Measuring Particulate Emissions from Combustion Sources

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Regulatory and Scientific Affairs Department

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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.

Method	Filter Temperature, ^o F	Catalyst Fines/Ash	H_2SO_4	NH ₄ Sulfates
EDA 5	248 + 25	Vac	Some	Vac
LPA J	248 ± 23	Tes	Some	ies
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

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

*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 NOx, 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?

Dilution Sampling System: Replicating Ambient Air

An alternate approach is to develop a method that attempts to replicate the physical conditions that occur in the atmosphere once the flue gases are emitted form the stack. Organic and inorganic vapors in a defined state of equilibrium at stack conditions (i.e., temperature, pressure, moisture level, concentration) will now cool and dilute in the sampling system to a new state of equilibrium representative of atmospheric conditions. For most combustion sources the change in temperature that occurs between stack and atmospheric conditions may be the most significant factor impacting the formation of secondary PM. This reduction in temperature not only allows the vapors to condense, but also allows reactions to occur that were inhibited at higher stack temperatures. Since the early 1970s, mobile source emissions have been quantified using a dilution tunnel sampling system that replicates atmospheric formation conditions (Federal Register, 1971). Small volumes of exhaust gas are cooled with 10-40 times their volume of cool air in a dilution tunnel. In addition to cooling the sample gas, the dilution air prevents the condensation of water, as the air absorbs moisture that would otherwise condense. After cooling, a short delay or residence time is allowed prior to sample collection.

While several of these dilution system samplers were developed in the 1970s and 1980s for research purposes, their size, weight, and bulk were a detriment for use at stationary sources that required rapid assembly in often elevated and cramped locations. However, recent technological advances resulted in a simplified design for these samplers, and led the API to sponsor an extensive series of tests using them at a number of gas-fired sources and fluid catalyst cracking units (FCCUs) from 1998 to 2004 (England, 2005, 2007, 2007). These tests were carried out simultaneously with measurements made using conventional PM stack sampling methods and provide a good comparison of the two approaches.

Condensable Particulate Formation

The methods developed by the EPA and other agencies to measure the condensable fraction of PM are designed to collect both organic and inorganic components. However, emissions of condensable organics are generally encountered only during manufacturing operations such as spray painting. Refinery combustion sources have extremely high combustion efficiencies, low stack gas CO concentrations, and typically contain extremely low levels of condensable organics (England, 2005). Emissions of filterable PM are associated with a wide range of particle size diameters, having a significant fraction greater than 2.5 microns in diameter, while condensable PM is formed at aerodynamic diameters equal to or less than 2.5 microns.

Condensable particulates that are typically emitted from refinery combustion sources are present in the vapor phase during combustion as SO_3 , SO_2 , and NH_3 and later condense at lower temperatures in the presence of water vapor as sulfuric acid or ammonium sulfates. The relative amounts of the sulfur oxides present depends on the sulfur content of the fuel, the oxygen levels, and the presence of any trace metal catalysts that convert SO_2 to SO_3 . In the

presence of water vapor SO₃ reacts to form H_2SO_4 , which can then condense as an aerosol or on the surfaces of fine particulate matter when the temperature drops below its dew point. The increasing use of NH₃ for NOx control adds another degree of complexity, as any ammonia slip can react with the SO₂ or SO₃, and water vapor to form condensed ammonium sulfates at temperatures from 350 - 450 °F (depending upon the concentrations of SO₂, SO₃, NH₃, and H₂O). The conditions leading to the formation and condensation of these sulfates were extensively analyzed (Burke, 1982). At that time, the main concern was formation of corrosive sulfate and bisulfate deposits in air preheaters caused by NH₃ injection to reduce NOx emissions from the upstream combustion unit. However, the analysis and conclusions from the Burke study are equally applicable to the present discussion of PM emissions measurement techniques.

Sampling trains that use aqueous impinger solutions after the PM filter to collect condensable PM have shown a positive bias in condensable results due to the conversion of SO_2 to SO_3 across the impingers at a rate that is higher than typically occurs in the atmosphere near the source. Furthermore, the conditions present in the impingers are not representative of those found either in the stack or in the atmosphere. Consequently, it is not surprising that the amount of PM measured from these sources varies widely, depending upon the measurement method used.

