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LABORATORY AND FIELD EVALUATION OF THE EPA METHOD 5 IMPINGER CATCH FOR MEASURING CONDENSIBLE MATTER FROM STATIONARY SOURCES

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On Friday, April 8, 1988, the EPA announced that it plans to propose a method for measuring PM_{10} emissions. The method will be proposed for inclusion in Appendix M of 40 CFR Part 51. Since all condensible emissions inherently form very fine particles in the PM_{10} size range and are considered PM_{10} emissions, a companion discussion in the Federal Register addressed three possible approaches for the measurement of condensible emissions. This paper presents the results of a laboratory study and field evaluation commissioned by the EPA, Emission Measurement Branch to evaluate the impinger approach. This approach collects the sample in impingers or condensers at ice bath temperatures, separates the sample into organic and inorganic fractions, and then evaporates the sample to dryness before weighing the residue. Specifically, the paper presents results for: a comparison of solvents currently specified by State and local air pollution control agencies in their methods for extraction of condensible organic material; an evaluation of solid sorbents for removal of condensible organic material; an evaluation of nitrogen purging for the removal of the sulfur dioxide collected with the sample; an examination of the composition of condensible matter collected in impingers (sulfate, sulfite, chloride, and nitrate content); and additional sample preparation procedures to remove other unwanted constituents.

Introduction

As stated in the Federal Register[1] on Friday, April 8, 1988, the U. S. Environmental Protection Agency (EPA) plans to propose a method for measuring PM_{10} emissions. The method will be proposed for inclusion in Appendix M of 40 CFR Part 51. All condensible emissions inherently form very fine particles in the PM_{10} size range and are therefore considered as PM_{10} emissions. The condensible matter described is primary condensible matter which is material that is a gas or vapor at the sampling location stack temperature and transforms into a liquid or solid immediately after leaving the sampling location to within a few seconds after it leaves the stack or duct.[2]

The approach for measurement of condensible particulate matter (PM_c) discussed in the Federal Register and the topic of this paper is the use of the Method 5 impinger catch. An advantage of the "impinger approach" is that it would allow the determination of both filterable emissions and condensible emissions simultaneously using the existing methodology and equipment. Additionally, this approach would provide the option to make compliance determinations regarding filterable particulate emissions while gathering data to develop a supporting data base for future condensible emission regulations.

The impinger approach involves use of impingers or condensers at ice bath temperatures for sample collection. For analysis, the impinger/condenser solution is extracted to separate the organic fraction from the inorganic fraction, both fractions are taken to dryness (organic fraction at ambient temperature and inorganic fraction at 105°C), and the residues are weighed to determine the amounts of organic and inorganic condensible matter. A disadvantage to this approach is that noncondensible gases may react with other gases or condensibles in the impinger solution to form PM_c that would not have otherwise formed (artifacts). A nitrogen purge of the impinger solution immediately after the test run had previously been suggested to aid in minimizing the amount of reaction products. The effectiveness of this procedure has been documented in this study.

The Emission Measurement Branch of EPA's Office of Air Quality Planning and Standards sponsored the study described herein to evaluate the impinger approach in the laboratory and the field. The principal objective of this work was to provide the required documentation to propose one or more methods for the measurement of condensible emissions. This study focused on two areas: (1) the impinger method which is currently used by State agencies to determine condensible particulate emissions, and (2) eliminating measurement of artifacts collected by the impingers. The major criteria for evaluating the sampling and analytical protocol were (1) precision and accuracy, (2) compatability with current sampling and analytical equipment, and (3) cost effectiveness.

Laboratory Evaluation

The laboratory evaluation conducted to develop a candidate protocol focused on (1) identifying the strengths and weaknesses of the condensible emission measurement methods already developed by state and local agencies and (2) eliminating the measurement of PM_c formed from noncondensible gases (artifacts). Based on the state methods, the laboratory analyses were partitioned to examine the determination of the organic condensible particulate matter and the determination of the inorganic condensible particulate matter.

The organic fraction extraction must remove all organic matter that would be boiled off during the drying phase (at 105°C) of the inorganic fraction. The initial evaluation of the organic extraction was conducted on aliquots of two impinger samples (from a coal-fired boiler and a wood-fired boiler) at three pH's (pH of actual sample, pH of 2, and a pH of 12). Each aliquot was extracted four times with the respective organic extractant and the individual extraction weights determined. The results for the extractions conducted at the pH of the sample showed that the extraction with methylene chloride or ether-chloroform, or the use of a C_{18} sorbent all remove a similar amount of organic matter from both samples (1.6, 1.9, and 1.3 mg from the coal-fired boiler sample and 16.0, 15.5, and 15.6 mg from the wood-fired boiler sample, respectively). The amount of organic matter extracted using freon was significantly less for the wood-fired boiler sample (2.0 mg). For each aliquot, the inorganic fraction was taken to dryness and the totals for condensible matter (organic plus inorganic) were similar for all methods of extraction (183, 175, 172, and 179 mg for the coal-fired boiler sample and 46.9, 44.8, 49.2 and 45.4 mg for the wood-fired boiler sample, respectively). The pH of the coal-fired boiler sample was approximately 2.5 and was 4 for the wood-fired boiler sample.

