Description of a Pseudo-Particulate Formation Mechanism in New EPA Method 202

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Introduction

The recent modifications promulgated by EPA to the Method 202 sampling system were thought to resolve most if not all of the significant limitations of "old" Method 202. These modifications, shown in Figure 5, include the re-design of the sampling system to include a glass-coil (modified Graham) condenser, two dry impingers, and an unheated condensable particulate matter (CPM) filter. The modifications were implemented in order to eliminate the significant CPM "artifacts" which often occurred in old Method 202.

In new Method 202, the CPM is collected in dry impingers after filterable particulate matter (FPM) has been collected on a filter maintained as specified in either Method 5, 17, or 201A. New Method 202 eliminates the use of water as the collection media in impingers and includes the addition of a condenser followed by a water dropout impinger immediately after the final in-stack or heated filter.

This article presents the results of a recently completely test program conducted on a coal-fired boiler using new Method 202, and discusses the potential for pseudo-CPM formation in the new method.

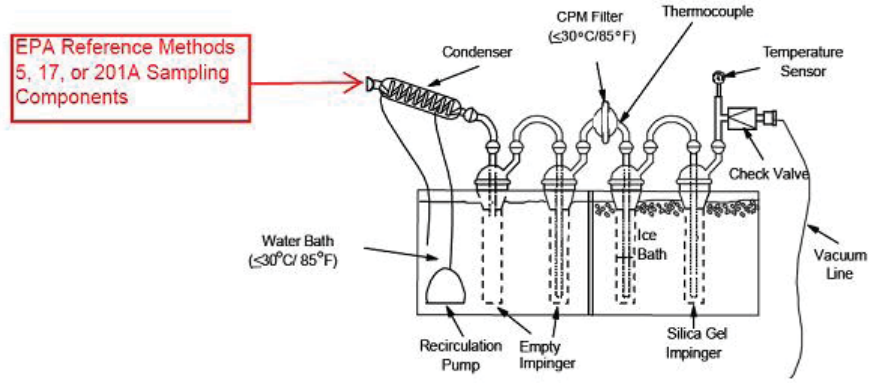

Figure 5. EPA Method 202 (New) Sampling System

Background on Old Method 202

Source emission testing experience since the promulgation of Method 202 in 1991 demonstrated that it was inappropriate to use water-filled impingers to cool the sample gas stream for CPM combustion sources having SO_2, NO_2 and/or soluble organic compound emissions. These gaseous contaminants can partially absorb in the impingers and chemically oxidize to form material counted as CPM in old Method 202. These artifact reaction products are not related to the primary emission of CPM from the source.

The potentially significant problems affecting the accuracy of old Method 202 included the following:

1. Dissolution of sulfur dioxide and nitrogen oxides into water with subsequent oxidation to form sulfates and nitrates in the impingers;
2. Dissolution of soluble organic compounds into water;
3. Penetration of submicrometer sized condensed particles through the impingers of the Method 202 sampling train;
4. Gas phase homogeneous reactions between ammonia and hydrogen chloride and/or between ammonia and sulfur dioxide in the cold, water-filled impingers.

Of these four sources of bias, the absorption and reaction of sulfur dioxide was most common. Since old Method 202 was originally promulgated, there was considerable concern that absorption of soluble sulfur dioxide and nitrogen dioxide and subsequent reactions of these dissolved gases occur within the aqueous phase in the impingers. These reactions

are important because these gases are considerably more soluble in cold liquids than in warm liquids. The 32°F to 68°F temperatures of the liquid in the impingers provide an ideal environment for the collection of soluble inorganic gases.