Conventional Measurement Methods: Filter/Impinger Sampling

In response to the needs of the New Source Performance Standards (NSPS) limiting emissions of criteria pollutants, the EPA has developed over a period of time a number of methods to measure PM emissions from a variety of sources. Of these, the following are of particular interest to the refining industry.

EPA Method 5

The initial source test method developed by the EPA, Method 5, dates back to 1971 shortly after the inception of the first group of NSPS (Federal Register, 1971). Method 5 uses a sampling probe together with a pitot tube to isokinetically traverse and sample the stack at a series of points to collect PM samples for a minimum of 1 hour period on an external glass fiber filter maintained at 120 ± 14 °C or 248 ± 25 °F (Figure 1).

Isokinetic sampling conditions are satisfied when the PM probe sampling velocity is adjusted to equal the stack gas velocity at the sample point. This ensures that the stack traverse provides a representative sample encompassing the full range of PM sizes present in the stack.

A compliance test on a process unit is defined as consisting of three test runs meeting the conditions of the method that are carried out during constant representative unit operating conditions. Method 5 only quantifies filterable PM, as somewhat arbitrarily defined by a collection temperature of 248 ± 25 °F, and did not directly address the measurement of condensable PM. This was primarily due to the fact that the best available control devices of that time were not able to reduce the condensable portion of the emissions. Consequently, a test method that included collection of any condensable fraction would not directly characterize the

performance capabilities of existing air pollution control equipment. A complete description of this method along with all the other EPA methods mentioned here can be found on the EPA website <u>www.epa.gov</u> under "Methods".



Figure 1. EPA Method 5 Sampling Train (U.S. EPA, 2000)

EPA Methods 5B and 5F

Quantifying only the filterable component of PM shifted the focus from atmospheric emissions to characterizing the performance characteristics of pollution control equipment. Several subsequent NSPS publications included source categories with significantly different source characteristics and control devices. Thus, FCCUs were recognized as a special category having the potential for sulfuric acid emissions that could not be controlled by then available PM control technology, dry electrostatic precipitators (ESP) or cyclone separators. To measure the effectiveness of these devices, Methods 5B and 5F were developed. These are similar to Method 5 except that the filter temperature is now at $160 \pm 5^{\circ}$ C or $320 \pm 10^{\circ}$ F, ensuring that no sulfuric acid would condense on the filter. The methods are essentially identical in practice and differ only in the analytical procedures used to determine the amount of condensable

ammonium sulfate PM that may have been collected on the filter. This amount is then subtracted from the total filterable PM measurement to obtain a filterable PM for reporting.

The temperature range for the formation of these sulfates shows that their formation depends on the stack gas composition (Burke, 1982). Assuming an SO_3/SO_2 fraction of 0.02 and SO_2 and NH₃ stack levels of 200 ppm and 20 ppm, respectively, sulfate condensation occurs at about 410 °F. For lower SO₂ concentrations, 10 ppm, and the same ammonia level, the condensation temperature drops to 350 °F. Consequently, EPA Methods 5B and 5F are expected to collect the condensable ammonium sulfates because the filter temperature used in these methods usually is below the ammonium sulfate dew point.

EPA Method 17

In another attempt to develop a method that directly determines filterable PM, Method 17 was introduced in the 1980s. This method is similar to the Methods 5B and 5F except for the filter location. While Methods 5B and 5F use a filter external to the stack, Method 17 uses an instack glass or quartz fiber filter to directly measure PM inside the unit (Figure 2).



Figure 2. EPA Method 17 Sampling Train (U.S. EPA, 2000)

Stack gas temperatures for process heaters and FCCU's are usually about 500 °F, which is above the sulfuric acid dew point. The sulfuric acid dew point in these systems depends upon the concentrations of water vapor and H₂SO₄, and can vary from 240 °F to 280 °F over a range of 1-10 ppm H₂SO₄ and 12-15% moisture content (Lundgren, 1978, Abel, 1946). These high stack temperatures are also above the formation temperatures for NH₄HSO₄ and (NH₄)₂ SO₄ (350-400 °F), so that in cases where ammonia is present, condensable species will not be collected. However, if the unit is equipped with a wet scrubber or an ESP and has a sampling temperature below 200 °F, all the ammonium sulfates and sulfuric acid would be collected on the filter. Consequently it is not surprising that PM emission results from the same unit could vary significantly, depending upon the measurement method used, the presence or absence of condensable sulfates, and the temperature of the sampling filter.

