

Characterization of Utility Boiler Contributions to PM_{2.5}

Glenn C. England

Energy & Environmental Research Corporation

18 Mason

Irvine, CA 92618

ABSTRACT

Emissions from coal-fired utility boilers may contribute significantly to ambient particulate concentrations, especially in the very fine (below 2.5 micron) particle size range. Ambient PM_{2.5} speciation studies often show that geologic materials, which comprise the majority of fly ash produced by coal combustion, make up only a small fraction of the particulate. Sulphate, nitrates, and organic compounds typically comprise more than 80 percent of the ambient PM_{2.5}. Therefore emission of secondary aerosol precursors (e.g., nitrogen oxides, sulfur dioxide, sulfur trioxide, ammonia, certain volatile organic compounds) contributes significantly to ambient PM_{2.5}. Coal-fired boilers emit both primary PM_{2.5} and secondary particle precursors. Because of the large quantity of gaseous fuels burned, even gas-fired devices may have potential to contribute significantly to ambient PM_{2.5}.

The chemical speciation of primary particles emitted from coal-fired boilers provides important markers that can be used to identify the relative contribution of a specific category of sources to regional ambient PM_{2.5}. Existing emission factors and speciation profiles for PM_{2.5} and PM_{2.5} precursors from combustion sources are often dated and incomplete. Also, the wide variety of coal mineral matter compositions, boiler designs and pollution control equipment makes site-specific emissions characterization the most reliable manner of attributing source contributions. A test protocol for developing PM_{2.5} emission factors and chemical speciation profiles has been developed. The paper discusses approaches for characterization of PM_{2.5} and PM_{2.5} precursors from stationary combustion sources and preliminary results of field measurements made using traditional and dilution sampling techniques. Results of tests on gas-fired units using both traditional source testing methods and a dilution sampling approach are presented and compared.

INTRODUCTION

In July 1997, the U. S. Environmental Protection Agency (USEPA) promulgated new National Ambient Air Quality Standards (NAAQS) for fine particulate matter and ozone, including a new standard for particles 2.5 μm or less in diameter, referred to collectively as PM_{2.5}. Although this standard was recently remanded by the U. S. courts, the EPA intends to appeal the decision and it is expected that this represents only a short delay in the implementation of the new NAAQS. USEPA is continuing to implement a national network to monitor and speciate ambient PM_{2.5} while litigation continues. In Canada, the development of Canada-wide ambient air quality standards for PM_{2.5} actively continues with passage in the foreseeable future likely¹. In Europe, the European Commission (EC) has proposed tighter standards for PM₁₀ and is considering new legislation on PM_{2.5}².

Chemical speciation of PM_{2.5} emissions provides important markers for determining the contribution of source categories to ambient PM_{2.5}. Also, it is widely believed that only certain components of PM_{2.5} cause the various adverse human health effects that have been observed. Chemical analysis of ambient PM_{2.5} samples collected in various parts of the United States and Canada show that sulfates, nitrates, carbon (elemental and organic) dominate in most urban and many non-urban areas; ammonium and mineral (soil) elements also are present^{3,4}. Organic compounds are important components of particulate matter and most of the particulate organic carbon is believed to reside in the fine particle fraction⁵. For example, in a study of the Los Angeles area organic compounds constituted approximately 30 percent of the ambient fine particle mass⁶.

Particles may be either directly emitted into the atmosphere (primary particulate) or formed there by chemical reactions and physical transformations (secondary particulate). The majority of primary emissions from combustion are found in the PM_{2.5} or smaller size range, especially with clean burning fuels, such as gas. Sulfates and nitrates are the most common secondary particles, although organic carbon can also result from volatile organic compounds (VOCs)⁷. The gaseous precursors of most particulate sulfates and nitrates are: sulfur dioxide (SO₂) and sulfur trioxide (SO₃); oxides of nitrogen (NO and NO₂, the sum of which is designated NO_x), respectively; and ammonia (NH₃). Secondary organic aerosol formation mechanisms are not well understood due to the multitude of precursors involved and the rates of formation which are heavily dependent on meteorological variables and the concentrations of other pollutants. It is believed, however that atmospheric transformations leading to the formation of secondary aerosol from gas-phase primary organic emissions may be very significant in some areas, particularly during the summertime.

The reliability of studies to apportion the contribution of regional sources to local ambient PM₁₀ and PM_{2.5} relies to a large extent on having accurate emission inventory and speciation data for model input. The Chemical Mass Balance Model is one common approach to particulate source apportionment, favored for its simplicity. This model relates chemical analysis of ambient air samples to sources based on emission profiles for those sources and other factors⁸. Generic source emission profiles, e.g. those developed by EPA for source-receptor modeling, are available for many source categories; however, these must be used with great caution since they may not accurately represent specific sources because of site-specific process differences, data based on measurements using older, less sensitive and selective techniques, and/or incomplete data. The National Research Council Committee on Research Priorities for Airborne Particulate Matter concluded that one of the 10 most important research priorities for fine particulate studies is to “develop advanced mathematical, modeling and monitoring tools to represent the relationships between specific sources of particulate matter and human exposures⁹.” Thus, there is a need for new source emission data for specific sources and locations using the latest measurement technologies to provide more reliable source apportionment results¹⁰.