Description of the Unit Tested

For the purposes of this discussion, the boiler tested will be identified as Unit A. Unit A is a solid fuel-fired steam generating unit that utilizes circulating fluidized bed (CFB) boiler technology to burn low sulfur Powder River Basin (PRB) coals. Unit A has a nameplate rating of approximately 400 MMBtu/hr. The boiler was designed for a maximum continuous rating of 300,000 lb/hr of steam flow at a pressure of 150 psig, and temperature of 450°F. Unit A is equipped with an in-bed limestone sorbent injection system for the control of SO_2 emissions and to protect internal waterwall surfaces from sulfide corrosion. Nitrogen oxides (NOx) are controlled by the low inherent combustion temperatures with staged combustion. Additional NOx control is provided by a selective non-catalytic reduction (SNCR) system, which injects ammonia (NH_3) into the appropriate high temperature region of the furnace for conversion of NOx to N_2 and H_2O. Figure 6 shows a process diagram of Unit A.

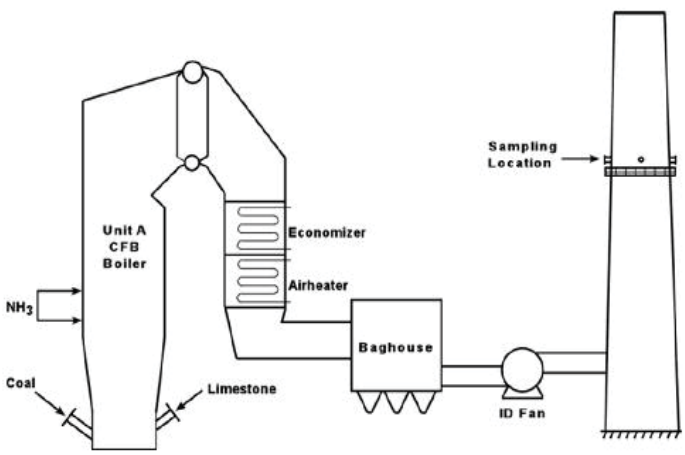

Figure 6. Process Diagram of Unit A

Description of Testing

CleanAir conducted compliance testing of Unit A in 2010. The compliance testing consisted of three (3) runs of EPA Method 5/202 for the determination of FPM/CPM, as well as simultaneous controlled condensation method (CCM) testing using CleanAir Method 8B (modified EPA CTM-013) for the determination of H_2SO_4. Unit A has operating permit limits for FPM, CPM, and H_2SO_4. All testing was conducted at the stack.

During the 2010 compliance testing of the Unit A, elevated condensable particulate matter (CPM) were detected in the back-half fraction of the EPA Method 5/202 sampling system. Utilizing ion chromatography (IC) analysis of the back-half fractions, it was determined that approximately 85% of the inorganic CPM consisted of ammonium sulfate compounds. These compounds were determined to be "artifacts" and should not be considered measured condensable material. This paper explains the formation mechanism for ammonium sulfate which is believed to have occurred in the Method 202 sampling system.

Discussion of the Pseudo CPM Formation Mechanism

The formation of the pseudo-particulate ammonium sulfate compounds which were found in the Method 202 "dry" impingers during the 2010 compliance testing of the Unit A boiler are the result of chemical reaction of dissolved sulfur dioxide (SO_2) and ammonia (NH_3).

This pseudo-particulate is the result of the dissolution (i.e. scrubbing) and subsequent reaction of flue gas SO_2 and ammonia NH_3 slip from the Unit A boiler selective non-catalytic reduction (SNCR) system which forms either ammonium bisulfate or ammonium sulfate according to the following reactions:

$$\mathbf{NH_3\ (gas) + SO_2\ (gas) + H_2O \rightarrow NH_4\ (liq) + HSO_3\ (liq) + time,\ O_2 \leftrightarrow (NH_4)HSO_4 \qquad (1)}$$

$$\mathbf{2NH_3\ (gas) + SO_2\ (gas) + H_2O\ (liq) \rightarrow NH_4\ (liq) + SO_3\ (liq) + time,\ O_2 \leftrightarrow (NH_4)_2SO_4 \qquad (2)}$$

Sulfur dioxide itself is a gas that readily dissolves in water. Once dissolved, it reacts with water to form new compounds called *sulfites*, according to the following reaction:

$$\mathbf{H_2O + SO_2 \leftrightarrow H+ + HSO_3^- \leftrightarrow 2H+ + SO_3^= \qquad (3)}$$

In solution with H_2O (water), SO_2 is called molecular SO_2, HSO_3^- is called bisulfite and $SO_3^=$ is called sulfite. The negative signs ($^-$ and $^=$) denote the negative charge of the bisulfite and sulfite ions (molecules with a charge are called ions). The double arrows (↔) of the equation denote that the reaction is at equilibrium.