Sulfuric Acid Emissions Measurements

Although the EPA did not require measurement of condensable PM prior to the development of the fine particle standard for ambient air, it was aware of the health effects of sulfuric acid aerosols. As such, the EPA recognized the need to have methods available to measure the condensable PM emissions from stationary combustion sources that burn sulfur-containing fuel. The principal SOx species emitted by these sources is SO₂; further conversion to SO₃ depends upon the fuel being burned, the amount of excess air used during combustion, and the type of combustion source. For refinery-gas fired heaters, SO₃ levels are typically less than 1% of the SO₂ present, but they can range up to 5% of SO₂ for FCCUs depending upon the metals levels in the crude being processed. For most stack gas compositions, the relatively large amounts of water vapor present (10-15%) will result in virtually all these S(VI) species being emitted as sulfuric acid (Lundgren, 1978). To attempt to measure these emissions, the EPA developed Methods 6 and 8, which are both impinger-based methods. These methods differ slightly in impinger design, but both are intended to collect SO₃/sulfuric acid as well as SO₂.

EPA Methods 6 and 8

In these methods, an initial impinger consisting of an 80% isopropyl alcohol (IPA) solution in water is followed by two additional impingers containing 3% aqueous hydrogen peroxide solutions. Any SO₃ or sulfuric acid present in the stack gas is captured in the IPA impinger and the SO₂ is then oxidized to sulfate and collected by the peroxide solutions. While these methods have generally worked well for most purposes, they have been troubled by the residual solubility of SO₂ in the IPA impinger solutions that can result in a positive bias when measuring low emissions levels of sulfuric acid. This problem becomes greater when NH₃ is also present in the stack, and laboratory studies have shown that NH₃ contributes an additional positive bias to sulfuric acid measurement using these methods (England, 2008)

Controlled Condensation System

The problems with Methods 6 and 8 led to the development of a new method for sampling SO_3 /sulfuric acid concentrations, the controlled condensation method (Figure 3).

In this method, an in-stack filter (> 500 °F) precedes a cooled condensation coil that lowers the filtered sample gas temperature to 167-185 °F, below the dew point of sulfuric acid. Droplets of condensed sulfuric acid are collected and rinsed from the coil while the SO₂ passes on and is collected in peroxide solution impingers. There are several published variations of the method, differing in the filter temperature and sulfate analysis procedures employed (Maddalone, 1979, Cheney, 1984). In contrast to the bias found for Method 8, the additional presence of ammonia in the sample stream does not contribute a positive bias to the sulfuric acid measurements using this method (England, 2008). This method has not been widely used for refinery source testing despite the fact that the EPA recognizes controlled condensation as a valid test method (Myers, 2007) and provides the method as NCASI Method 8A in the list of Conditional Test Methods provided in the EMC section of the EPA website (www.epa.gov/ttn/EMC). As such, operators of refinery combustion units are encouraged to insist that regulatory agencies accept it for testing inasmuch as the current EPA Methods 6 and 8 are subject to a positive bias and not sufficiently accurate at low SO₂ concentrations.



Figure 3. Controlled Condensation Method Sampling Train (SO₃) (Maddalone, 1979)

Importance of Measuring PM 2.5 Emissions and Condensable PM

The EPA's increasing concern about the health effects of inhaling PM ultimately led to the development of new National Ambient Air Quality Standards (NAAQS) for fine PM, defined as having an aerodynamic diameter equal to or less than 2.5 microns equal to or less than 2.5 microns as measured by EPA Reference Methods (Federal Register, 1997). This occurred along with the development of new emission sampling methods, Methods 201 and 201A that included in-stack cyclones ahead of an in-stack filter (Figure 4) to quantify different PM size fractions: total PM, PM 10 and PM 2.5. These methods were designated as Conditional Test Method 40 (CTM 040) and, more recently, as Other Test Method 027 (OTM 027).