COAL-FIRED UTILITY BOILER EMISSIONS

Coal-fired boilers emit both primary particles and secondary particle precursors which contribute to ambient PM_{2.5}. Since primary particles typically comprise a very small fraction of ambient PM_{2.5}, the contribution of primary particle emissions to ambient PM_{2.5} may be insignificant compared to emissions of SO₂, SO₃, and NO_x, and ammonia. However, the chemical speciation of primary emissions, especially elements found in the coal mineral matter and fly ash, may serve as a good marker for individual sources burning different coals. The quantity and distribution of major and trace elements found in coal mineral matter vary over a tremendous range across different coals. Figure 1 compares the speciation profile measured on three coal-fired boilers in Colorado, expressed as the percentage of each species relative to the loading of PM_{2.5} mass on a filter collected in a dilution tunnel sampler¹¹. The vertical bar represents the mean of replicate measurements, and the dot represents the standard deviation. A good marker is considered one for which the standard deviation is much less than the average. Of the anions measured, sulfate, chloride and potassium are consistently good markers, while ammonia and nitrates only appear in some cases. Clearly, sulfates, chlorides and potassium can be explained by their common presence in the coal mineral matter. However, nitrates normally would not be expected in source emissions since most of the nitrogen oxides present typically exist as nitric oxide (NO). Also ammonia should not be present unless it is added to the stack gas, either for control of nitrogen oxides or for electrostatic precipitator performance enhancement. Other major coal mineral matter constituents such as aluminum, silicon, calcium and iron appear in the emissions profile with good confidence. However, these common earth elements are not unique to the coal-fired power plant emissions hence their use as markers may be questionable. The fraction of organic and elemental carbon in each of the three tests was generally significant.

The distribution of particle sizes in the stack gas depends not only on the coal mineral matter but on the characteristics of the boiler, the air pollution controls, and the definition of a particle. Figure 2 compares the particle size distribution before and after an electrostatic precipitator of a 600 MW wall-fired unit equipped with an electrostatic precipitator and burning an eastern U. S. bituminous coal. The particle size upstream of the electrostatic precipitator shows only 2 to 6 percent of the particles below 2.5 microns. At the stack downstream of the electrostatic precipitator, 40-50 percent of the particles are below 2.5 microns. If condensible particles such as sulfuric acid mist also are included in the particle size distribution, these can dominate the small particle size range. For example, Figure 3 compares particle size distribution measured in the stack of a petroleum fuel fired boiler equipped with a scrubber. The measurements were made using tandem cascade impactors, one heated above the acid dewpoint and the other heated below the acid dewpoint but above the moisture dewpoint such that acid particles would condense in one but not the other. The difference in the particle size distributions shown in the figure represents the condensible particles, and it can be seen that the contribution to the fine particle loading is very significant. Thus, the definition of "particulate matter" - especially with respect to condensible particles - becomes very important when establishing contributions to ambient PM_{2.5}. For many coal fired boilers in the U. S., sulfate particulate and condensible sulfuric acid mist have been excluded from the definition of particulate matter emissions; for PM_{2.5} source apportionment, this may be inappropriate.

Organic compounds may be present in emissions from coal-fired boilers as products of incomplete combustion. Organic aerosols in the atmosphere result from condensation of heavier organic compounds present in the source combustion products and atmospheric reaction of volatile organic compounds to form heavier, condensible organics. Organic compounds with a carbon number greater than 7 are believed to be key contributors to secondary and condensible primary organic aerosols¹¹. Tests for "air toxics" conducted over the past several years provide a partial database of volatile and semivolatile organic compound emissions for several classes of utility boilers. Such tests normally seek to quantify a specific list of compounds rather than to speciate the total organic mass and so there are no data for many of the organics of interest from a PM_{2.5} perspective. The data which do exist suggest that the concentration of organic compounds is very low compared to other emitted substances; however, the importance of even small concentrations could be significant in certain regions of the country given the large volume of flue gas emitted.

SOURCE CHARACTERIZATION TEST METHODS

Source characterization approaches for particulate matter fall into two general categories: source-level sampling and ambient-level sampling. In the former, samples of the exhaust gas from the source are collected and analyzed. In the latter, the exhaust gas is first diluted with air to near-ambient levels and then samples are collected and analyzed. The general sampling and analytical principles for characterizing particulate mass, size, and composition are similar for the two types of measurements, but the specific approaches differ due to the differences in pollutant concentrations and background gas composition. In the context of regulatory enforcement, source-level sampling is currently the accepted approach for total suspended particulate and PM₁₀ measurements for stationary sources, while ambient level sampling using dilution is the accepted approach for mobile source particulate emission measurements. This research program is aimed at establishing ambient level sampling as an acceptable, even preferred, approach for characterizing stationary source contributions to ambient fine particulate.