Solubility of Ammonia and Sulfur Dioxide in Water

Many gases are soluble in water, particularly NH_3 and SO_2. The solubility of SO_2 and NH_3 in water are shown in

Figures 7 and 8, respectively.

New Method 202 requires that the dry impingers are operated at a temperature less than 85°F (29°C). In practicality, these impingers are typically operated in the temperature range of 60°F to 84°F (16°C to 29°C). This temperature range is below the dew point temperature of the flue gas. All gases have a dew point that is dependent on the temperature, pressure, fuel type and sulfur content. Below the dew point temperature, the gas/vapor will start to condense into liquid. The dew point temperature of a flue gas having a water vapor content of 17% vol. H_2O, such as the stack gas of the Unit A boiler, would be approximately 128°F (53°C).

Ammonia gas has a high affinity for water. As seen in Figure 8, its solubility in water at 68°F (20°C) is approximately 520 mg/g. The solubility of sulfur dioxide in water at 68°F (20°C) is approximately 120 mg/g. The presence of ammo-

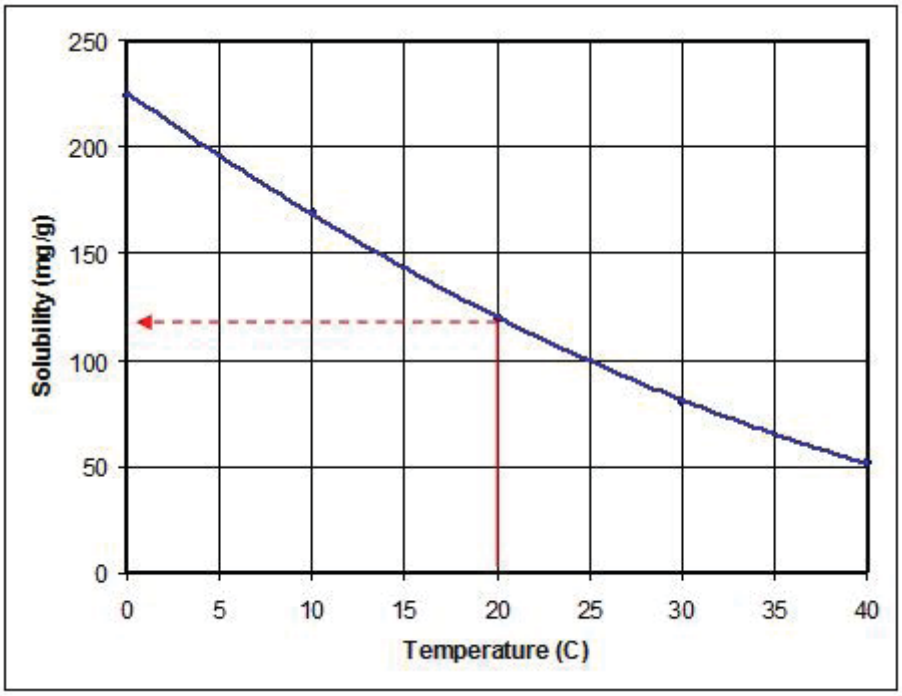

Figure 7.
Solubility of SO_2 in Water

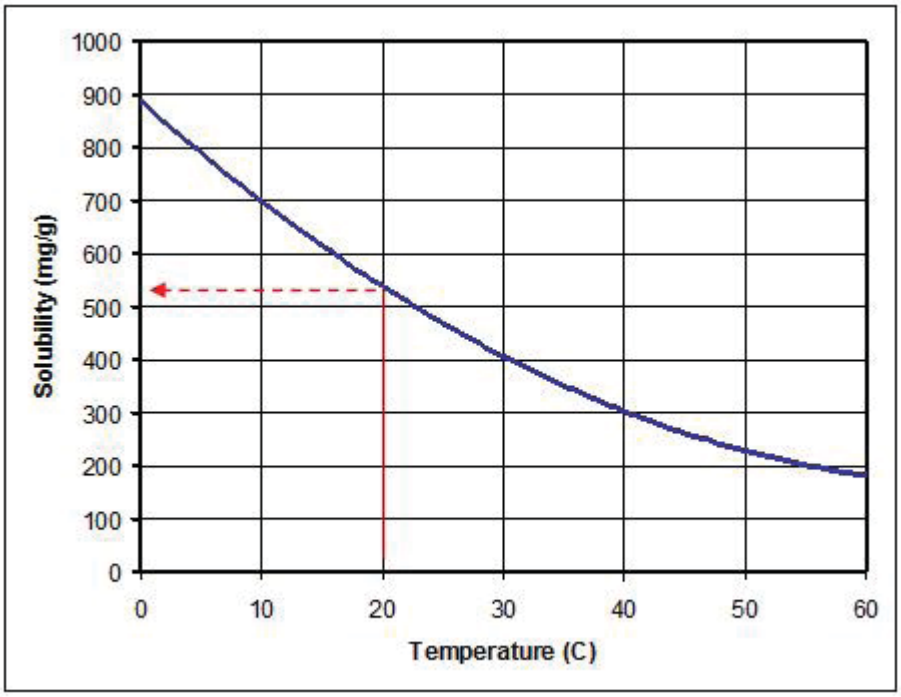

Figure 8.
Solubility of NH_3 in Water

nia in the gas stream enhances the solubility (absorption) of SO_2 – in the condensate. So much so that bubbling the gas through the liquid does not have to occur.

Ammonia, being extremely water soluble, will first absorb into the condensate elevating the pH. This slight elevation in pH will greatly enhance artifact generation through scrubbing of sulfur dioxide, forming various dissolved ammonium sulfate salts.