At the same time, advances in emissions control technology resulted in the development of improved wet scrubbers and wet ESPs capable of capturing fine PM. The PM 2.5 fraction of the total PM emissions had a large component of condensable PM, as the physics of condensation leads to the formation of small-size particles. Consequently, the EPA reconsidered methods for determining condensable PM and returned to their original proposal for Method 5, including aqueous impingers after the heated filter to collect the condensable PM. With the promulgation of this method, the EPA believed that it had procedures to quantify the emissions of condensable PM and filterable PM into the atmosphere, as well as the means to determine the effectiveness of control technologies designed to reduce them (Myers, 2006).



Figure 4. EPA OTM 027 Sampling Train (U.S. EPA, 2004)

EPA Method 202 and its Modifications

The method promulgated by the EPA for measuring condensables was published as Method 202. Method 202 measures condensable PM by bubbling a pre-filtered gas sample through a series of impingers partially filled with water and placed in an ice bath. The impinger solutions are then evaporated and dried to determine the net residue weight. The method includes a number of blanks (de-ionized water, dichloromethane, and a filter) used to correct the test results. In an attempt to correct some of the difficulties present in the original draft first proposed in 1971, the new method included a nitrogen purge of the impingers after completion of the test to remove any residual SO_2 from solution to prevent its conversion to sulfate. The inclusion of a different solvent, dichloromethane, was also thought to result in improved extraction of any organic condensable PM present. In the years following its publication, this method was widely adopted by state and local regulatory agencies for compliance testing to measure condensable PM in a sampling train along with filterable PM, thereby determining total PM emissions. However, it soon became apparent that measurements of condensable PM made with Method 202 were higher than anticipated for gas-fired sources, and its accuracy was questioned (Corio, 2000). Evidence grew that the nitrogen purge was very important but not effective in preventing conversion of dissolved SO₂ to condensed sulfates, which subsequently could react with dissolved ammonia to form ammonium sulfates prior to actual analysis. In addition, any NH_3 in the emissions gas, either as a consequence of its use as a

particle conditioning agent for ESPs or as ammonia slip from installed nitrogen oxides control technology, reacts with SO_2 in the impinger solutions to increase the measured sulfates and further bias the apparent condensable emissions rate.

In response to these concerns, research studies were carried out to modify Method 202 to avoid conversion of SO_2 to sulfate in the impinger solutions (Richards, 2005). In this optimized Method 202 (Figure 5), the gas entering the sampling train is first contacted on the surface of an indirect condenser to a temperature below 68 °F using cold water recirculated from the impinger case.

With this modification, the only contact between gaseous SO₂ and condensed water is with condensed material on the surfaces of the indirect heat exchanger. A large knockout or dry impinger follows the condenser to quickly separate the sample gas from the condensed water. The sample gas stream then passes through two empty Greenberg-Smith impingers to ensure complete droplet knockout and condensable PM formation upstream of the condensable PM filter. The filter collection is combined with the rinses of the empty Greenberg-Smith impingers. All of the condensed material is then extracted from the combined sample and analyzed in accordance with standard Method 202 analytical procedures. Laboratory tests have shown that this procedure avoids artifact formation in gas streams containing SO₂, NOx, and NH3 (up to 15 ppm) associated with the standard method. While these results are promising, very few field tests have been carried out to establish the method on a firm basis. As evaluation and possible modifications of optimized Method 202 is ongoing, readers are advised to consult the EPA website to learn of new developments regarding the current status of optimized Method 202. EPA has termed this method as OTM 028 and has made it available on its website.



Figure 5. Optimized EPA Method 202 Sampling Train (Richards, 2005)

South Coast Air Quality Management District Method 5.2

While it is not the intention of this report to review the various state and local regulatory approaches to measuring PM emissions, no report would be complete without mentioning the South Coast Air Quality Management District (SCAQMD) method for measuring filterable and condensable PM, Method 5.2 (SCAQMD, 1989). Although this method uses the same equipment as EPA Method 5, this method specifies that the external filter to be maintained at about 190 °F. Due to the low filter temperature, SO₃ in the flue gas will be collected as sulfuric acid and ammonium sulfates (where the stack gas contains ammonia) on the filter. Hence, collected condensables cause a positive bias in the filterable portion using Method 5.2. This bias can be very significant (>50%) for FCC units operating in the SCAQMD due to very low stack emissions limits for PM.