Source-Level Sampling

The most common approach to source-level sampling for particulate matter is EPA Method 5 or Method 17¹². Methods based on similar principles are used in other countries. Using an in-stack filter according to EPA Method 17 (Figure 4a), solid and liquid particles present at the stack temperature are captured on the filter. EPA Method 5 (Figure 4b) employs

a filter external to the stack heated to a constant temperature, typically 250°F or 320°F, which allows particulate to be defined independent of the stack gas temperature. Heating the filter avoids condensation of moisture or acids, depending on the temperature selected. These methods measure primary particles that are filterable at the filter temperature. Condensible particulate is usually defined as the amount of material collected in a series of iced impingers downstream of an in-stack filter and includes both ultra-fine particles which pass through the filter and vapors which condense at the ice bath temperature. EPA Method 202¹³ is an example of this approach. Impinger methods for condensible particulate are subject to substantial artifacts that do not occur in atmospheric processes, especially when ammonia, SO₂, sulfates and/or chlorides are present in the exhaust, and thus may not provide an accurate measure of primary condensible particles. These effects are especially significant for coal-fired boilers due to the relatively high SO₂ concentrations present in the flue gas. Particle size is usually measured using in-stack cyclones or cascade impactors, e.g. using EPA Method 201A¹³ (Figure 4c), or occasionally using heated out-of-stack cyclones. While these methods may provide regulatory agencies a means of enforcing emission limits defined using the same methods, they may not be generally applicable to all sources and may be biased high or low due to interferences and artifacts.

Source-level measurement methods also exist for secondary particle precursors. NO_x and SO₂ emissions can be characterized using continuous gas analyzer systems. SO₃ can be measured by high-temperature filtration of the sample to remove solid particles, followed by cooling to a temperature below the H₂SO₄ dew point (but above the moisture dew point) and subsequent filtration to remove condensed acid mist¹⁴. Gaseous ammonia can be trapped in sulfuric acid impingers and subsequently analyzed by ion chromatography, although the sample must be filtered at stack temperature to avoid biases due to formation or decomposition of solid/liquid ammonium compounds. Gas-phase organic compounds usually are measured by adding a sorbent trap which strips organics from the gas onto the sorbent (Figure 4d). The sorbent is subsequently analyzed in the laboratory.

Ambient-Level Sampling

Source-level sampling methods tend to underestimate or overestimate the contribution of the source to ambient aerosols because they do not account for aerosol formation which occurs after the gases leave the stack. Ambient-level sampling for source characterization involves diluting the exhaust gas and subsequently sampling and analyzing the diluted gas using ambient air methods. This has one advantage over source-level sampling in that results are directly comparable to measurements of ambient air samples. If the dilution is performed in a manner which simulates conditions in the exhaust plume, then particles which form in the plume can be characterized also. Ambient air methods are similar in general principle to source-level measurements for combustion devices, but somewhat simpler because provisions in source-level methods to eliminate problems caused by the high gas temperatures, high moisture content, higher pollutant concentrations and interfering major and minor gases are not necessary.

Investigators have been using dynamic dilution samplers to investigate the impact of emissions on atmospheric aerosols for more than 20 years. While dilution sampling has become the standard reference method for automotive emissions, it has been employed only in research applications for stationary combustion sources. Dynamic dilution samplers for stationary source studies draw a hot exhaust gas sample continuously into a chamber where is mixed with a continuous flow of filtered ambient air. The diluted sample is then drawn through multiple filters or sorbents, which strip particles and/or selected gases from the sample. These are then taken to an analytical laboratory for analysis. A wide variety of dilution tunnel designs has been employed by various researchers, depending on the focus of their studies¹⁵. A wide range of construction materials, dilution ratios, total residence times, and physical configurations are represented. Designs developed prior to the mid-1980's focused primarily on characterizing particulate mass in sources with high particulate concentrations. As health

impact studies began to associate health effects with specific components of ambient particulate mass, dilution sampler designs evolved to allow characterization of particle size and chemical composition.

In 1989, Hildemann et al.¹⁶ introduced a dilution sampler design specifically designed for characterizing organic aerosols in very low concentrations. The key features of this system were: 1) it did not contain any plastic or rubber materials that could leach organics into the system or prevent thorough decontamination of the system; 2) it allowed for a relatively large sample size to facilitate detailed chemical analysis of organic compounds; 3) it allowed for dilution and cooling of the sample fully to ambient temperature; 4) the dimensions and the flow rates in the system were selected to minimize particle and vapor losses onto the walls; and 5) it provided for long sample residence times. Dilution ratios of at least 40:1 were used to assure adequate mixing between the sample stream and the dilution air, in addition to cooling the sample to essentially ambient temperature. An analysis of aerosol condensation, coagulation and nucleation rates in samples with low particle concentrations revealed that diffusion of condensing vapors to particle surfaces is relatively slow; hence, the design incorporates an additional residence time chamber providing a total of approximately 80-90 seconds residence time to facilitate condensation of low-concentration aerosols. The design has been used by Hildemann and others¹⁷ to generate detailed organic aerosol speciation data for several types of sources.

TEST APPROACH

A test protocol developed for characterizing the total contribution of stationary sources to ambient PM_{2.5} (Figure 5) is expected to be applicable to a broad range of fossil-fueled stationary combustion sources, but has significant benefits for sources with very low PM concentrations. This test protocol was recently demonstrated at two gas-fired units and a comparison of the in-stack and dilution tunnel methods was made¹⁸. In addition to primary PM_{2.5}, samples for organic and inorganic secondary aerosol precursors (e.g. NO_x, SO₂, volatile organic compounds) also were collected and analyzed. The dilution tunnel used in these tests (Figure 6) follows the Hildemann and Cass design discussed above. The diluted sample was collected on Teflon membrane, and quartz filters for particulate mass, inorganic species and elemental/organic carbon analysis. Gaseous organic compounds were collected on Tenax sorbent for volatile compounds and polyurethane foam/XAD-4 sorbent for semivolatile compounds, and analyzed by gas chromatography with mass spectrometry, Fourier transform infrared absorption, and photoionization detection. Elements were determined on Teflon membrane filters by X-ray fluorescence. Ions were determined on quartz filters by ion chromatography. Organic and elemental carbon were determined on quartz filters by thermal-optical reflectance.