The excess ammonia is the chemical driving force, greatly increasing the solubility of SO_2. This is occurring in a thin film, without bubbling through the solution. This is due to ammonia's affinity for water, forming a basic solution that wants to attract and react with the acidic SO_2 gas.

Analytical Determination of Ammonium Sulfate and Correction of Inorganic Results

The post-test analysis of the inorganic CPM fraction of the Method 202 samples consisted of taking a 20-ml aliquot of the dry impinger liquid and associated rinse prior to the gravimetric analysis which includes the extraction and evaporation steps. This aliquot was analyzed for both anions and cations using Dionex ion chromatography (IC) in CleanAir's analytical laboratory. The only anions and cations identified by IC were sulfate ($SO_4^{=}$) and ammonium (NH_4^{+}), respectively.

Using the results from the IC analysis, it was determined that Run 1 had a stoichiometric excess of ammonium, and Runs 2-3 had an excess of sulfate. Equation 4 below was used to make this determination:

$$\text{mg } SO_4^{=} \times \frac{1 \text{ mol } SO_4}{96.0 \text{ mg } SO_4} \times \frac{2 \text{ mol } NH_4}{1 \text{ mol } SO_4} \times \frac{18 \text{ mg } NH_4}{1 \text{ mol } NH_4} = \text{mg } NH_4 \text{ required} \qquad (4)$$

As a simplification that expresses the most conservative results, we assumed that ammonium sulfate was formed preferentially in all three Runs. This assumption seemed reasonable given the concentrations of the reactants, and the pressure and temperature of the impinger. The chemical reaction equation for the formation of ammonium sulfate is as follows:

