel efforts have been made by other agencies, consultants, and industry groups. First, a dilution method

was developed. This method is designed to emulate the natural formation of condensable particles.⁹ It uses no impingers, but dilutes the stack gas sample with cool, dry air so that condensable particles can form before the entire diluted sample stream is drawn through a filter for collection.

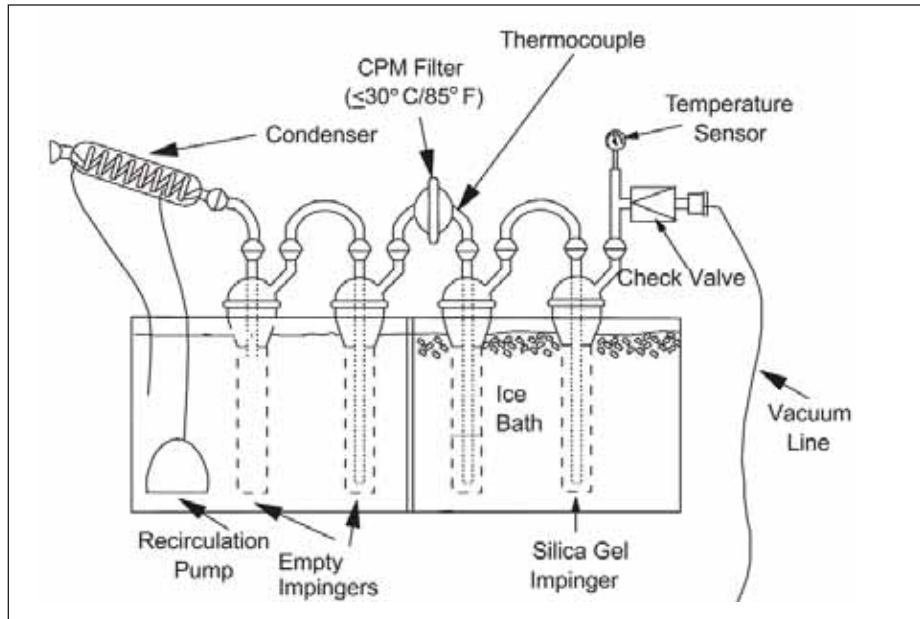
Dilution techniques have been used to measure condensable emissions from mobile sources since the 1970s. However, the sampling systems used were much too large to be practical for stack emission sampling, where the stack platform space and weight capacity is limited. In 2004, EPA developed a conditional test method CTM-039 to provide dilution apparatus and techniques that would be practical for stack sampling.¹⁰ The agency considers the method to be the “gold standard” for the measurement of primary PM_{2.5} emissions. However, the method requires the use of new, expensive equipment and has seen limited use in the field so far. The early results show that the method does have great potential for improved measurements,¹¹ so development work will continue.

Meanwhile, the PM_{2.5} NSR Implementation Rule requires accounting of the condensable emissions by 2011. For that reason, EPA has proposed a “dry impinger” method, known as “other test method” OTM-028, that can be implemented more quickly, as it uses standard stack sampling gear with a few important additions.¹² Many testing programs are currently being conducted to determine the method’s precision and accuracy and to study its potential for improved measurements.¹³

The Proposed Method

EPA has developed Method OTM-028 (also known as the “dry 202” or the “new 202” method) to replace the existing Method 202. This method collects the condensables not by bubbling the sample gas through chilled impingers with water, but by condensing into empty impingers, as shown in Figure 4.

In Method OTM-028, moisture and condensable PM collect in the impingers and on a backup filter, but there is no bubbling of gases through water.⁷



This minimizes gas-liquid contact, so that much lower amounts of precursor gases are collected as artifact. Laboratory studies indicate the collection of 40–80% less sulfate artifact, or even as much as 85–95% less artifact for some high-SO₂ samples.¹⁴

Figure 4. Sampling apparatus impinger train for EPA Method OTM-028.

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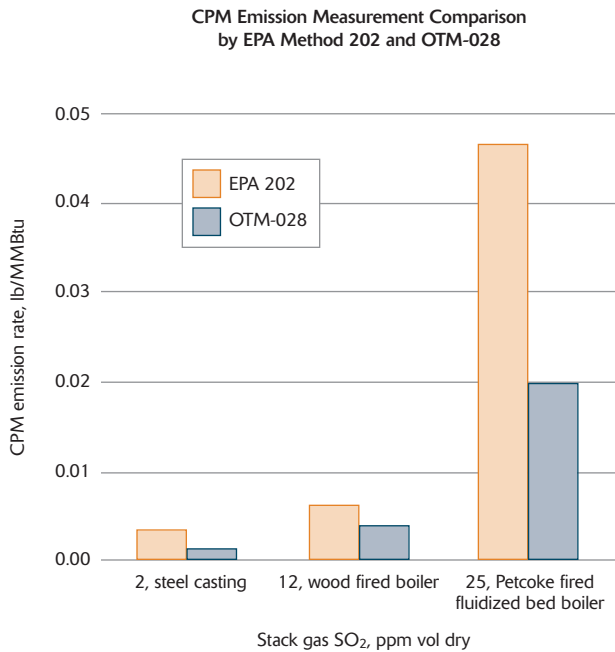


Figure 5. Results from concurrent tests on a variety of sources.

