Particulate Emissions-
Combustion Source Emissions Dependent on Test Method

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Particulate emissions from combustion sources can be quantified by type and size: filterable, condensible, PM, and PM_{10}. Permit limits for both pulverized coal boilers (PC) and circulating fluidized bed boilers (CFB) do not always provide adequate clarification regarding what type of particulate is addressed by the limits. Critical to this issue is the prescribed test method, and the potential for error introduced by the test method that can misreport compounds such as ammonium bisulfate and sulfur dioxide as particulate emissions (Methods 5, 201, 202, etc.). This paper will summarize recently established PM_{10} permit limits, describe the inherent problems of PM_{10} test methods, and provide considerations for emission inventories.

Summary of Recent PM_{10} BACT Determinations

Through numerous Freedom of Information Act (FOIA) requests, the PM_{10} permit limits were found for several recently permitted coal-fired boilers across the country. As shown in Figure 1 and Table 1, the limits for both filterable and condensible are often the same or lower than the limits for filterable only.

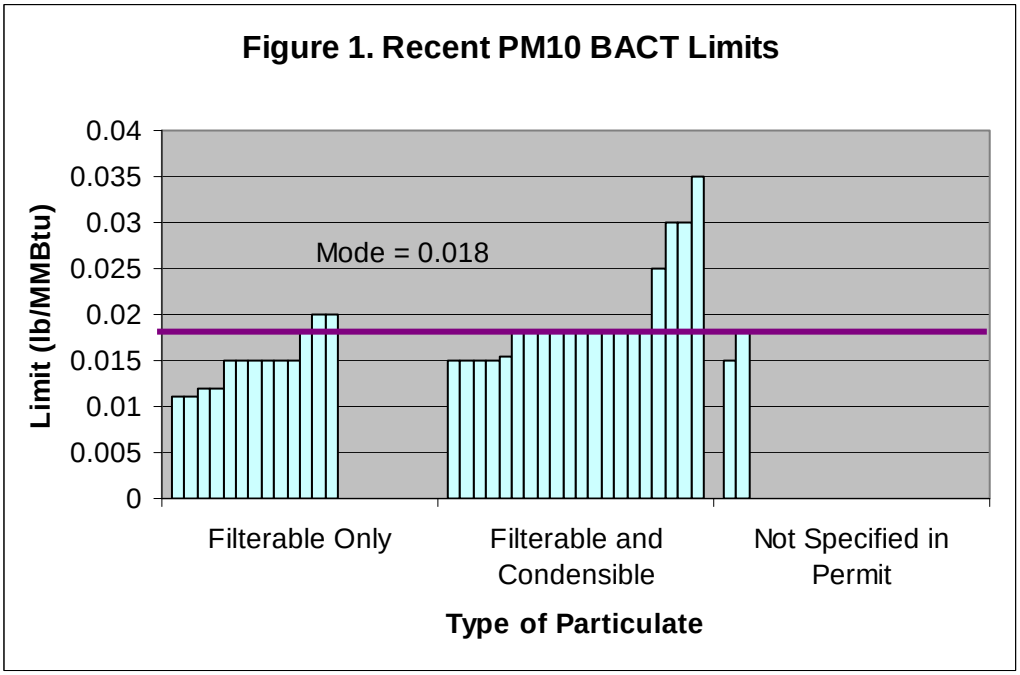

Table 1. Particulate Limits for Recently Permitted Coal-Fired Boilers.