An Alternate Approach: Replicating the Atmosphere with Dilution System Sampling

The methods described in the preceding pages are all based on collecting filterable PM on a filter maintained at various elevated temperatures and subsequently collecting any condensable PM in an aqueous impinger solution. Needless to say, this does not replicate the conditions or correspond to the processes leading to the formation of PM in the atmosphere downwind from

these sources. Researchers have long been interested in developing a PM source test method that more closely represents PM formation phenomena that occur as the exiting stack gas interacts with the atmosphere. This has been achieved for mobile source emissions measurements, which have been quantified since the 1970s with dilution tunnel sampling systems that cool and condense exhaust gas with 10-40 times their volume of cool filtered air. This additional air also prevents condensation of water as the dilution air absorbs moisture that would otherwise condense. After cooling the air sample and providing a short residence time in a mixing chamber, the PM is collected on filters identical to those used for sampling ambient air. While early versions of dilution sampling systems for stationary sources were bulky, heavy, and operationally complex, recent systems have reduced both the size and the complexity of these units, making them easier to use for refinery source testing.

In recent years, the design developed at the Desert Research Institute (DRI), based on earlier work by Hildemann at the California Institute of Technology, has gained wide acceptance as a means of measuring PM emissions and species emitted from combustion sources (Hildemann, 1989). After a review of the PM sampling methods available (England, 1998), the API initiated a series of tests to determine PM2.5 emissions using this dilution sampling system (Figure 6) for gas-fired refinery process heaters, boilers, steam generators, and FCCUs. A small in-stack cyclone having a cut-point at 2.5 microns was used to ensure that only PM 2.5 samples would be collected.



Figure 6. DRI Dilution Sampler (Chow, 2004)

This program was extended to include other sources in 2000 and supported by a multistakeholder consortium that included the US Department of Energy, the Gas Research Institute, the New York State Energy Research and Development Authority, and the California Energy Commission (England, 2005, 2007, and 2007). All testing and analyses in this program were carried out by the Environmental and Energy Research Corp, a division of General Electric Corp. (GE), and DRI. In addition to dilution system sampling, the test program obtained concurrent samples at all locations using the conventional EPA filter with impingers to collect filterable and condensable fractions allowing comparison of results from these different approaches.

During the course of this program, modifications were made by the GE team to the original dilution sampler design that resulted in a smaller, more compact version (Figure 7).



Figure 7. GE Compact Dilution Sampler (England, 2004)

The results obtained by the compact version were shown to be equivalent to those obtained using the larger unit. Both these samplers replicate atmospheric mixing conditions so that the distinction between "filterable" and "condensable" PM vanishes, and only equilibrated PM is collected on the sampling filters.

This dilution system was used in sampling gas-fired sources for which the PM emissions were virtually all less than 2.5 microns. Emissions from sources, such as FCCUs, that have a broader PM size distribution range can also be measured with this sampler by simply removing the cyclone and thereby collecting PM over the entire size distribution present. In this case, however, it is important that the sample probe isokinetically traverses the stack to ensure collection of a representative sample of the emissions. At the present time, a method describing the use of this compact sampler, "Dilution Test Method for Determining PM 2.5 and PM 10 Mass in Stack Gases", WK- 8124, is being considered by the ASTM. After it has been approved, the EPA has indicated that it would be an acceptable method for compliance testing.

The National Research Council (NRC) endorsed dilution system sampling in reports recommending that the EPA continue developing these types of samplers for stationary source PM emissions (NRC, 1998, 1999, 2001). Development efforts were accelerated by the growing concern over the inaccuracy of condensable PM results obtained using Method 202, and ultimately resulted in the development of EPA's new Conditional Test Method 39 (CTM 39) for PM sampling. CTM 39 uses a more compact sampler than that developed by GE (Figure 8), but uses a larger diameter filter to collect PM than the GE system.