Source-level sampling for total particulate, PM₁₀, PM_{2.5} and condensible particulate was performed concurrently with dilution tunnel sampling, providing a direct link between the results obtained with the two approaches. In-stack particle size distribution was measured using in-stack cascade impactors. PM_{2.5} precursor measurements also included SO₂ and NO_x. Tests on coal-fired boilers also would include SO₃, ammonia, and particle size distribution.

Comparison Of In-Stack And Dilution Methods

Figure 7 compares PM_{2.5} mass measured by the dilution tunnel and the in-stack methods (EPA 201A/202) for the gas-fired boiler and gas-fired process heater. The amount of filterable particulate collected using the in-stack methods was essentially below the overall method detection limit at both sites. However, condensible particulate matter (CPM) as determined by EPA Method 202 was measurable. Analysis of the impinger contents suggests most of the measured CPM can be accounted for in sulfates and chlorides; however, it is believed these results may be biased high due to SO₂ absorption in the impingers. Due to differences in the fuel gas sulfur content, SO₂ concentration at the boiler site was approximately

8 ppm, while SO₂ at the process heater site was less than 0.3 ppm. The sulfate concentration in the impinger contents and CPM mass also was higher for the boiler than for the process heater site. Total PM_{2.5} mass obtained with the dilution tunnel are much lower than the total filterable plus CPM mass obtained with the in-stack methods. The dilution tunnel should capture all of the filterable plus any aerosols which condense under simulated plume conditions. The striking difference between the dilution tunnel and in-stack method results and the observations noted above suggest that EPA Method 202 may yield significantly biased results even for sources with very low SO₂ concentrations. The values of total particulate agree qualitatively with results reported by EPA in its emission factor database for natural gas combustion in external combustion devices. However, assuming the EPA results were obtained using the same methods, a similar bias may be present in those data.

SUMMARY

The sampling methodology should result in an improved characterization of source contributions to ambient PM_{2.5}, especially for sources with low particulate concentrations. Coal-fired boilers present unique challenges because of the large amount of condensible particles that may be present and because of the tremendous range of coal compositions, mineral matter speciation, and emission control equipment designs. Generic emission factors and speciation profiles therefore should be used with extreme caution for source apportionment. Developing site-specific emission factors and speciation profiles would provide the most reliable input to source apportionment studies and will ensure that coal-fired utility boilers are not unfairly targeted for emission reductions.

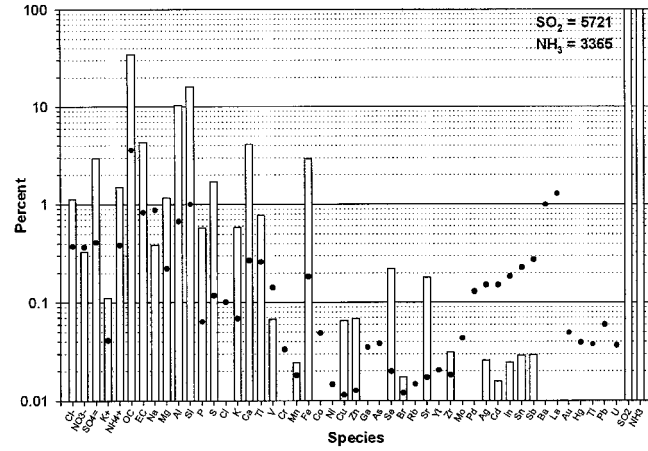
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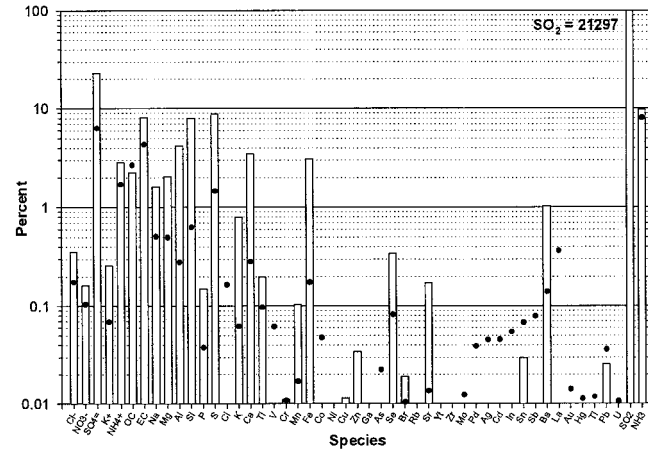
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(a) Unit 1 Boiler - ESP with ammonia injection



(b) Unit 2 Boiler - ESP with wet scrubber



(c) Unit 3 Boiler - fabric filter with dry scrubber

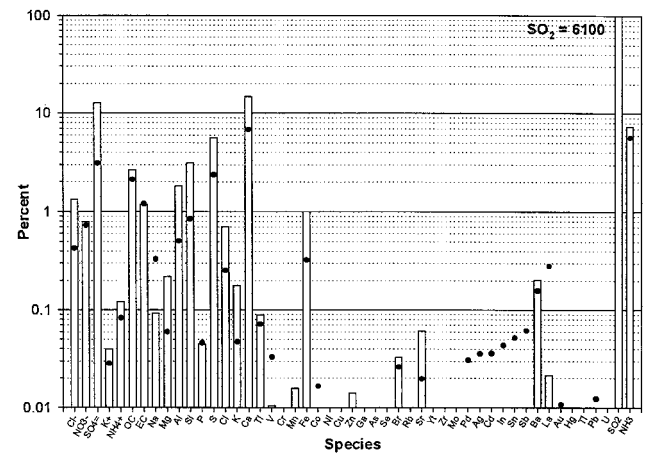


Figure 1. Coal-fired boiler source profiles derived for northwestern Colorado¹¹.