Facility	Particulate Type	Year Issued	Boiler Type	Operational?	Permit Limit (lb/mmBTU)
AES Puerto Rico #1	f/c	1998	CFB	yes (& tested)	0.03
AES Puerto Rico #2	f/c	1998	CFB	yes (& tested)	0.03
Corn Belt Energy	f only	2002	PC	no	0.02
Council Bluffs (Mid America)	f/c	2003	PC	no	0.025
Elm Road Generating Station #1 (WE-Energies)	f/c	2004	PC	no	0.018
Elm Road Generating Station #2 (WE-Energies)	f/c	2004	PC	no	0.018
EnviroPower IL - Benton #1	f/c	2001	CFB	no	0.015
EnviroPower IL - Benton #2	f/c	2001	CFB	no	0.015
Hawthorn 5 (KCP&L)	f/c	1999	PC	yes (& tested)	0.018
Holcomb Unit #2 (Sand Sage Power, LLC)	f/c	2002	PC	no	0.018
Indeck-Elwood LLC #1	f/c	2003	CFB	no	0.015
Indeck-Elwood LLC #2	f/c	2003	CFB	no	0.015
Intermountain Power Unit #3	f only	2004	PC	no	0.012
JEA Northside #1	f only	1999	CFB	yes (& tested)	0.011
JEA Northside #2	f only	1999	CFB	yes (& tested)	0.011
Kentucky Mountain Power, LLC (EnviroPower)	Not Specified	2001	CFB	no	0.015
Longview Power (GenPower)	f/c	2004	PC	no	0.018
Plum Point Power Station	f/c	2003	PC	no	0.018
Prairie State	f/c	2005	PC	No	0.035
Red Hills #1 (Choctaw Generation)	f only	1998	CFB	yes (initial testing waived)	0.015
Red Hills #2 (Choctaw Generation)	f only	1998	CFB	yes (initial testing waived)	0.015
Rocky Mountain Power (Hardin Generator Project)	f only	2002	PC	no	0.015
Roundup #1 (Bull Mountain)	f only	2003	PC	no	0.015
Roundup #2 (Bull Mountain)	f only	2003	PC	no	0.015
Santee Cooper/Cross Unit 3	f/c	2004	PC	no	0.018
Santee Cooper/Cross Unit 4	f/c	2004	PC	no	0.018
Sevier Power (Nevco Energy)	f/c	2004	CFB	no	0.0154
Spurlock (E. KY Power Coop)	f only	2002	CFB	no	0.015
Thoroughbred #1	f/c	2002	PC	no, Permit under litigation	0.018
Thoroughbred #2	f/c	2002	PC	no, Permit under litigation	0.018
Two Elk	f only	2003	PC	no	0.018
Whelan Energy Center Unit 2-Hastings	Not Specified	2004	PC	no	0.018
Wisconsin Public Service - Weston 4	f/c	2004	PC	no	0.018
WYGEN I (Black Hills)	f only	1996	PC	yes (& tested)	0.02
WYGEN II (Black Hills)	f only	2002	PC	no	0.012

Inherent Problems of Particulate Test Methods

Initial testing for PM_{10} is required of coal-fired boilers to confirm that they meet their permit limits. The permit usually specifies which test method is required. EPA standard reference methods are usually called out and are briefly discussed in Table 2 along with some alternate methods.

Table 2. EPA Reference Methods for Testing

Method	Particulate Size	Particulate Fraction	Method Notes
Method 5[1]	Any size	Filterable	Measures all particulate matter that is collected on a glass fiber filter at a temperature of approximately 120 ºC; combustion products that are in the vapor phase at this temperature, although they may contribute to ambient particulate matter concentrations, are not measured.
Method 201A[2]	PM_{10} or smaller	Filterable	Measures all particulate matter having an aerodynamic diameter equal to or less than nominally 10 micrometers (PM_{10}) that is collected on a glass fiber filter at the stack temperature. Method 201A excludes particles having an aerodynamic diameter nominally 10 micrometers or greater and therefore generally yields a slightly smaller result than Method 5.
Method 202[3]	PM_{10} or smaller	Condensible	Measures particulate matter that condenses at a temperature of approximately 20 ºC after passing through a filter such as that used in Method 5 or 201A. The total PM_{10}, which is the combined result of performing Method 201A and Method 202 simultaneously, may be substantially different than the PM measured by Method 5, or thePM10 measured by method 201A.

Compliance issues can arise when testing to verify compliance with a limit that includes both filterable and condensible emissions. For coal-fired boilers (or any sources with sulfur in the exhaust gas), Method 202 can provide an erroneously high result due to the creation of "artifacts". These artifacts consist of ammonia and sulfate compounds created in the sampling system:

- Oxidation of SO_2 to SO_3 in the "back half" impinger

[1] http://www.epa.gov/ttn/emc/methods/method5.html
[2] http://www.epa.gov/ttn/emc/methods/method201a.html
[3] http://www.epa.gov/ttn/emc/methods/method202.html

- NH_3 slip from SNCR or SCR reacts in the impinger to form ammonium bisulfate NH_4HSO_4
- Absorption of soluble NO_x components (e.g., N_2O_5)

Artifacts and are a known quantitative error in Method 202. This artificial particulate is formed by the measurement technique itself and would not form particulate matter in the atmosphere when the flue gas is cooled to atmospheric temperature. Several studies have been performed and reported similar results. (Mega symposium, 2004)

This is a serious developing issue within the utility industry. As the permit limits for particulate are tightened, and as technology advances related to the control of filterable particulate, the relative contribution of condensable particulate increases. This may be partly due to the fact that less filterable particulate is available to serve as a condensation nucleus, resulting in less particle growth and a resultant increase to the amount of fine particulate . This issue has come to the forefront recently because current PSD BACT limits are becoming increasingly restrictive. For utility boilers, a large portion of the filterable particulate is removed from the flue gas stream, resulting in a significant portion of the PM_{10} emissions consisting of condensable particulate matter. It has been shown that determining the condensable PM_{10} emissions using Method 202 may over-state that actual emissions, or quantity of particulate that would be created from ambient mixing and cooling of the gas stream.