Figure 8. EPA Dilution Sampling System: Conditional Test Method 39 (U.S. EPA, 2004)

However, because of the larger filter, the tare weight of the CTM 39 filter is much greater than that of the GE unit. As a result, the gravimetric mass of the PM, measured as the difference between two relatively large numbers, is less precise than that determined using the GE sampler. This may not be a serious problem for sources having relatively high PM emissions, such as FCCUs or coal-fired utility boilers, but it may be more of an issue for gas-fired units that have much lower PM emissions.

Dilution System Sampling Results: Mass Emissions and Speciation

The extensive studies carried out by GE at a number of gas-fired sources, using both dilution and conventional sampling systems, make it possible to compare and draw conclusions about PM mass emissions using these approaches. Furthermore, as the design of the dilution sampler makes it relatively straightforward to collect samples for chemical analysis, extensive data regarding the composition of the emissions were obtained. This analysis is much more difficult with the conventional filter/impinger sampling methods because of background contamination levels.

Mass Emissions

Although the gas-fired external combustion units (heaters, boilers, and turbines) were all fired on low sulfur natural or process gas with SO_2 stack gas levels less than 5 ppm, this low concentration of SO_2 was still enough to cause a significant bias in the condensables fraction measured by Method 202. The PM mass emissions determined using conventional sampling were found to be more than 10 times greater than those obtained using the dilution system. These results have been summarized (England, 2007) in the peer-reviewed literature and should provide useful guidance to regulators assessing the real impact of PM emissions from these sources in non-attainment areas.

Dilution system PM emissions measurements were carried out at two FCCUs. However, because the sampler used was somewhat bulky, no attempts were made to traverse these stacks. As a result, the data obtained were not necessarily representative of the actual stack emissions for particles with diameters >2.5 microns. (England, 2001, 2003). Additional FCCU studies that traverse the stack are required to better assess the use of the new compact dilution systems for FCCU applications.

The SO₂ artifact was also present in PM emission tests carried out by GE for the API on several natural gas-fired reciprocating internal combustion engines at a production field (England et al., 2004). These units were fueled using natural gas having an extremely low sulfur content, 0.4 ppmv, about an order of magnitude lower than the natural gas used for other units tested in the program. As a result, PM emissions measured by Methods 201/202 at this site were only about two times higher than those obtained using the dilution system.

Chemical Speciation

Dilution sampling systems are especially suited for chemically characterizing the mass emissions from combustion sources. After equilibration with the dilution air in a residence chamber samples can be collected on a series of filters, sorbent cartridges, and/or gas sampling canisters attached to the sampling manifold, as shown in Figure 9. Analyses of the stack gas emissions for the units tested in the API and multi-stakeholder program were carried out using procedures established for ambient air sampling (England, 2002, 2003, 2004, 2005). Samples collected on Teflon filters were weighed to determine mass emissions and subsequently analyzed for metals content by x-ray fluorescence analysis. Samples collected on glass-fiber filters were thermally analyzed for elemental and organic carbon, and samples collected in canisters and sorbent cartridges were analyzed for individual organic compounds. The speciation information on the metals and organic compounds concentrations present in the source emissions can then be used in subsequent health effects studies to assess the epidemiological impact of these emissions. At the outset of the API project, it was hoped that characteristic species present in the emissions from the sources tested might be found. If present, such species could be used in source attribution studies based on ambient air analyses to assess the contribution of these sources to ambient air quality. However, for the various gas-fired sources tested, this did not prove possible. PM and organic emissions from these units were found to be extremely low, with metals contents essentially equivalent to those found in the ambient dilution air. No characteristic "marker species" could be identified.



Figure 9. Dilution Sampling System: Collection System for Speciation (England, 2003)

Emissions from FCCUs are inherently more complex than those from gas combustion units, as these emissions result from combustion of spent coke on catalyst particles in the regenerator. Here, too, no characteristic organic species were found in the stack emissions (England, 2001, 2003). In fact, data from the earlier study were used to refute a contention by EPA Region 6 that FCCUs were a significant source of benzo-a-pyrene emissions. X-ray analysis of the PM

emissions from these sources showed that they were dominated by silica and alumina, with the presence of rare-earth elements typical for the cracking catalyst used in the specific FCCU. A recent publication describes application of this approach for analyzing contributions to ambient air concentrations in Houston (Kulkani, 2006).