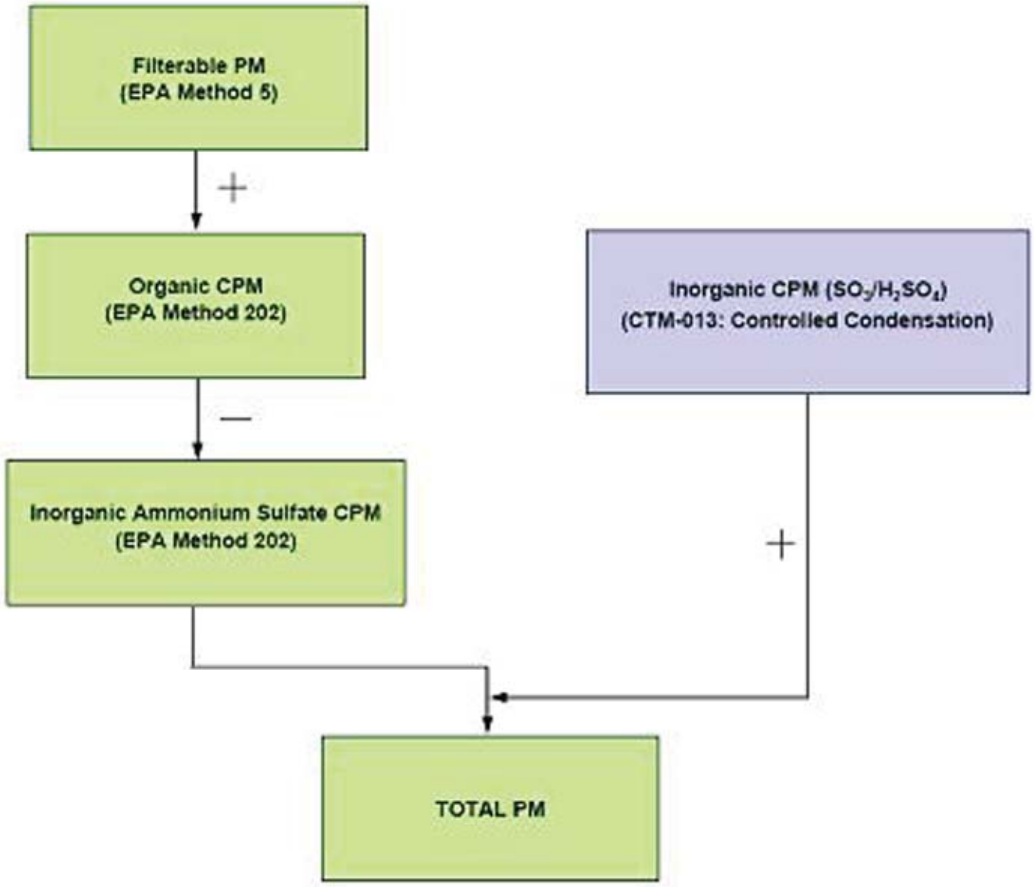

Figure 9. Total Particulate Matter Determination Flow Chart

performed by Hansen were intended to simulate combustion-produced SO_2 discharged into a fog cloud.

In the Hansen apparatus shown in Figure 13 (page 16), a warm, humidified, particle-laden air stream is introduced axially through the bottom plate of the cylindrical glass chamber of 16 cm inside diameter, 150 cm height. It mixes with an annular flow of cold, dry dilution air to produce the cloud by cooling the mixture below the resultant dew point.

Sodium chloride (NaCl) and propane soot particles (~ 5-15 $\mu g/m^3$) were used as cloud condensation nuclei. Cloud liquid water content was varied between 0.2 and 3 g/m^3. SO_2 and NH_3 concentrations were 0.6 and 1.1 ppm, respectively. The contact time between the SO_2 and the cloud drops was varied from 8 s to 3 min. Up to 80% of the input SO_2 can be oxidized to sulfate within short contact times in the presence of NH_3 and when the water is in the condensed cloud-drop phase. Negligible sulfate formation was observed in the absence of the liquid phase regardless of the presence or absence of NH_3. No significant dependence of the oxidation on the cloud condensation nuclei type nor the contact time was found.