Possible Corrections

Nitrogen Purge in Method 202

Method 202 allows for a nitrogen gas purge to correct for these artifacts by removing the dissolved SO_2:

> The one hour purge with dry nitrogen should be performed immediately following the final leak check of the system. Even low concentrations of SO_2 in the exhaust gas will dissolve into the impinger solution and if not removed by nitrogen purging will result in a positive bias.
>
> Neutralizing the inorganic portion to a pH of 7.0 determines the un-neutralized sulfuric acid content of the sample without over correcting the amount of neutralized sulfate in the inorganic portion. These neutralized sulfates (such as $(NH_4)_2SO_4$ or NH_4SO_4) would be created in the exhaust gas upon dilution cooling in the ambient air and result in fine particulate formation. Ion chromatography, for SO_4 measures both the amount of neutralized and un-neutralized SO_4 contained in the impinger solution prior to the addition of NH_4OH and therefore introduces a negative bias.
>
> The presence of free ammonia and HCl in the exhaust gas will form Ammonium Chloride that produces fine particulate upon dilution and cooling in the ambient air.[4]

[4] http://www.epa.gov/ttn/emc/methods/method202.html

However, the nitrogen purge may not eliminate the artifacts completely. Some SO_3 and SO_4 remain as well as ammonium chlorides, and even a small quantity of artifacts can affect the test results.

New Methods (Controlled Condensate)

The problems measuring condensable particulate emissions from combustion sources have been identified for combustion turbines as well, and EPRI and others have developed and proposed alternative test methods that attempt to simulate atmospheric condensation. One alternative that has been suggested because it was once an approved test method is Method 8A. This test method was originally developed for the pulp and paper industry, and is no longer an approved EPA standard test method. The intent of this test method is to cool the sample to 150ºF by passing it though a glass coil. The intended result is that the H_2SO_4 and SO_3 acids will condense and be measured as condensible particulate. Most of the artifacts, including the artificial SO_2 byproducts will not be created. Although EPA has not approved an alternate method to simulate atmospheric condensation, the results from a test of this type can be helpful in quantifying the effect of artifacts or pseudo-particulate created in Method 202.

Precedents

AES Puerto Rico recently experienced problems complying with their original particulate limits. The draft permit established a permit limit (for a CFB unit) of 0.015 lb/mmBTU, and specified Methods 201 and 202 for the compliance test. The applicant commented that tying this low emission rate to a test method that includes condensable emissions is inappropriate. EPA responded by setting a second limit of 0.05 lb/mmBTU if the limit of 0.015 lb/mmBTU could not be achieved. Initial testing of the unit showed levels approximately double the limit of 0.015 lb/mmBTU. Subsequently, their permit limit was modified to 0.03 lb/mmBTU. The complete decision can be found at http://www.epa.gov/eab/disk11/aespur.pdf.

The recently issued permit (1/14/05) for Prairie State in Illinois (pulverized coal boilers) established a limit of 0.035 lb/mmBTU for PM_{10} filterable and condensible with a stipulation that the limit may be lowered to 0.018 lb/mmBTU after initial testing.

Typically, one would expect that particulate matter (PM) would include particulate smaller than 10 microns (PM_{10}) as a subset of the total. But at the Tucson Electric Springerville Unit the PM limit is almost one fourth (1/4) of the limit for PM10. The difference is that the condensable portion is not included in PM. The agency established a limit of 0.055 lb/mmBTU for PM10, and specified method 202 which includes condensable. For PM, the permit limit is only 0.015 lb/mm, and specifies Method 5, or filterable only.

Emission Inventory Considerations

Using an emission limit for particulate must be qualified with type of particulate. For combustion sources, this is best defined by identifying the test method used to determine the emission rate. Method 5 particulate is PM filterable only. Method 201 particulate is filterable particulate less than 10 microns, etc. The following are recommendations for pro-active steps that can be taken

to try to minimize the problems related to the determination of particulate from combustion sources:

- Particulate emission estimates for airborne particulate with a potential to affect ambient concentrations, should include filterable and condensable particulate less than 10 microns only.

- All emission estimates for particulate resulting from combustion sources should include both filterable and condensible emissions, and specify the compliance test method.

- Particulate emissions are only equivalent if the same test method is used.

- Factors to adjust a filterable only estimate to a filterable and condensable estimate need to consider the relevant test method.

- Method 202 results may have a potential to overestimate emissions from sources with SO2 emissions because of the creation of pseudo-particulate within the sampling train.

- Consideration should to be given to the development of test methods that provide consistent results.