Separate aliquots from each sample were adjusted to a pH of 2 and then extracted. The organic results for the samples extracted at a pH of 2 were similar to those extracted at the actual sample pH for all organic extractants. The pH of the remaining inorganic fractions of these aliquots were readjusted to pH 12 and then reextracted with each solvent. At a pH of 12, approximately 25% more organics were extracted. For both the coal-fired and wood-fired boiler samples, the third and fourth extractions at each pH using each solvent removed significantly (greater than 10%) more organics. However, total condensible matter results indicate that the organic matter not removed by the solvent or the C_{18} cartridge is probably not removed at 105°C.

Since it was later found that the inorganic artifacts could be removed from the impinger sample and the pH adjustment does not affect the total condensible matter measured in the organic plus the inorganic fractions, no further evaluations were conducted with the organic fraction.

In determining the inorganic matter collected in the impinger solution, it was important (1) to eliminate the effect of SO_2 in the stack gas dissolving to form a mixture of bisulfates and sulfites ($SO_3^=$) which can react to form sulfate ($SO_4^=$) and collecting in the impinger solution and (2) to develop an analytical method for determining the amount of inorganic condensible particulate in the impinger solution after removal of the organic matter. The inorganic fractions of 10 impinger samples were bubbled with 200 ppm SO_2 cylinder gas for 2 h and then were purged with nitrogen gas. The purge gas stream exiting the sample was monitored during the purge using a calibrated continuous SO_2 gas analyzer. Aliquots of each sample taken before the addition of SO_2, before the nitrogen purge, and after the nitrogen purge were analyzed by ion chromatography (IC) for $SO_3^=$ and $SO_4^=$. Eight samples were similarly treated except that an air purge was used. Based on these experiments, it was determined that the SO_2 in the stack gas would form $SO_3^=$ in the impinger solution during sampling; and only later, over a period of several days, does the $SO_3^=$ convert to $SO_4^=$. By SO_2 monitoring of the nitrogen purge, it was found that a rate of 20 lpm for 60 minutes is effective in removing all the SO_2. Purging with air proved unsatisfactory for samples with a pH greater than 3.

Since the sulfuric acid collected in the impingers cannot be accurately weighed as a condensible due to its interaction with water (hygroscopic), many state methods require addition of ammonium hydroxide (NH_4OH) to the impinger solution which binds with the sulfate ion in the acid to form ammonium sulfate (NH_4SO_4). There are two potential problems with this approach. One is that other acid gases which are not primary condensibles may react with the ammonia to form PM. The other is that the ammonia added to the sample must be subtracted from the final weight since it is not part of the original sample.

NH_4OH was added to the inorganic fraction of a number of impinger samples. One set of samples were analyzed for chlorides (Cl^-) by IC before and after this addition. The IC analysis of the fractions with NH_4OH added showed that the ammonium ion reacts with the Cl^- in the sample to form NH_4Cl and, as a result, HCl would be measured as condensible matter. Since HCl is not considered primary condensible matter, no Cl^- should be included in the final weight. To resolve this problem, the analytical protocol was modified. Various impinger samples were initially taken to dryness, the residues redissolved, and then NH_4OH was added. Aliquots were analyzed for Cl^- before and after drying and after the NH_4OH addition. This approach consistently eliminated the Cl^- (during drying) and yielded a stable sulfate that could be accurately weighed.

To correct for the additional weight due to ammonia, state agency methods usually determine the ammonia added to the samples by analyzing the sample for $SO_4^=$ by IC and then calculating the stochiometric weight of ammonia bound to this ion. Acidometric titration was examined as an alternative technique for this determination. Aliquots of the inorganic sample fraction were titrated with 0.1 N NH_4OH to a pH of 7.0 using a pH meter and using bromothymol blue as the endpoint indicator. The $SO_4^=$ in these aliquots was then analyzed by IC and the ammonia was calculated using the two titrations and the IC analysis. Both titration techniques proved comparable to the IC analysis.

Based on the work described above, a draft protocol was developed for measurement of condensible particulate emissions using the Method 5 impinger catch. This protocol was evaluated in the field test programs described in the following section.

Field Evaluation

The field evaluation test results were used principally to (1) determine the effect of a posttest nitrogen purge for removing dissolved SO_2, (2) determine the precision (standard deviation) of the sampling and analytical protocol, (3) evaluate the effectiveness of heating to remove chlorides, (4) compare the $SO_4^=$ content of the inorganic fraction as determined by IC versus NH_4OH titration, and (5) determine the effect of a posttest nitrogen purge on the removal of organic matter.