Quantitation and Precision

The standard EPA methods for collecting PM emissions on filters have been in use for decades and the precision of the results derived from these measurements is generally regarded as no better than $\pm 15\%$. However, emissions measurements on sources such as gas-fired process heaters that have inherently lower PM emissions will have greater uncertainties. This higher uncertainty is due to the low mass of material collected relative to the large filter (147 mm diameter) on which the particulate is collected. Measurements made for these sources with the GE dilution sampler are more precise because the PM is collected on smaller filters that are used for ambient air sampling (47 mm diameter), and which have a tare weight that is about 1/10 that of the larger filter.

The results of the API multi-stakeholder test program included a review of the accuracy and precision attained with the GE dilution sampler (England, 2005). This program showed that no significant bias occurred for data obtained using the dilution sampler. In particular, for the low PM 2.5 concentrations characteristic of gas combustion (approximately 0.05 to 0.3 mg/dscm), 95 percent confidence intervals from \pm 28% to more than \pm 200% were observed, with most of the results for each test set was between \pm 41% and \pm 87% (25th to 75th percentile). While these uncertainties appear higher than those conventionally attributed to EPA methods, they are not surprising as these units have very low PM emissions. By comparison, the variations found in this program for the EPA methods for these units are greater than 200% (England, 2005).

Only two studies using the GE dilution system have been carried out for FCCUs (England 2001, 2003), so it is too early to establish any precision estimates for FCCU application. However, since the PM emissions from these sources are much higher than those from gas-fired combustion sources, one could expect the precision to be similar to that of conventional testing. In all cases, however, the skill and care of the emissions testing personnel are key elements in obtaining precise and accurate results.

Guidance for Source Operators: Which Method Do I Use and When?

The preceding discussion has reviewed the range of methods used to measure PM emissions, including "condensable" species comprising PM 2.5 from combustion units. This discussion has summarized how the measurements for an individual source can vary due to the measurement technique used and the associated thermodynamics and chemistry leading to the formation of "condensable" PM. Condensables can form by:

- Conversion of vapor phase SO₂ to sulfates in the impinger solutions
- Reaction of vapor phase SO₂ with NH₃ in impinger solutions to form sulfates

• Reaction of species present in the vapor phase at stack gas temperatures (350-500 °F) to form PM at the lower filter temperatures (160-250 °F) used for sample collection, e.g. ammonium sulfates from NH₃, and SO₂, or H₂SO₄

The extent to which these mechanisms become problematic depends upon the composition of the combustion gas being sampled. In the case of a gas-fired process heater or IC engine burning natural gas with negligible S-fuel content, all of the methods discussed are likely to provide similar PM results, subject to measurement uncertainties. However, even for gas-fired units with low S-fuel content, results obtained using EPA Method 202, which attempts to determine condensable PM, will severely overstate actual PM emissions because of SO₂ conversion to sulfates in the impingers. The problem is more complicated for FCCU's, with their complex combustion gas mixture containing SO₂, SO₃, and NH₃ along with catalyst fines. Here, depending on the filter temperature and the use of collecting impingers, the measured PM values can vary widely, with conventional EPA methods yielding higher PM emissions values than those provided by dilution samplers due to the above-mentioned reactions that lead to formation of sulfuric acid and sulfates.

For units using wet-scrubbers for PM control, the presence of condensable moisture will cause problems for the current dilution sampling methods, thereby limiting their use in this application. Both the EPA and GE samplers use in-stack cyclones to avoid collecting particles great than 10 microns. However, these in-stack cyclones could also trap and remove fine particles collected in the agglomerated water droplets. A simple, practical approach may be to eliminate the cyclones and collect all PM on a filter as in Method 17. As the wet scrubber is expected to have collected the bulk of all the large particles, this approach would collect all PM emitted by the source and provide a conservative value for the total PM 2.5 emitted (by virtue of including some larger sized PM that may pass the scrubber and end up on the collection filter). Further research and discussion to develop the most representative PM measurement technique for wet scrubber stacks is warranted.

