



Project Summary

Development of Sampling Methodology for Dilution Air Sampling of Condensible Emissions from Stationary Sources

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This report describes the initial development of a technique using dilution of stack gas with conditioned ambient air for measurement of the particulate mass of condensible emissions from stationary sources. The methodology developed is designed for widespread application to measure emissions which are in the vapor phase at temperatures greater than that of the Method 5 filter and which immediately condense to the particulate phase upon mixing in a temperature controlled chamber with air that has been cooled, dried, and filtered.

The front half of the condensibles air dilution train (CADT) is a Method 5 probe and filter. The portion of the train for collection of condensibles (back half) includes a dilution air injection cone and a mixing chamber followed by a separate filter for condensibles. The temperature selected for the filter for condensibles is 20°C, and the dilution factor is 15:1 on a volume basis, high enough to prevent condensation of moisture.

The filter for condensibles is desiccated for 24 h in a Teflon envelope before weighing. This limits the evaporative loss of substances condensed during sampling. For sources where H_2SO_4 is present, a procedure was selected for correcting the weight for moisture retained by H_2SO_4 .

The selected protocol was tested in the field at a site with predominantly organic condensible emissions. The CADT was operated simultaneously and collocated with Method 5 trains which used another protocol, the impinger approach, for condensible emissions.

The mass of condensible emissions measured by the CADT ranged from 25.2 to 27.6 mg/dscm. The average difference between the two approaches was 2%. The standard deviation of the differences was 15%. The precision of the dilution approach (standard deviation of replicate sampling runs) was estimated to be 15%.

This Project Summary was developed by EPA's Atmospheric Research and Exposure Assessment Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The PM_{10} ambient air particulate standard has created a need for measurement methods for PM_{10} emissions (particulate matter of nominally 10- μm aerodynamic diameter and smaller) from stationary sources. Previously, techniques have been developed for measurement of PM_{10} emissions present at process stack conditions. Some emissions in the vapor phase at stack conditions are converted to the condensed phase immediately upon discharge into ambient air. Substances condensed in stationary source emissions are believed to be primarily incorporated with particles less than 10 μm in diameter. Because of the emphasis on PM_{10} , the need for a practical and precise source test method for the condensible component of emissions has become important.

The term condensibles is used to refer to materials in the vapor phase at stack condi-



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tions which immediately convert to and persist in the solid or liquid phase when sampled with the source test methodology. This particulate matter and that sampled at stack conditions are referred to as "primary" particulate emissions. This portion of the ambient particulate burden is distinguished from "secondary" particulate emissions, which are the results of slower reactions, such as conversion of SO_2 to sulfates and photochemical formation of organic smogs.

Based upon a literature review of current approaches for such source measurements, two approaches were recommended for research and development. One recommended approach was dilution cooling of extracted process exhaust gas with conditioned ambient air. The other was use of the Method 5 back half (impinger catch) with standardized procedures for recovery of condensibles. It was pointed out that for the definition of condensibles to be precise (i.e., for a consistent definition of emission rates of condensible material from the source), conditions, including the sampling temperature at which the sample is obtained, must be within specified limits. Sampling conditions should be independent of the local ambient conditions at the time of the sampling because, as they vary, these local conditions may cause varying amounts of condensation. Examples of local conditions which vary include background pollutant levels, adsorption or absorption processes, and meteorological variables, all of which may contribute to the actual amount of stack emissions converted from the vapor to particulate phase at any given time. Specific source sampling conditions and hardware for measurement of condensibles were selected for the practical and theoretical aspects described in this report. Therefore, condensible emissions are defined only in terms of the recommended sampling methodology.

This report describes the initial development effort for measurement of condensible emissions by air dilution. Selection of specific procedures for widespread use with emphasis on measurement of the mass of condensible emissions from stationary sources was the major goal of this project.

Development Approach

Sampling Hardware and Sampling Procedure

The condensibles air dilution train (CADT), fabricated and assembled for testing in the field, includes the front half of a Method 5 train, nozzle, probe, and filter. Measurements with the CADT provide values for condensibles relative to current values obtained with Method 5. The condensibles

portion of the train includes a heated sample orifice meter, dilution air injection cone and mixing chamber, and the filter for condensibles. The sample orifice meter is heated to prevent cooling of the sample gas prior to entering the dilution air injection cone.

The sample orifice meter serves the same purpose as that used in Method 5, the monitoring of sample flow rate required to maintain isokinetic sampling. In addition, it serves the purpose of the dry gas meter in Method 5; the total sample gas volume is measured at this point, before dilution of the sample. This is accomplished with digital electronic integration of the square root of the signal from a differential pressure transducer. The operator enters a scale factor calculated directly from the usual sample and ambient gas parameters and orifice ΔH_0 to provide digital readout of flow rate and accumulated sample volume. The front half of the CADT is operated by the same protocol as Method 5. Alternately, it is designed to be operated according to the constant sampling rate (CSR) procedure for PM_{10} .

The selected temperature at which the condensibles filter is to be maintained is 20°C and the selected dilution factor is 15:1 on a volume basis (corresponding to near 20 on a mass basis). The dilution factor was chosen to be high enough to avoid condensation of water while limiting the size of the train components for practical use. The diluter was based on a 50% scaleup of one developed previously to provide high turbulence and uniform mixing. The mixing chamber was sized to provide a residence time of approximately 2 s.

