

Measuring Particulate Emissions from Combustion Sources

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Executive Summary

The principal measurement methods for sampling particulate matter (PM) from stationary combustion sources generally consist of a sampling train that includes a heated filter maintained at a variety of elevated temperatures, followed by a series of aqueous impinger solutions used to collect material that is in the vapor phase within the stack, but could condense and form PM immediately after entering the atmosphere. These two fractions are commonly referred to as “filterable” (e.g. fly ash or catalyst fines) and “condensable” (e.g. sulfuric acid, semi-volatile organics, or ammonium sulfates), PM. Since the early 1970s, the EPA has proposed a number of methods to determine PM emitted from combustion sources and these are discussed in this report. Most of the attention was initially centered on measuring filterable PM as this material was considered to comprise the major fraction of PM emissions subject to removal by control technology.

The EPA methods and their variants differ primarily in the temperature of the collecting filter, leading to accumulation of different amounts of material on the filter (depending upon the species present in the stack gas). A summary of the operating temperatures and impact on condensables accumulation (Table 1) indicates the biases that can occur between the principal PM measurement methods employed today.

Table 1. PM Emissions Measurement Methods & Filter Temperatures: Will the Component Be Collected on the Filter?

Method	Filter Temperature, °F	Catalyst Fines/Ash	H ₂ SO ₄	NH ₄ Sulfates
EPA 5	248 ± 25	Yes	Some	Yes
EPA 5B, 5F	320 ± 10	Yes	No	Yes
EPA 17	Stack temp.	Yes	No*	No*
EPA OTM 27	Stack temp.	Yes	No*	No*
SCAQMD 5.1/5.2	190	Yes	Some	Yes
Dilution Sampler	Ambient	Yes	Yes	Yes

*Stack temperatures are generally > 500 °F for units without wet scrubbers. Units equipped with wet scrubbers have stack temperatures < 200 °F and are likely to collect some H₂SO₄ and all NH₄ sulfates.

SCAQMD refers to the South Coast Air Quality Management District.

After the introduction of the National Ambient Air Quality Standards (NAAQS) for fine particulate matter, regulatory interest shifted to methods that also measured the condensable fraction (consisting of PM having aerodynamic diameters equal to and less than 2.5 microns). Accurate measurements of these emissions became important as regulators sought to ensure attainment of PM ambient air quality standards by controlling source emissions. This paper discusses the technical basis of the resulting biases for both filterable and condensable PM for the various test methods

The American Petroleum Institute recognized the importance of this issue in 1997, initiating a review of the appropriate test method before undertaking a comparative testing program for PM 2.5 emissions from refinery sources. Measurements were made using a conventional cyclone/filter/impinger method (EPA Methods 201A and 202) along with a newly developed dilution system sampler. This new sampler seeks to represent atmospheric conditions by diluting and mixing stack gas with clean ambient air, and collecting the resulting PM on filters similar to those used in ambient air sampling. Initial results from this program showed the cyclone/filter/impinger method had a significant positive bias that overstated the emissions of condensable PM because some of the stack gas SO₂ was converted to sulfate PM in the impinger solutions. This program was expanded in 2000 with the participation of several other organizations: US Department of Energy, Gas Research Institute, California Energy Commission and the New York State Energy Research and Development Authority. By the conclusion of the test program in 2004, the emissions of over a dozen combustion units had been measured. These studies confirmed the initial findings and demonstrated that the dilution system method provided more accurate and reproducible emissions data than those from filter/impinger methods.

In addition to providing more accurate PM emissions data, the dilution system readily provides a means of chemically characterizing these emissions in terms of their metals and organic content. Emissions from gas-fired sources were found to be significantly lower than those obtained using conventional test methods. The particulate matter collected was found to consist mainly of semi-volatile organics with no significant contribution from any poly-nuclear aromatics or metals. Emissions from catalytic cracking units were dominated by catalyst fines with their characteristic metals content, sulfuric acid, and to a lesser degree semi-volatile organics.

While dilution system sampling has been endorsed by a committee of the National Research Council and the EPA, the sampling devices are not widely available at present. In the interim, a series of alternative options are provided as guidance to refinery source operators. These recommendations are:

- Use EPA Method 202 cautiously; it has a serious problem with positive bias caused by SO₂ to sulfate conversion. While the EPA recognizes this, it is not clear that all state and local regulatory agencies do. Therefore, it is important to ensure that these agencies are also aware of the deficiencies of this method when used for compliance testing.
 - The EPA has accepted a revised version of Method 202 to minimize the formation of artifact sulfate that appears promising. However, it has not been extensively field tested

and the presence of NH_3 in combustion emissions may lead to a positive measurement bias

- PM emissions from gas-fired process heaters, boiler, and IC engines can adequately be determined by a method that only collects the filterable PM. This is supported by extensive testing, which shows that the condensable fraction for these sources is negligible.
- PM emissions from catalytic cracking units are probably best treated on an individual basis as their operating characteristics differ widely, leading to a range of combustion gas compositions. API studies have shown that emissions of semi-volatile organics are only a minor component compared to catalyst fines and condensable sulfur species (e.g., sulfuric acid and sulfate salts). Consequently a prudent approach to measuring these PM emissions is to focus on the major species using a combination of EPA Method 17 and the controlled condensation sampling system.

Introduction: Filterable and Condensable Particulate Emissions

Since the inception of the Clean Air Act, the petroleum refining industry has been faced with the need to determine criteria pollutant emissions from combustion sources. While some of these species, such as NO_x, SO₂ and CO remain in the vapor phase during and after combustion and are relatively simple to measure, particulate matter (PM) measurements are much more challenging. This is because while some PM such as fly ash or catalytic cracking catalyst fines is clearly solid material that is readily collected and measured on a sampling filter, other species that may exist in the vapor phase during combustion can later condense into aerosols downstream from the combustion zone. This can occur before or after any control devices, depending upon the temperature and composition of the combustion gases. Consequently, it has been customary to refer to PM as being composed of two PM components, filterable and condensable, the relative amounts of each depending on the stack gas composition and temperature, control devices in use at the unit, and the method for measuring PM. While measuring filterable PM is relatively straightforward (i.e., PM collected on a filter), condensable PM is a more esoteric quantity and its contribution to total PM emissions is very much dependent upon the choice of the measurement method. The EPA apparently recognized this issue, and until the interest in measuring and controlling PM 2.5 emissions emerged in the 1990s, their PM sampling methods were centered on measuring only filterable PM (Myers, 2006). At the time that these methods were originally instituted, the best available pollution control devices were mainly limited to filterable PM and could not control the condensable portion of PM emissions (Federal Register, 1975). As interest in the health effects associated with PM emissions increased, efforts were centered on determining the contribution of the PM 2.5 fraction which was believed to most responsible for these effects and principally composed of condensable matter (Federal Register, 1991). This report will review the conditions leading to the formation of condensable particulate matter from stack gas components along with the methods used to measure PM emissions from refinery combustion sources.

Principal Measurement Approaches

Filter/Impinger System: Directly Sampling Stack Gas

Historically the EPA has promulgated a series of sampling methods based on a combination of filters and aqueous impingers to collect the filterable and condensable PM present in stack emissions. While these methods are somewhat complex and cumbersome compared to those used to measure gas phase species like SO₂, sampling equipment for them is now available from a number of suppliers and the commercial stack testing community is very familiar with their use. From the outset, a number of questions remained about this approach: was an iced water bath an appropriate medium to collect species present as vapors in the stack gas that would later cool and condense at atmospheric temperatures, and could reactions within the impinger solution or during the subsequent analytical procedure lead to the formation of artifact PM?