

PM2.5 EMISSION CHARACTERIZATION FOR STATIONARY SOURCE GAS COMBUSTION

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KEYWORDS: PM2.5, source characterization, emission factors

ABSTRACT

Reliable PM2.5 source apportionment will require accurate inventories of speciated emissions from stationary sources. Although gas combustion is typically thought of as a "clean" process, the enormous quantities of gas burned in boilers, process heaters, and engines could make even small emissions concentrations significant. This study shows that current methods for measuring emission factors and speciation profiles from gas fired sources may have significant artifacts leading to overestimation of emissions. Chemically speciated results using an improved test protocol for natural gas- and refinery gas-fired boilers and process heaters are presented.

INTRODUCTION

New ambient air standards for particles 2.5 μm or less in diameter, referred to collectively as PM2.5, will motivate regulators to identify and control emission sources contributing to ambient PM2.5. Sulfates, nitrates, and carbon (elemental and organic) dominate PM2.5 composition in most urban and many non-urban areas; ammonium and elements also are present^{1,2}. Combustion devices are believed to be the most significant source of PM2.5.

The majority of primary emissions from combustion is often found in the PM2.5 or smaller size range, especially for devices equipped with particulate emission control equipment and for clean burning fuels such as gas. The predominant gaseous precursors of secondary particulate sulfates and nitrates are: sulfur dioxide (SO_2) and sulfur trioxide (SO_3); oxides of nitrogen (NO and NO_2 , the sum of which is designated NO_x); and ammonia (NH_3). Secondary organic aerosols formed from volatile organic carbon compounds also may be very significant in some areas, especially during the summertime when photochemical activity is high³.

Methods for identifying sources of ambient PM2.5 employ modeling approaches, which range from simple to complex. The chemical "fingerprint" of a source's emissions can be used to apportion the contribution of regional sources to local ambient PM2.5 using chemical mass balance models, one example of such methods. These relate the chemical speciation profile of ambient air samples to sources based on speciation profiles for all sources in the modeled area. Reliable results require complete speciation profiles for every source⁴.

The quality of source emissions data which presently exist is often questionable because of: a lack of data for different process configurations to account for site-specific differences; data based on measurements using older, less sensitive or selective techniques; and/or incomplete profiles. 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 results^{2,5}.

GAS-FIRED COMBUSTION SOURCES

Combustion of gaseous fuels in steam boilers, process heaters, gas turbines and stationary reciprocating internal combustion engines accounts for a major fraction of fossil fuel combustion in the U.S. Most if not all petroleum refinery boilers and process heaters in the U.S. are gas fired. Petroleum refining is the most energy-intensive of the major energy-consuming industries in the U.S., consuming 3.3 Quads of energy in 1994⁶. The majority of this was accounted for by combustion of gaseous fuels. There is widespread use of reciprocating engines and steam generators in exploration and production activities. Many refineries are situated in or near areas where ambient PM2.5 levels are predicted to exceed the new NAAQS.

Based on 1982 data gathered in southern California, petroleum industry equipment is believed to be a minor source of carbonaceous aerosols in ambient fine particulate matter⁷. Organic compounds may be present in emissions from gas-fired sources as products of incomplete combustion. Organic aerosols in the atmosphere result from semivolatile organic compounds ($>\text{C}_{20}$) present in the source combustion products and atmospheric reaction of volatile organic compounds ($>\text{C}_7$) to form heavier, condensable organics⁸. Tests for "air toxics" conducted over the past ten years provide a partial database of volatile and semivolatile organic compound emissions for several classes of petroleum industry sources. Recent pilot-scale tests indicate that the yield of selected organic compounds from gas combustion is extremely low under operating conditions representative of good operating practice normally found throughout the industry⁹. Emissions of BTX (the sum of benzene, toluene and xylene), formaldehyde, and PAH (the sum of 16 polycyclic

aromatic hydrocarbons) derived from pilot scale tests of a single refinery heater burner and field tests of petroleum industry boilers and process heaters reveals a range of emissions typically near or below detection limits, even when the most sensitive test methods available are used. Compared to boilers and process heaters, stationary reciprocating internal combustion engines (RICE) have relatively high average PAH emission factors – on the order of 0.1 lb per million Btu of gas fired. PAH emissions from asphalt blowing are slightly lower than stationary RICE. PAH emission factors for refinery boilers, process heaters, gas turbines, and coke calciners are approximately an order of magnitude lower. While these types of data may provide a clue to sources of ambient aerosol precursors, the tests usually looked only for specific compounds deemed toxic or carcinogenic, ignoring many other organic compounds such as fuel fragments that may contribute to ambient organic aerosols.

Tests of industrial gas-fired boilers and gas turbines in which particulate emissions measurements included both the filterable and condensable particles show that the condensable fraction is significant, sometimes exceeding the filterable fraction¹⁰. The contribution of the condensable fraction is even more pronounced for oil-fired sources. For example, tests of distillate oil-fired industrial boilers showed condensable particulate matter amounted to several times the filterable particulate. A comparison of fine organic carbon emissions from an oil-fired industrial boiler showed total condensable organic aerosol was 7 to 16 times higher than the filterable organic fraction.