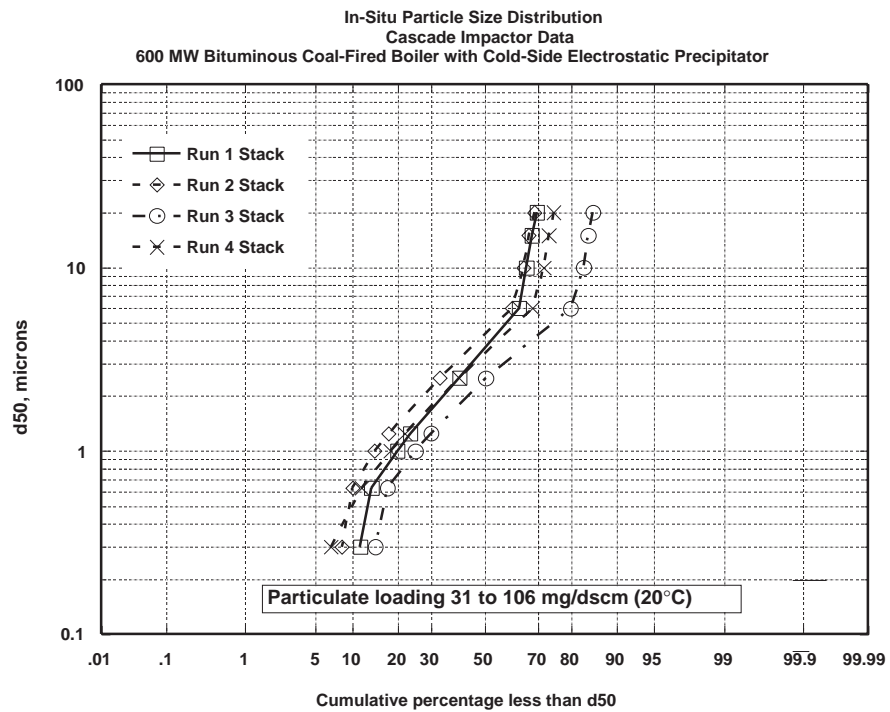
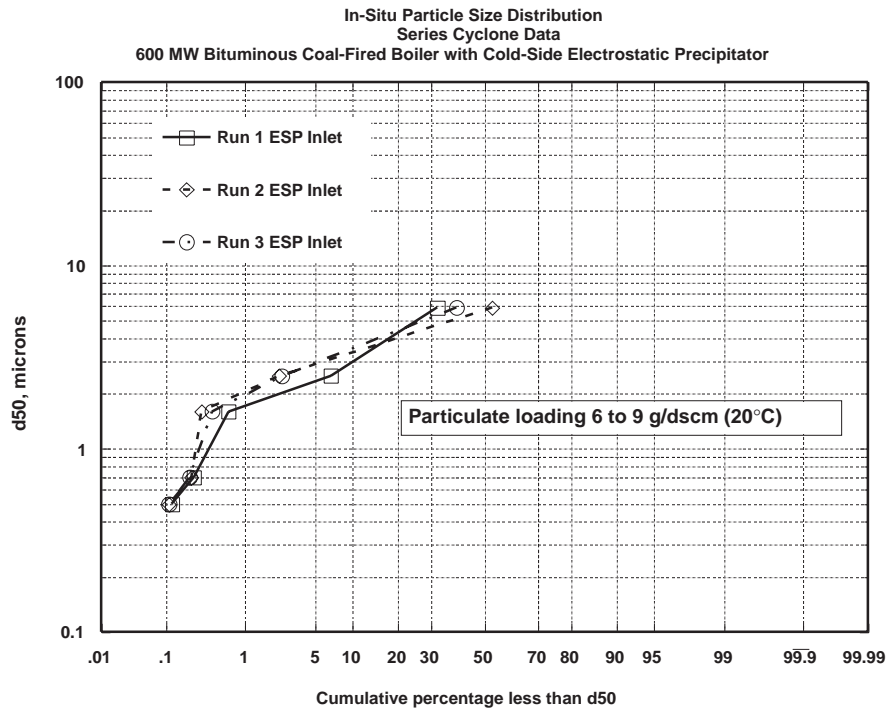


Figure 2. Size distribution for particles present at flue gas temperature (163°C).