Conclusions

The following conclusions have been made based upon the test results and research conducted on this issue:

- The reactions in equations 1 and 2 are dependent on dissolution of SO_2 and NH_3 in water and the temperature of the impingers; they would not normally take place anywhere in or beyond the stack exit. A nitrogen purge will have no effect in removing the ammonia salts once formed. The only way to account for these pseudo-particulates is to quantify the ammonium salts in the impinger catch using ion chromatography or selective ion electrodes, and account for them using a stoichiometric mass balance.

- The excess ammonia is the chemical driving force, greatly increasing the solubility of SO_2. This is occurring in a thin film, without bubbling through the solution. Because of ammonia's affinity for water, a basic solution is formed in the impingers that attracts and reacts with the acidic SO_2 gas forming ammonium salts.

- The particulates found in the impinger are not found in the stack since the two reacting compounds must be in gaseous form to pass through the initial (EPA Method 5) particulate filter.

- The ammonium salts are not formed by condensa-

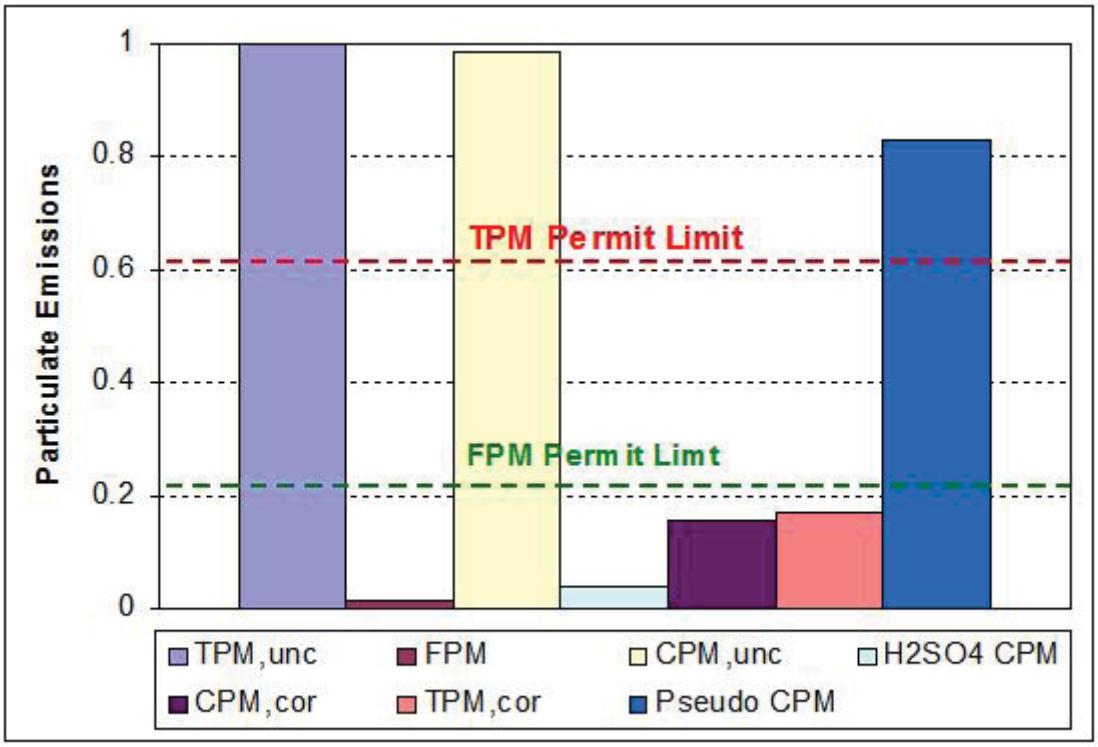

Figure 10. Run 1 Results Summary

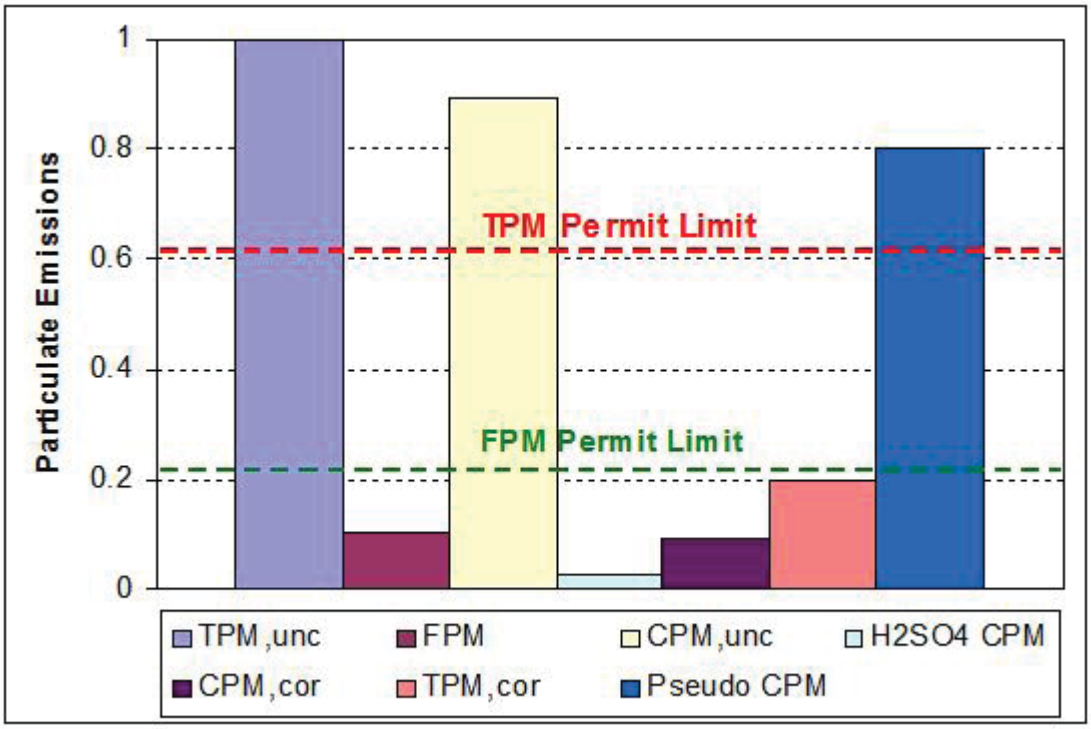

Figure 11. Run 2 Results Summary

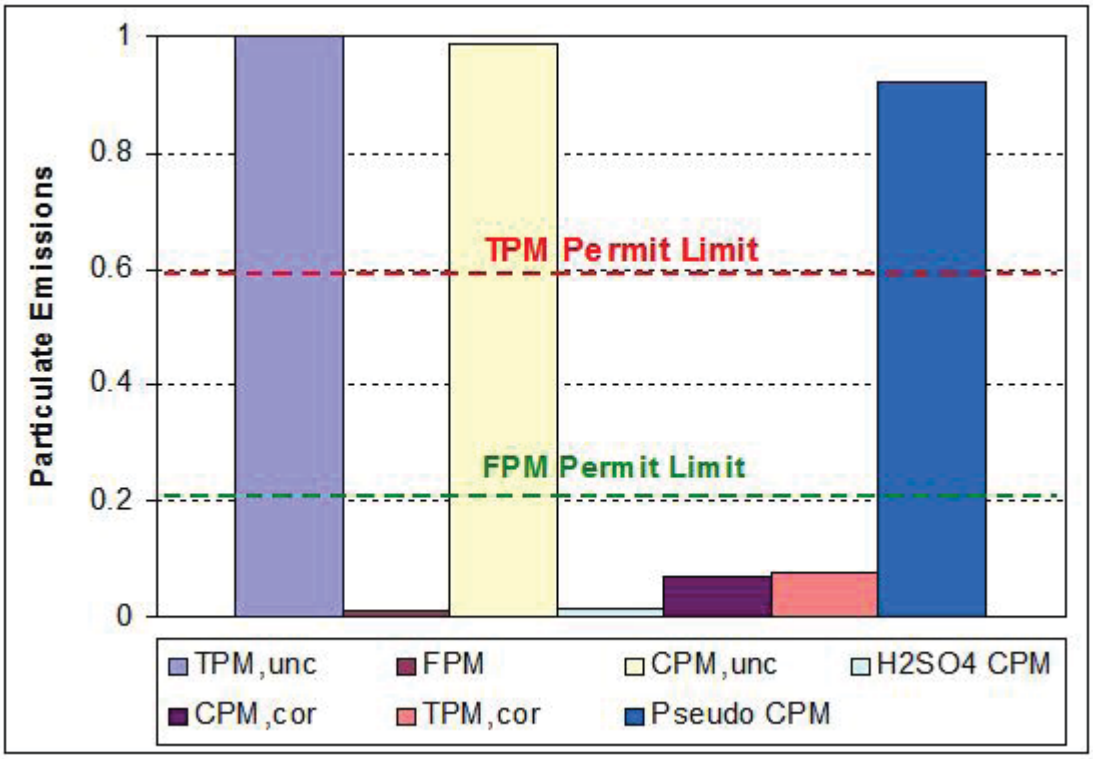

Figure 12. Run 3 Results Summary

tion, but rather require a reaction between dissolved SO_2 and NH_3, in the presence of water.

- The artifact CPM formation mechanism described in this document is likely to occur in any source that has appreciable levels of free ammonia in the flue gas, coincident with low sulfuric acid concentrations.