SOURCE CHARACTERIZATION TEST METHODS

Source characterization approaches for particulate matter fall into two general categories: source-level sampling and ambient-level sampling. 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 gas temperature, 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.

Source-Level Sampling

The most common approaches to source-level sampling for particulate employ an in-stack filter or a filter external to the stack and heated to a constant temperature (e.g., EPA Method 17 or Method 5).¹¹ Heating the filter avoids condensation of moisture and/or acid aerosols, depending on the temperature selected. These methods define primary particles that are filterable at the filter temperature.

Condensable particulate is frequently defined as the amount of material collected in a series of impingers in an ice bath downstream of an in-stack filter and includes both fine particles which pass through the filter and vapors which condense at the temperature of the gas leaving the impingers (typically 60-70°F).^{12, 13} Impinger methods for condensable particulate are subject to substantial artifacts¹⁴ that do not occur in atmospheric processes, especially when ammonia, sulfates and/or chlorides are present in the exhaust, and thus may not provide an accurate measure of primary condensable particles.

PM₁₀ and PM_{2.5} are commonly measured using in-stack cyclones or cascade impactors^{13, 15}, or occasionally using heated out-of-stack cyclones.¹⁶ While these methods may provide regulatory agencies a means of enforcing emission limits defined using the same methods on a specific type of source, they may not be generally applicable to all source types and may be biased high or low due to interferences and artifacts. Further, the methods may allow subtraction of sulfate or chloride captured in the impingers as a matter of policy, which may not be appropriate when conducting source apportionment studies for PM_{2.5}.

Source-level measurement methods also exist for secondary particle precursors. NO_x and SO₂ emissions can be characterized using continuous gas analyzer systems. SO₂ 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 mist¹⁷. 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 using a sorbent trap, which strips organics from the gas onto the sorbent. The sorbent is subsequently analyzed by thermal desorption of the organic compounds into a gas chromatograph/mass spectrometer system for quantification and speciation.

Dilution Sampling

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 at least one major advantage over source-level sampling in that results are directly comparable to ambient air measurements. If the dilution is performed in a manner which simulates conditions in the exhaust plume, then particles which form in the plume are represented in the sample. 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 temperature, high moisture content, higher pollutant concentrations and interfering major

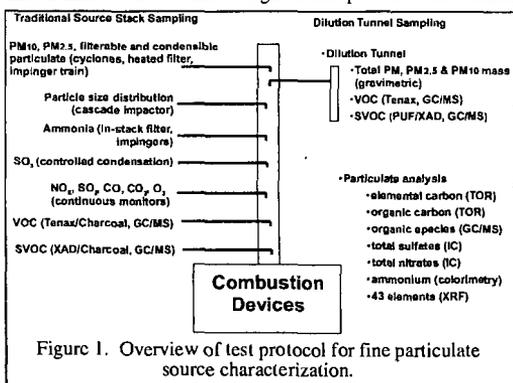
and minor gases are not necessary. Because of the comparatively low temperature of ambient air and diluted source samples, a greater range of sampling media such as Nylon and Teflon membrane filters can be used. This simplifies and extends the range of chemical speciation measurements.

Dynamic dilution samplers for stationary source studies draw a hot exhaust gas sample continuously into a chamber where it is mixed with a continuous flow of conditioned ambient air or pure inert gas. The diluted sample is then drawn through multiple filters, sorbents or denuders, which strip particles and/or selected gases from the sample. These are then taken to an analytical laboratory for analysis.

Hildemann et al.¹⁸ introduced a dilution sampler designed specifically for characterizing organic aerosols at 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 organic 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 others¹⁹ to generate detailed organic aerosol speciation data for several types of sources.

TEST APPROACH

Tests were performed on a gas-fired boiler and a gas-fired process heater in refineries. Both units were fired on refinery process gas. Both in-stack and dilution tunnel methods were included in the test matrix (Figure 1). The dilution tunnel used in these tests follows the Hildemann design discussed above. The diluted sample was passed through various collection media as illustrated in the figure. Volatile organic compounds were collected on Tenax sorbent, and analyzed by gas chromatographic separation and flame ionization detection of individual hydrocarbons for peak quantification, and/or combined mass spectrometric/Fourier transform infrared detection for peak identification. Semivolatile organic compounds were collected on quartz filters followed by



polyurethane foam (XAD-4 sorbent, which were extracted and analyzed by electron impact gas chromatography/mass spectrometry, using Fourier transform infrared detection, mass selective detection, and multiple ion detection for compound identification and quantification. Elements were determined on Teflon membrane filters by energy dispersive 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 condensable particulate was performed concurrently and co-located with dilution tunnel sampling, providing a direct comparison between the results obtained with the two approaches. PM_{2.5} precursor measurements during the gas-fired unit tests included SO₂, NO_x and volatile organic compounds. In a separate test of a fluid catalytic cracking unit not reported here, particle size distribution was measured using *in situ* cascade impactors and PM_{2.5} precursor measurements also included SO₂ and NH₃.