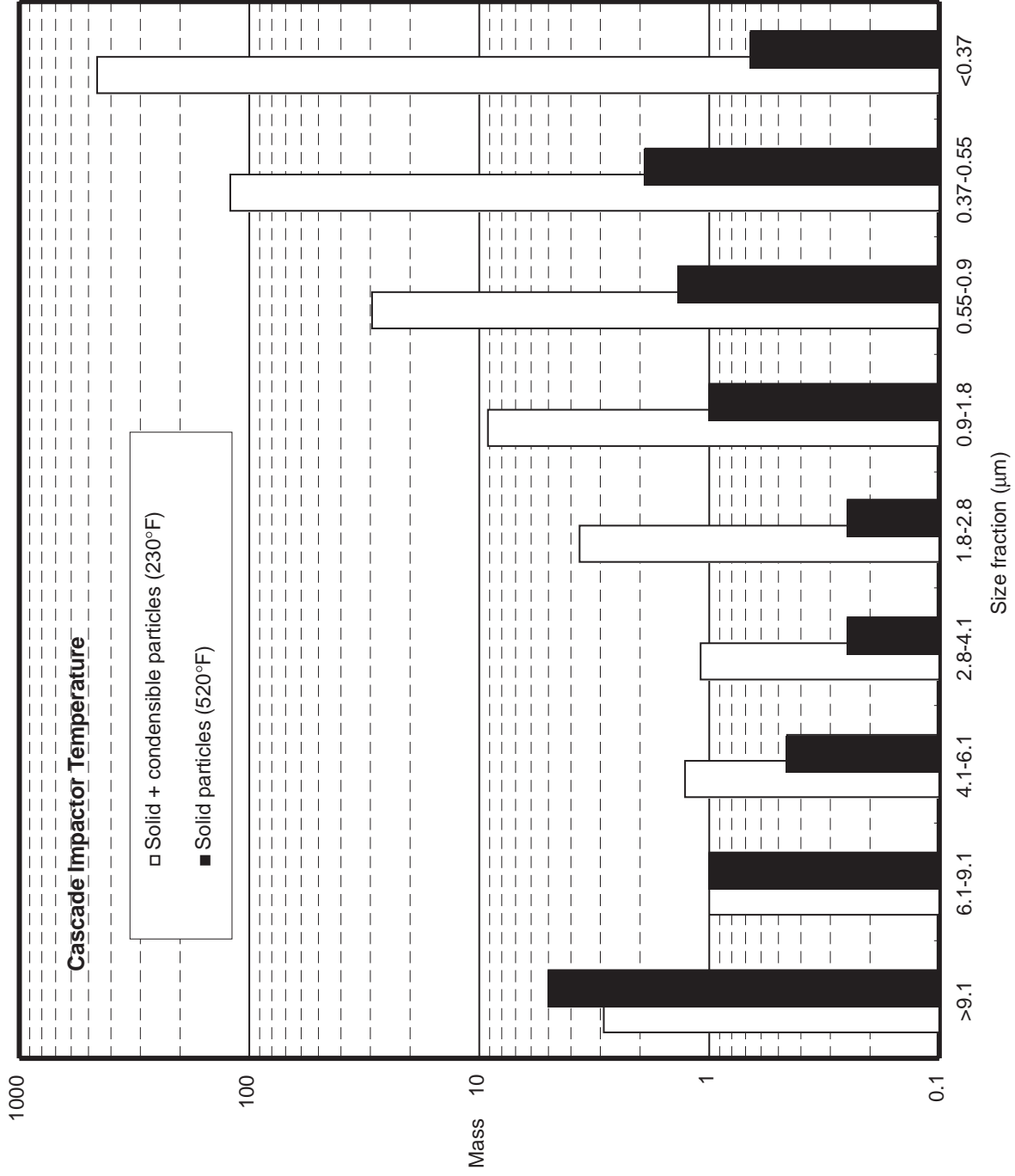
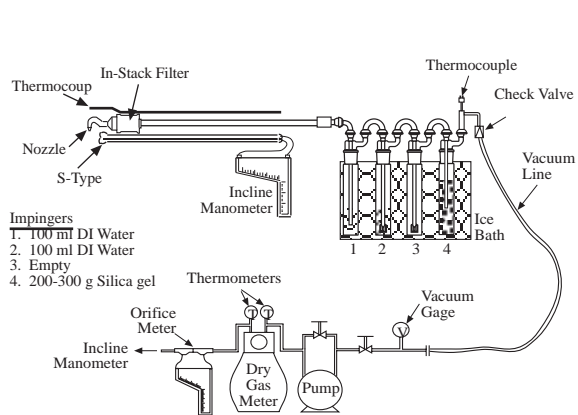
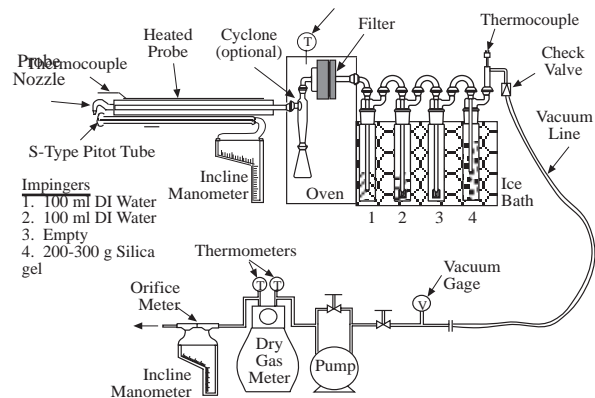