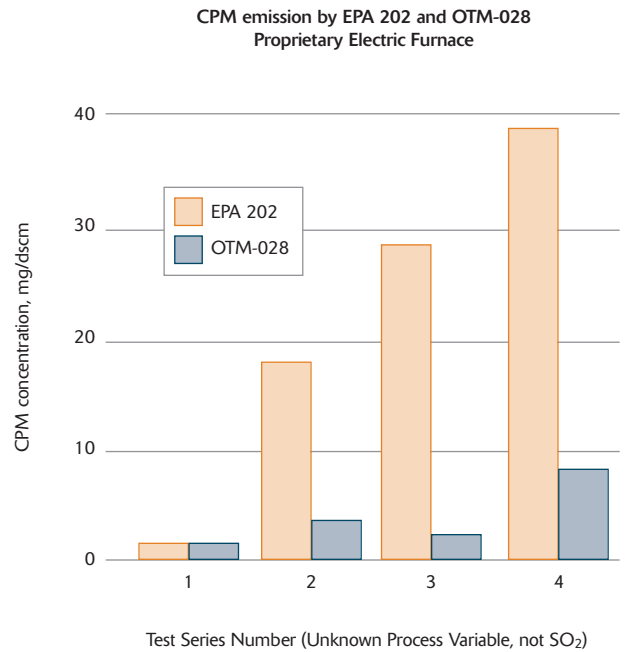


Figure 6. Comparison of Method 202 and OTM-028 results from concurrent test runs.

Table 1 summarizes the basic features of the existing and developmental methods.

OTM-028 Test Results

Method OTM-028 has been used recently on a variety of emission sources to determine its results and whether it performs as expected. The hypothesis is that OTM-028 would provide lower results than the existing Method 202, since it would collect less artifact mass from noncondensable gases dissolving in the impinger contents.

Actual test results from the existing Method 202 and from OTM-028 are presented in Figure 5. There are not enough available data to provide for a systematic, scientific evaluation. The figure includes data from paired, direct-comparison test runs from three different emission sources. Each data point represents the average of three test runs.

The results shown in Figure 5 have been arranged according to the SO₂ concentration in the stack gas. The first data set was from a steel casting operation with no particulate emission control device installed, less than 2 parts per million (ppm) SO₂, and batch operations with a “burst” of emissions. The second data set was from a wood-fired boiler with 12-ppm SO₂, which included a dry

electrostatic precipitator for particulate control and ammonia injection for the selective noncatalytic reduction (SNCR) of NO_x emissions. The third source was a fluidized-bed boiler burning petroleum coke, which included SO₂ concentrations of 25 ppm, SNCR for NO_x control, and a baghouse for control of filterable particulate emissions.

Additional testing programs have been conducted on a proprietary electrically heated furnace that has extremely low SO₂ emissions. The results from those sets of tests, which included concurrent sampling by Method 202 and OTM-028, are presented in Figure 6. A different “chemistry” affected these results, so the x-axis in this case represents an unknown process condition variable, and the y-axis is the concentration of condensable PM in units of milligrams per dry standard cubic meter.

Each data point shown in Figure 6 represents the average of three test runs, and each run included concurrent sampling using both methods. A proprietary chemical variable other than SO₂ was varied from low to high for test series 1 to 4. These results indicate the potential for OTM-028 to provide lower results, perhaps by mitigating some artifact bias, even with the presence of noncondensable gases other than SO₂.

Table 1. Features of various EPA methods for measurement of condensable PM emissions.

Method	Sample Collection	Condensation Temperature
Existing Wet impinger EPA 202	Bubble sample through water in impingers immersed in ice bath, backup filter and post-test nitrogen purge to reduce artifact are optional ⁸	Not directly measured, but outlet temperature < 68 °F
Dry impinger OTM-28 (proposed as a replacement for EPA 202)	Draw sample through condenser coil and empty impingers to avoid bubbling of sample through condensate. Backup filter to collect particles and post-test nitrogen purge to reduce artifact are required ¹⁰	Condenser and impingers in water bath, so filter outlet temperature < 85 °F
Dilution CTM-039	No impingers; sample diluted and cooled with dry air, backup filter to collect particles, including condensables ¹²	Dilution air cooled to keep filter outlet < 85 °F

Conclusion

The results presented indicate that Method OTM-028 may perform as expected. That is, the artifact from SO₂ or other noncondensable gases may be reduced from that measured using the existing Method 202. The method appears to have the potential to provide results that are more representative of actual condensable PM emissions.

The results presented in this article are from a limited number of testing programs. Professional emission testing companies are presently conducting additional testing programs for their clients, EPA, and other agencies. Much more data will become available and much will be learned over the next several months. **em**

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