The tests demonstrated that the dilution tunnel approach could be successfully applied to stationary industrial sources. One of the practical challenges to the tests was limited space on the stack sampling platform for placement of the dilution tunnel and ancillary equipment. These sites were selected in part due to the relatively generous sampling platforms available (a half-circle platform with two sample ports at the boiler site, and a full-circle platform with four sampling ports at the process heater site). However, there are many gas-fired sites where such generous access is not available since stack sampling of gas-fired sources is not universally required. Because of the limited space on the boiler site's platform, the dilution tunnel tests and in-stack method tests could not be performed concurrently; instead, they were performed on different days. Process operating data indicated similar process conditions during all tests. Better access was available at the process heater site, so these tests were performed concurrently. Each test run at both sites was six hours in duration, with a total of three runs for each measurement. In addition to stack samples, a single ambient air sample was collected near the combustion air inlets at each site for comparison.

PRELIMINARY COMPARISON OF IN-STOCK AND DILUTION TUNNEL RESULTS

The amount of filterable particulate collected using the in-stack methods was essentially near or below the overall method detection limit (Figure 2). However, condensable particulate matter (CPM) as defined by EPA Method 202 was measured at much higher levels. Analysis of the impinger contents from the boiler test suggests a large fraction of the measured CPM can be accounted for in sulfates and chlorides (Figure 3); however, the mass of sulfates based on the impingers is much greater than that based on the dilution tunnel filters. It is believed the impinger results may be biased high due to dissolved SO_2 in the impingers. Due to differences in the fuel gas sulfur content, SO_2 concentration at the boiler site was approximately 8 ppm, while SO_2 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 PM2.5 mass obtained with the dilution tunnel was much lower than the total filterable matter plus CPM mass obtained with the in-stack methods. The dilution tunnel should capture all of the filterable matter plus any aerosols that 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 results are significantly biased. 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.

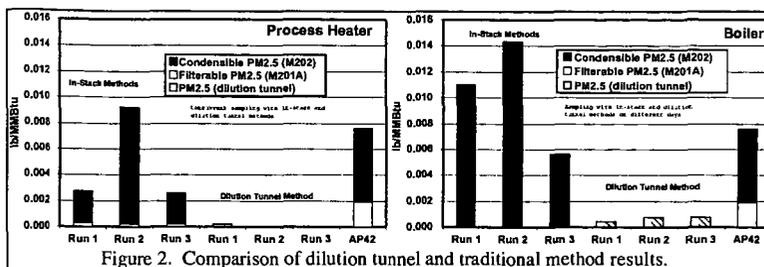


Figure 2. Comparison of dilution tunnel and traditional method results.

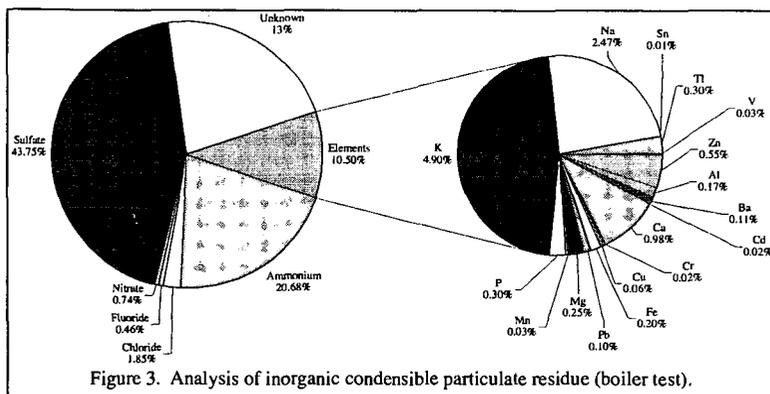


Figure 3. Analysis of inorganic condensable particulate residue (boiler test).

SUMMARY

The sampling methodology described in this paper should result in an improved characterization of source contributions to ambient PM2.5, especially for sources with low particulate concentrations. The test results suggest that traditional source testing methods may significantly overestimate particulate emissions, especially the ultrafine condensable particle fraction. This may be due to analytical method artifacts associated with application of methods designed for much higher particle concentrations. Since particle condensation mechanisms are dependent on both vapor concentration and temperature, dilution tunnel methods provide conditions that more closely represent true atmospheric condensation conditions compared to impinger condensation methods.

ACKNOWLEDGEMENT

The authors wish to acknowledge the contributions of the test personnel, especially Robert Zimmerman and Stephanie Wien of GE-EER, and the staff of the host facilities who graciously allowed us access to the units for testing. The authors gratefully acknowledge the American Petroleum Institute, the U. S. Department of Energy, and the Gas Research Institute for co-funding this work.

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