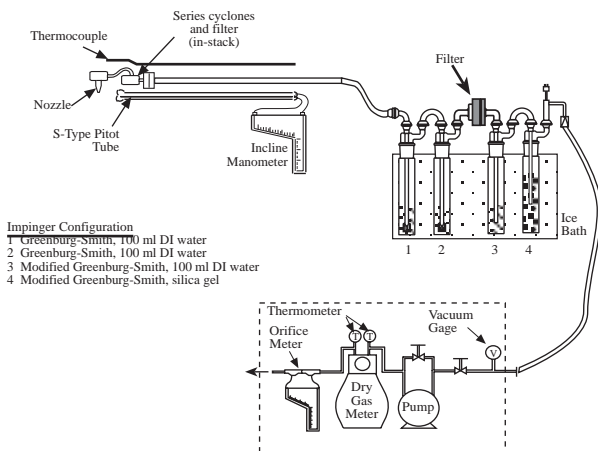
Figure 3. Comparison of particle size distribution with and without condensable aerosols.



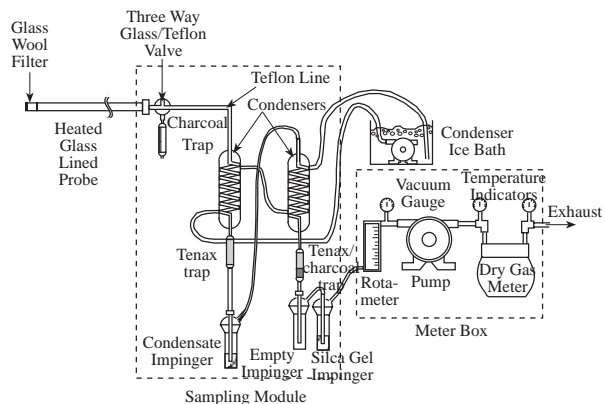
(a) EPA Method 17 sampling train.



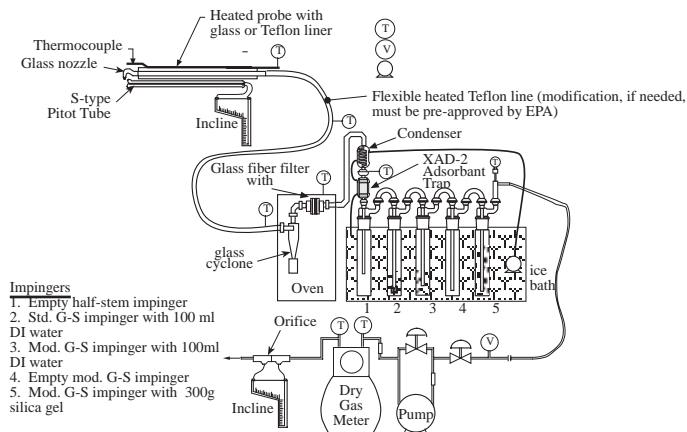
(b) EPA Method 5 sampling train.



(c) EPA Method 201A/202 sampling train.



(d) EPA Method 0030 Volatile Organic Sampling Train.



(e) EPA Method 0010 Modified Method 5 (SVOC) sampling train.

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Figure 4. Source-level sampling approaches.