The dilution air consists of ambient air conditioned by cooling in an ice bath condenser and filtering. The temperature of the dilution air must be controlled at a temperature low enough to obtain the desired temperature (20°C) of the combined sample and dilution gas. During sampling the flow rate of the dilution air is varied with the sample flow rate to maintain the volume dilution factor, including changes of the absolute pressure in the diluter due to increase of the differential pressure across the Method 5 filter.

Exploratory Laboratory Measurements for Analytical Procedures

It is expected that sampling for condensibles will provide particulate samples with significant differences from those addressed by Method 5 analytical procedures; in particular, the volatility of condensible samples will be higher. Difficulties in obtaining satisfactory sample

weights due to substantial variations have been attributed to evaporation of substances collected during sampling runs and to adsorption or absorption of water by hygroscopic substances such as condensed sulfuric acid. It is relevant that desiccation to minimize the contribution of adsorbed or absorbed water may lead to the removal of a proportionately larger mass of other condensed substances than is experienced with Method 5 samples.

Laboratory measurements of simulated filter samples were performed to define procedures for determining weights of samples of condensibles. Measurements were performed to evaluate the rate of desiccating water in presence of other substances from quartz filters, which were chosen as the media for collecting condensible samples.

Field Evaluation

The first field test of the condensibles air dilution train was performed at the stack of a wood chip dryer used in the production of particleboard. The particulate control device on this source is an electrically augmented gravel bed filter. This stack was chosen because it was expected to have predominately organic emissions. The CADT was operated simultaneously and collocated with multiple Method 5 trains operated by another procedure, the impinger approach, for condensible emissions.

Results

The common analytical procedure of desiccating to remove adsorbed or absorbed moisture and weighing for determination of sample mass was selected. The rate of evaporation of substances condensed during sampling and absorption or adsorption of moisture during weighing was controlled by keeping the condensible filter in a Teflon envelope. The specified time of 24 h for desiccation of the condensibles sample provided adequate evaporation of moisture but limited evaporation of test substances which were used to simulate stack condensible emissions.

Measurements with solutions of sulfuric acid indicated that the rate of evaporation of water was sufficient for drying in 24 h at which time the mass ratio of $\text{H}_2\text{O}/\text{H}_2\text{SO}_4$ approached that for water of hydration causing the evaporation rate to become very small. For samples containing 10 to 60 mg of H_2SO_4 , the ratio of $\text{H}_2\text{O}/\text{H}_2\text{SO}_4$ after 24 h of desiccation was found to be in the range of 27 to 43%. For sources where H_2SO_4 is present, the analytical determination of the mass of H_2SO_4 by extraction and titration can be used to obtain a correction for

moisture retained by H_2SO_4 after desiccating the sample for 24 h.

In the field test the condensible emissions measured using the dilution approach ranged from 25.2 to 27.6 mg/dscm in five sampling runs performed over three days. On average the two approaches agreed; the results from the dilution air approach were 2% lower than the results from the impinger approach. The standard deviation of the difference was 15%. The precision of the impinger approach in this field test was 3%, expressed as standard deviation of replicate runs. The estimated precision of the dilution approach was 15% in this field test. Blank runs following the protocol for the dilution approach indicate that 5% of this variation of the dilution approach was the result of errors associated with loading and unloading filters.

Conclusions and Recommendations

In the initial phase of development of the dilution air approach for measurement of condensibles, a sampling train was designed and fabricated. Procedural details were identified from analysis of the fundamental nature of the dilution approach. Laboratory studies of desiccation of simulated condensible samples were conducted, and

the train and procedures were evaluated in a field test. The results of the field test at a site with predominantly organic condensible substances gave reasonable results. The close agreement with the impinger approach and the fundamental differences in the two approaches suggest that condensible emissions for the site tested were composed of particulate matter that is not subject to subtle changes.

The laboratory investigation of sample analytical procedures for mass determination indicated that some materials may evaporate significantly during desiccation of the sample to remove adsorbed or absorbed water which is in excess of combined water or water of hydration in the following formula $\text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$. However, these are limited to substances with volatility or equilibrium vapor concentrations greater than or comparable to that of water. Also, it was concluded that for excluding water of hydration from the measured sample mass, the most appropriate method was a moderate correction for sample mass determined gravimetrically based on the amount of H_2SO_4 found through titration. EPA is considering condensible methodology named the impinger catch (IC) approach in which water of hydration in addition to H_2SO_4 will be included as condensible emissions. If the IC approach is adopted, then inclusion

of water of hydration as condensibles will likely become a part of the gas dilution methodology. This would eliminate the titration step from the gas dilution procedures.

It is recommended that further testing be performed at other sources, particularly a source expected to emit sulfates for the next test. Extended laboratory measurements are recommended to determine if the recommended correction for water retained by H_2SO_4 after 24 h of desiccation is accurate for higher levels of initial water vapor concentration. In addition, although other hygroscopic substances which may be present in condensibles are expected to retain substantially less water than H_2SO_4 , measurements should be performed to quantify their retention of water under the conditions adopted in the procedures.

Multiple filter holders should be fabricated so that condensibles filters are loaded and unloaded in the laboratory rather than at the sampling site to minimize errors due to handling. Some modifications of the condensibles air dilution train (CADT) are recommended. Improved thermal insulation of the heated sample orifice meter is needed to better maintain the condensibles filter at the adopted reference temperature, 20°C. In addition, improved mobility is needed for traversing.

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*The complete report, entitled "Development of Sampling Methodology for Dilution Air
Sampling of Condensable Emissions from Stationary Sources," (Order No. PB91-
129 742/AS; Cost: \$15.00, cost subject to change) will be available only from:*

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