- Cloud chamber research by Hansen showed that SO_2 and NH_3 will not react in the absence of liquid water droplets.
- Work of Hansen indicates that SO_2 and NH_3 would not react immediately at the exit of a stack to form CPM.
- The EPA should acknowledge that significant positive biases related to the interaction of SO_2-NH_3-H_2O can occur in new Method 202, and should allow for quantification and correction of these biases using procedures similar to those outlined in this article.

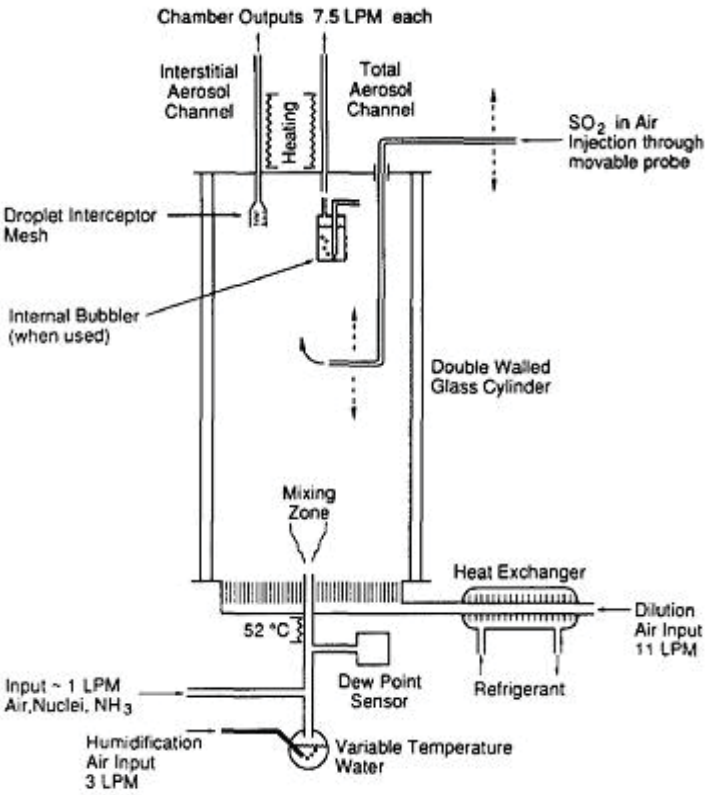

Figure 13. Schematic Diagram of Hansen Cloud Chamber Apparatus

For further information contact Scott Evans at sevans@cleanair.com

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