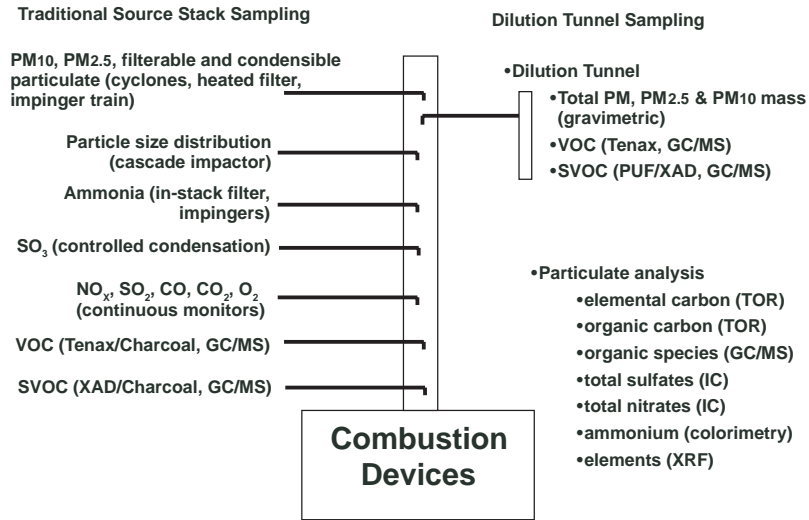
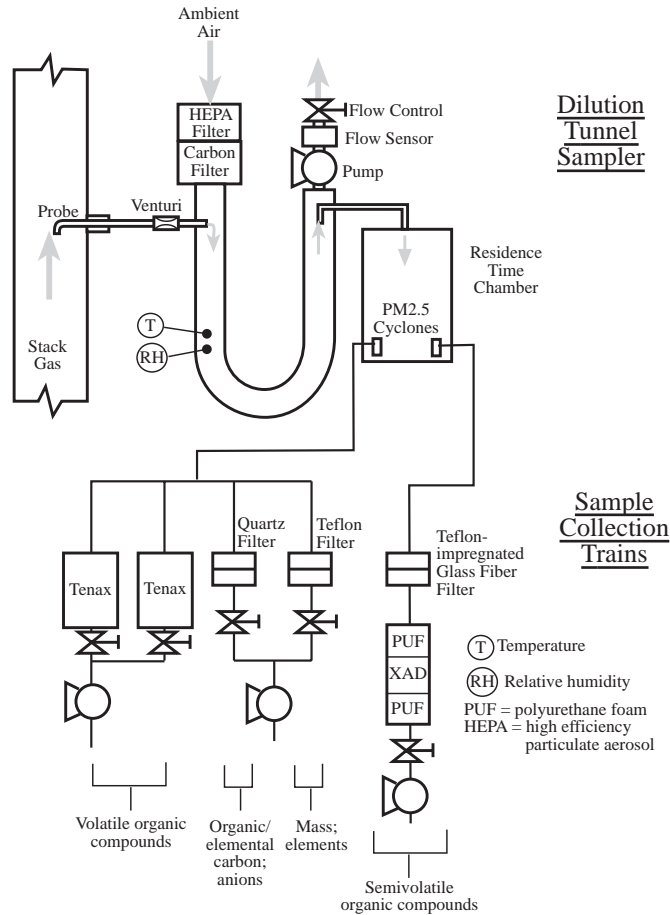
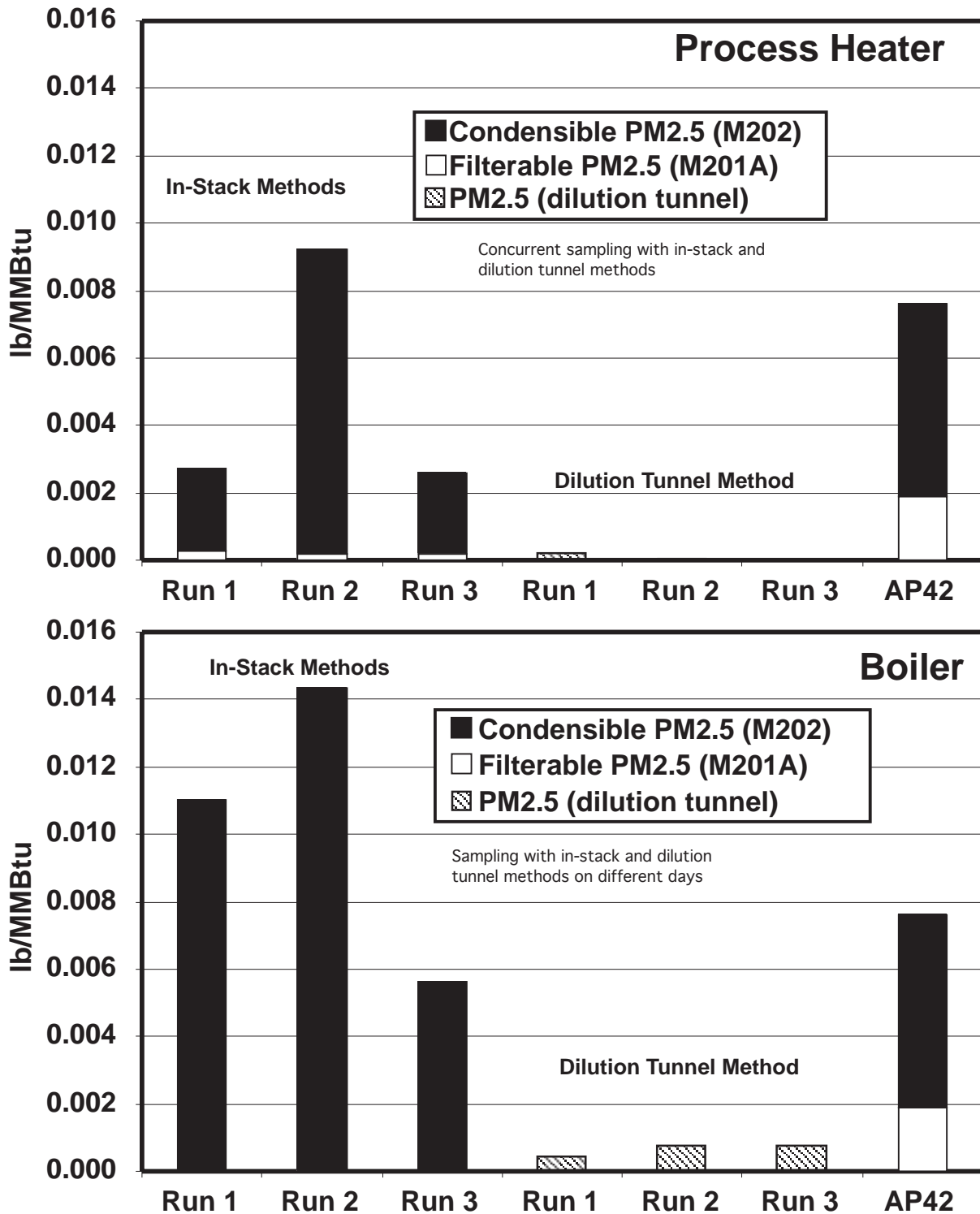


Figure 5. Overview of organic aerosol/PM_{2.5} measurement protocol.



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Figure 6. Dilution sampling system for measuring fine particulate emissions from stationary combustion sources.



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Figure 7. Comparison of PM2.5 emission rate measured using in-stack and dilution tunnel methods¹⁵.