While it is generally accepted that dilution samplers will provide the most accurate PM emission results (with the possible exception of wet scrubbers), these units are not readily available for use by qualified emissions testing contractors. Until such time, source operators are faced with the question of which method to use for source testing at their facilities. The following options are recommended:

- While the EPA recognizes the inadequacies of Method 202 for determining emissions from combustion units with measurable SO₂ emissions, it is not clear that all state and local regulatory agencies are aware of these problems. Therefore, it is important to ensure that these agencies are also aware of the deficiencies of this method when used for compliance testing. This report is intended to provide source operators with alternatives that provide more representative emissions determinations
- Laboratory testing of the revised Method 202, or OTM028, using dry impingers looks promising for sources with SO₂, but this method has not been extensively field tested. It

also is unclear whether the presence of NH_3 would lead to formation of additional artifacts. Consequently, use of the revised Method 202 by itself cannot be recommended at present.

- For gas-fired process heaters, boilers, and IC engines, the simplest and best option is to collect PM emissions using a method that does not attempt to determine condensable PM. Based on the results of the API multi-stakeholder testing program, PM emissions from these sources are very low, consisting of low levels of non-toxic semi-volatile organics and elemental carbon (England, 2005). Any "filterable only" PM testing method is apt to be acceptable, with the main problems being random error caused by extraneous PM such as rust or bird droppings on the filter and analytical uncertainties associated with the determination of small quantity of PM mass collected on a large-mass filter.
- FCCU's are probably best approached on an individual basis as their operating characteristics differ widely, leading to a range of combustion gas compositions. Between 1998 and 2002, the API sponsored PM 2.5 emissions tests at two FCCUs. In both studies, PM emissions essentially consisted of catalyst fines and sulfuric acid, with organic species and elemental carbon comprising very minor components. This suggests that organics are not likely to be significant in PM emissions from these sources, and that a prudent approach would be to focus on measuring sulfuric acid and catalyst fines emissions separately, and to avoid attempting to measure "condensable" PM using a flawed method.
 - Catalyst fines should be collected on a filter, either at stack temperatures (assuming that there is no wet scrubber upstream from sample collection) as in Methods 17 and 201, or on an externally heated filter of at least 320 $^{\circ}$ F as in Method 5B and 5F. This avoids collection of sulfuric acid on the filter and ensures that the filter collects only catalyst fines and ammonium sulfates that can form if NH₃ is present in the stack gas.
 - Sulfuric acid should be determined independently using the controlled condensation sampler that avoids any artifacts resulting from reactions with NH₃. Experience has shown that in the presence of NH₃, artificially higher values of sulfates are reported using EPA Methods 6 and 8.

The filter/impinger methods described in this report can result in the formation of ammonium sulfates during the sample collection process, and thereby cause a positive bias in the apparent emissions from combustion units that use NH₃ for NOx control or ESP conditioning. Some regulatory agencies, such as the SCAQMD, are not troubled by this fact as they believe that, since all emitted NH₃ and SO₂ ultimately react in the atmosphere to form sulfates, they are correctly regulating these emissions. However, PM emissions are defined by the EPA as those directly emitted from the stack or immediately formed thereafter as a result of condensation in the atmosphere (e.g., sulfuric acid). Stationary source emissions testing methods are designed to measure these primary particulate emissions and not the secondary particulate matter that is formed many hours later in the atmosphere, far downwind from the source, as a result of reactions between gaseous precursors such as NH₃ and SO₂.

This review has attempted to summarize the methods available for determining PM emissions for stationary combustion sources. Because vapor phase species in the flue gas at stack temperature conditions can later condense to form aerosols at atmospheric conditions, measuring PM emissions is a more complex problem than measuring other criteria pollutants (e.g., NOx, CO, or SO₂). The summary provided herein may not make recommendations for testing methods that should be applied for a specific source, but it should help source operators educate local regulators and to negotiate with them using a technically-sound basis in order to obtain acceptable and, more importantly, representative compliance source testing methods.

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