The evaluation testing was performed at a coal-fired boiler and a wood-fired boiler using five quadruplicate train (quad-train) runs during each test. To evaluate the effect of the posttest nitrogen purge, two of the trains from the first two quad-train runs did not undergo a posttest purge; the other two trains had the posttest nitrogen purge conducted. To evaluate the precision of the sampling and analytical protocol, all four trains in the last three quad-train runs were subjected to a posttest purge. All five quad-train runs were about 2 h in duration. Aliquots of each sample were taken for IC analysis of $SO_4^=$, $SO_3^=$, Cl^-, and NO_3^- prior to extraction, prior to titration of the inorganic fraction, and after the gravimetric analysis of the inorganic fraction. The emissions sampled from the coal-fired boiler contained mostly inorganic condensibles and those from the wood-fired boiler contained mostly organic condensibles.

During the first field test, the coal-fired boiler was burning a 2% sulfur coal. The controlled emissions were sampled using the draft condensible protocol at a location following the fabric filter. At the wood-fired boiler, sampling of the controlled emissions using the draft protocol was conducted at a location following an electrified fabric filter.

The $SO_4^=$ concentration in the purged coal-fired boiler samples was compared to that in the corresponding unpurged quad-train samples using a Student's t test and the null hypothesis. A significant difference was found at the 95% confidence level. The $SO_4^=$ concentration in the unpurged samples from Runs 1 and 2 were 340% and 180% higher than the average $SO_4^=$ level of 2 mg/m^3 in the purged samples. The sulfate condentration was near the limit of detection for the wood-fired boiler samples (< 0.07 mg/m^3). These results coupled with the laboratory evaluations demonstrate that the use of the nitrogen purge satisfactory removes the dissolved SO_2 collected in the impinger liquid. The results for the unpurged samples for the coal-fired boiler were not used for the determination of precision, because the inorganic fraction (sulfate) was shown to be significantly different. The standard deviation for the sampling and analytical protocol averaged 1.1 mg/m^3 for an average stack concentration of 3.5 mg/m^3 at the coal-fired boiler and 2.1 mg/m^3 for an average stack concentration of 13.0 mg/m^3 at the wood-fired boiler.

Based on the IC analysis of sample aliquots taken at various stages in the sample preparation process, the Cl^- concentration (not a condensible particulate species) of the coal-fired boiler samples was reduced from a level of about 100 mg/m^3 to a level of about 0.02 mg/m^3 by drying the sample at 105°C prior to the addition of NH_4OH. These results were also supported by the laboratory results, which showed that the majority of the HCl collected can be removed by taking the inorganic sample fraction to dryness prior to the addition of NH_4OH.

Without removal of the dissolved SO_2 by purging and the HCl by drying, the weight of the condensibles for the boiler sample would have been about 120 mg/m^3 instead of the actual weight of about 4 mg/m^3.

Since the results for total condensibles were much lower than had been anticipated, comparison of the IC results to the gravimetric determinations discussed below was not as close as had been expected.

The IC analysis and titration techniques for ammonia determination did not agree as well as they had in the laboratory evaluation. The average calculated ammonia values for the coal-fired boiler samples were 0.95 mg/m^3 by IC, 0.67 mg/m^3 by titration using an endpoint indicator, and 0.41 mg/m^3 by titration using a pH meter. For the wood-fired boiler, the values were 0.03 mg/m^3 by IC and 0.11 mg/m^3 by titration. These differences are not as significant when compared to the typical particulate concentration levels for a compliance determination of about 30 to 50 mg/m^3. An additional evaluation test at a source with high sulfate levels would provide a more accurate comparison.

To determine if the nitrogen purge was removing any of the organic matter, the organic condensible results were compared for the purged and unpurged sample pairs in quad-train Runs 1 and 2 in both field evaluations using a Student's t test and the null hypothesis. The t tests indicated that the organic values for the purged and unpurged samples were equivalent at the 95% confidence levels. Therefore, the nitrogen purge did not effect (or purge out) the organic condensibles.

Conclusions and Recommendations

The results of the laboratory and field evaluations lead to several conclusions/recommendations.

1. A nitrogen purge should be conducted at the rate of 20 lpm for 60 minutes at the end of a test run when SO_2 is present in the flue gas. An air purge is not recommended.

2. The sample should be dried at 105°C prior to the addition of NH_4OH. If this procedure is followed, the sample may be analyzed for Cl^- following the final weight determination, which is subtracted from the final weight and reported as secondary condensible matter.

3. The weight of ammonia added to the sample may be determined by (1) using the IC analysis for $SO_4^=$ according to EPA Method 5F or (2) titrating the sample to a pH of 7.0 using 0.1 N NH_4OH and a pH meter.

4. Extract the organic matter from the aqueous impinger contents using methylene chloride. The use of ether-chloroform would also be acceptable.

5. When the determination of condensible matter includes both organic and inorganic fractions, the pH of the sample need not be adjusted prior to extraction, and the extraction should be repeated three times.

This method applies to the determination of particulate emissions, from stationary sources, which condense between 120°C (the standard solid particulate matter filter temperature) and 0°C (the temperature of the impinger ice bath). Collection of particulate samples is conducted according to EPA Method 5 followed by a gaseous nitrogen purge of the impinger contents. Analysis of the organic and inorganic fractions of the impinger contents allows determination of emissions which condense at temperatures below the filter temperature.

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